ARYL/CYCLOHEXYL MAGNESIUM INITIATED POLYMERISATIONS OF METHYL METHACRYLATE:

A KINETIC, MECHANISTIC, MOLAR MASS AND STEREOREGULATION STUDY

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Finally, and most importantly, I dedicate this thesis to my parents who have unceasingly supported and encouraged me throughout the course of my studies.

This thesis contains no material which has been accepted for the award of any other degree/diploma in any university and that, to the best of my knowledge and belief, does not contain material published or written by any other person, except where due reference is made in the text.

Mark Fisher

ABSTRACT

The polymerisation of methylmethacrylate (MMA) has been examined using as initiators Grignard reagents and dialkyl/diaryl magnesium compounds synthesised from the following halides: bromobenzene, bromomesitylene (2-bromo-2,3,5 trimethyl benzene) and bromocyclohexane.

Polymer products formed indicate that discrete, different active centres exist which propagate via an eneidic pathway. Studies have been conducted with a view to determining the effects on the nature and proportion of different active centres due to variations in reaction solvent composition, temperature, bromide to active bond ratios and initiator solvent. Characterisation of polymer products was completed using Gel Permeation Chromatography (GPC) and Nuclear Magnetic Resonance (NMR). Stereoregular polymer is favoured using Grignard reagents in non-polar solvent and is usually accompanied by broad molecular weight distributions. The amount of residual THF in de-etherated Grignard reagent/toluene initiator solutions seems to be an important factor in determining isotactic content. Polymer formed by initiators in THF generally have narrower molecular weight distributions and lower isotacticity than for analogous reactions in toluene, although some anomalies are apparent. Dialkyl/diaryl magnesium compounds also provide polymer products of narrower molecular weight distribution and isotacticity, even for polymerisations conducted in toluene.

Kinetic experiments have been conducted on polymerisations initiated by MsMgBr, PhMgBr and Ph_2Mg in toluene, using ^1H NMR spectroscopy to monitor the time dependence of monomer conversion. Dilatometry has been utilised to determine the external order of reaction with respect to both monomer and active bond concentration at 250K using PhMgBr. Current theories substantiating a rapid initiation process using Grignard reagents seem not to apply, with the constitution of the initiator probably playing an important role in the proposed slow initiation process. Termination of growing chains is an important factor in kinetic analysis. The ^1H NMR technique for the determination of time dependent monomer conversion has been modified in preliminary experiments using ^{13}C-carbonyl enriched monomer, enabling the possibility of observation of reaction rates, side product formation and time dependent microstructure.

Variable temperature studies on the constitution of Grignard reagents in THF and toluene have been undertaken. The presence of the Schlenk equilibrium has been confirmed and under some circumstances the presence of associated species has been inferred.

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CHAPTER 1

1. INTRODUCTION

The object of this chapter will be to briefly introduce the problems inherent in anionic and/or pseudoanionic polymerisations, with emphasis on organomagnesium initiated reactions, which will be examined in this thesis. A more comprehensive revue of material relevant to individual chapters will be found at the beginning of each. Extensive reviews of anionic/pseudoanionic polymerisations are already well documented[1,2,3,4] and will not be fully examined here.

The prospect of controlling molecular weight, molecular weight distribution and microstructure of polymethylmethacrylates (pMMAs) is desirable for a number of reasons:

(1) The monomer is relatively inexpensive and commercially available.

(2) Control of these variables leads to the ability to produce polymer with well defined physical and mechanical properties.

(3) Potential exists for the production of stereoblock polymer, the physical and mechanical properties of which are still relatively unknown[5] and requiring of further study.

(4) The blending of narrow distribution pMMAs of known molar mass and microstructure enables modification of physical properties for each of the different compon-

ents of the blend, so that a mixture can be "tailor-made" in its response to such parameters as crazing, fracture and impact resistance. Some narrow molecular weight pMMAs produced in this thesis have been used extensively by Truong[6] in the study of the mechanical properties of these blends.

The variety of initiators capable of polymerising MMA is diverse, with the choice of initiator playing a critical role in the degree of control over the polymer produced. Alkyl and aryl metal compounds are useful initiators for stereospecific polymerisation and present the possibility for control of the above properties of pMMA. For example, by variation of solvent conditions from apolar to polar, microstructure covers the range from isotactic to stereo-block (at intermediate polarity), and finally to distributions favouring syndiotactic placements in polar solvent.[7] Other factors such as temperature (Chapter 4) and the presence or absence of supporting electrolyte may be just as critical. Some organometallic initiators allow direct control of molecular weight and molecular weight distribution by virtue of the "living" nature of polymer chains produced. These reactions have been examined by Szwarc,[8] and are so named because of the absence of termination effects. Under these circumstances molar mass is strongly dependent upon the reaction time and narrow molecular weight distributions arise.

An important distinction to be made among organometallic initiators concerns the nature of the bond formed

between the growing chain end and the metal. The ionic or covalent character of this bond in solution is an important factor in determining whether the terms anionic or pseudoanionic should be applied to a polymerisation. Whichever mechanism operates, all the evidence indicates that stereoregular pMMA is only formed in systems where the metal atom is sufficiently close to the active site to influence the mode of approach, aspect of presentation of the monomer, the mode of double bond opening and rotation of the active chain end.

The reactive salts of highly electropositive metals of Group I (Na,K,Cs) can be considered to participate in typically anionic polymerisation with free ions (polar solvent), ion pairs and solvent separated ion pairs being present and in equilibrium with each other at the active chain end. Müller and Schulz[9] represent the growing end under these circumstances as:

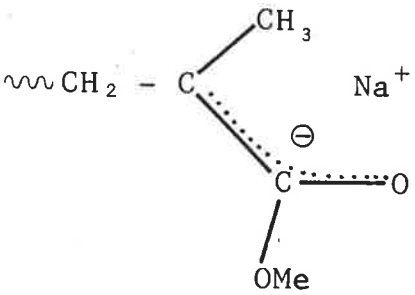


Fig. 1.1

Szwarc[10] and Schulz[11] have demonstrated that styrene polymerisation initiated by aryl sodium complexes in ether is also a true free ion-ion pair mechanism. Stereoregular polymerisations producing isotactic polymer are enhanced by the suppression of free ions so that conditions of

non-polar solvent, low temperature and inert, supporting electrolyte favour ion pair formation and stereoregular growth. The organometallic salts of these Group I metals suffer, however, under such conditions due to low solubility and heterogeneous polymerisations result.

The concept of pseudoanionic polymerisations reflects uncertainty in the degree of ionic or covalent character at the growing chain end. Under the extreme circumstance of covalent character, monomer addition at the growing end is believed to occur by insertion into that bond. Pseudoanionic polymerisations are evident among organometallic initiators when the metal atom is of intermediate electropositivity i.e., using alkyl and aryl compounds of lithium, magnesium and aluminium as initiators. However, the decision as to whether alkyl/aryl metal initiators produce active sites propagating through ionic/covalent forms is not absolutely defined by the ionic/covalent properties of the initiator in solution. Those compounds (e.g., benzyl lithium) where the alkyl or aryl group is stabilised by charge delocalisation will certainly possess ionic character in solution, particularly in organic solvents of relatively high dielectric constant. Under these circumstances initiation of polymerisation may occur via the carbanion, but thereafter the nature of the interaction between the growing end and the metal is dependent on the nature of the metal, the dielectric constant of the solvent and the ability of the last added monomer residue to stabilise potential negative charge.

Using alkyl lithium compounds as initiators for butadiene polymerisation, Bywater and Worsfold[12] have defined two ion-like isomeric forms for the growing end:

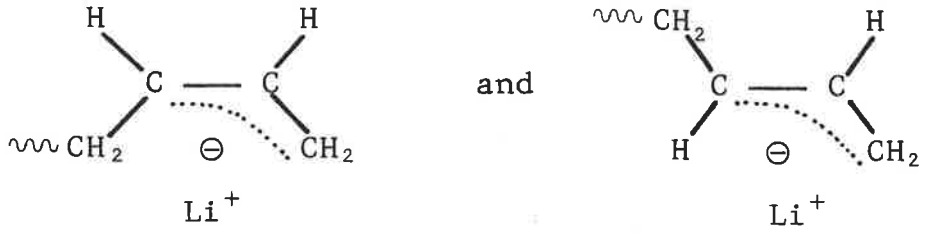


Fig. 1.2

According to these workers, confirmation of this ion-like end is made by analysis of model compounds of the form:

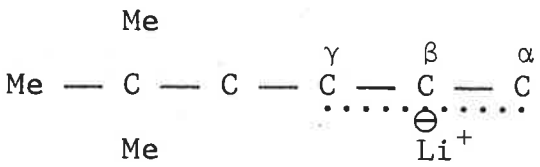


Fig. 1.3

Calculation of charge densities, based upon a comparison of ^{13}C chemical shifts with the α, β and γ sites of hypothetically ionised allyl potassium, indicate that both α and γ sites possess excess charge density.[13] Some hindered rotation of the $\alpha(C)-\beta(C)$ bond was also noted, in confirmation of partial double bond character. Care needs to be taken, however, in implying that chemical shift data solely reflect electron density at a given site. Factors such as differences in solvation and in intramolecular effects as a result of differences in aggregation complicate such an observation, with the quantitative data being, strictly speaking, only relative to the chosen standard.

The views of the above workers are in at least partial contradiction with the interpretations of Fraenkel and coworkers,[14] who view the site as a covalent form:

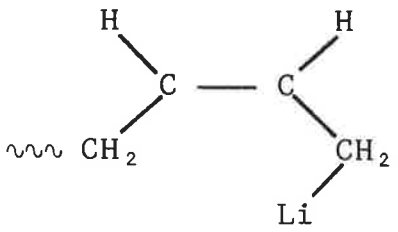


Fig. 1.4

The proposed σ bond nature of the C_α-Li bond was corroborated by examination of ^{13}C enriched model compounds of butadiene polymerisation, of the form:

$$nBu - \overset{\delta}{C} - \overset{\gamma}{C} - \overset{\beta}{C} - \overset{\alpha}{C} - Li$$

Fig. 1.5

Predominantly, 1,4 addition was noted, with a ratio of cis/trans forms equal to 3 found in benzene and cyclopentane. Lithium was concluded to be bound at the α position with no evidence of γ bound lithium, although these workers could not rule out the possibility of partial ionic character.

Current terminology tends to associate pseudoanionic polymerisations with those reactions proceeding by insertion of the monomer unit into the covalent carbon-metal bond at the growing chain end. Trialkyl aluminium reactions with 1-alkenes are believed to proceed via such a mechanism,[15] based upon the Ziegler-Aufbau reaction[16] prototype:

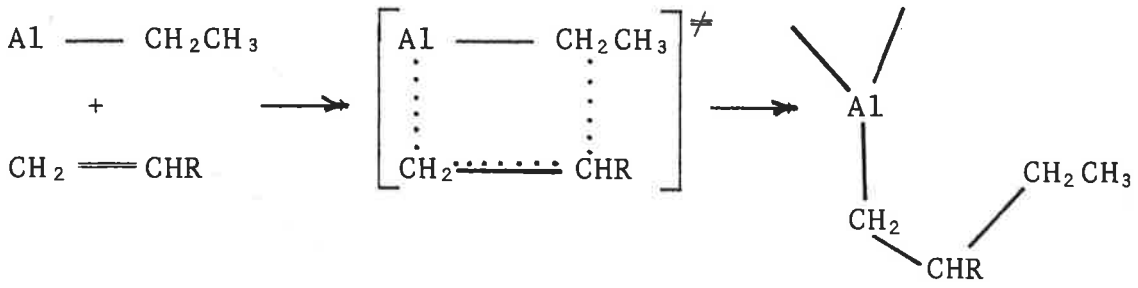


Fig. 1.6

The polymerisation of MMA by alkyl/aryl magnesium compounds, subject to study in this thesis, is also believed[17] to proceed via a monomer insertion reaction. This observation is partially supported by conductance studies on ethereal solutions of Grignard reagents, which indicate[18] only trace amounts of ionised material. Anions and cations, both containing magnesium, constitute this trace ionised material, with extensive association of these entities into ion pairs and ion triplets likely.[19] Stronger evidence for an insertion mechanism during propagation lies with the kinetic evidence of Bateup[20] and Mair.[21]

Complications in the behaviour of alkyl/aryl magnesium compounds in the presence of halide ion arise due to the presence of the Schlenk equilibrium:[22]

$$R_2Mg + MgX_2 \rightleftharpoons 2RMgX \qquad \text{Equn. 1.1}$$

so that at least two different types of RMg bond exist. Both forms of the initiator represented in Equn 1.1 are capable of initiating polymerisation of MMA, with propagation believed to be occurring by monomer insertion in both moderately polar (THF) and apolar (toluene) solvent.[20,21]

A definition of the bond character between metal and growing chain end is useful in attempting to understand

and control the properties of stereoregularity, molar mass and molar mass distribution of pMMA formed. Equilibria between active sites, such as those present in ionic systems, affect these properties:

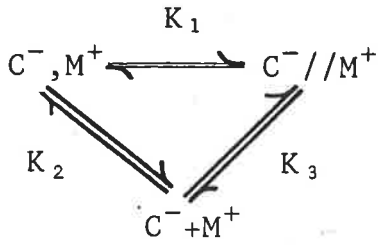


Fig. 1.7

with the model for such equilibria based upon that of Grunwald [23] for free ions, contact and solvent separated ion pairs. If all these entities exist then the position of the equilibria, their relaxation times and relative reactivities of each of these polymerisation active states are important in considering the polymer products formed. If the time that a growing site spends in each state is significantly longer than the time taken for monomer addition, then that portion of the growing chain inherits the stereochemical features typical of that state. Rapid exchange between states would provide polymer chains where the addition of the last monomer unit is independent of prior additions to the chain (i.e., Bernoullian statistics). Molar mass distributions will be broadened as a result of these equilibria, with broad unimodal distributions arising in the case of rapid exchange.

In addition to the possibility of equilibrating active centres, the presence of discrete, non interacting active centres propagating with their respective rates and

stereospecificities has been noted in some systems. Grignard reagent initiated polymerisations of MMA, particularly in apolar solvent, have been shown[17,20,21] to produce broad molecular weight distributions as a result of the operation of such independent centres. Similarly, nBuLi initiated polymerisations of MMA[24] and ethyl methacrylate[25] in apolar solvent show the presence of independent centres, with fractionation studies in the nBuLi/MMA system revealing differences in tacticity across the broad molar mass range of the resultant polymer.

Apart from considerations of solvation equilibria inherent in typically ionic polymerisations (Fig. 1.7), Grignard reagents, by virtue of the presence of the Schlenk equilibrium (Equn 1.1), imply that at least two different potential active centres, RMgX-like and R_2Mg-like, may operate. The relative proportion of polymer products arising at these centres will again be dependent on the position of the equilibrium, its lability and the relative reactivities of the two different R-Mg bonds. The potentiality for anionic systems to produce stereoregular polymer at low temperature may not necessarily apply, particularly if the Schlenk equilibrium favours, at higher temperature, one or other forms of the initiator which is highly stereodirecting. This aspect will be expanded upon in Chapters 3 and 4.

The formation of aggregates in organometallic initiator solutions affects both the efficiency of the initiation process and the properties of the polymer

produced. Higher aggregates are generally[3] of low reactivity, while the breakdown into less associated species usually enhances the reactivity of the organometallic compound drastically.[26] The slow release of potential active centres from less reactive or inert forms may then be responsible for considerable broadening of the molecular weight distribution, although, in systems where no termination is evident, narrow distributions can still be attained provided the polymerisation is carried on to sufficiently high molecular weights.[3] If discrete, independent potential active centres, propagating at their own rates and stereospecificities, are released from these high order associates then broad molar mass distributions seem assured. The implications of initiator association cannot be neglected even at low concentration. In hydrocarbon solutions examination of colligative properties has established that n-butyllithium[27] and ethyllithium[28] are hexameric at concentrations up to .1M, with no significant breakdown of aggregates at concentrations as low as 10^{-5}M. Although no examinations were attempted in this thesis to determine the degree of association of Grignard reagents/ dialkyl/diaryl magnesium compounds, the significance of this result for alkyllithium compounds may equally apply to magnesium systems, particularly at low temperature.

The presence of terminating chains present another means by which molar mass distributions may be broadened with consequently greater variation in the physical properties of the polymer produced. Early work in the field of anionic and pseudoanionic polymerisations failed to recog-

nise the critical nature of trace impurities on the occurrence of termination, but refined experimental techniques by Szwarc and co-workers[8] established the presence of "living" polymerising systems from which narrow molecular weight distribution polymers are accessible. Despite all care in experimental procedure, however, some systems[29] are prone to the effects of termination. While the possible terminating mechanisms in the anionic polymerisations of methacrylic acid esters are well established - intramolecular cyclisation, reaction of the growing chain end with the monomer carbonyl unit and to a lesser extent chain grafting reactions - the reasons why some systems show a tendency to terminate at a particular molar mass remains unsolved. A full discussion of the mechanisms of chain termination is found in Chapter 5.

The means of stereochemical, molecular weight and molecular weight distribution control in organomagnesium initiated polymerisations of MMA, where different, independent centres are operating,[17,30] rests ultimately with an identification of those centres. Direct access to this information is not possible using currently available experimental techniques, due to the low concentration of active sites, so that the properties of those centres must be indirectly inferred from kinetic examinations and the variations of microstructure, molecular weight and molar mass distribution as a function of overall solvent constitution, temperature, initiator solvent and in the case of Grignard reagents, the halide to active bond ratio.

These indirect observations constitute the objectives of this thesis, and include a ^{13}C NMR examination of the phenyl (Ph) and mesitylene (Ms) magnesium initiator solutions as well as a cursory NMR study of the cyclohexyl (chex) magnesium bromide initiator, in an attempt to correlate any changes in their constitution with the changes in the type of polymer product formed.

1.1 Side Reactions

The proceeding chapters of this thesis deal almost exclusively with the reaction of organomagnesium compounds and MMA leading to the formation of polymer products, i.e., the 1,4 addition at the initiation stage, as depicted in Fig. 1.8:

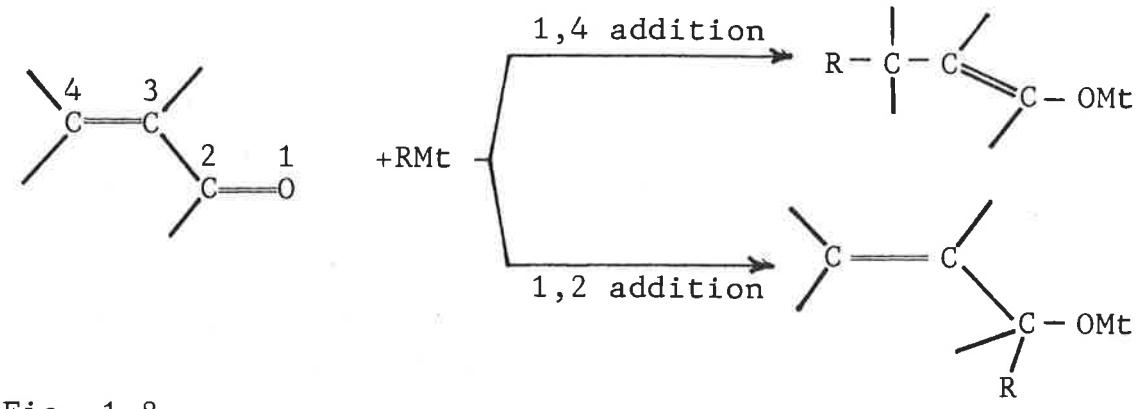


Fig. 1.8

The possibility of the 1,2 addition does have some consequences on those sites producing polymeric material, however:

(1) In addition to the formation of potentially inactive aggregates of organometallic initiator,[3] the efficiency of initiation of sites leading to polymer products is reduced by the consumption of active bonds at the carbonyl group. This efficiency may be

further reduced in the reaction of organomagnesium compounds with an ester functionality, due to the possibility of a 2-fold 1,2 addition at this site:

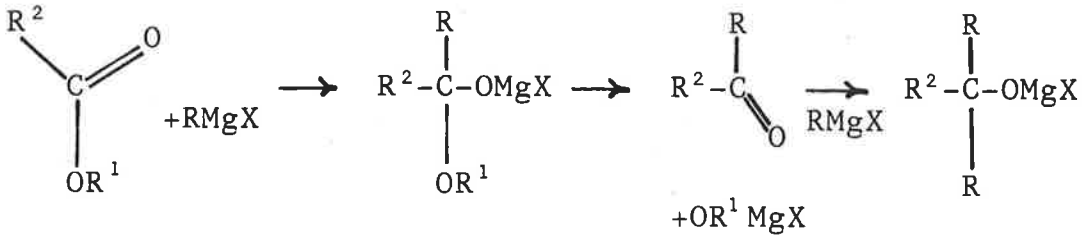


Fig. 1.9

(2) For α, β unsaturated esters the side product of 1,2 addition is the alkoxide group. In polymerisations of MMA with nBuLi the methoxide ion has been found to initiate polymerisation in THF[31] but not in toluene.[32] Conclusive evidence as to whether methoxide ion is a potential initiator in organomagnesium systems is yet to be presented.

(3) Hatada and co-workers[33] have noted in nBuLi polymerisations of MMA that butyl isopropenyl ketone, resultant from 1,2 addition, is capable of acting as a comonomer in the polymerisation. This is also conjectural in organomagnesium systems.

Conflicting kinetic evidence is available on the mechanism of Grignard reagent addition to saturated carbonyl moieties. Their addition to ketones has been observed to be either overall second[34] or third[35] order. Second order kinetics has been attributed to either a simple bimolecular reaction or a unimolecular decomposition of their complex, of the form:

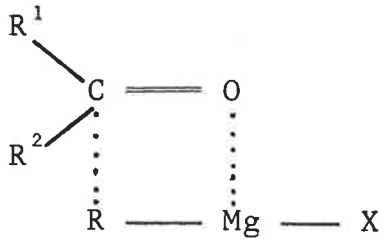


Fig. 1.10

Overall third order kinetics, with first and second orders with respect to ketone and Grignard reagent respectively, has been interpreted in terms of a six-membered transition state:

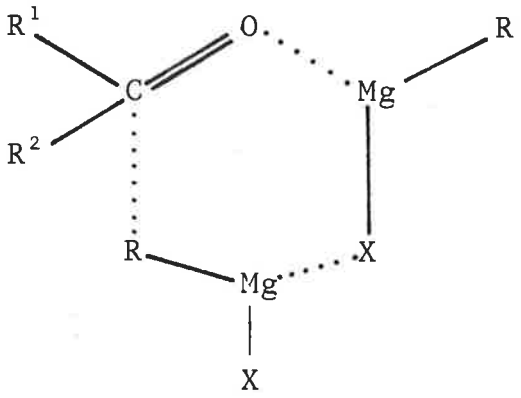


Fig. 1.11

The discrepancy between orders of reaction may have arisen as a result of trace impurities or alternatively from factors which may have varied the degree of association of the Grignard reagent.

The factors determining the ratio of 1,2 to 1,4 addition in α,β unsaturated systems are not fully defined. Gilman and Kirby[36] and Hauser[37] have shown in the reaction of phenyl compounds of Group II and IA metals with benzalacetophenone that the preference for mode of addition is dependent on the polarity of the carbon-metal bond. The more reactive, essentially ionic organometallics of Group I and II metals favour 1,2 addition, while the less

reactive, essentially covalent phenyl lithium and PhMgBr favour 1,4 addition. Other important factors appear to be the nature of the substrate, solvent polarity and temperature.

This, then, summarises the relevant material that needs to be considered in an evaluation of parameters affecting the nature of polymer produced. Clear definition of these parameters will also provide indication of the mechanism of monomer addition, which is particularly important in the case of reactions producing stereoregular polymer.

CHAPTER 2

2. PREPARATION OF REAGENTS AND VACUUM LINE PROCEDURES

Special procedures were required for the preparation of reagents used in this thesis due to the extreme sensitivity of Grignard reagents and corresponding dialkyl/diaryl magnesium compounds, as well as the actual polymerising systems, to the presence of water and oxygen. In addition, maximum purity of solvents, with regard to other organic impurities, had to be maintained. Szwarc and co-workers[1] have noted that the presence of any impurities may drastically affect the potentiality of living systems which may be present in alkyl/aryl metal/MMA polymerisations.

2.1 Purification of Reactants and Solvents

(a) Methylmethacrylate (MMA ; Fluka ; AR)

Stabilised monomer was washed 4-5 times with 10% w/v sodium hydroxide, to remove the stabilising quinol, and then washed with water until neutral to indicator paper. Removal of water from the monomer was facilitated by an initial coarse drying procedure over anhydrous $MgSO_4$. Following this, the monomer was placed over calcium hydride (CaH_2) for a period of at least one week, degassed three times using a freeze/thaw cycle and then distilled *in vacuo* into storage containers. The monomer was distilled, prior to use in polymerisations, into a vessel containing a sodium mirror and benzil.[2] The MMA/sodium benzil solution produced a crimson-purple coloration indic-

ative of the absence of moisture and oxygen in the system. Monomer was left over sodium benzil for 3-4 minutes (longer times were avoided because this organometallic compound induces slow polymerisation) before distillation into dispensing containers, which were kept refrigerated at -20 °C. Subsequent to any polymerisations a small amount of monomer was added to water to ensure no spontaneous radical polymerisation had occurred during the storage period.

(b) Alkyl/aryl bromides (Fluka ; AR)

Bromobenzene (PhBr), bromomesitylene (MsBr; 2-bromo-1,3,5-trimethylbenzene) and cyclohexylbromide (chexBr) were refluxed for at least 12 hours over CaH_2 before distillation, the middle fraction only being used for Grignard reagent preparation. The high boiling point of MsBr (225°C; 1AT) necessitated its distillation at reduced pressure. Grignard reagent preparation using these alkyl/aryl bromides was attempted immediately after distillation.

(c) Tetrahydrofuran (THF ; BDH ; AR)

This solvent was refluxed over lithium aluminium hydride (LAH) for a minimum of 12 hours, which served the dual purpose of removing both water and quinol stabiliser. This was then distilled, the middle fraction collected, and then refluxed over sodium benzophenone to produce either a purple (sodium benzophenone radical anion) or crimson (radical dianion) coloration after 12 hours. Distillation, followed by a triple degassing procedure (3 freeze/thaw cycles), produced purified THF which was

distilled in vacuo into a storage vessel containing a sodium mirror and benzophenone. THF was distilled from this storage vessel into dispensing containers prior to use in polymerisations.

(d) Toluene (BDH ; AR)

Purification of this solvent was identical to the method used for THF, except that CaH_2 was used as the initial drying agent.

(e) 1,4 Dioxane (BDH ; AR)

This reagent was dried by refluxing for 12 hours over CaH_2. Distillation was aided by the use of an antifrothing nitrogen stream. The distillate was triply degassed and then decanted in vacuo on to sodium benzophenone. The final distillation from this drying agent into storage vessels ready for use was made difficult by the formation of a solid dioxane "crust" at the surface of evaporation, but was finally achieved by frequent agitation at the surface.

(f) Magnesium (BDH turnings: "For Grignard Reagents" with Fe content < .01%)

Magnesium turnings were refluxed for 12 hours in dry THF/toluene to remove any grease present on the surface of the turnings. The magnesium was subsequently collected and dried in a vacuum oven prior to use.

(g) Deuterated Solvent and Solvent for NMR Purposes

i) Dimethylsulphoxide-d_6 was used straight from the supplied ampoules in a 30%w/w solution with o-

dichlorobenzene, as a solvent for ^1H tacticity determinations at 400K.

ii) o-dichlorobenzene (BDH; AR) NMR investigation revealed that this solvent was quite suitable for use, without further purification, in ^1H tacticity determinations. In particular, no major impurity peaks were present at chemical shifts corresponding to α CH_3 of pMMA, where ^1H tacticity determinations were made.

iii) Chloroform - $CDCl_3$ was dried over $4A^o$ molecular sieves and was used, together with 3% TMS internal standard, as the solvent for determinations of microstructure at 300K, using ^{13}C NMR spectroscopy.

iv) Tetrahydrofuran -d_8, for use in NMR kinetic runs and for investigation of initiator constitution, was dried over LAH with frequent agitation, triply degassed and distilled twice before storage in vacuo.

v) Toluene - d_8, used in a similar manner to THF - d_8, was dried over CaH_2 before degassing and distilling (twice) into an appropriate storage vessel.

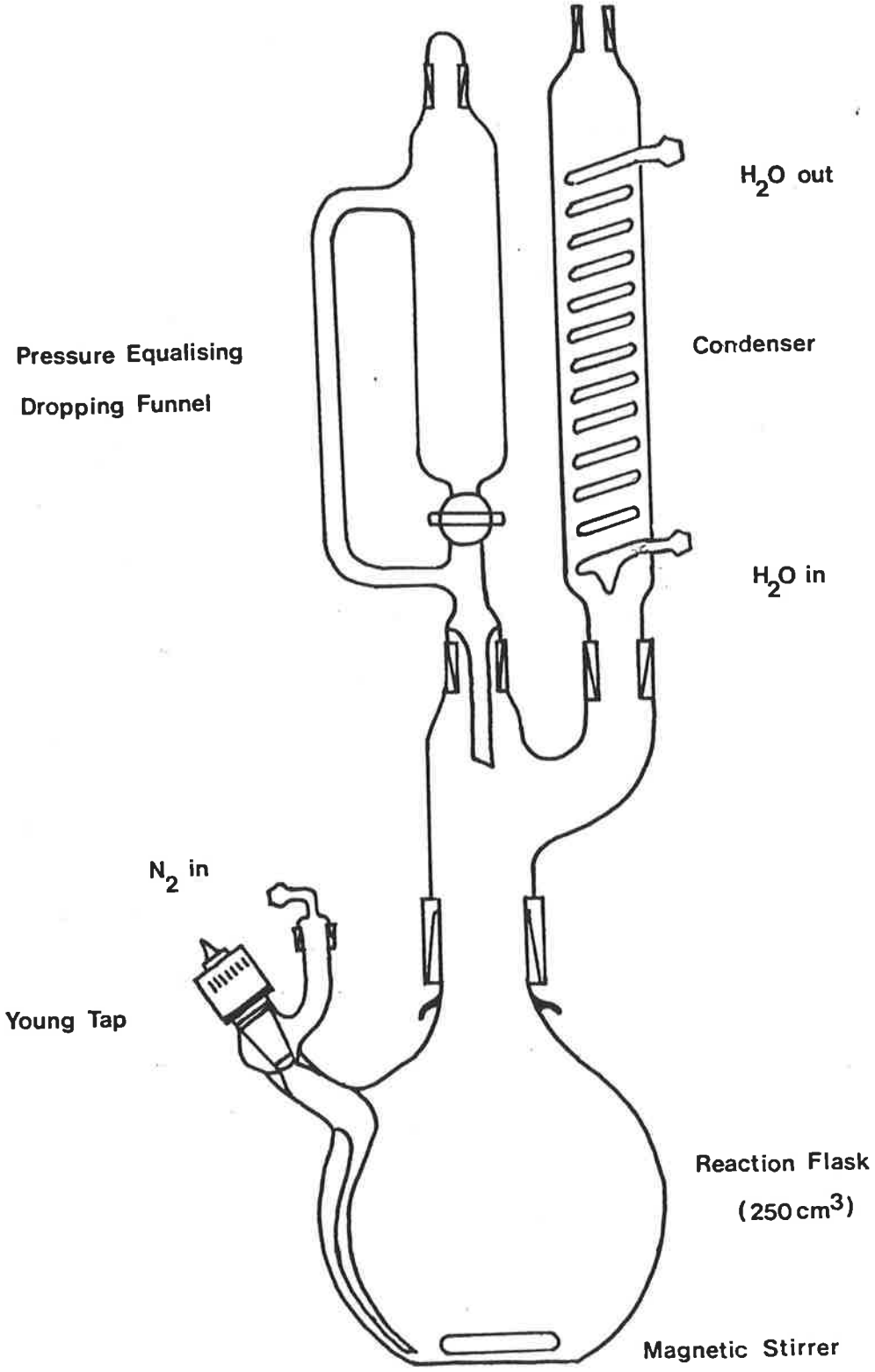
2.2 Preparation of Initiator Solutions

(a) Grignard Reagents

The apparatus used in initiator synthesis is depicted in Fig. 2.1. All glassware, prior to reaction, was heated for 12 hours at 120°C to remove traces of adsorbed water. Grignard reagents were initially prepared in THF freshly distilled from sodium benzophenone prior to use, and

placed in the reaction flask of Fig. 2.1 together with a magnetic stirrer and purified magnesium turnings (in 2-3-fold excess of the stoichiometric requirement). High purity, dry nitrogen (99.9%) was passed through the bleeder system, depicted in Fig. 2.1, and maintained throughout the course of the reaction to prevent oxidation/hydrolysis of the Grignard reagent. Freshly purified alkyl/aryl bromide was placed in the pressure-equalising dropping funnel and added dropwise to the magnetically stirred solution of THF/magnesium turnings. In all cases some initial heating was required to initiate reaction, but thereafter no difficulties were experienced, the alkyl/aryl bromide being added to maintain a steady THF reflux. Following addition of all the bromide, the reaction mixture was heated for a further 15-20 minutes to ensure completion of reaction and then allowed to cool for 10 minutes (this cooling procedure was enhanced by increasing the flow rate of high purity nitrogen to increase the rate of THF evaporation). Particular reference is made to this cooling period because Mair,[3] preparing the terBuMgBr initiator solution, has noted fundamental differences in pMMAs formed by initiator solutions decanted from residues before and after cooling. These differences are almost certainly related to the uptake of magnesium bromide ($MgBr_2$; refer to Chapter 3 for a discussion of the Schlenk equilibrium) which tends to precipitate preferentially during cooling. After cooling and removal of condenser and dropping funnel, a porosity 2 (JENA) sintered glass filter was mated with the reaction vessel, and, with maintenance of nitrogen atmosphere, this

Fig 2·1 Grignard Reaction Vessel



apparatus (Fig. 2.2) was inverted and placed on the general purpose vacuum manifold (Fig. 2.6; described later) ready for transfer to the Grignard storage vessel (Fig. 2.3). The coarse filtration procedure was accelerated by momentarily exposing the solution to vacuum and was effective for the removal of unreacted magnesium and the small amount of $MgBr_2$-rich material arising from the cooling procedure. After transfer to the storage vessel the initiator was degassed 3 times using a freeze/thaw cycle. Following overnight standing fine deposits of colloidal magnesium were evident which were filtered (porosity 4 filter; JENA) in vacuo using the filter stick depicted in Fig. 2.4, and collected in another storage vessel using the general purpose vacuum manifold (Fig. 2.6). Initiator/THF solutions were wrapped in aluminium foil and stored in a dark cupboard when not in use.

(b) Diaryl Magnesium Compounds

Preparation of these compounds required the addition of 1,4 dioxane to the corresponding Grignard reagents, which precipitated $MgBr_2$ as the bis-dioxane complex. The bromide concentration of the Grignard reagent was determined using Volhard's method[4] (refer to section 2.4: Characterisation of Initiator Solutions) and to this was added an amount of 1,4 dioxane in slight excess of 1:1, to ensure complete removal of bromide. The white magnesium bromide bis-dioxane precipitate was filtered using the porosity 4 filter (Fig. 2.4). Tests on the resultant filtrate revealed that bromide was efficiently removed in

Fig2·2 Coarse Filtration

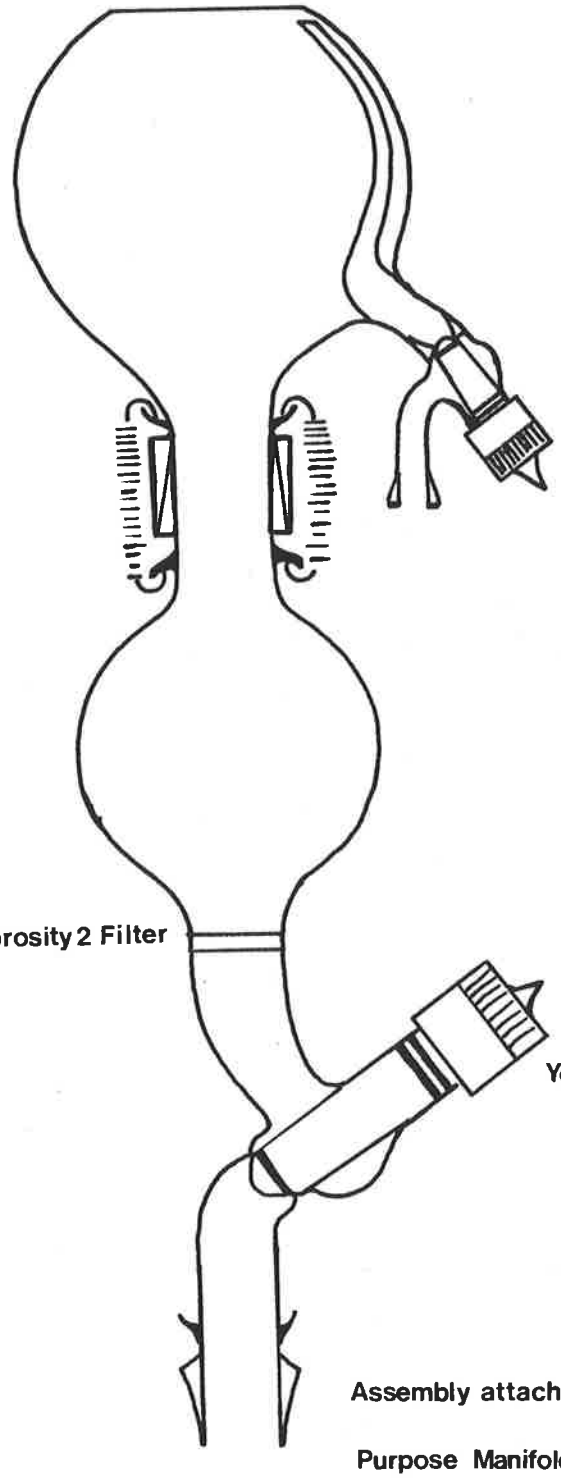


Fig 2·3 Grignard/Solvent Storage Vessel

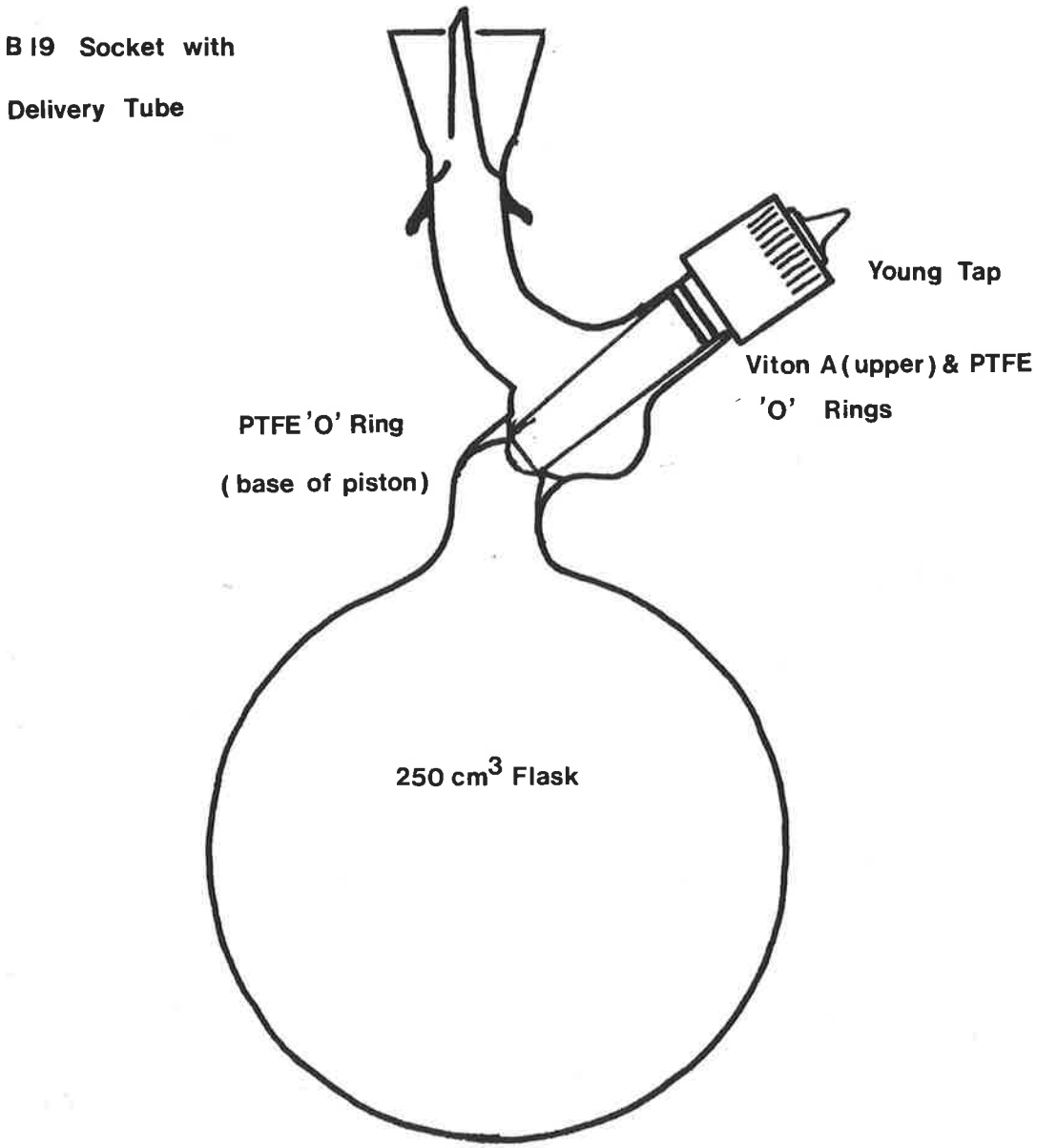
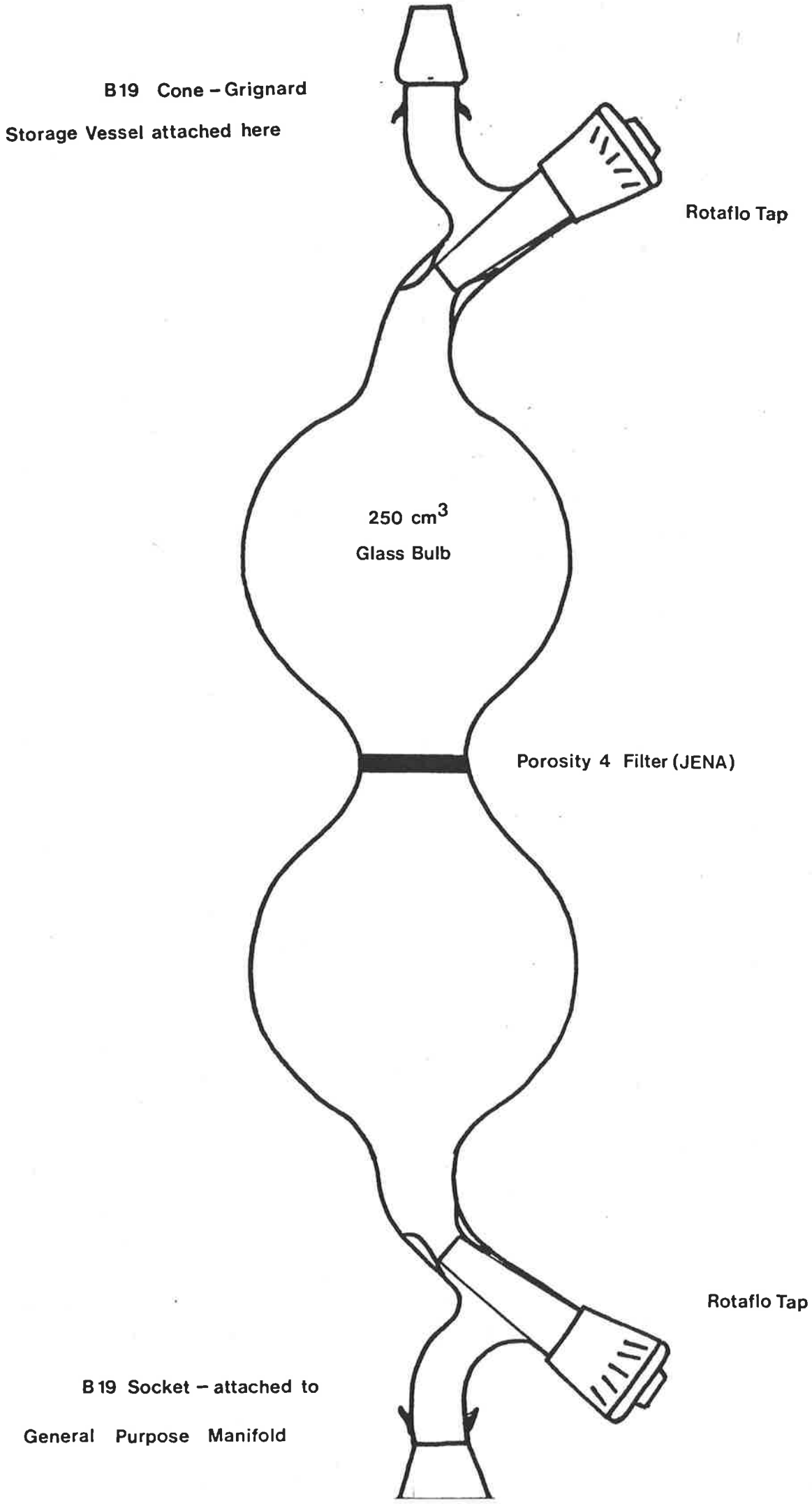


Fig 2·4 Vacuum Filter Stick



the case of PhMgBr, but the MsMgBr system provided persistent trace amounts of bromide despite further additions of 1,4 dioxane. The implications of this result on the NMR of initiator solutions and polymer products is explained in Chapters 3 and 4, respectively.

(c) De-etheration of Grignard and Diaryl Compounds

i) The use of Grignard reagents, in non-polar solvent, as initiators for MMA polymerisation, produces stereoregular polymer of high molar mass.[3] For this reason, initiator solvent (THF) was replaced with toluene. This involved the in vacuo distillation, with gentle heating, of THF from the initiator using the general purpose vacuum manifold (Fig. 2.6), leaving behind a concentrated slurry to which toluene was added. Not all material was found to be soluble in the predominantly non-polar solvent, and bromide rich precipitates were filtered from the resultant solution using the porosity 4 filter stick (Fig. 2.4). The amount of THF remaining after replacement with toluene is critical in the determination of the bromide to active bond ratio, which in turn is important in determining the type of pMMAs formed with these initiators. The THF content of initiator solutions was determined using a PERKIN-ELMER F11 Flame Ionisation Gas Chromatograph using a 2 metre metal column packed with 10% apiezon on varaport 80-100 with oven temperature: 90° C, injector temperature: 40° C and nitrogen carrier gas flow rate: 25ml. min^{-1}.

ii) Under normal circumstances, initiator/toluene solutions prepared under the conditions of (i) were used in

polymerisations. However, referring to the methods of Tsvetanov,[5] an extensively de-etherated PhMgBr solution was prepared by heating a THF solution of this Grignard reagent for 8 hours at 343K under high vacuum (10^{-3} - 10^{-4} Torr). The NMR character of this initiator is discussed in Chapter 3. It has been shown[6] that extensive heating of terBuMgBr produces HMgBr and 2 methyl propene, but such reactions are unlikely for aryl magnesium bromides.

iii) Diaryl magnesium compounds in toluene were formed by de-etheration of diaryl magnesium/THF solutions, analogous to (i) above. Some precipitation was again evident which was removed by in vacuo filtration.

2.3 Preparation of Magnesium Salts for Addition to Polymerisation Reactions

(a) Magnesium Bromide

i) The preparation of anhydrous $MgBr_2$ in THF was achieved using the same method and apparatus (Figs. 2.1, 2.2) used for Grignard synthesis. Ethylene dibromide (1,2-dibromo-ethane) was dried over CaH_2, distilled, and the middle fraction of this distillate added to a stirred solution of excess magnesium turnings in THF, reacting according to the equation below:

$$Mg + Br\,CH_2\,CH_2\,Br \xrightarrow[\text{Initial heat}]{\text{THF}} MgBr_2 + CH_2\,CH_2\uparrow \qquad \text{Equn 2.1}$$

ii) Extensively de-etherated $MgBr_2$ /toluene solutions were prepared, for additions to initiator solutions to supplement bromide content, in an identical fashion to extensively de-etherated PhMgBr (see above). The solubility of

$MgBr_2$ in toluene under these conditions is very low, with Volhard's method predicting the bromide content, for the filtrate from a saturated solution, of $.01_5$ M at ambient temperature.

(b) Magnesium Methoxide ($Mg(OMe)_2$)

Magnesium methoxide in THF was prepared to test the effect of possible polymerisation side product, methoxide ion, on stereochemical and GPC aspects of pMMA formed with Grignard reagents.

Methanol (CSR; AR) was dried in vacuo over $4A^{o}$ sieves for a period of one month, with intermittent shaking, to remove water. This was then distilled in vacuo, with the middle fraction being retained for further reaction. Methanol/THF ($44.9x10^{-3}$ moles of methanol) was added in vacuo to a solution of Ph_2Mg/THF ($51.4x10^{-3}$ moles of PhMg bonds) to produce a white $Mg(OMe)_2$ precipitate. Solvent was twice evaporated from this precipitate before replacement with THF. In vacuo filtration of the supernatant THF through a porosity 4 filter produced a solution showing no evidence (^1H NMR) of hydroxylic protons of residual methanol. The solubility of magnesium methoxide in THF was low, but evaporation of some of the THF filtrate did reveal the presence of white, solid $Mg(OMe)_2$ in small amounts. Attempts to prepare $Mg(OMe)_2$ in toluene failed, in agreement with other workers.[7]

2.4 Characterisation of Initiator Solutions

Determination of the active C-Mg bond content[4] of an organomagnesium system involved the acidification of a known volume of initiator solution with a standard acid solution, and back-titrating the remaining unreacted acid in solution with standard base:

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X \qquad \text{Equn 2.2}$$

$$Mg(OH)X + HCl \longrightarrow MgXCl + H_2O \qquad 2.3$$

or

$$R_2Mg + 2H_2O \longrightarrow 2RH + Mg(OH)_2 \qquad 2.4$$

$$Mg(OH)_2 + 2HCl \longrightarrow MgCl_2 + 2H_2O \qquad 2.5$$

and $[R\text{-}Mg]_o = 2[R_2Mg]_o + [RMgX]_o$ for a Grignard solution, with the individual concentrations dependent on the equilibrium constant for the Schlenk equilibrium (refer to Chapter 3).

Halide content of initiator solutions was determined using Volhard's method,[4] requiring acidification of the initiator solution with dilute nitric acid, reacting with excess standard silver nitrate and back-titrating the excess $AgNO_3$ with potassium thiocyanate, using ferric ammonium sulphate as an indicator.

2.5 High Vacuum Systems

Improvement in the design of high vacuum glassware has been made possible by development of high vacuum greaseless taps and joints which provide excellent sealing qualities, not only at ambient temperatures, but at low temperatures as well.

Greaseless taps provided by YOUNG GLASSWARE were used constantly on storage vessels for both monomer and initiator solutions (Fig. 2.3), and in particular did not fail for monomer storage vessels refrigerated at -20°C. This tap was utilised extensively on high vacuum manifolds as well, and is best illustrated in Figs 2.6 and 2.7. Efficient sealing is reliant upon compression between the glass surface of the barrel and the PTFE "O" ring at the end of the piston. Increased compression, required in storage vessels at lower temperature, was facilitated by further tightening of the threaded piston in the glass barrel. At the threaded end of the piston 2 "O" rings, PTFE and Viton A, both insensitive to solvents used in this thesis, prevented leakage of air into the system through the thread, so that the whole tap system could be placed in/on a vacuum line without leakage.

Under ambient conditions ROTAFLO taps proved as effective as YOUNG taps, and were frequently used on storage or reaction vessels maintained at room temperature.

Greaseless Viton A "O" ring cones were used on vacuum manifolds (Figs 2.6 and 2.7) as sites of attachment for reaction vessels and storage containers. Utilisation of "O" rings at these joints partially eliminated the possibility of contamination of reaction components with trace amounts of water, which is always present in high vacuum grease. In some instances the use of high vacuum grease proved unavoidable.

2.6 High Vacuum Pumping System

Fig. 2.5 shows the basic pumping system used for all experiments in this thesis. An EDWARDS 3 stage rotary oil pump was used in conjunction with two in-series, three stage, glass mercury diffusion pumps to provide high vacuum in the system. The two diffusion pumps were capable of being isolated from the backing pump and the remainder of the line during evacuation by the inclusion of a by-pass for the rotary oil pump, facilitated by the inclusion of the three indicated YOUNG taps. Alternatively, when high vacuum was required, the backing pump and diffusion pumps could all be directed to an in-series configuration by manipulation of the taps. Two liquid nitrogen traps were included to protect the diffusion and oil pumps from contamination by solvent vapours.

The general purpose and reagent dispenser manifolds (Figs 2.6 and 2.7, respectively) were attached to this pumping system using a YOUNG greaseless ball and socket joint with an accompanying Viton A "O" ring.

2.7 High Vacuum Manifolds

The vacuum manifolds (Figs 2.6 and 2.7) both extensively employ YOUNG taps and greaseless Viton A "O" ring cones.

(a) General Purpose Manifold

This manifold (Fig. 2.6) was used continually for such procedures as:

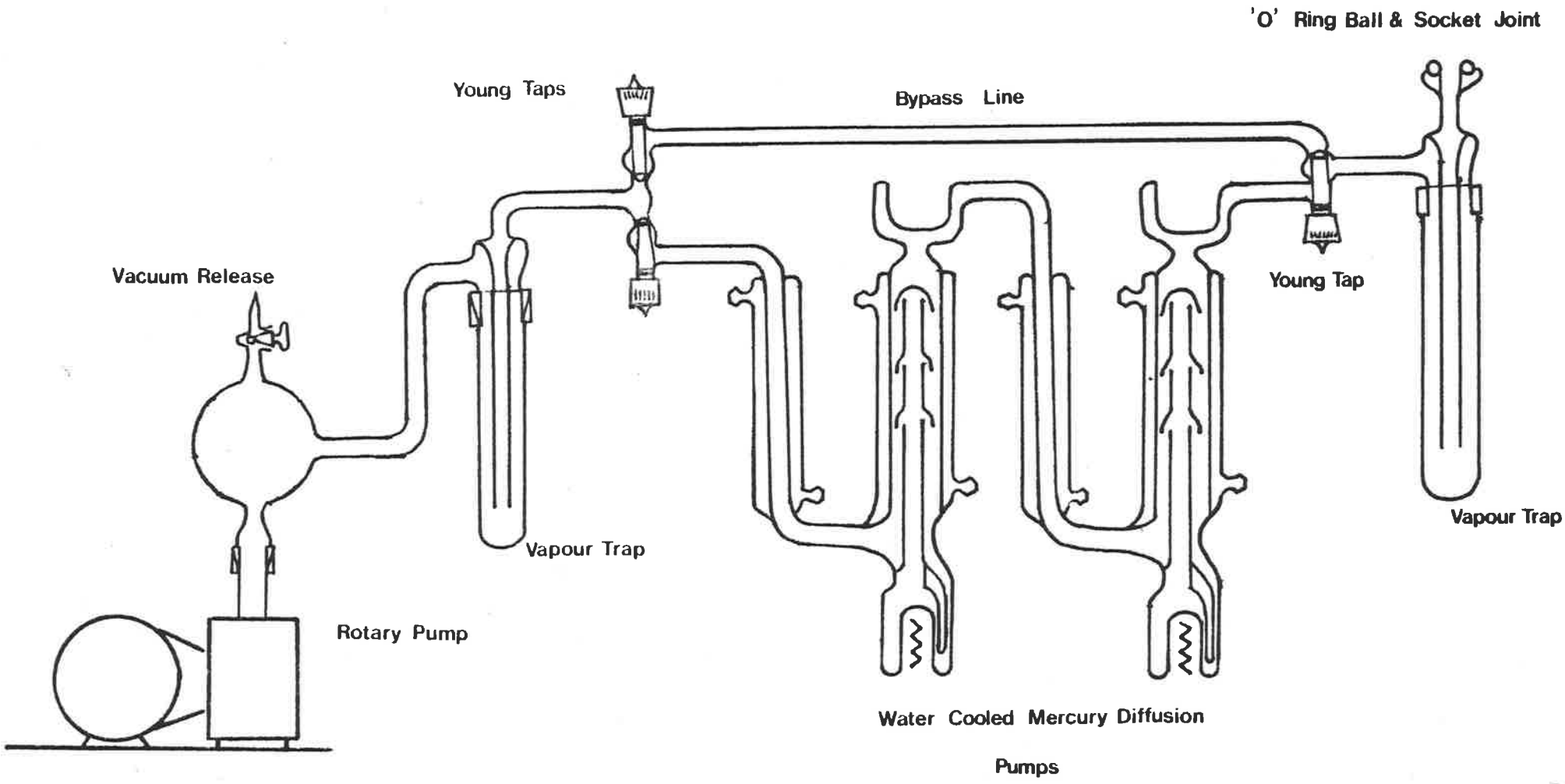


Fig 2·5 High Vacuum Pumping System

Fig. 2.6 (opposite): General Purpose Manifold

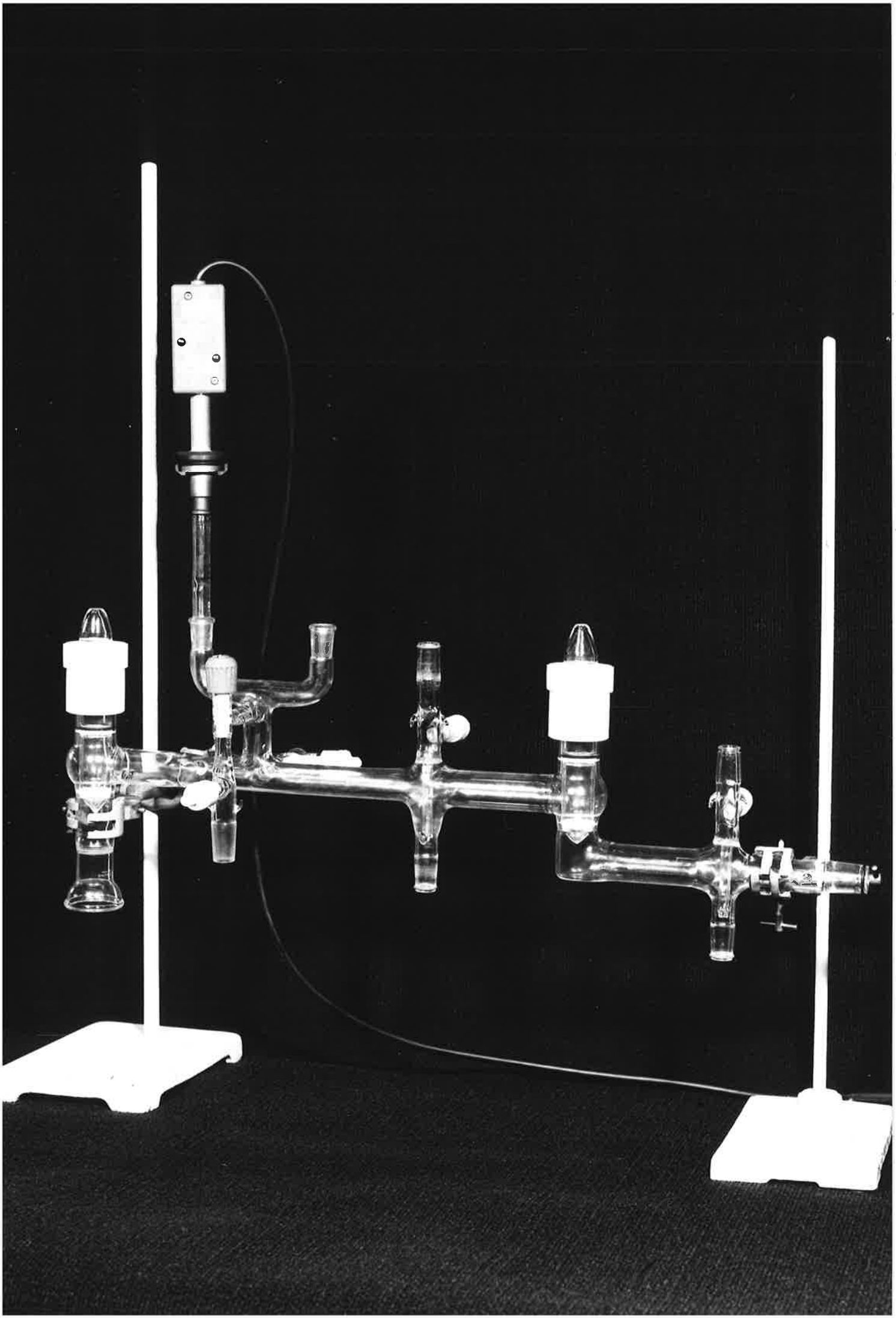
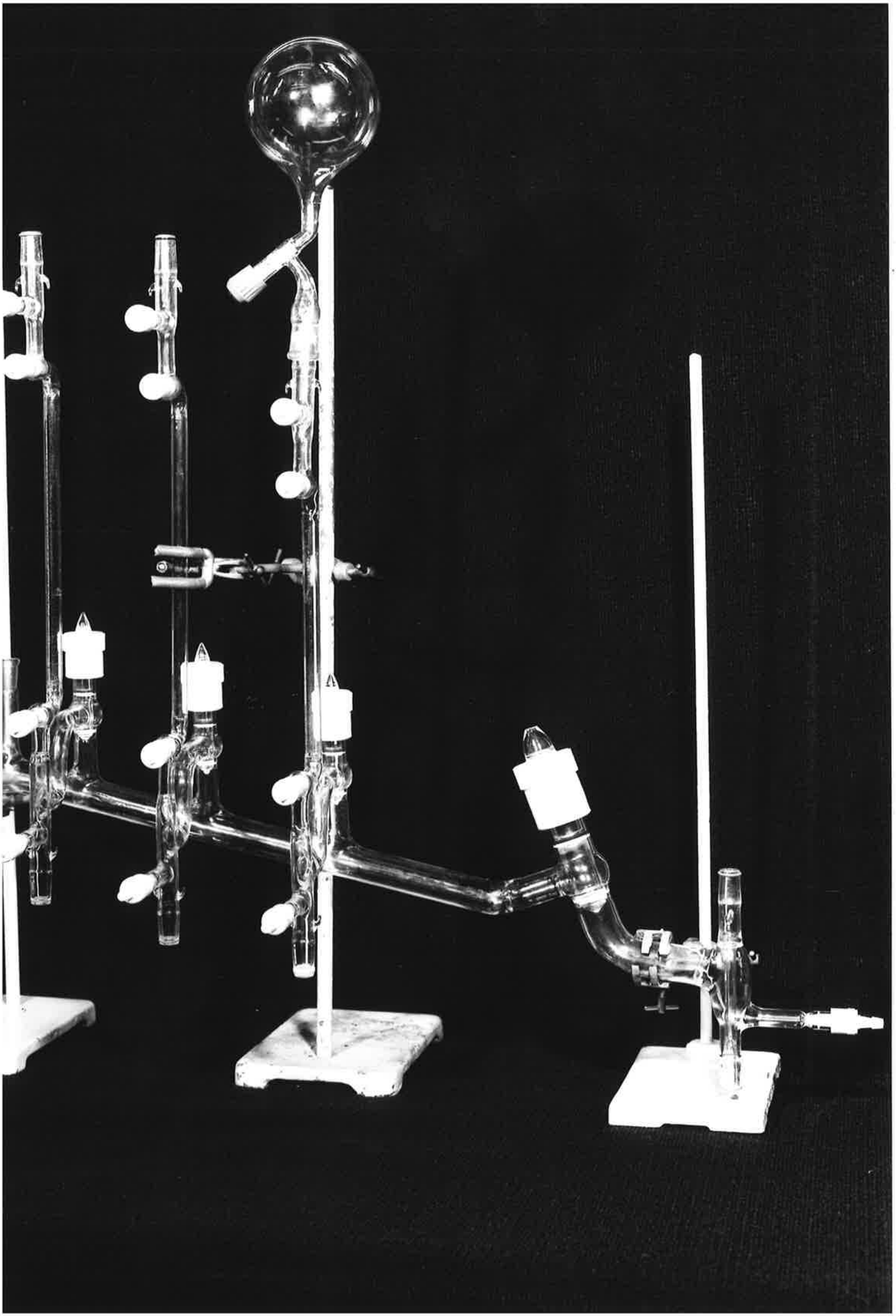


Fig. 2.7 (opposite): Reagent Dispenser Manifold



(1) Freeze/thaw degassing procedures for purified monomer/solvent.

(2) Transfer of filtered Grignard/diaryl magnesium reagents from the filter stick (Fig. 2.4) to storage containers (Fig. 2.3).

(3) Distillation of deuterosolvents where a short path length is important.

(4) Preparation of sealed NMR tubes for the examination of Grignard and diaryl magnesium compounds.

(5) Solvent replacement procedures for initiator solutions.

(b) Reagent Dispenser Manifold

This manifold (Fig. 2.7) was interchanged with the general purpose manifold at the greaseless ball and socket joint of the high vacuum pumping system (Fig. 2.5) when required. It consists of three totally isolable burettes designed to deliver monomer, THF and toluene from dispensing vessels (Fig. 2.3), at the top of each burette arm, into the desired reaction vessel (refer to next section) attached to the manifold at the greaseless joints at the base of the burettes. Approximate delivery volumes were checked by weight before introduction of a new component at the next vacuum burette. In addition to the vacuum burettes, a site (Fig. 2.7, far right) is available for the introduction of initiator solution into the reaction vessel.

Extent of vacuum in both manifold systems was measured with an EDWARDS PR10-S sensor with thermo-resistivity heads.

In common to both manifolds are the YOUNG vacuum release taps, placed near sites of attachment, to enable easy release of reaction vessels, etc.

2.8 Reaction Vessels

Four different types of reaction vessel were used to conduct polymerisations, and these are depicted in Fig. 2.8(a) and (b), Fig. 2.9 and Fig. 2.10.

(a) NMR Scale Reactions

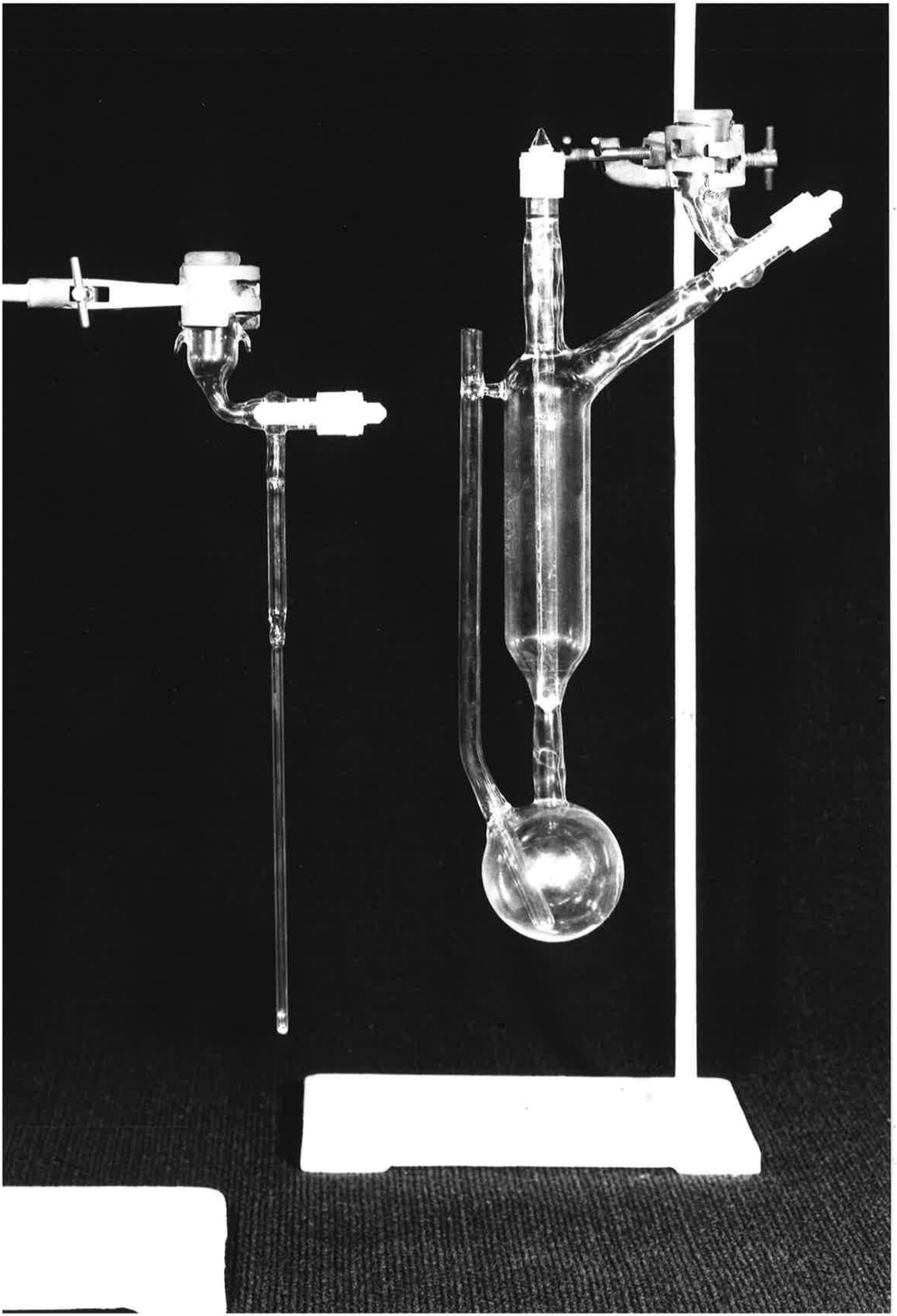
Kinetic aspects of the polymerisations of MMA by organomagnesium compounds were studied using NMR on reaction volumes of approximately $1cm^3$. Fig. 2.8(a) shows the 5mm NMR tube and accompanying YOUNG tap prior to addition of reagents using the vacuum manifolds. A small dumb-bell shaped glass insert, designed to rest below the NMR probe region, has been incorporated to aid mixing of reagents at initiation, and a constriction above the NMR tube has been added to enable efficient sealing of the tube after addition of reagents.

Aspects of the filling procedure of this reaction vessel have been expanded upon in Chapter 5, but this basically involves the *in vacuo* introduction of initiator in deuterosolvent, freezing, followed by addition of monomer/solvent on to the frozen initiator and subsequent

Fig. 2.8 (opposite):

(a) NMR reaction tube with constriction for *in vacuo* sealing and glass insert for ease of mixing.

(b) Large Scale Single Sample Reaction Vessel.



sealing of the tube. This tube was then kept frozen in liquid nitrogen until ready for initiation.

(b) Large Scale Single Sample Reaction Vessel

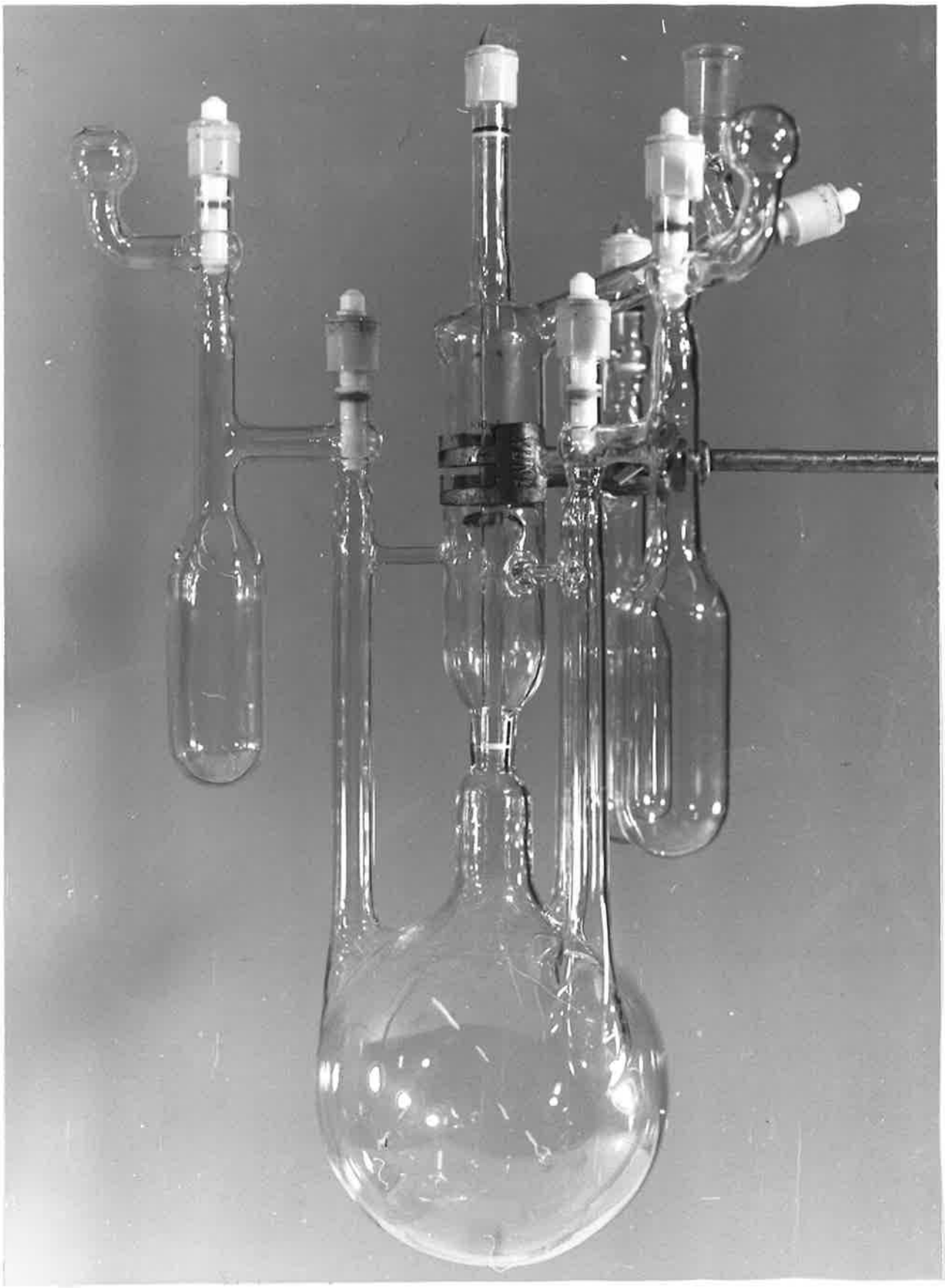
This reaction vessel (Fig. 2.8(b)) was the most frequently used and consists of two compartments, separated by a modified YOUNG compression joint, where the glass piston of an ordinary YOUNG tap has been extended to provide a central shaft traversing the upper compartment of the reaction vessel. This shaft culminates in a PTFE "O" ring seal in the narrow region between upper and lower compartments. The extended seal showed no sign of failure, even at a reaction temperature of 200K. The glass insert into the bottom compartment of the reaction vessel, suitable for the placement of a temperature probe, could be optionally used to monitor the temperature of the reaction mixture.

Monomer/solvent (THF/toluene) was introduced into the lower compartment of the reaction vessel and initiator in either THF or toluene into the upper portion, using the reagent dispenser manifold (Fig. 2.7).

(c) Multiple Sample Reaction Vessel

This vessel (Fig. 2.9) is identical to that of Fig. 2.8(b), except that side-arms have been added to the lower portion of the reaction vessel to enable decantation of samples of the reaction mixture into peripheral containers, followed by isolation from the main flask using a YOUNG tap. Termination of these samples was facilitated by

Fig. 2.9 (opposite): Multiple Sample Reaction Vessel



the addition of methanol from the small glass bulbs at the top of Fig. 2.9.

The importance of this reaction vessel lies with its ability to produce the same initiation condition for each sample, enabling a coherent examination of microstructure and molar mass to be made from the same reaction as a function of conversion.

(d) Delayed Addition Reaction Vessel

This reaction container (Fig. 2.10) has a third compartment added to accommodate an extra reaction component, to be added some interval after initiation of polymerisation. It was used intermittently to study the effect of delayed addition of THF and potential side products on polymerisations conducted in toluene.

2.9 Constant Volume Dispenser

Kinetic dilatometry studies, in particular, are reliant upon reproducible delivery of initiator solutions into the reaction vessel. Fig. 2.11 shows the dispenser used for constant volume additions of initiator solution into the reaction vessel. The initiator storage vessel is mounted on the upper B19 cone and this assembly attached to the reagent dispenser manifold (Fig. 2.7; far right), in addition to the appropriate reaction vessel. Initiator solution is run into the dispenser *in vacuo*, such that a constant volume is attained between the lower YOUNG tap of the dispenser and the lip of an outlet in an internally annealed tube. In this manner volumes of 11.0cm^3 (±3%; 25°

Fig 2·10 Delayed Addition Reaction Vessel

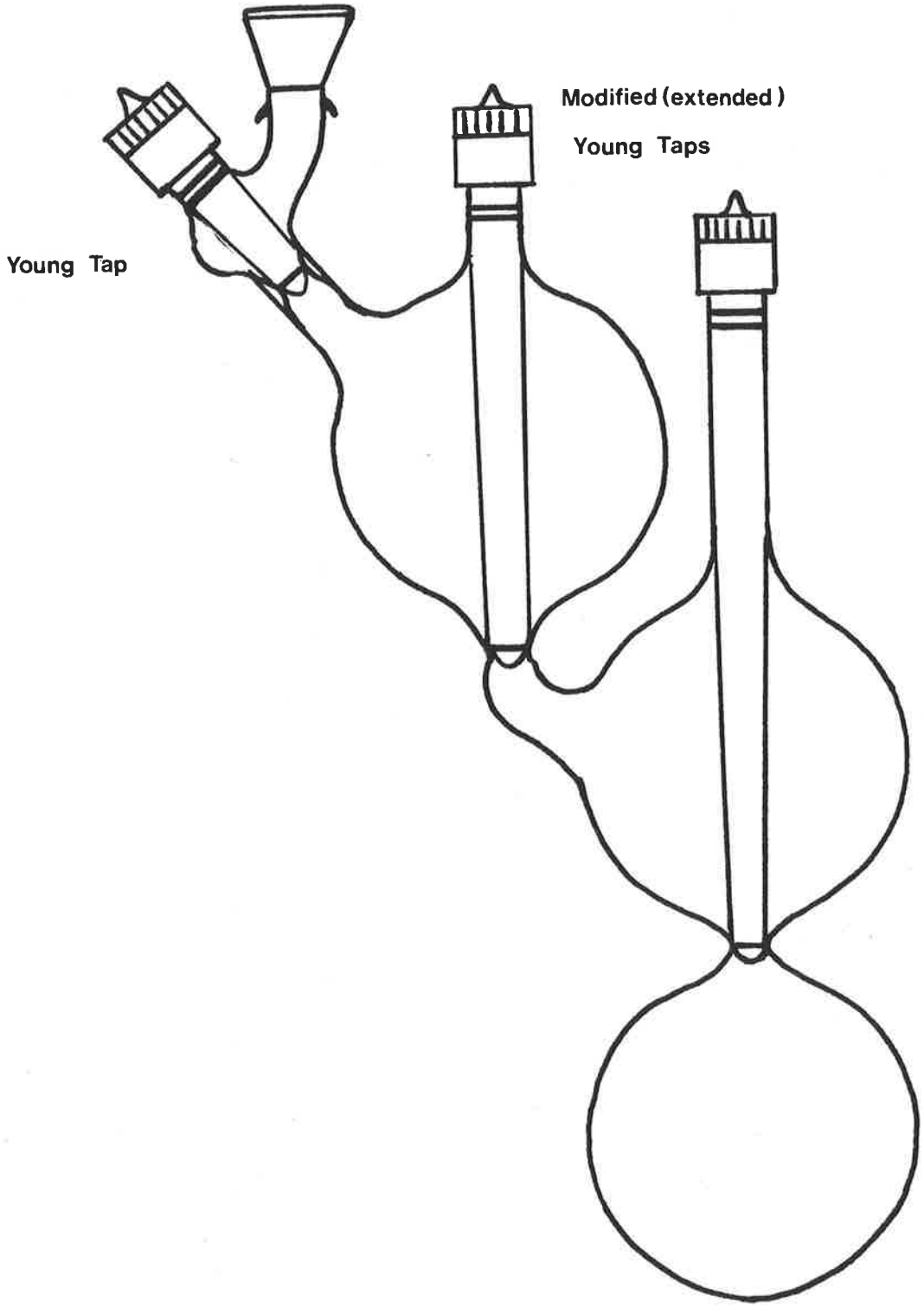
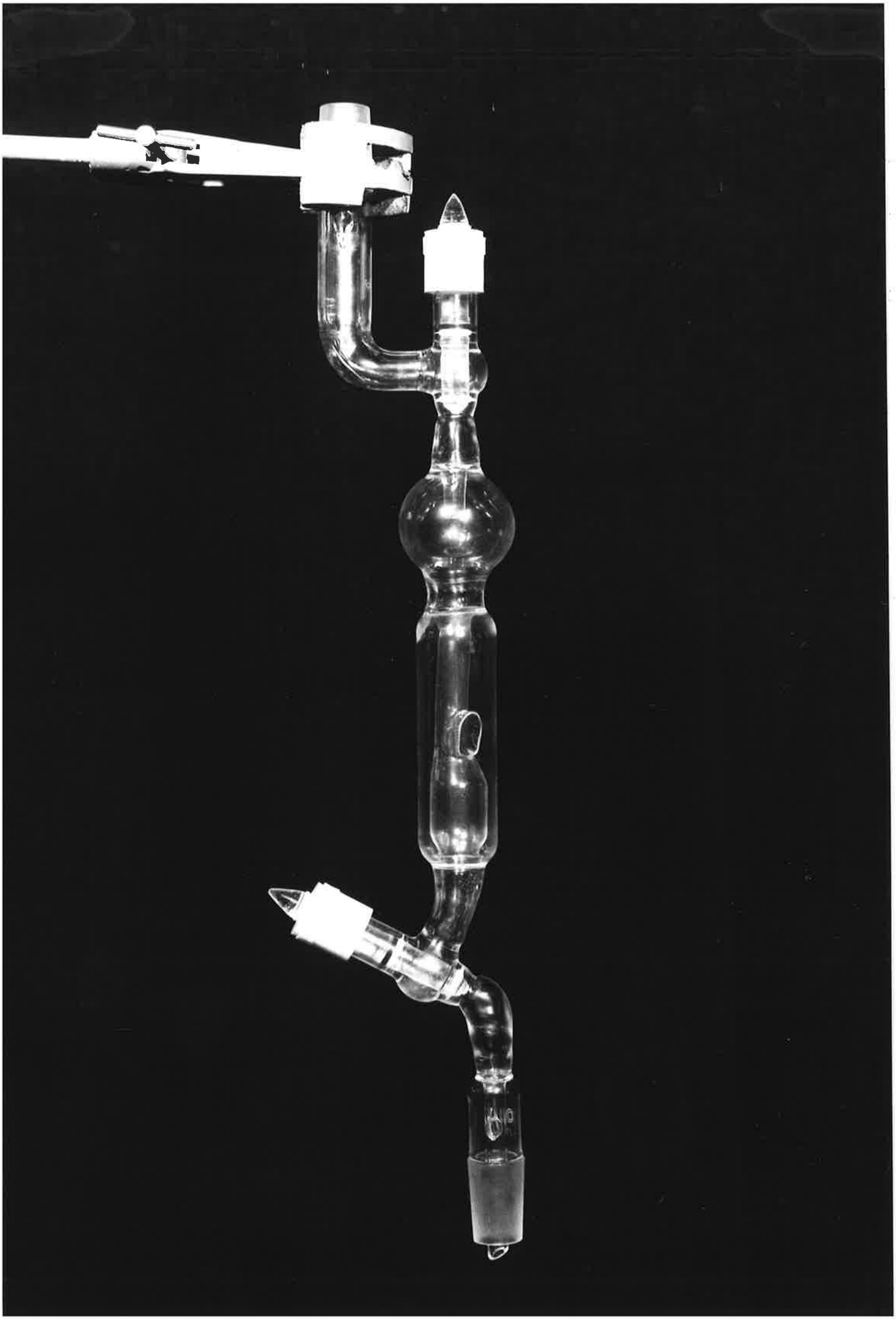


Fig. 2.11 (opposite): Constant Volume Dispenser

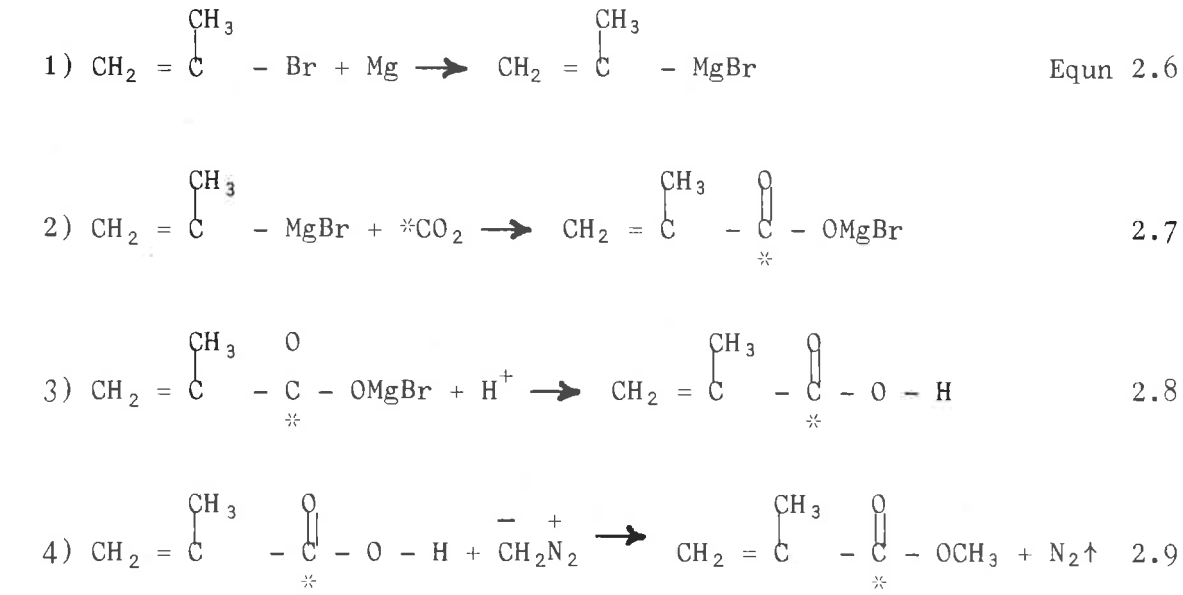


C) of initiator could be dispensed into the upper compartment of a reaction vessel.

2.10 ^{13}C Enrichment of MMA

Preliminary kinetic experiments using ^{13}C NMR were attempted using monomer enriched at the carbonyl carbon. This site of enrichment was chosen on the basis of a consideration of relative chemical shifts of monomer and polymer carbonyl resonances, impingement of solvent resonances on resonances associated with the site of enrichment, and spin-lattice relaxation times at possible sites of enrichment. This will be discussed fully in Chapter 5.

The reaction sequence used for enrichment was:



Equn 2.6

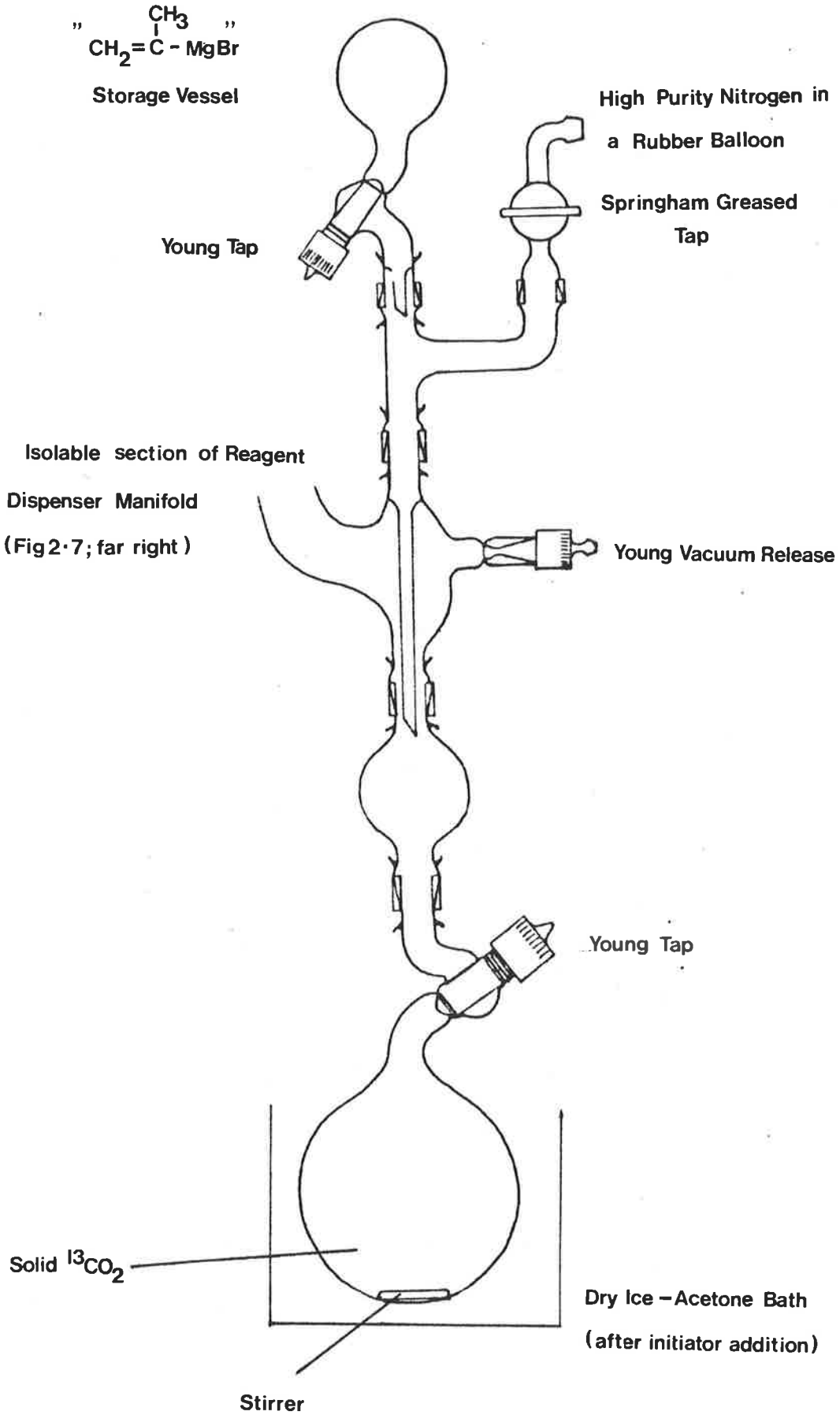
Equn 2.7

Equn 2.8

Equn 2.9

The bromide, 2-bromopropene, and magnesium turnings were purified in a manner analogous to those mentioned in 2.1(b) and 2.1(f) and the Grignard reaction was carried out in THF using the apparatus of Fig. 2.1. The Grignard reagent so formed was filtered, transferred to a storage vessel and degassed.

Fig 2·12 ^{13}C Enrichment Apparatus (MMA)



Enriched CO_2 (BOC; 91 atom per cent ^{13}C; 1 litre; 1 atmosphere) was transferred *in vacuo* to a one litre container with an attached YOUNG tap, and the apparatus for the second reaction step was assembled on the vacuum line as shown in Fig. 2.12. Carbon dioxide was maintained as a solid by immersion of the reaction vessel in liquid nitrogen, and the Grignard reagent prepared in step 1 was run *in vacuo* into the glass bulb above the YOUNG tap of the reaction vessel. At this stage the vacuum line was adjusted to positive pressure by allowing high purity nitrogen from the rubber balloon to enter the line, and the Grignard reagent was added to the reaction vessel. The liquid nitrogen bath was removed, replaced with a dry ice-acetone bath, and the reaction mixture stirred for 10 hours at -75° C. The resultant solution was acidified with ammonium chloride, and methylated in situ with diazomethane using standard procedures. Fractional distillation under reduced pressure yielded ^{13}C enriched monomer.

CHAPTER 3

3. THE PROPERTIES OF GRIGNARD REAGENTS IN SOLUTION

3.1 Introduction

The nature of Grignard reagents in solution is still a contentious question. Their discovery, by Grignard in 1900,[1] has been followed by some intensive examination. The postulate, by Schlenk and Schlenk,[2] concerning the existence of an equilibrium between a halogenated organomagnesium species, RMgX (X=Cl,Br,I), and the corresponding dialkyl/diaryl magnesium entity is well regarded, even today:

$$R_2Mg + MgBr_2 \underset{K_{Schlenk}}{\rightleftharpoons} 2RMgX \qquad \text{Equn 1.1}$$

Alternatively, Jolibois[3] has suggested the following equilibrium, with an unsymmetrical dimer being proposed.

$$R_2Mg + MgBr_2 \rightleftharpoons R_2Mg.MgBr_2 \qquad \text{Equn 3.1}$$

Equilibrium constants, calculated at various temperatures,[4] have reinforced the validity of the Schlenk equilibrium (Equn 1.1), with several parameters determining the position of this equilibrium:

(1) Temperature: Parris and Ashby[5] believe that at lower temperature the Schlenk equilibrium favours the dialkyl magnesium species. In this thesis, if the microstructure of pMMAs formed under the same solvent conditions are an indication of the nature of the initiator, then lower temperatures using the MsMgBr initiator favour less stereoregular polymer, showing

similarity to those produced using Ms_2Mg (refer to Chapter 4).

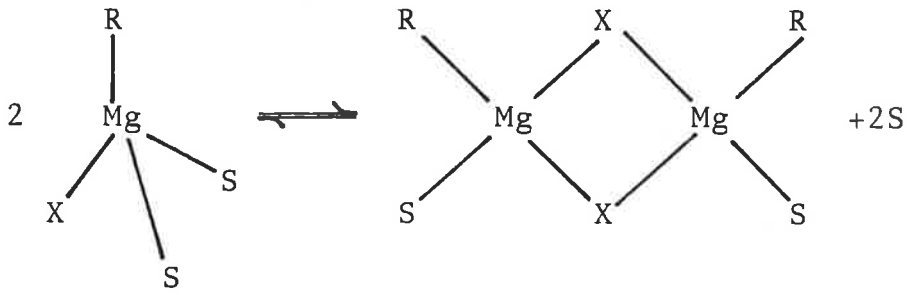
(2) Solvent: As an example, diethyl ether tends to favour the RMgX species to a greater extent than in higher polarity THF.[4]

(3) Halide: Solvent plays an important role in determining the magnitude of the halide effect, being less pronounced in THF than in diethyl ether.[4] In diethyl ether EtMgBr has K=480, while EtMgI has K > 630[4] at the same temperature.

(4) Alkyl/aryl group: This effect is again more pronounced in diethyl ether than THF.[4] In diethyl ether, for example:

PhMgBr has K = 55 while
EtMgBr has K = 480 under the same conditions.

The Schlenk equilibrium cannot be divorced from association equilibria, so that under conditions where these make a significant contribution they must be taken into account. Different states of association are believed[6] to be involved in alkyl lithium/hydrocarbon monomer reactions, and may be just as important in MMA polymerisations using Grignard reagents as initiatiors. In the case of these initiators it is normally assumed, on the basis of comparison with $Et_n Al_2 X_{6-n}$ (X=halide) systems,[7] that association occurs mainly through a double halide bridge, which is believed to be more stable than a double carbon bridge involving two Mg-C-Mg-two electron bonds:

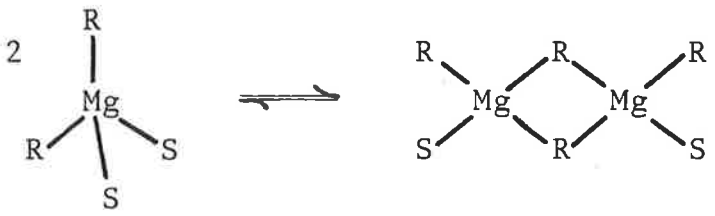


Equn 3.2

X = halide

Variation of the halide group produces a consequent variation in the tendency to associate. In diethyl ether, alkyl and aryl magnesium chlorides and alkyl magnesium fluorides remain dimeric over the whole concentration range examined.[8] Bromo and iodo magnesium alkyls tend to generally favour greater rate of change in association as a function of increasing concentration under the same conditions.[8] In THF, alkyl magnesium chlorides, bromides and iodides remain monomeric over a wide concentration range, while alkyl magnesium fluorides are dimeric[8] (due to the strong bridging ability of the fluoride, basic THF is prevented from cleaving the bridge).

It has been claimed[8] that in ether solvents, alkyl/aryl magnesium halides show a greater tendency to associate than their dialkyl/diaryl counterparts. Association through bridging hydrocarbon groups is not precluded, however, with the less bulky the alkyl/aryl entity the more likely the formation of associates e.g., dimethyl magnesium is dimeric in diethyl ether[8] at reasonably low concentrations, indicating bridging methyl groups:



Equn 3.3

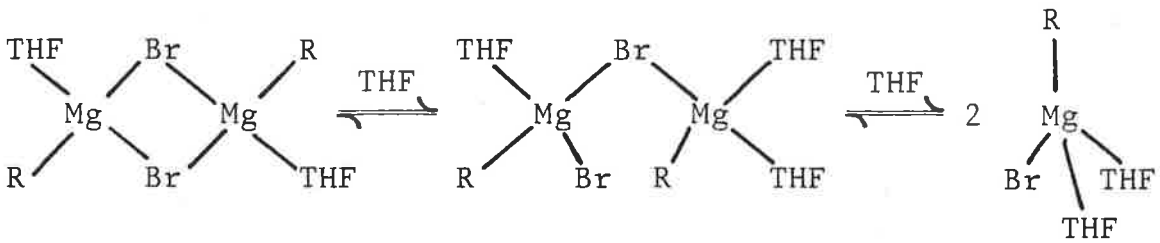
R = Me

S = Et_2O

In THF, dialkyl/diaryl magnesium compounds remain monomeric over a wide concentration range. [8]

The implications of the alkyl/aryl bridging system are of importance in an NMR study of these species. Since the alkyl/aryl group is involved in an electron deficient bond, nuclei in this environment are deshielded and should appear in a lower field position compared to the alkyl/aryl group of the monomer. Thus downfield shifts appearing in dialkyl/diaryl magnesium compounds are assignable as associates (not necessarily dimers). The non-bridging alkyl/aryl groups appearing at terminal magnesium atoms of associates may not have chemical shifts at much variance from those of monomeric dialkyl/diaryl magnesium species. In ^{13}C NMR studies of both Grignard and dialkyl/diaryl magnesium species described in this thesis, no splitting of the upfield alkyl/aryl resonance could be observed, which is consistent with the observation that the terminal resonance of associates and the monomer alkyl/aryl resonances could not be resolved at 22.62MHz. Although considerable study [8] has been carried out on the association of alkyl/aryl magnesium halides and their equivalent dialkyl/diaryl analogues, particularly in Lewis base solvents, the behaviour of these compounds in non-polar solvents, and especially at lower temperatures, is less well defined.

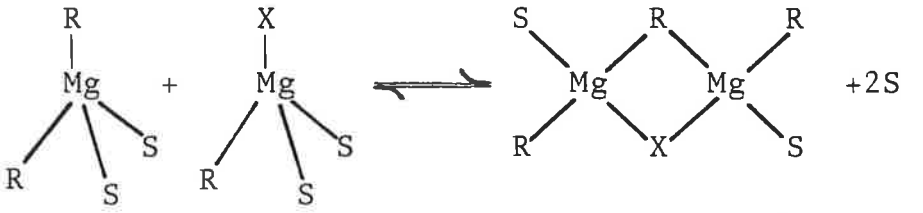
Such aspects represent vital parameters in these investigations, where highly stereoregular polymers have been produced at moderately low temperatures in non-polar media using aryl magnesium bromides. Examination of dialkyl/diaryl magnesium compounds in such solvents at room temperature have concluded that di-n-pentyl[9] and di-sec-butyl magnesium[10] compounds are dimeric in benzene. If complexing solvent is present, in equivalent amounts or more, then R_2Mg compounds appear to exist[13-17] as monomers, dimers or equilibrium mixtures of both, depending on the concentration of the electron donor and its nucleophilicity. Westera and co-workers[18] have examined the degree of association of alkyl magnesium bromides in the presence of an electron donor in benzene using Van Vulpen's method (a vapour pressure technique). They concluded, in the case of ethyl magnesium bromide, that when one equivalent of THF was present in benzene, dimers were predominant, even though the initial concentration of active bonds was only .02M. Addition of THF saw rapid disruption of these associated species, which they postulated to occur in the following manner:



Equn 3.4

The presence of mixed halo/hydrocarbon bridges in Grignard reagent solutions (see below) has no experimental

basis, although, given the existence of halo and alkyl/aryl bridges there is no obvious reason why they should be totally precluded:



Equn 3.5

In the terBuMgX/THF systems (X=Cl,Br), studied by NMR in this laboratory by Mair,[19] the methyl ^{1}H resonance at 90MHz was seen to be split into 4 distinct proton environments at 290K, which were ascribed to the following possible species:

(1) ^{1}terBuMgX $(THF)_2$

(2) $^{2}terBu_2Mg$ $(THF)_2$ X = Cl,Br

(3) (THF)^{3}terBuMg^{4}terBu MgBr(THF)
X

with (3) representing an intermediate dimer between (1) and (2). Implicit in this assignment is the assumption that terminal and bridging terBu groups of the associates of (2) are indistinguishable from environments (3) and (4) of the dimer (3). The observation of 4 peaks in this system was found to be dependent on the active bond concentration and the X/RMg ratio at 90MHz resolving power. Ashby,[5] using a 60MHz spectrometer, observed only two broadened peaks in this system at this lower resolution.

Implicit in the above discussion has been the assumption that the geometry of the alkyl/aryl magnesium species in the Schlenk equilibrium is tetrahedral or distorted tetrahedral in nature. The origins of this assumption lie chiefly with crystallographic data where, for example, PhMgBr has been observed[20] as a tetrahedral dietherate moiety. This may not be necessarily so in solution, with Driessen and Heijer[21] having isolated a six co-ordinate species, $Mg(THF)_6(SbCl_6)_2$ - the large counter ions being required to stabilise the weakly co-ordinating THF ligands. However, all reference material cited on alkyl/aryl magnesium compounds in this thesis has assumed 4-co-ordinate geometry, a practice continued here.

Study of the Grignard reagent, isobutyl magnesium bromide/THF, by Hagias[22] has shown that the Schlenk equilibrium and concurrent associative processes are dependent on the active bond, C-Mg, concentration and the bromide to active bond ratio. This serves to reinforce the necessity of defining both of these parameters in any NMR discussion of Grignard reagent systems, as well as ensuring that they are defined when these reagents act as polymerisation initiators. An ^1H NMR study of the isobutyl magnesium bromide system[22] has revealed the following:

(1) For a Grignard solution characterised by parameters [RMg]=.4M and [Br]=.3M, observation of the methylene resonance reveals a pair of doublets with a coalescent temperature of 285K, indicating the onset of slow exchange between R_2Mg and RMgX.

(2) With [RMg]=.4M and [Br]=.1M, the methylene signal indicated, in addition, a low field signal matching almost exactly the field position of an associated bridging R group of di-isobutyl magnesium.

(3) For the di-isobutyl magnesium system a simpler pattern of methylene doublets emerged. At high concentration, [RMg]=.70M and [Br]=0, a predominant downfield doublet was evident - probably due to deshielded, bridging isobutyl groups, with a much less predominant upfield signal due to monomeric entities and terminal isobutyl groups of associates. At lower concentrations, [RMg]=.27M and [Br]=0, a reversal in intensities with respect to the methylene doublets was noted, with the high field signals (monomeric and terminal R groups of associates) predominating over the low field doublet (bridging R groups of associates). This is consistent with a monomer species favoured at low concentration.

(4) Thermodynamic evidence, based upon variable temperature ^{1}H NMR studies of the isobutyl magnesium bromide/THF system, indicates that the Schlenk equilibrium proceeds, in the direction of dialkyl magnesium, with a nett increase in solvation (Equn 1.1), consistent with an observed loss of entropy. The extra solvation of $MgBr_2$ (Equn 1.1) appears to be a controlling factor in this system, as is also the case of the terBuMgCl system examined by Parris and Ashby. [2]

The ensuing discussion on 6-membered ring Grignard reagents serves to substantiate the theories to date.

3.2 Experimental

As detailed in Chapter 2, Grignard reagents were prepared under high purity nitrogen from alkyl/aryl halides and finely divided magnesium turnings in THF. In this study Grignard reagents have been prepared from the following cyclic bromides: Bromobenzene (PhBr), bromomesitylene (MsBr), and cyclohexyl bromide (chexBr). Corresponding dialkyl/diaryl species were produced by the addition of 1,4 dioxane to these Grignard reagents. In an attempt to secure complete removal of $MgBr_2$ as the bis-dioxane complex, the molar addition of dioxane was always such that it was in slight excess of the molar quantity of bromide present, as determined by Volhard's method (Chapter 2). Some difficulty was experienced in the total removal of bromide from the MsMgBr system. When a large excess of 1,4 dioxane was added in some preparations, Volhard's method predicted the presence of bromide in slight excess of inherent experimental errors involved in Volhard's procedure. This is in agreement with other workers[19,23] who have viewed 1,4-dioxane as sometimes unreliable for the total removal of halide. No such problems were associated with the PhMgBr system where bromide removal was achieved within the level of sensitivity of the Volhard test.

Solvent replacement procedures were often used to examine the nature of Grignard reagents in non-polar toluene solution, which involved evaporation of THF from the alkyl/aryl magnesium compound, followed by <u>in vacuo</u>

decantation of toluene. Such a procedure introduced another parameter into the discussion of Grignard reagents; the question of how the extent of de-etheration affects the constitution of the Grignard or dialkyl/diaryl species. Extensively heat treated PhMgBr systems (see later), prepared in a similar manner to Tsvetanov,[24] represent the extreme case of de-etheration procedures. Under these circumstances precipitates arise, on replacement of solvent THF with toluene which, while rich in bromide, retain a small active bond content. The supernatant toluene solution is therefore rich in active bonds and deficient in bromide. Work done by Mair[19] and the author on the nature of Grignard's reagents in solution, as reflected by the nature of pMMA formed using the organomagnesium compounds as initiators, shows that THF is vital for the uptake of bromide. For the PhMgBr system, provided the mole percentage of THF in toluene lies within 5-10%(GLC), then the bromide to active bond ratio will remain constant, within error, between different batches of initiator. Molecular weight distributions and microstructures of pMMAs formed using these different batches as initiators for polymerisation are also quite similar. If the PhMgBr system is more extensively heat treated than this, a bromide deficient initiator solution results on replacement of THF with toluene, with pMMAs formed using this initiator having, in particular, tacticities quite different from those formed using initiator with 5-10%THF. The microstructure and molar mass distribution variations are thus sensitive to changes in the nature of the initiator/initiator solvent.

3.2.1 Aryl/Alkyl Magnesium Solutions for the NMR Experiment

As aryl/alkyl magnesium compounds are both air and moisture sensitive, it is essential that experiments be carried out *in vacuo* in sealed NMR tubes. It has been acknowledged [25] that atmospheric oxygen can produce alkoxides capable of fast exchange reactions at the magnesium centre.

NMR tubes (10mm) were prepared in the following manner:

(1) RMgX/THF/d_8-THF (internal lock) solutions were prepared by dilution of the stock solution to the required concentration with THF. The active bond and bromide content were determined at this stage. This was then decanted *in vacuo* into an NMR tube attached to a YOUNG tap (similar to the one shown on the reaction kinetics NMR tube (Fig. 2.8(a))). Some THF was evaporated from the NMR tube and replaced with an equivalent amount of d_8-THF (LAH dried) by distillation. All material added to the tube was checked by weighing and concentrations recalibrated accordingly. The contents of the tube were then frozen and the tube sealed at the constriction while drawing a vacuum of 10^{-3}-10^{-4} Torr.

(2) R_2 Mg/THF/d_8-THF: as for (1) above but with 1,4 dioxane added and filtration prior to decantation into the NMR tube.

(3) RMgX/Toluene/d_8 - Toluene: in most cases this was prepared by gentle de-etheration, to provide a final mole per cent THF of 5-10%. These solvent replacement procedures were often accompanied by some precipitate, which was filtered from the solution after the addition of dry toluene. Bromide and active bond concentrations were determined at this stage, followed by decantation of the solution in vacuo into the NMR tube. After d_8-toluene solvent replacement, the tube was sealed and concentrations recalibrated as in (1).

(4) R_2 Mg/Toluene/d_8 -Toluene: same as for (3) above, except that the de-etheration was carried out on R_2 Mg/THF.

3.2.2 Choice of Nucleus for NMR Investigation

All NMR spectra recorded here were produced on either BRÜKER HX90E or BRÜKER WP80 Fourier Transform spectrometers using 5mm (^{1}H-HX90E) or 10mm (^{13}C-HX90E, WP80) probes. Both spectrometers possessed facility for broad band decoupled and off-resonance decoupled experiments, which were used extensively for ^{13}C analysis of Grignard reagents. Variable temperature studies of these reagents were completed using the HX90E spectrometer solely.

Inherent difficulties arise in a discussion of ^{1}H spectra of many six membered ring systems. Extensive long-range coupling between protons on the ring present an almost indecipherable picture of the Grignard reagent system. Such a problem could have been remedied by deuter-

ating selected sites around the ring - a proton study has been achieved for the PhMgBr system by other workers[26] at ambient temperature using selective deuteration around the ring. Clearly, a study of the Grignard reagent system would most effectively be observed by examination of the site adjacent to the magnesium atom and yet aryl magnesium compounds lack protons here.

Resonance studies using the ^{13}C nucleus are, however, suitable for the study of these aryl magnesium compounds. Most polymerisations were carried out using these initiators and, therefore, they have been extensively studied using ^{13}C NMR. Only a cursory examination, using ^{1}H and ^{13}C NMR, has been used here for the chexMgBr system.

Studies of aromatic Grignard reagents using ^{13}C NMR are not without problems. Since C(1), attached to the magnesium atom, has no attached protons, spin-lattice relaxation of this nucleus using a Pulsed Fourier Transform technique may present problems (ideally we require the magnetisation vector to return to the Z' axis via spin-lattice relaxation before initiation of the next pulse). To diminish this effect smaller pulse angles were used (ca.20°) and a large number of accumulations taken. Solution concentrations (with respect to active bond content) were maintained in the vicinity of .4M-.6M, and 10mm tubes were employed to maximise the amount of material in the probe region. The field strengths of the two spectrometers are:

BRÜKER HX90E	^{1}H : 90MHz
	^{13}C : 22.62MHz
BRÜKER WP80	^{1}H : 80MHz
	^{13}C : 20.1 MHz

3.3 Results and Discussion

3.3.1 A Study of Extensively De-etherated PhMgBr in d_8-Toluene

Work carried out by Tsvetanov[24] using Grignard reagents as initiators in the polymerisation of acrylonitriles produced a novel method for the preparation of heat treated Grignard initiators. On the basis of this work an extensive de-etheration procedure was carried out on stock PhMgBr/THF([PhMg]=.78M; Br/PhMg=.95), involving the prolonged heating of this initiator for 10 hours at 80° C and .001 Torr. Replacement of solvent THF with toluene produced a precipitate which was filtered in vacuo. On the occasions on which this procedure was performed, a determination of the active bond and bromide content consistently gave the following result:

$$\frac{[Br]}{[PhMg]} = .38 \pm .05$$

When the precipitate from the de-etheration was redissolved, the number of moles of active bonds in this precipitate, together with the number of moles of active bonds taken up by toluene, equalled (±5%) the total number of active bonds initially present. Extensive heat treatment, therefore, did not deactivate the initiator in any way.

An ^1H NMR study of extensively de-etherated PhMgBr in d_8-toluene (99.7%) was done, with a representative spectrum appearing in Fig. 3.1. It is obvious that despite extensive heating, residual THF is still present. This is in agreement with other workers[27,28] who noted that Grignard reagents tenaciously retain ether. Note the absence of fine structure on the residual α methyl proton resonance of toluene is well resolved, indicating optimal shimming of the spectrometer.

In addition, an ^1H NMR spectrum of d_8-toluene was produced and a "ratio of undeuteration"

$$\text{i.e.,} \quad \frac{\text{undeuterated aromatics (toluene)}}{\text{undeuterated methyl (toluene)}}$$

was evaluated from integrated areas. From the integrated area of the residual α CH_3 peak in extensively de-etherated PhMgBr/d_8-toluene a corrected area in the aromatic region could be evaluated, using the "ratio of undeuteration", corresponding to aromatic protons associated with the aryl magnesium compound (i.e., minus the effect of residual aromatic protons in d_8-toluene). From this a value for the ratio, THF molecules: PhMg units, could be calculated:

$$\text{Ratio} \qquad \text{THF} \quad : \quad \text{Phenyl}$$

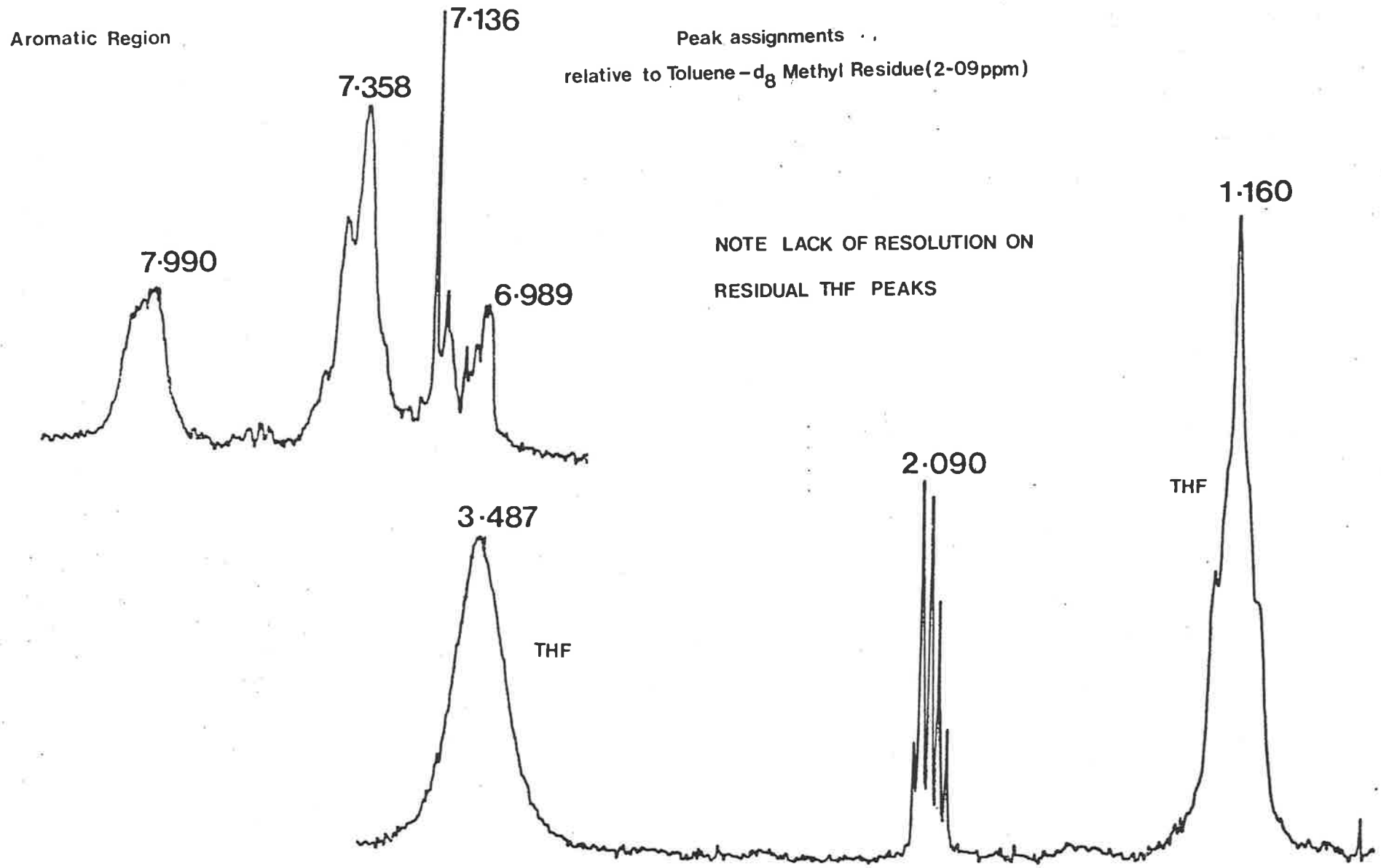
$$\frac{\text{Average Area } \alpha, \beta \text{ THF}}{4} \quad : \quad \frac{\text{Corrected Aromatic Area}}{5}$$

For extensively de-etherated PhMgBr/d_8-toluene the following quotient was obtained:

$$\frac{\text{moles}_{\text{THF}}}{\text{moles}_{\text{Phenyl}}} = \mathbf{0.8} \pm 20\%$$

Fig 3·1 90 MHz ^1H Spectrum of Extensively De-etherated

Phenyl Magnesium Bromide/Toluene-d_8

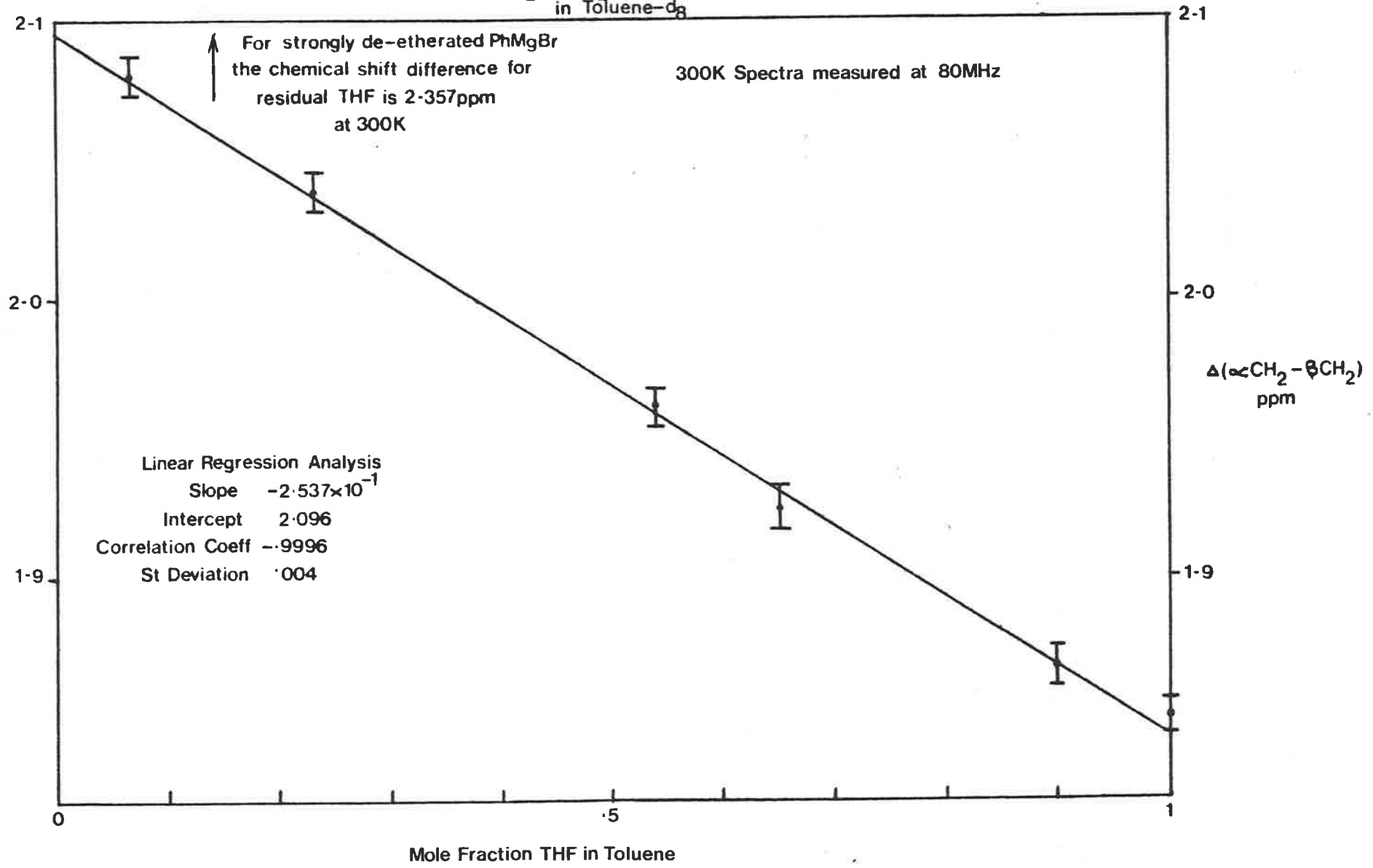


The broadening and loss of resolution of the THF resonances seemed suggestive of an exchange reaction between free and bound forms of THF, so a variable temperature ^1H NMR study was carried out in an effort to alter the exchange rates. However, little change in resolution was observed during this procedure. The broadening must be due to factors other than exchange, or the exchange process is observed but has a low activation energy.

Fig. 3.2 shows a plot of internal chemical shift differences between α and β THF peaks as a function of mole fraction THF in d_8-toluene.[29] If the line of best fit is extrapolated to infinite dilution of THF, the maximum internal chemical shift difference measures 2.096ppm ($\pm$.004ppm). The internal chemical shift difference for extensively de-etherated PhMgBr/d_8-toluene is 2.357ppm - a discrepancy of about 23Hz at 90MHz field strength.

Extensively de-etherated $MgBr_2$/d_8-toluene, formed in an analogous manner to the Grignard reagent, was also examined subsequent to its formation via the Grignard reaction between 1,2-dibromoethane and magnesium in THF (refer to Chapter 2). It was sparingly soluble in toluene, with the filtrate from a saturated solution giving a bromide content of .01$_5$M($\pm$20%). An ambient ^1H NMR examination revealed that some THF still remained with an internal chemical shift difference of 2.078ppm - quite different to that observed in extensively de-etherated PhMgBr/d_8 - toluene. The internal chemical shift difference is close to that of a THF/d_8-toluene mixture with $\chi_{THF/tol} \sim .07$

Fig3·2 Plot of $\Delta(\alpha CH_2 - \beta CH_2)$THF in ppm for various mole fractions in Toluene-d_8



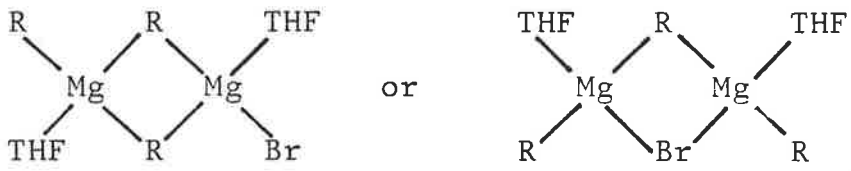
(Fig. 3.2), suggesting that it is not strongly co-ordinated. Spin-spin coupling of the THF resonances was clearly evident, in contrast to the extensively de-etherated PhMgBr.

If the following are assumed to be true:

(1) That remaining THF in extensively "de-etherated" PhMgBr is strongly bound.

(2) That little free magnesium bromide remains in solution based upon the very low solubility of extensively de-etherated $MgBr_2$.

then two possible permutations for the structure of this initiator in solution, consistent with Br/PhMg = .38±.05 and THF/Ph = 0.8±20%, are the dimer associates:



3.3.2 ^{13}C Spectra of Alkyl/Aryl Magnesium Reagents

3.3.2.1 General Comments

A discussion of the ^{13}C spectra for aryl and cyclohexyl magnesium systems is pre-empted by the following observations:

(1) Where these reagents have been studied in THF, peak assignments (in ppm) have been taken relative to the β THF resonance, taken as 25.30ppm. This assignment has been made independent of temperature, and as such any peak assignments made relative to this remain

approximate, until such time as the relationship between the chemical shift of the β THF carbon and TMS, as a function of temperature, is examined.

(2) Where these reagents have been studied in toluene as the predominant solvent species, peak assignments have been made relative to the methyl carbon of toluene, taken as 20.40ppm. As in (1) above, chemical shift data will not be strictly relative to TMS until further study is undertaken.

(3) In contrast to butyl magnesium systems studied in this laboratory,[19] the phenyl and mesitylene systems may, during the formation of the Grignard reagent, give rise to relatively non-volatile side products. It has been acknowledged for some time[30] that the formation of Grignard reagents involves the formation of alkyl/aryl radicals, and as such radical coupling reactions forming diphenyl and dimesitylene represent possible side reactions in Grignard synthesis. They did not appear to exist in measurable amounts in the above systems. However, trace amounts of benzene and mesitylene were observed in the approximately 1M stock solutions of Grignard reagents in THF (1 mole per cent; GLC). Two possible reasons for the existence of these compounds can be offered:

(a) Although stringent conditions were maintained during the formation of organomagnesium compounds, infrequent contact with trace amounts of high vacuum grease was unavoidable. Proton abstraction from the

small amount of water in this grease may be responsible for the presence of benzene and mesitylene.

(b) Okubo[31] noted that, in the reaction of benzyl magnesium chloride with ketones, the benzyl radical was produced and was capable of abstracting protons from solvent THF. This may also occur in the Grignard synthesis.

3.3.3 The ^{13}C Spectra of Phenyl Magnesium Systems

Phenyl magnesium systems studied are depicted in Fig. 3.3, measured at 300K. Due to the uncertainty in the effect of bromide on the spectra obtained, both active bond and bromide contents have been stated for each system.

A comparison between Fig 3.3A and Fig. 3.3B shows a feature common to all the phenyl magnesium systems studied: a marked downfield shift of the C(1) carbon resonance from 122.29ppm (C(1)-Br) to 167.07ppm (C(1)-Mg) for the Grignard reagent (Fig. 3.3B). Off resonance decoupling experiments have verified that the low field signal in Fig. 3.3B is due to the C(1)-Mg site. Peak assignments relative to the position on the aromatic ring are (Fig. 3.3B):

Table 3.1:

ppm	Origin of Resonance
167.07	C(1)-Mg
140.41	C(2,6)-ortho
124.80	C(3,5)-meta
125.25	C(4)-para

These assignments are in accordance with work carried out by Jones.[32] Carbon chemical shifts have been shown by

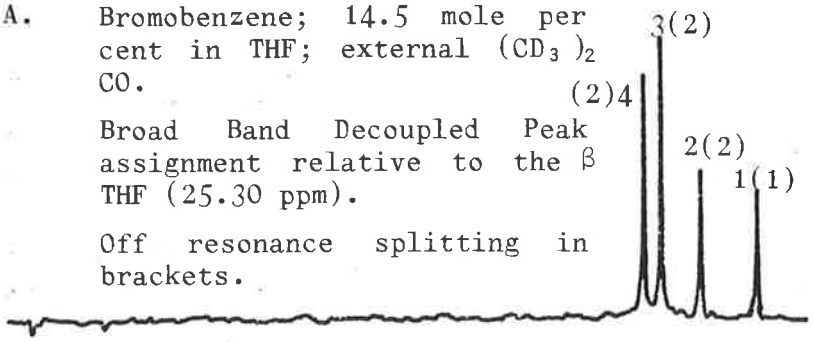
Fig. 3 .3: ^{13}C (20.1MHz) Spectra of the Phenyl System

300K

A. Bromobenzene; 14.5 mole per cent in THF; external $(CD_3)_2CO$.

Broad Band Decoupled Peak assignment relative to the β THF (25.30 ppm).

Off resonance splitting in brackets.



	ppm	Origin
1.	122.29	C(1)-Br
2.	126.84	p C
3.	130.00	m C
4.	131.40	o C

B.

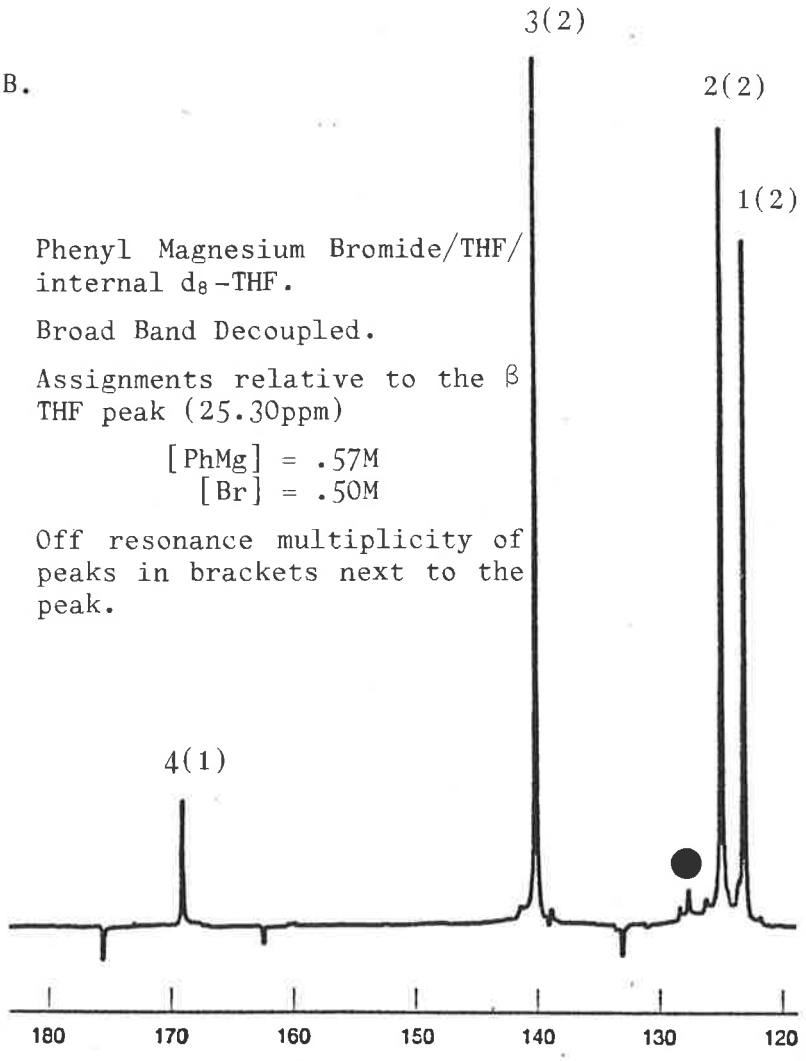
Phenyl Magnesium Bromide/THF/ internal d_8-THF.

Broad Band Decoupled.

Assignments relative to the β THF peak (25.30ppm)

[PhMg] = .57M
[Br] = .50M

Off resonance multiplicity of peaks in brackets next to the peak.



	ppm
1.	124.25
2.	124.80
3.	140.41
4.	167.07

The region denoted by a black dot infers the presence of trace amounts of benzene.

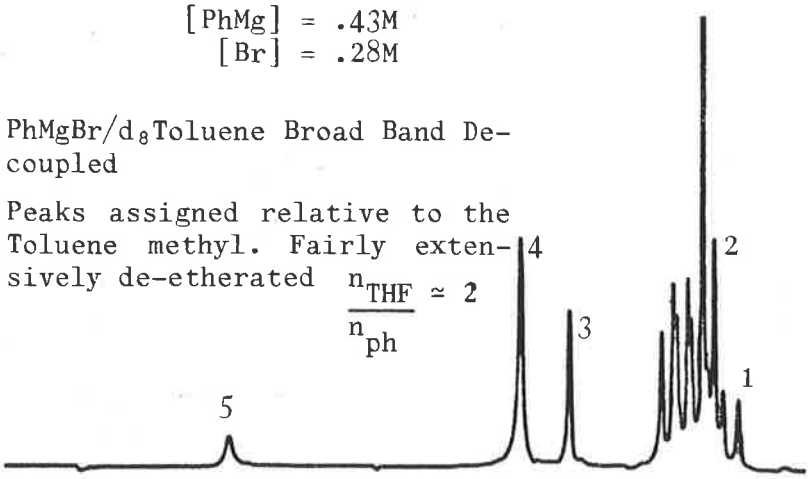
Fig. 3.3 (cont'd): ^{13}C (20.1MHz) Spectra of the Phenyl System (cont'd).

C.

[PhMg] = .43M
[Br] = .28M

$PhMgBr/d_8$Toluene Broad Band Decoupled

Peaks assigned relative to the Toluene methyl. Fairly extensively de-etherated $\frac{n_{THF}}{n_{ph}} \simeq 2$



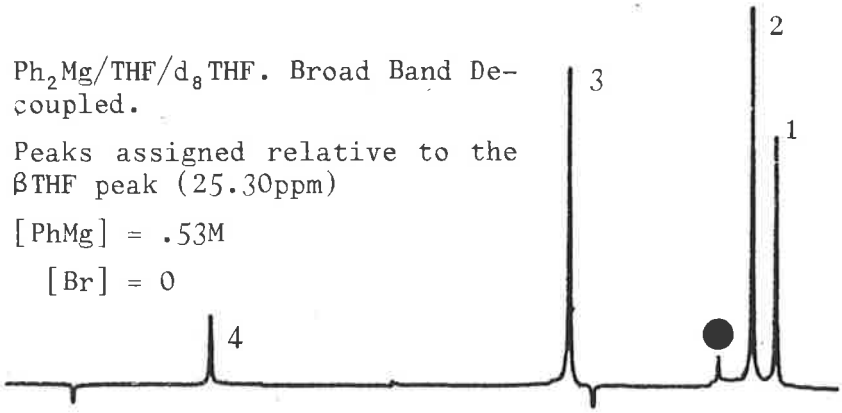
ppm
1. 124.07
2. 126.01
3. 137.67
4. 141.68
5. 165.31

D.

$Ph_2Mg/THF/d_8THF$. Broad Band Decoupled.

Peaks assigned relative to the βTHF peak (25.30ppm)

[PhMg] = .53M
[Br] = 0



ppm
1. 123.62
2. 125.38
3. 140.39
4. 168.99

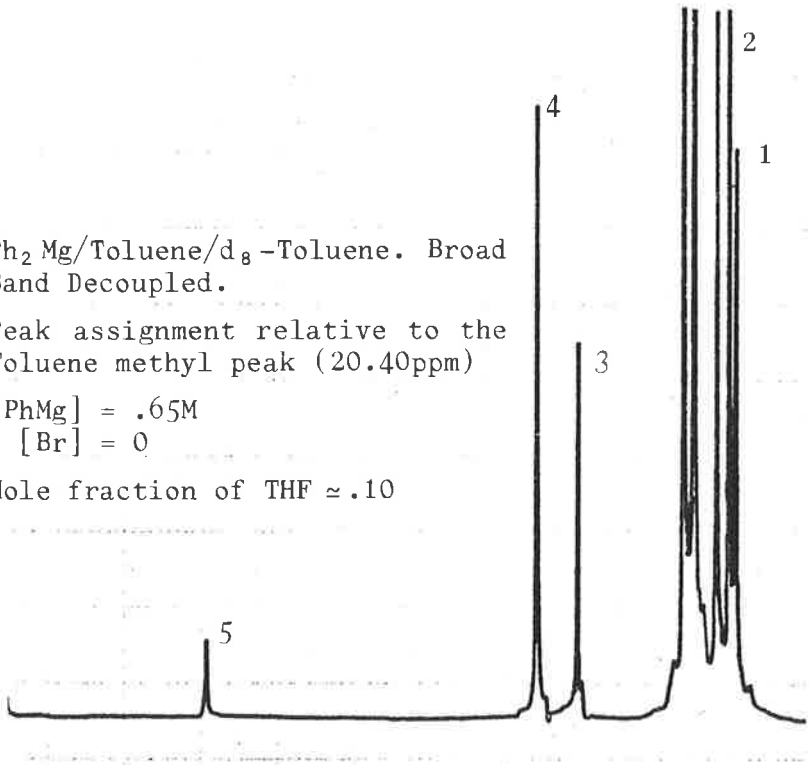
E.

$Ph_2Mg/Toluene/d_8$-Toluene. Broad Band Decoupled.

Peak assignment relative to the Toluene methyl peak (20.40ppm)

[PhMg] = .65M
[Br] = 0

Mole fraction of THF ≃ .10



ppm
1. 124.25
2. 124.80
3. 137.00
4. 140.41
5. 167.07

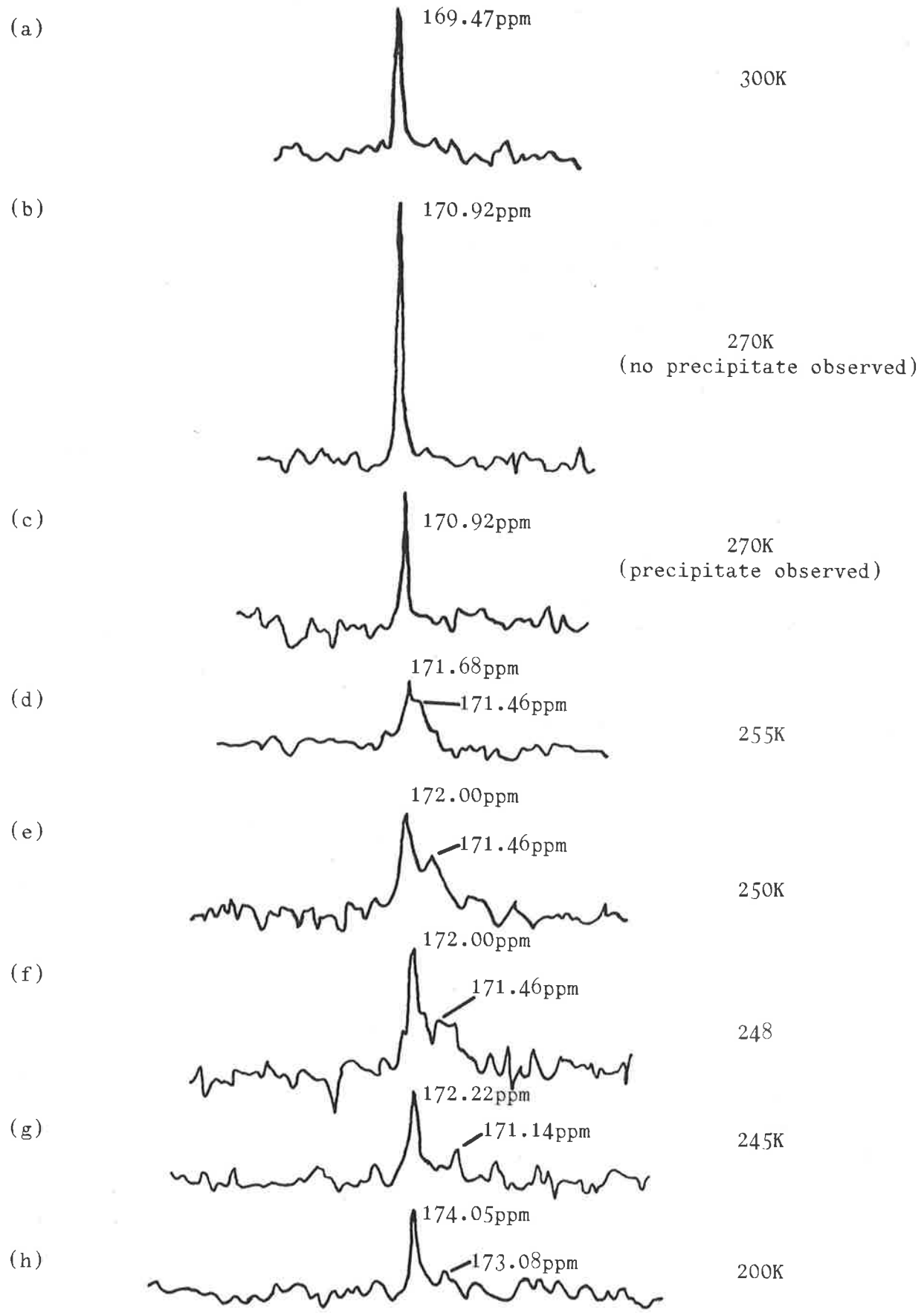
Karplus and Pople[33] to be dominated by a paramagnetic screening term in the Saika-Slichter equation.[34] In conjunction with this, Jones[32] has noted that, relative to benzene (128.7ppm), the C(1) and C(2,6) carbons are deshielded, and has interpreted these observations as indicating the presence of the phenyl carbanion, although it was noted that these species probably existed as solvated aggregates.

Fig. 3.3C, where prolonged heating procedures have been applied to the Grignard reagent, shows some anomalies. Despite optimum spectrometer characteristics, line broadening of some peaks (4 and 5; in particular 5) is seen. Whether this represents a coalescence phenomenon between two or more chemically distinct sites is speculative and is further confused by variable temperature observations, considered later in this chapter (Fig. 3.5), where the 270K line width narrows with respect to that of Fig. 3.3C, without showing any evidence of a two(or more)-site exchange process. This phenomenon may arise as a consequence of hidden partner broadening, which has been noted in some exchanging systems[35] (see later; Section 3.3.3.2).

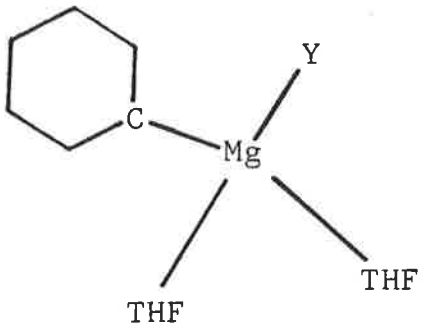
3.3.3.1 Variable Temperature Study of PhMgBr/THF/d_8-THF

A variable temperature NMR study at 22.62MHz was made of the PhMgBr/THF/d_8-THF system, with active bond and bromide contents as indicated in Fig. 3.3B. Temperature effects for the C(1)-Mg site are indicated in Fig. 3.4, which shows the presence of a rapid exchange process occurring at high temperatures with consequent narrow line

Fig. 3.4: ^{13}C (22.62MHz) Spectra of C^1-Mg for $PhMgBr/Ph_2Mg/THF/d_8THF$
Assignments relative to β THF (25.30ppm)



width, grading to a coalescence temperature at about 255K. Two sites are evident at lower temperatures under conditions of slow exchange between these states. It is unlikely that an observation of isomers, resultant from whole-ring rotations of the phenyl group, is being seen in this situation, principally because the phenomenon is being observed at C(1)-Mg, which is spatially invariant in the tetrahedral system below:



An ^{1}H NMR study of the terBuMgBr system by Mair[19] has similarly concluded, on the basis of integrated intensities of peaks under conditions of slow exchange, that the origins of exchange lie with effects other than rotational conformations of the molecule.

A more realistic interpretation lies in a discussion of the entity Y in the above diagram i.e., an acceptance of the postulated existence of the Schlenk equilibrium, with Y representing either a phenyl or a bromide group. Evans and Khan,[36] using ^{19}F resonance spectroscopy of pentafluorophenyl magnesium bromide in diethyl ether, observed two parafluoro triplets at 22°C which coalesced to a single triplet at 94°C. Additions of bis-pentafluorophenyl magnesium to this system revealed that the high field signal corresponded to the diaryl magnesium entity,

with the low field signal correlating with aryl magnesium bromide. It will be shown in a later section on the mesitylene magnesium bromide system that, at least for the C(1)-Mg resonance, a similar observation holds. Mesitylene and phenyl magnesium systems are thought not to differ in this regard. For the terBuMgBr system[19] the opposite effect has been shown to exist.

Consideration of two other factors is required in Fig. 3.4:

(1) Intermittent precipitation was sometimes noted. However, probably due to a supersaturation effect, it was possible to produce the spectra of Fig. 3.4 in the absence of precipitation. Spectra 3.4(b) and 3.4(c) show that precipitation primarily causes a loss of signal intensity.

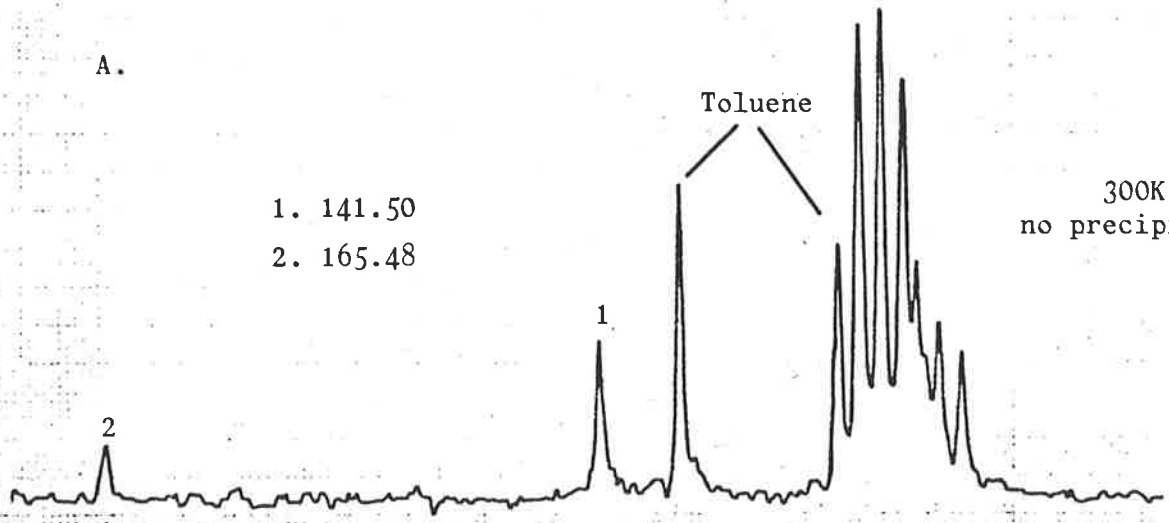
(2) At low temperatures there is an apparent broadening of the upfield signal associated with the C(1) of diphenyl magnesium, perhaps indicating the likelihood of a second coalescence involving the onset of slow exchange between monomeric and associated forms of diphenyl magnesium. This line broadening phenomenon at low temperature is more readily observed in the mesitylene magnesium bromide system discussed later.

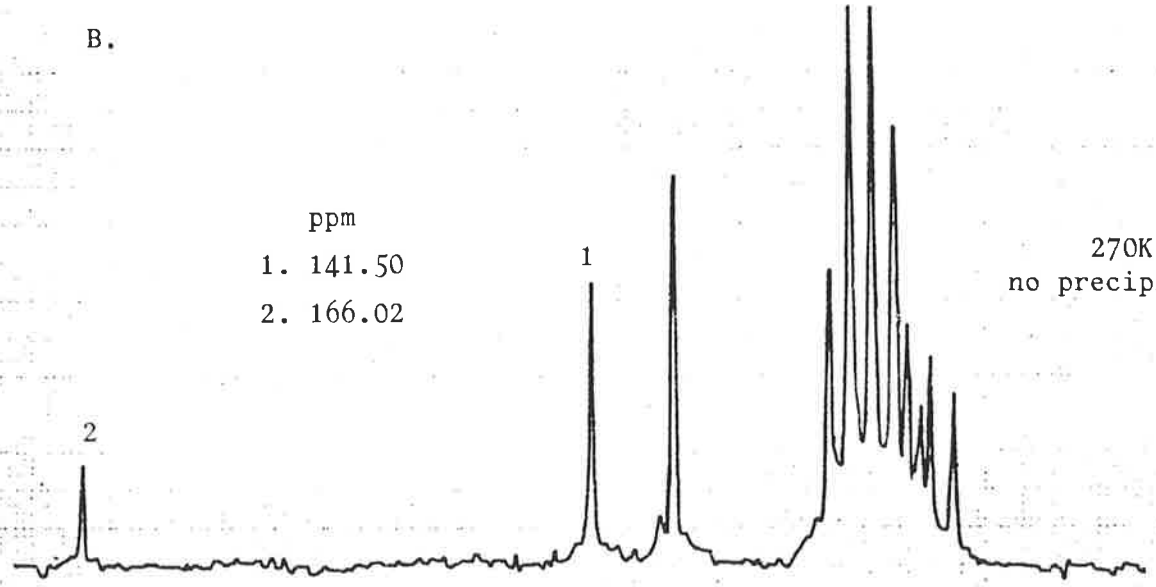
3.3.3.2 Variable Temperature Study of PhMgBr/d_8-toluene/residual THF

The 300K ^{13}C spectrum of this system is shown in Fig. 3.3C and the active bond and bromide contents are as indicated. A variable temperature analysis is presented in Fig. 3.5.

Fig. 3.5: ^{13}C (22.62MHz) Broad Band Decoupled Spectra of PhMgBr/Schlenk/d_8 Toluene

Peak assignments relative to the Toluene methyl (20.40ppm)





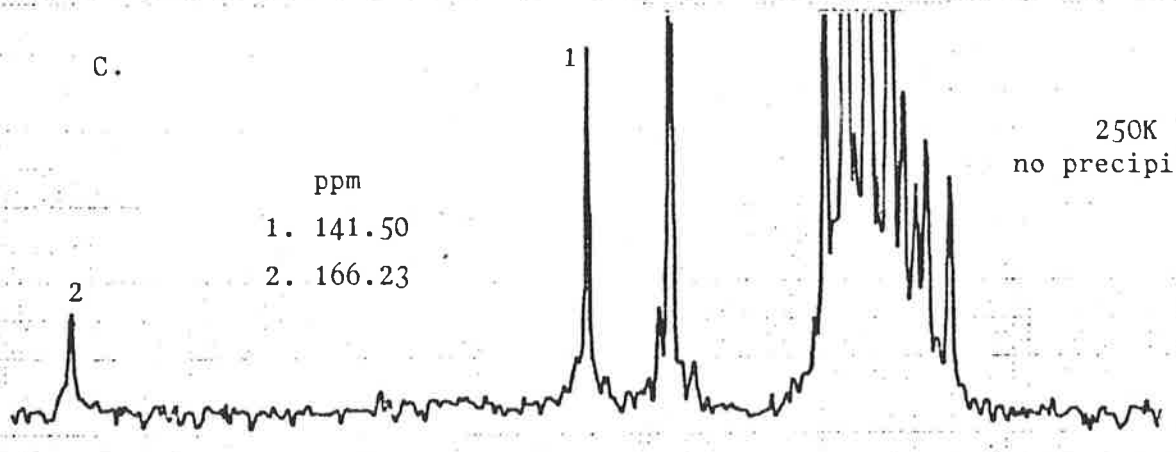
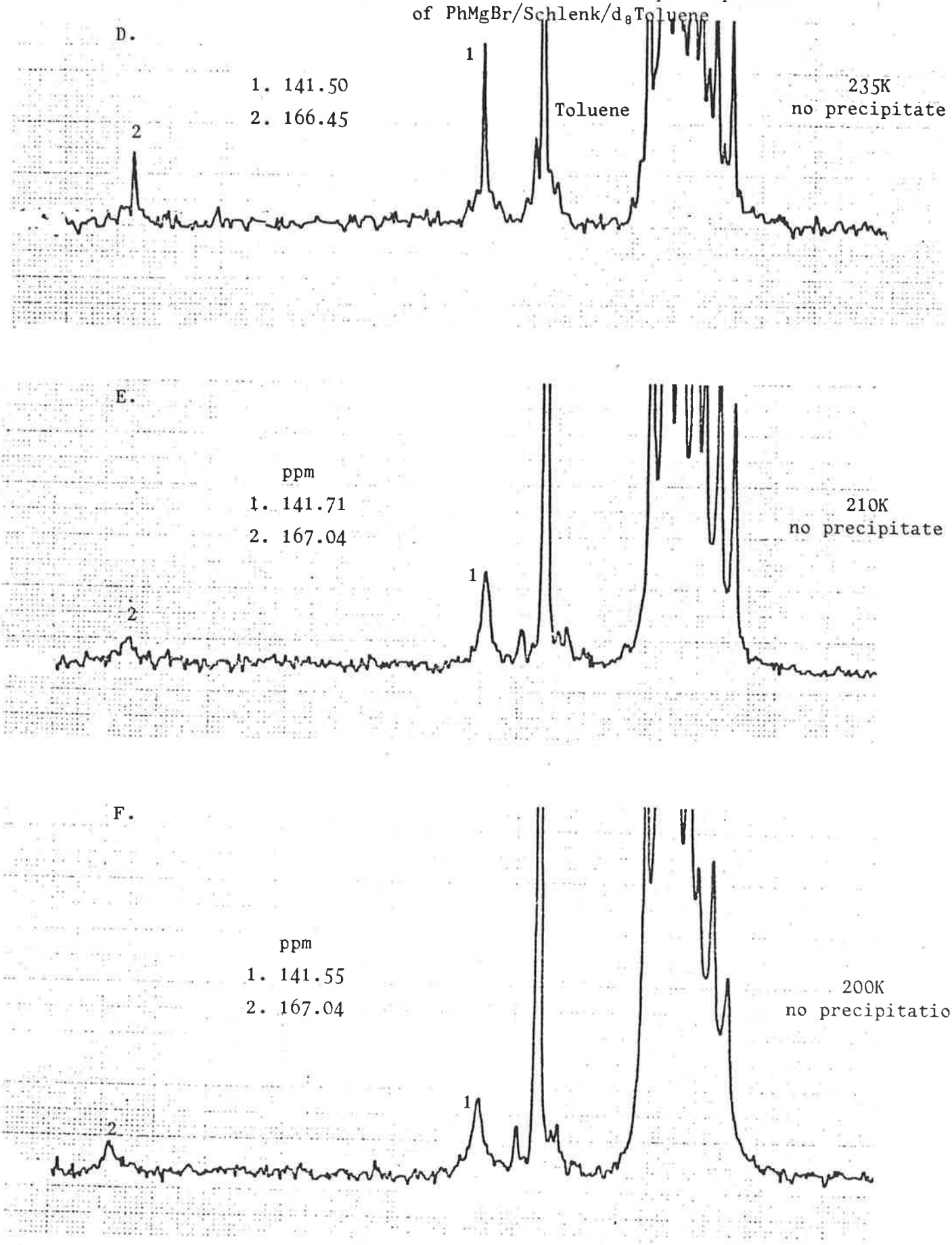


Fig. 3.5 (cont'd): ^{13}C (22.62MHz) Broad Band Decoupled Spectra of PhMgBr/Schlenk/d_8Toluene



The origin of the line broadening in peaks 1 and 2 at 300K (Fig. 3.5A), followed by line narrowing at lower temperature appears to lie with a real chemical effect, rather than an instrumental problem inherent in the shimming of the spectrometer. This behaviour may be explainable on the basis of "hidden partner broadening", which has been observed by Hagias[35] in the isobutyl magnesium bromide/THF/toluene system. Hidden partner broadening is closely related to the concepts of resolution (implying the chemical shift difference between partners in an equilibrium process) and sensitivity (involving the prospect of sensing the different partners in the equilibrium, especially when the population of one of the components is low). If the chemical shift difference is small and the population of one of the components is low after the onset of coalescence, then line broadening at the onset of slow exchange (Fig 3.5A) may produce, at lower temperature (Fig. 3.5B), a peak with narrower line width but with the predominant site only, clearly evident. The solution to this problem lies with the utilisation of high resolution, high field NMR spectrometers.

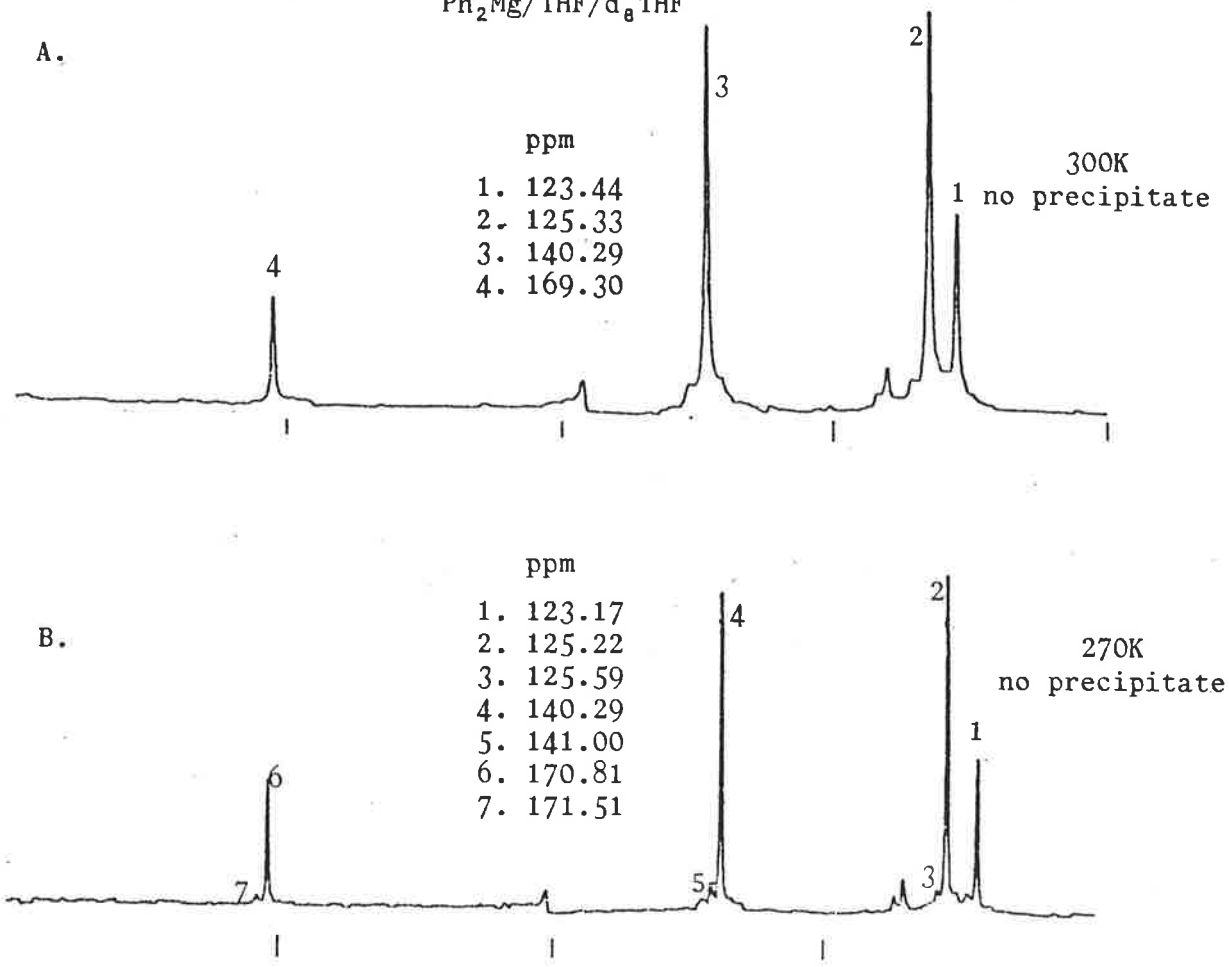
Unlike the PhMgBr/THF/d_8THF system (Fig. 3.4), where a coalescence temperature of ca. 255K was noted, a gradual broadening of the phenyl resonances (peaks 1 and 2, Fig. 3.5C-F) is seen with successive decrements in temperature, indicating the approach to another slow exchange process between chemical entities.

Confusion arises as to which coalescence phenomenon in Fig. 3.5 represents the Schlenk equilibrium. If the continued broadening of resonances at lower temperatures corresponds to the onset of slow exchange in the Schlenk equilibrium process (which appears to be so, based upon a comparison of the MsMgBr/toluene/d_8-toluene system, discussed later in this chapter), then the coalescence temperature in this solvent appears lower than for the PhMgBr/THF system. However, the discrepancy in active bond contents and Br/PhMg quotients for these two systems negates an effective comparative study between the two systems. Additionally, the role that THF plays in the lability of any equilibrium may also be important; in the case of the MsMgBr system (see later), it appears that the lability of the Schlenk equilibrium is increased (i.e., lower coalescence temperature) when toluene becomes the predominant solvent (greater than 90 mole per cent), given similar active bond and bromide concentrations).

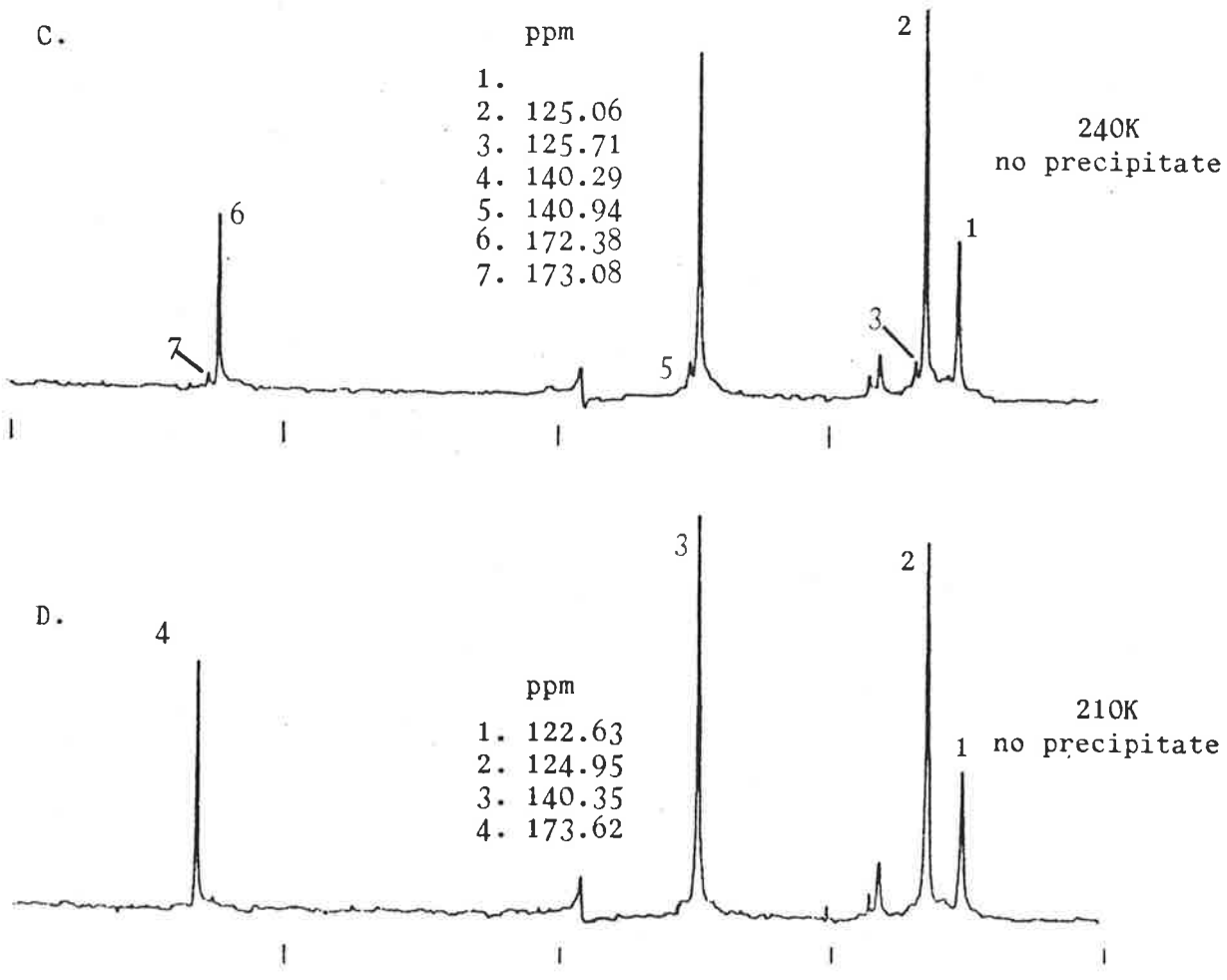
3.3.3.3 Variable Temperature Study of Diphenyl Magnesium/THF/d_8-THF

Active bond and bromide contents for this system are as indicated in Fig. 3.3D, with variable temperature spectra reported in Fig. 3.6. These spectra remain almost invariant with temperature, although minor peaks (3,5,7) in Fig. 3.6B and Fig. 3.6C are evident. Such minor peaks emphasise the deficiency of the ^{13}C technique - dealing with responsive nuclei at low abundance. These minor peaks indicate relative deshielding with respect to the major peaks, as would be the case for bridging phenyl groups in

Fig. 3.6: ^{13}C (22.62MHz) Broad Band Decoupled Spectrum
$Ph_2Mg/THF/d_8THF$



PEAK ASSIGNMENTS RELATIVE TO β THF (25.30ppm)



associated species. A better interpretation of this system could be achieved via an NMR study of the ^{13}C enriched phenyl Grignard reagent (probably most economically achieved by bromination of ^{13}C-benzene followed by formal Grignard synthesis).

3.3.3.4 Variable Temperature Study of Diphenyl Magnesium/toluene/d_8-toluene/residual THF

Fig. 3.3E summarises the active bond and bromide evaluations for this system. Fig. 3.7A-D and Fig. 3.8A-D represent variable temperature analyses of the aromatic Grignard region and the THF/toluene methyl region, respectively. Fig. 3.9A and Fig. 3.9B are spectra accumulated and stored at 210K after 3000 scans and represent aromatic and THF regions, respectively. They should be referred to Figs 3.7D and 3.8D which are continuations of the same data accumulation procedure at 210K.

In these spectra the following points are worth noting:

(1) Fig. 3.8 shows the presence of 1,4-dioxane, at 67.99 ppm in Fig. 3.8A, which is unavoidable if totally bromide free diphenyl magnesium is desired.

(2) Residual THF accounts for about 10 mole per cent (GLC) of the solvent and is indicated by resonances 1 and 3 in Fig. 3.8A.

(3) There appears to be a correlation between the observation of precipitation and the appearance of downfield shoulders on the THF peaks (Fig. 3.8C, peaks 2 and 5) and accompanying downfield shoulders on the

Fig. 3.7 (B.B.) ^{13}C Spectra for Aromatic Region of $Ph_2Mg/Tol/d_8Tol$; 22.62 MHz

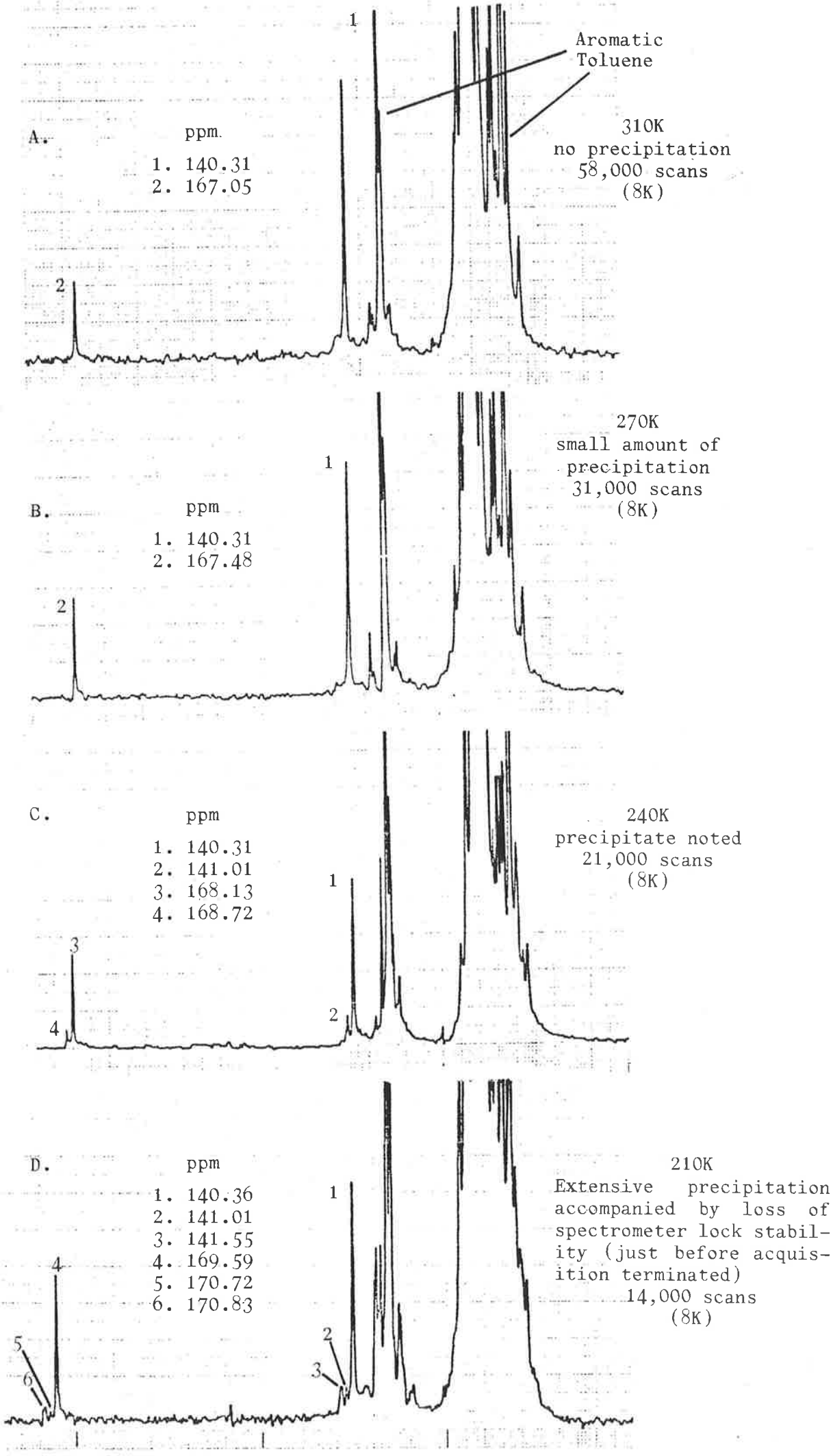
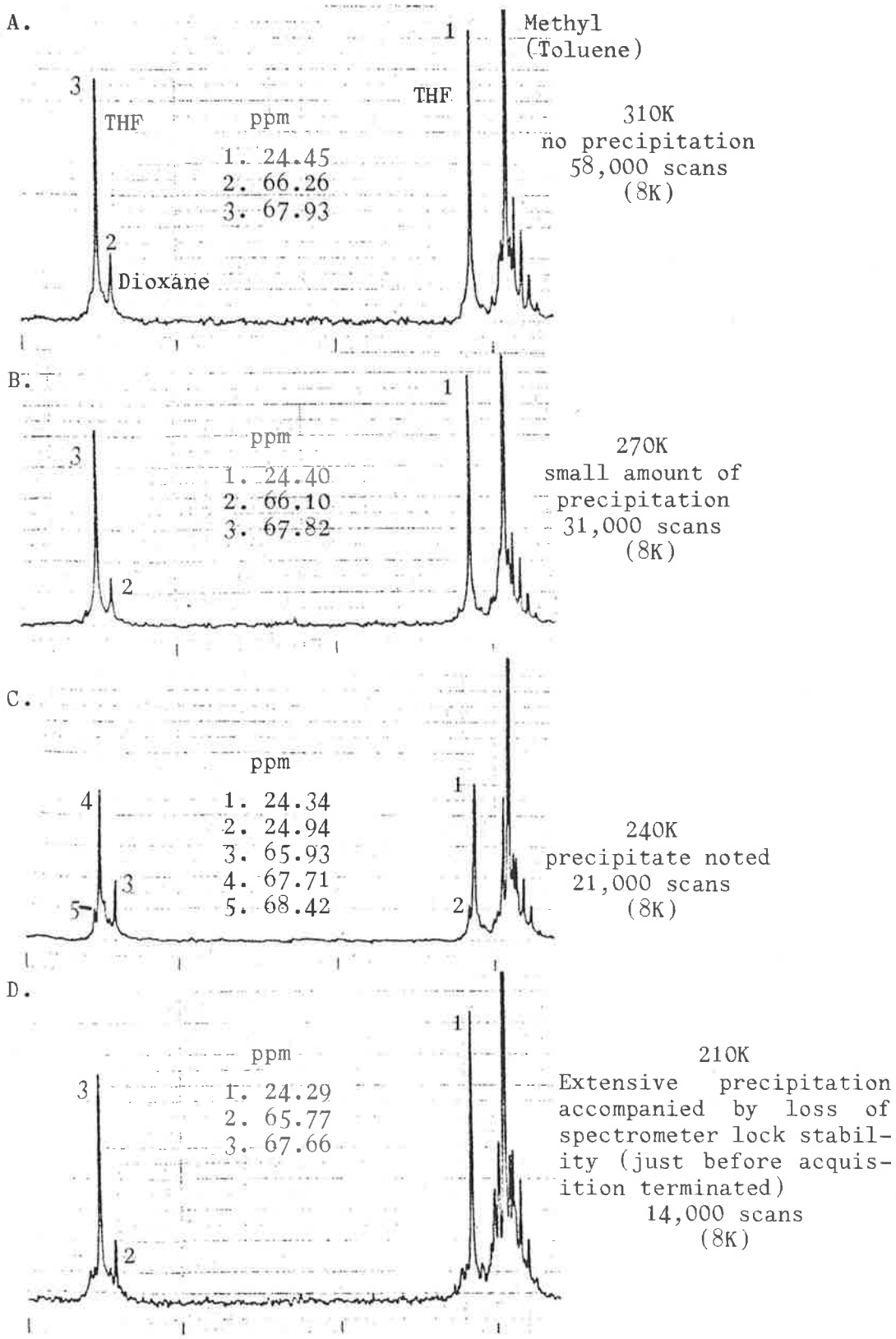


Fig. 3.8: (B.B.) ^{13}C Spectra of THF/Dioxane Region of Ph_2Mg/Toluene/d_8Toluene; 22.62MHz



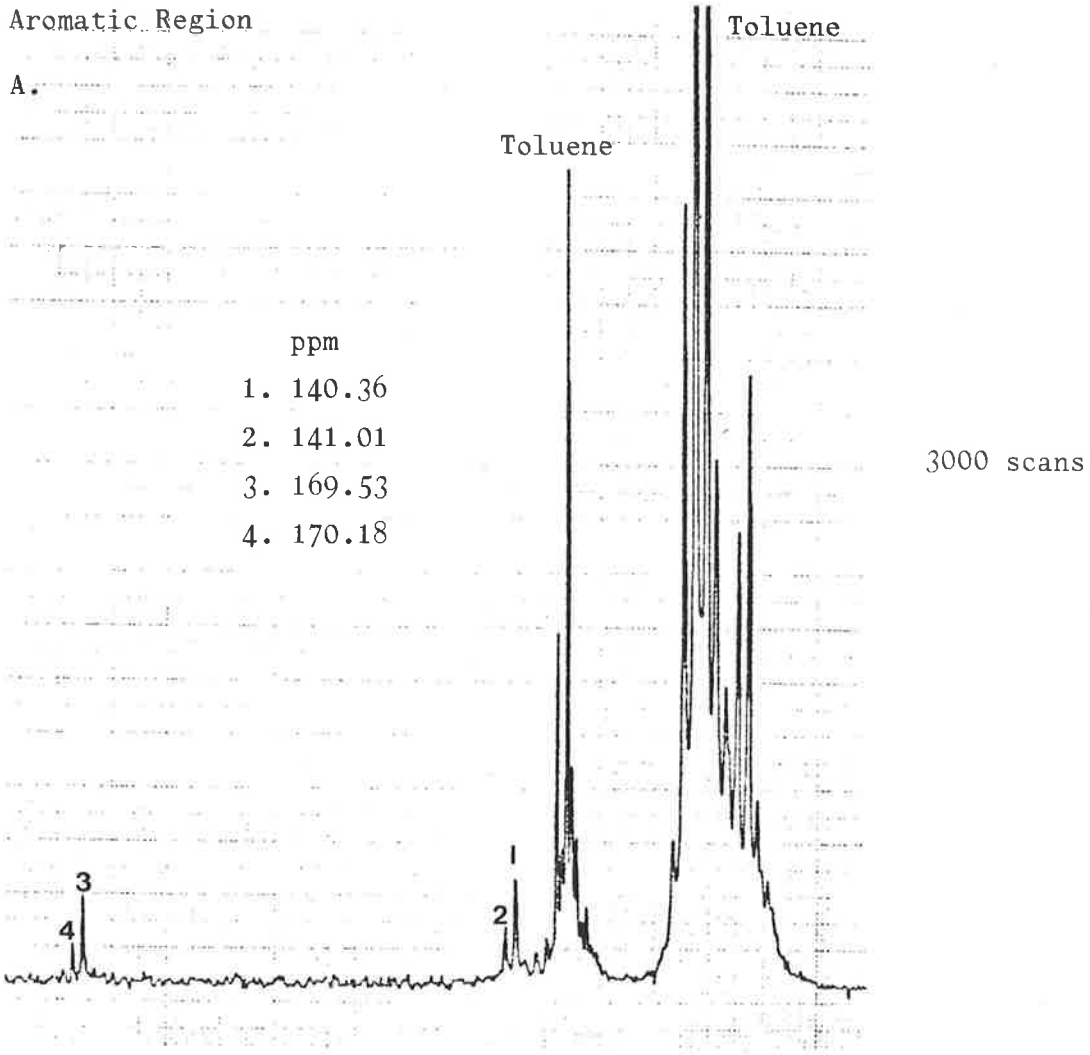
All assigments relative to the toluene methyl (20.40ppm) at all temperatures.

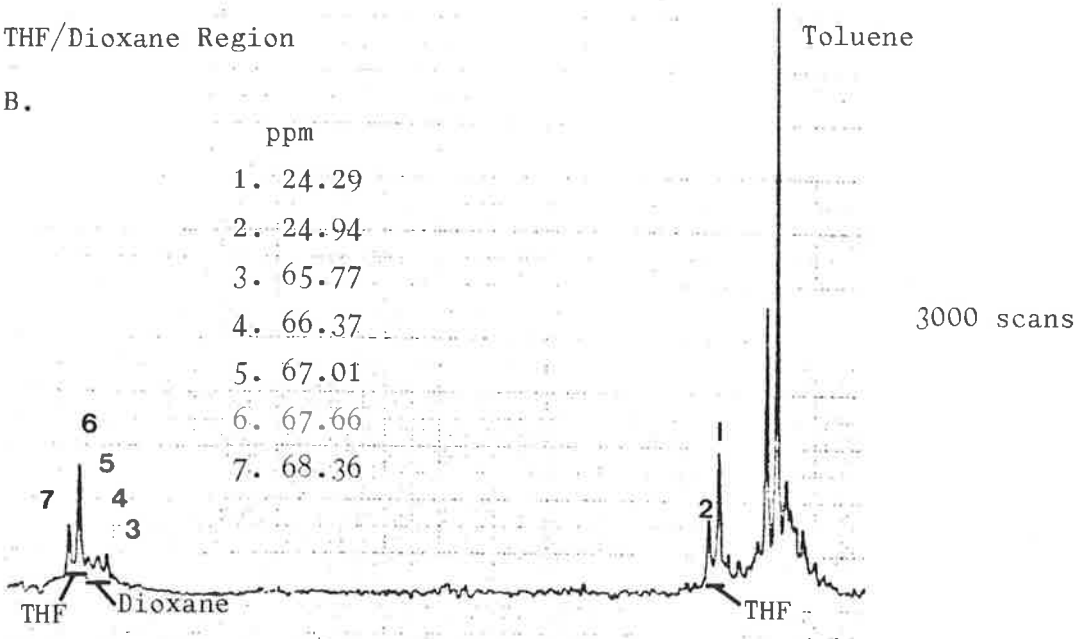
Note the appearance of fine structure on the THF peaks at lower temperature.

Fig. 3.9: ^{13}C Spectrum of Ph_2Mg/Toluene/d_8-Toluene

210K
22.62MHZ

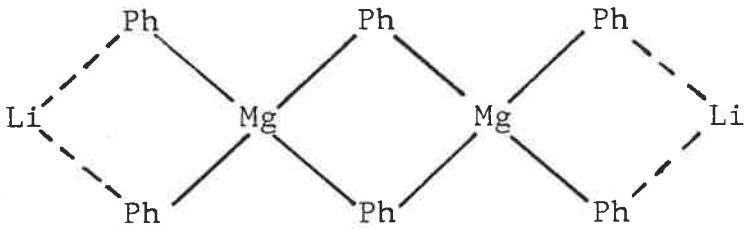
Peak assignments relative to Toluene methyl (20.40ppm)





Spectrum "D" in the previous 2 figures represents a continuation of accumulation after f.i.ds were stored at 3000 scans (above).

phenyl magnesium peaks (Fig 3.7C, peaks 2 and 4). This observation is made unequivocal at 210K in Fig. 3.9, where, prior to the massive precipitation observed in Figs 3.7D and 3.8D, distinctly defined downfield peaks are visible. These downfield peaks probably denote bridging phenyl groups, with phenyl bridged associates representing precursors to the precipitation process. Thoennes and Weiss[37] have prepared and characterised, by solid state means, the following compound:



indicating that phenyl bridges are possible in our system. The persistence of these downfield peaks (broadened slightly by field inhomogeneity as the volume of precipitate increases) probably indicates that solvent is capable of retaining some of the lower order associates in solution (Fig. 3.7D). No discernment of the degree of association is possible using NMR, but "polymeric" Me_2Mg has been postulated[38] in solution, and it is conceivable that Ph_2Mg precipitates by formation of these extended units. The persistence of the upfield peaks (e.g., peaks 1 and 3; Fig. 3.7C) over the whole temperature range seems to imply that the original, possibly monomeric, form of Ph_2Mg is still the predominant species in solution after equilibrium has been attained, even at 210K.

(4) The peak associated with 1,4 dioxane is also split, indicating that it exists in a bound form as well as THF. In polymerisations of MMA using initiators in THF, the presence of 1,4 dioxane does not affect active centres, since it can be assumed that THF is a stronger solvating agent than dioxane. This is perhaps most clearly demonstrated by Schulz et al.[39] in the anionic polymerisation of styrene using sodium as counterion. In a non-polar solvent such as toluene, where solvating agents are in low concentration, this may not be so. For an eneidic polymerisation where discrete, different propagating centres operate exclusively with respect to each other, an entity with dioxane co-ordinated at the active polymerising site could behave differently to an analogous site where THF complexation is evident, thus affecting such parameters as microstructure, molar mass distribution and rate of reaction.

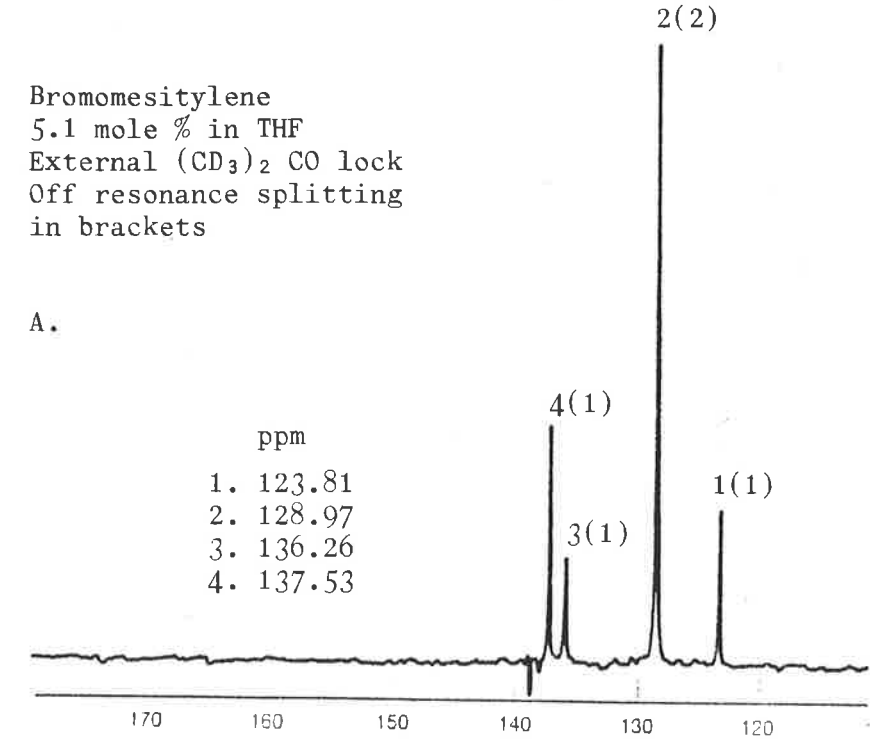
3.3.4 ^{13}C Spectra of Mesitylene Magnesium Systems

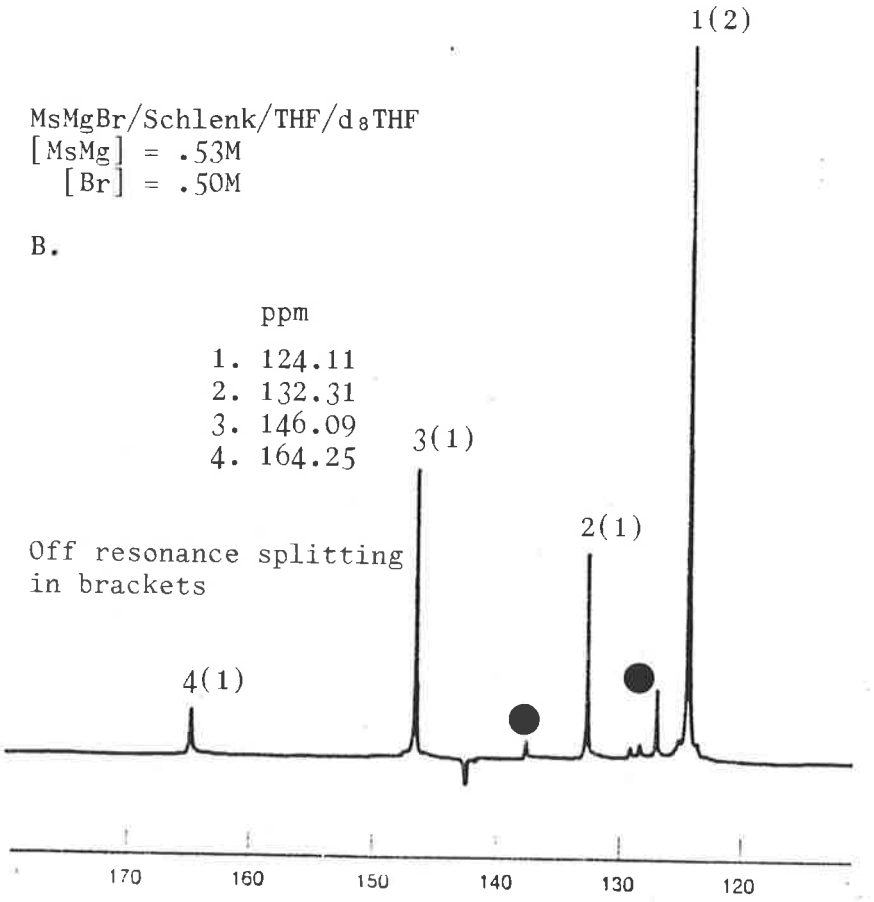
The mesitylene magnesium systems studied are shown in Fig. 3.10, measured at 300K. Bromide and active bond concentrations are shown, and apply to the variable temperature spectra studied later in this chapter. By analogy with the phenyl system, the low field peak of Fig. 3.10B (peak 4) is certainly the C(1)-Mg resonance, while off-resonance doublet character suggests that the high field resonance (peak 1) is that of the m-carbon environment. Peak 3, based upon arguments by Jones[32] is assigned as the o-carbon resonance, with peak 2 representing the p-carbon

Fig. 3.10: ^{13}C (20.1MHz) Broad Band Decoupled Spectra of the Mesitylene System

300K

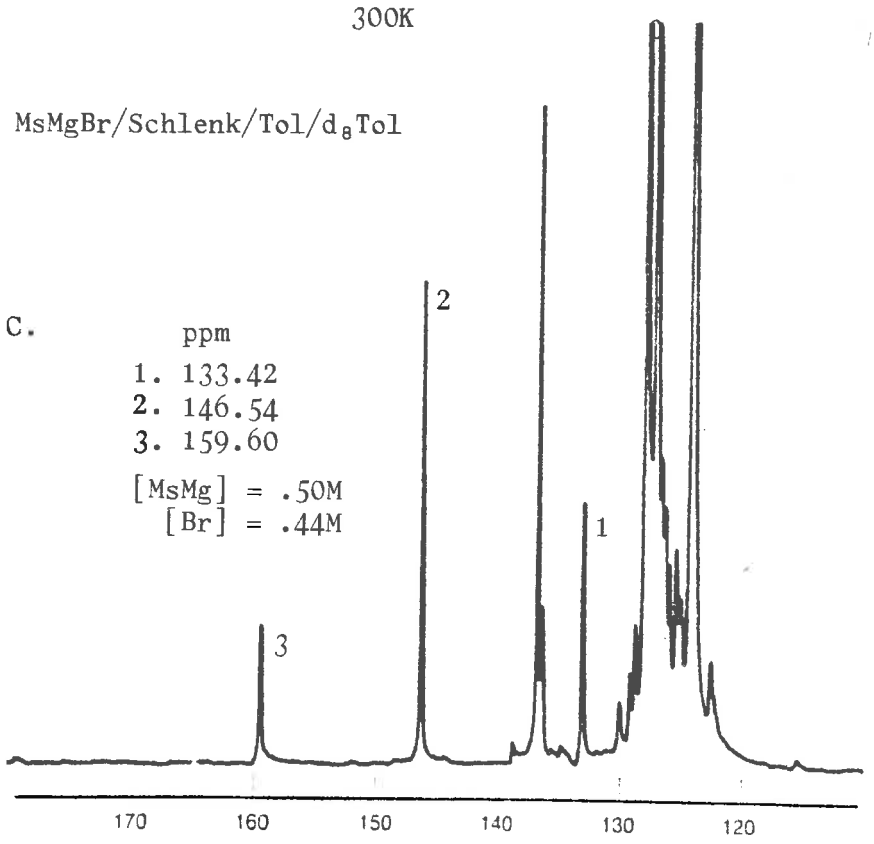
Peak assignment relative to β THF (25.30ppm)

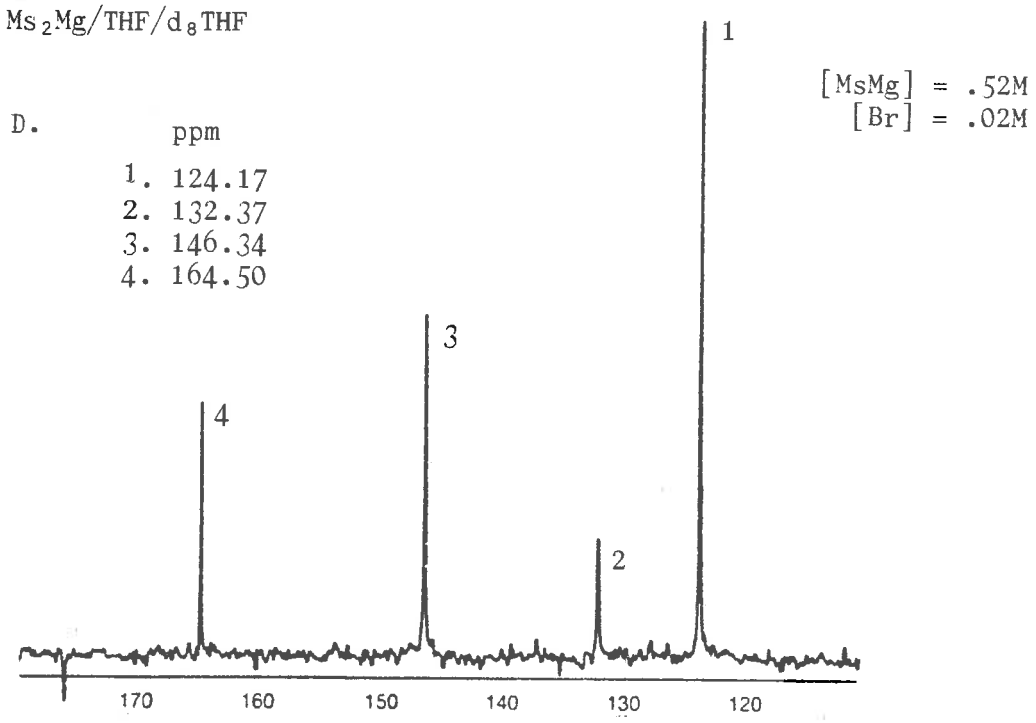




Black dots denote the presence of mesitylene.

Fig. 3.10 (cont'd): ^{13}C (20.1MHz) Broad Band Decoupled Spectra of the Mesitylene System





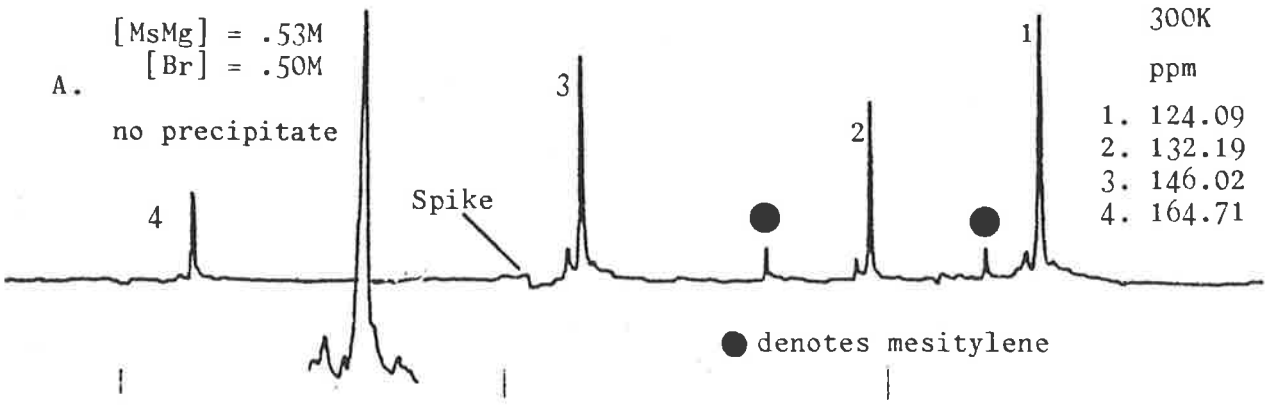
site. Impurity resonances (denoted by black dots in Fig. 3.10B) represent side-products of the Grignard synthesis. These peaks (at ca. 126.7 and 137.2ppm) correspond precisely to the field positions of mesitylene in THF and arise in an analogous manner to benzene in the phenyl magnesium system. Fig. 3.10C and Fig. 3.10D represent typical spectra of MsMgBr/toluene/d_8-toluene and Ms_2Mg/THF/d_8-THF for the given bromide and active bond concentrations. Addition of 1,4 dioxane is an imprecise method of producing Ms_2Mg as trace amounts of bromide remain in evidence.

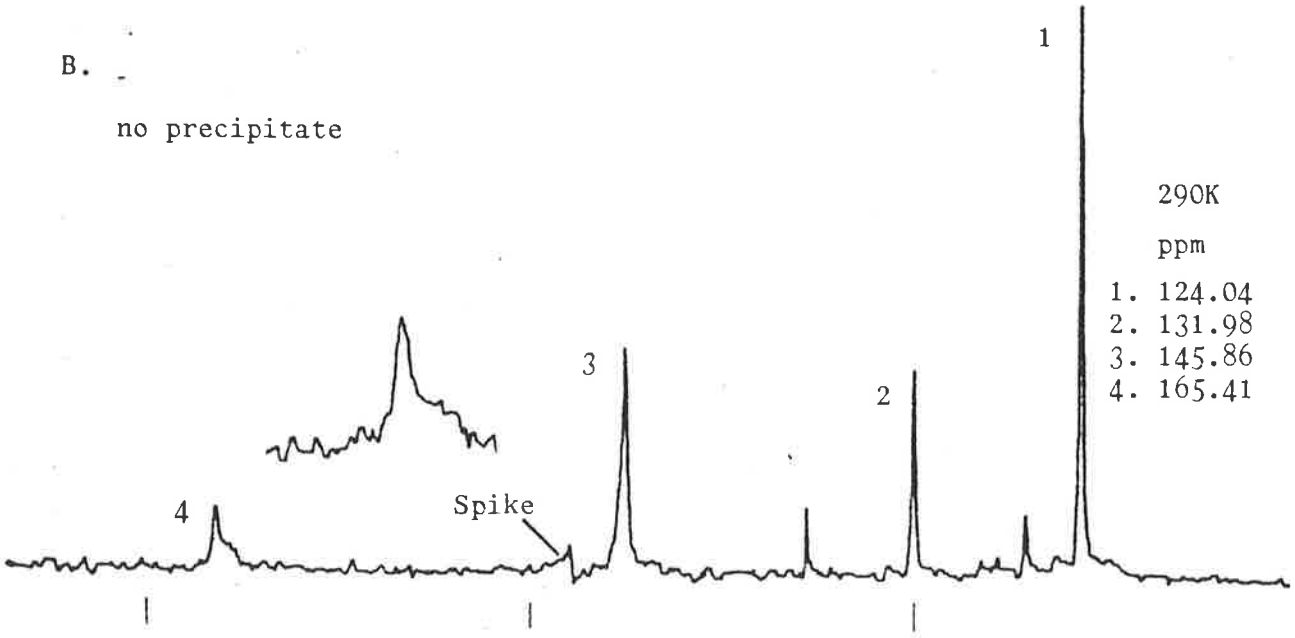
3.3.4.1 Variable Temperature Study of MsMgBr/THF/d_8-THF

Variable temperature ^{13}C spectra for this system are shown in Fig. 3.11A-F. The four principal resonances show distinct broadening at 290K, the approximate coalescence temperature, with the downfield C(1)-Mg resonance showing two distinct environments at 280K. This two-site process is taken to infer the presence of the Schlenk equilibrium with exchange between RMgX and R_2Mg. The effect is apparently transferred to other ring carbons much more effectively than its phenyl counterpart, where this effect was only primarily noticeable at C(1)-Mg, although the upfield m-carbons remain fairly unresponsive, even in the mesitylene system. The exchange effect at the o and p-methyl groups of mesitylene remains unobserved due to overlap by the β THF carbon resonance.

The actual mechanism for the exchange process in the Schlenk equilibrium has been viewed, in the light of exchange processes between organomagnesium compounds and

Fig. 3.11: ^{13}C (22.62MHz) Broad Bank Decoupled Spectra of the MsMgBr/Schlenk/THF/d_8THF System. Peak assignment relative to β THF (25.30ppm).





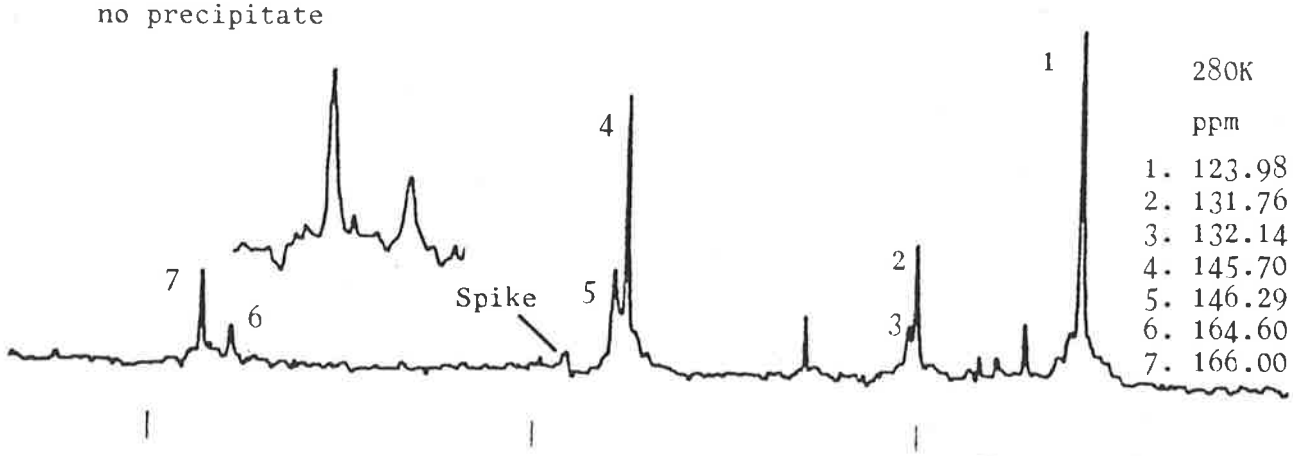
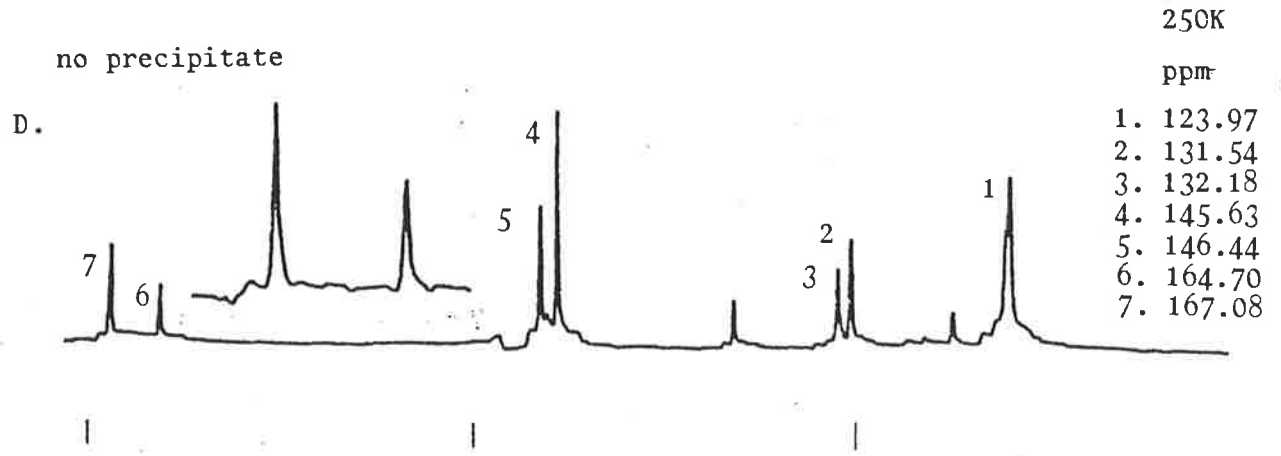
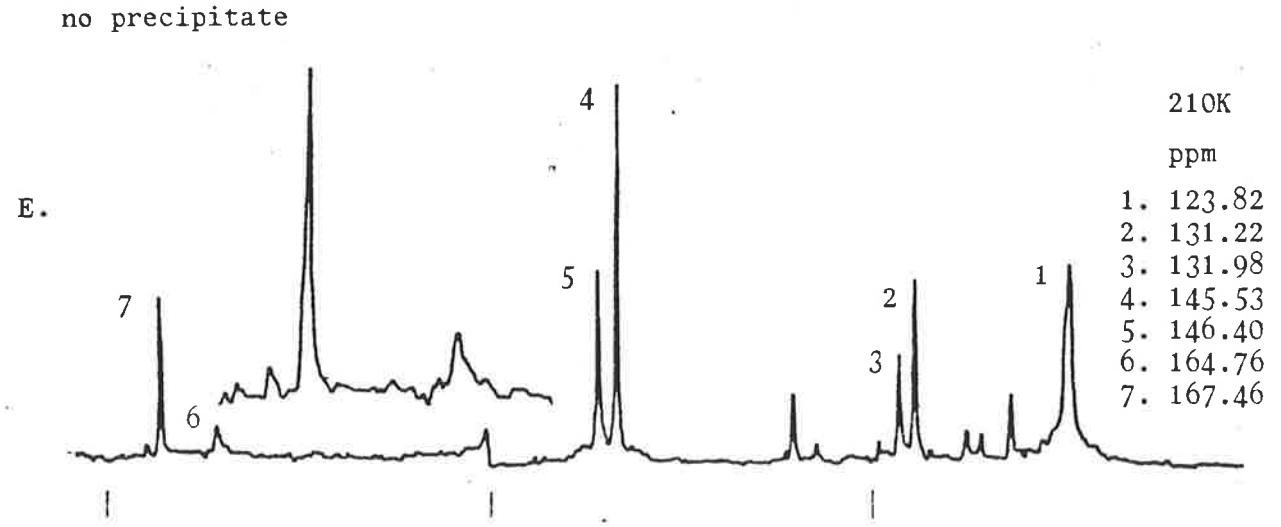
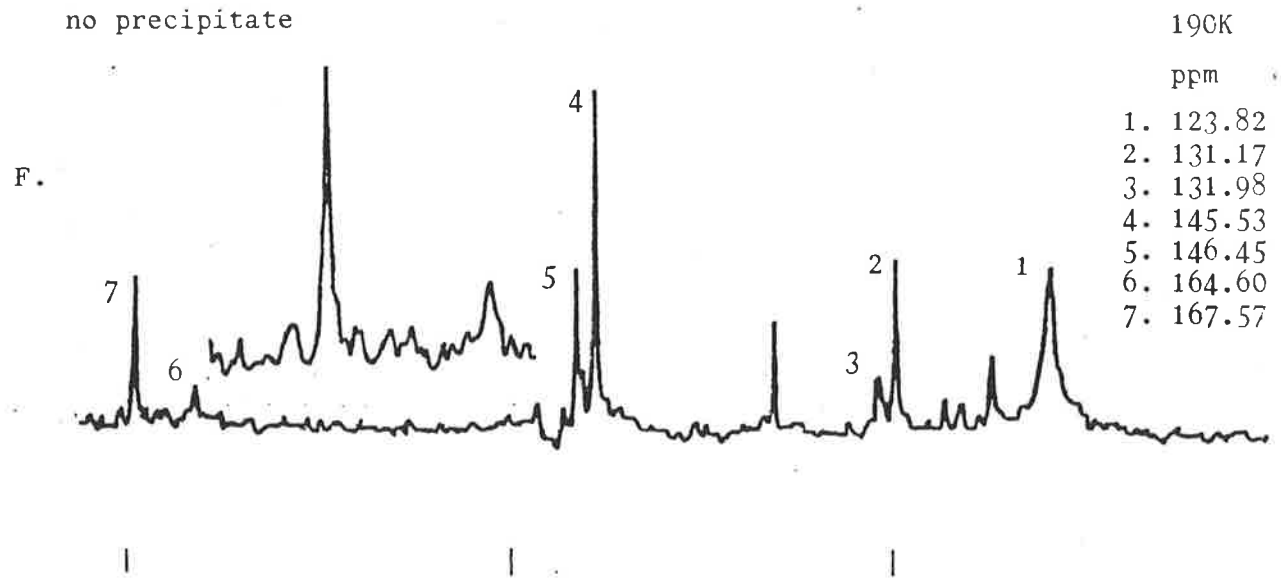


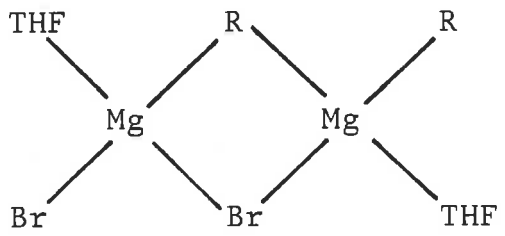
Fig. 3.11 (cont'd): ^{13}C (22.62MHz) Broad Band Decoupled Spectra of the MsMgBr/Schlenk/THF/d_8THF System. Peak assignment relative to the β THF (25.30ppm)







alkyl mercury halides, as occurring by a bimolecular mechanism.[25,40] Ashby[5] proposed that an intermediate in this process was a mixed bridge structure of the form:



the stability of which was important in determining the rate of exchange. A comparison of coalescence temperatures for the PhMgBr and MsMgBr systems is given in Table 3.2, below:

Table 3.2:

	Active Bond Content	Br/RMg	Approx. Coalescence Temp.
Phenyl	.57M	.87	∿ 255K
Mesitylene	.53M	.94	∿ 290K

If the exchange process is bimolecular then the rate of exchange is determined by the equilibrium concentrations at a given temperature, which is in turn dependent on the active bond content and the Br/PhMg quotient. If at the cited coalescence temperatures for the two systems in Table 3.2, the equilibrium concentrations are similar, then the variation in coalesence temperatures will give an insight into the effect of the aryl group on the lability of the Schlenk equilibrium. Given this qualification, it appears that the increased stericity of the aryl group retards the rate of exchange between $\underline{R}MgBr$ and $\underline{R}_2Mg$. In partial support of the observation that steric effects are important in determining the lability of the Schlenk equil-

ibrium are the examinations of Hughes and Vogler,[41] who noted that α branching in organomercury reagents was much more effective in inhibiting exchange than β branching. It has been noted[5] that terBuMgCl and $terBu_2Mg$ exist as two distinct ^1H resonances at 315K and yet CH_3MgCl gives only one signal at 173K, in support of increased stericity favouring slower exchange.

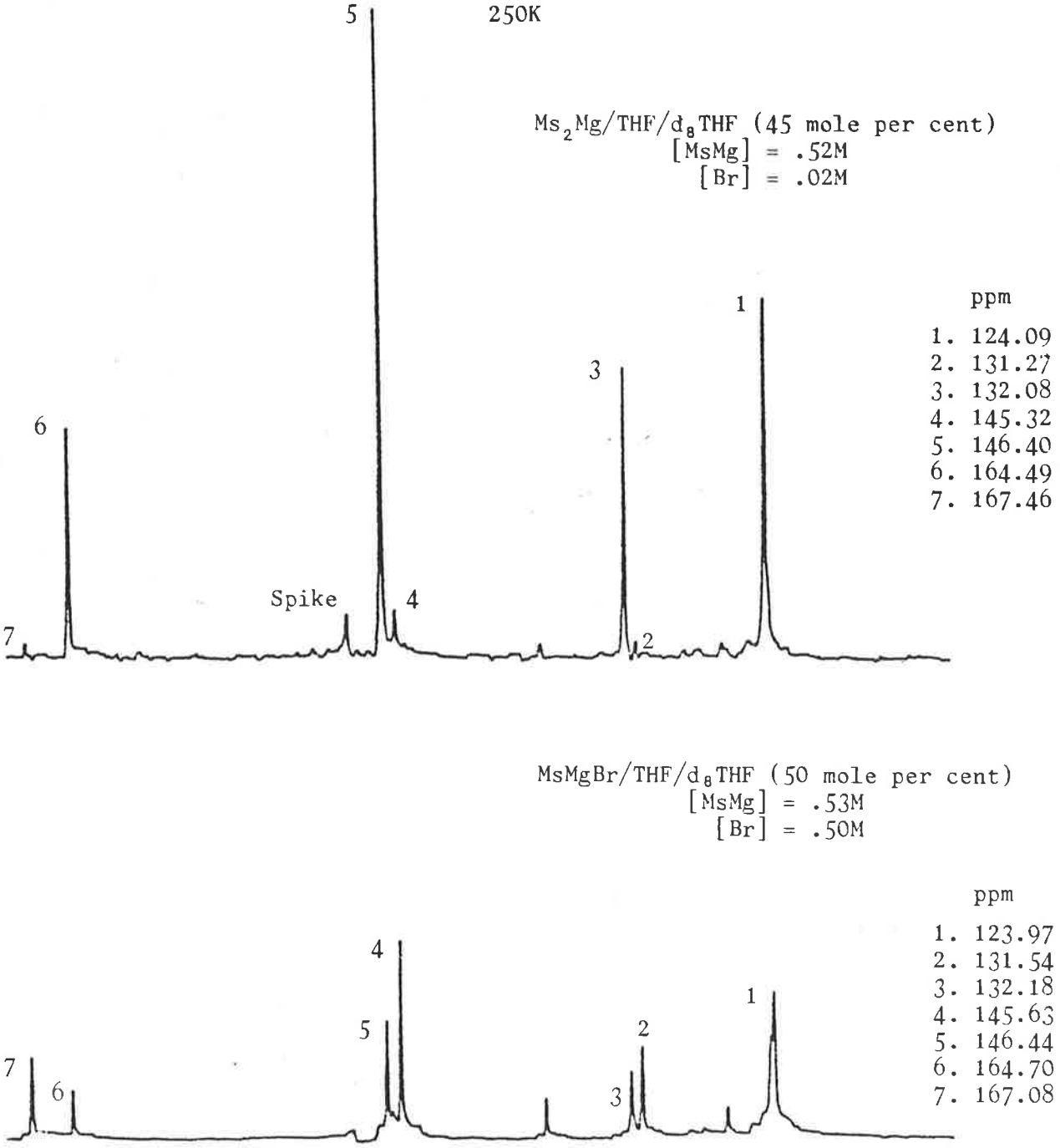
A comparison of the C(1)-Mg resonances (peaks 6 and 7) in Fig. 3.11D and Fig. 3.11E reveals that the upfield peak shows broadening with decreasing temperature, a feature in common with the PhMgBr/THF system (Fig. 3.4). This broadening suggests the onset of slow chemical exchange, probably between monomeric and associated forms. Fig. 3.12 indicates, on the basis of chemical shift correlation and observance of peaks due to trace amounts of bromide in the Ms_2Mg system, that the upfield peak of the C(1)-Mg doublet is due to the $\underline{R}_2Mg$ species (although this is reversed for the other mesitylene magnesium peaks).

3.3.4.2 Variable Temperature Study of MsMgBr/ toluene/d_8-toluene/residual THF

Spectra relevant to a variable temperature discussion of this system appear in Fig. 3.13A-F and Fig. 3.14A-F, and represent the aromatic/Grignard region and the residual THF/toluene methyl/o-methyl(MsMg) regions, respectively. Active bond and bromide contents are as indicated in Fig. 3.10C.

Examination of the C(1)-Mg resonance (peak 3, Fig. 3.13) reveals that the exchange process between Ms_2Mg and

Fig. 3.12: A comparison between ^{13}C (22.62MHz) Spectra of $Ms_2Mg/THF/d_8THF$ and $MsMgBr/THF/d_8THF$



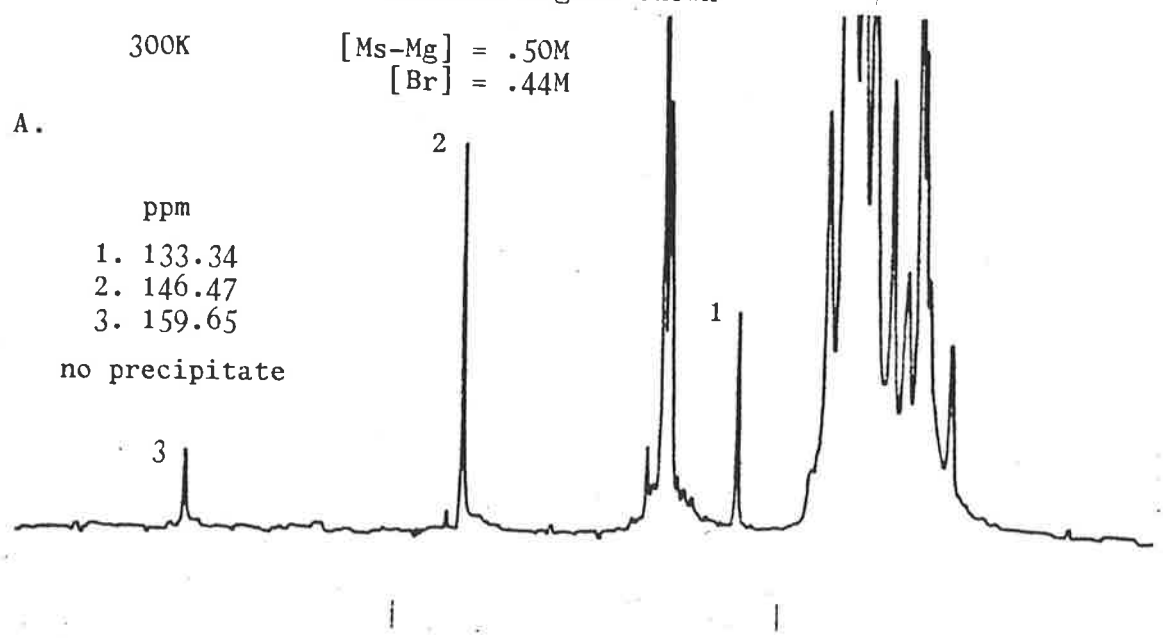
Correlation of Spectra based on chemical shift data reveals the following concerning the $MsMgBr/THF/d_8THF$ system:

That for the doublets (2,3) and (4,5) the downfield entity represents the resonance associated with the di-mesitylene species (upfield associated with brominated aryl magnesium).

For the doublet (6,7) this appears to be reversed with the downfield signal based on the brominated aryl magnesium.

Minor peaks (2,4,7) in the diaryl magnesium spectrum are believed to be due to aryl magnesium bromide.

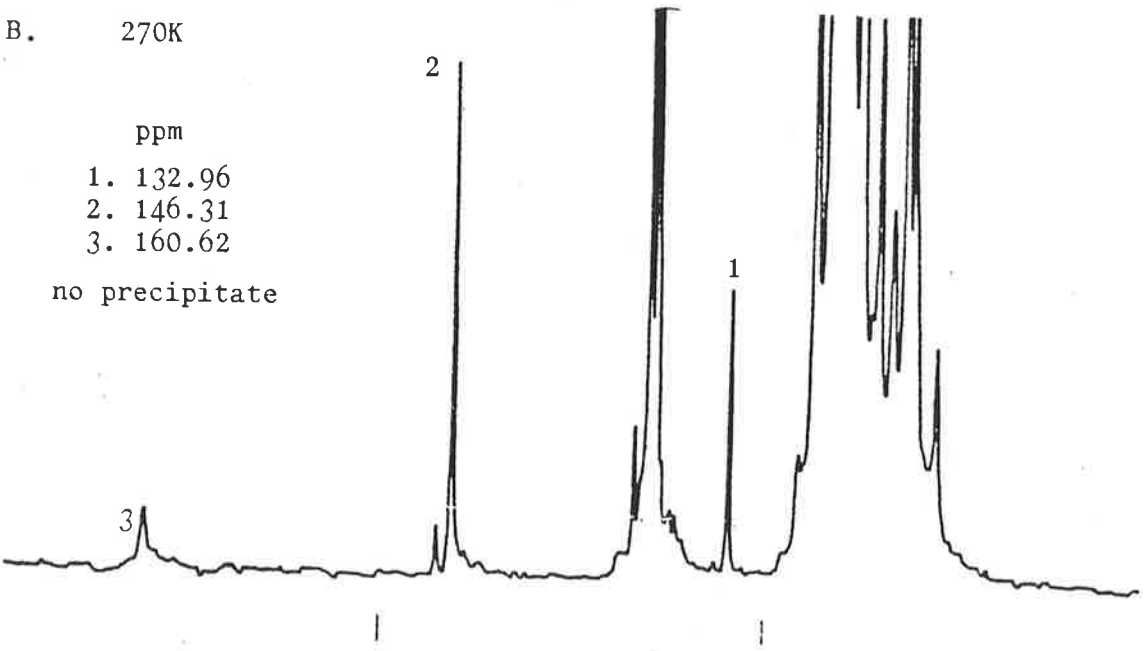
Fig. 3.13: ^{13}C (22.62MHz) Broad Band Decoupled Spectra
of MsMgBr/Schlenk/Tol/d_8Tol
Aromatic Region Shown



ppm

1. 133.34
2. 146.47
3. 159.65

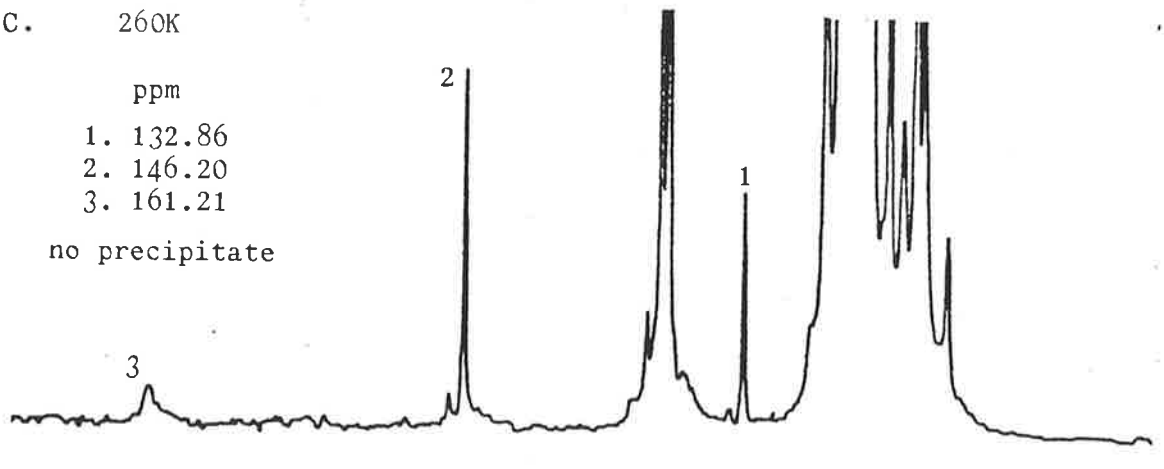
no precipitate



ppm

1. 132.96
2. 146.31
3. 160.62

no precipitate

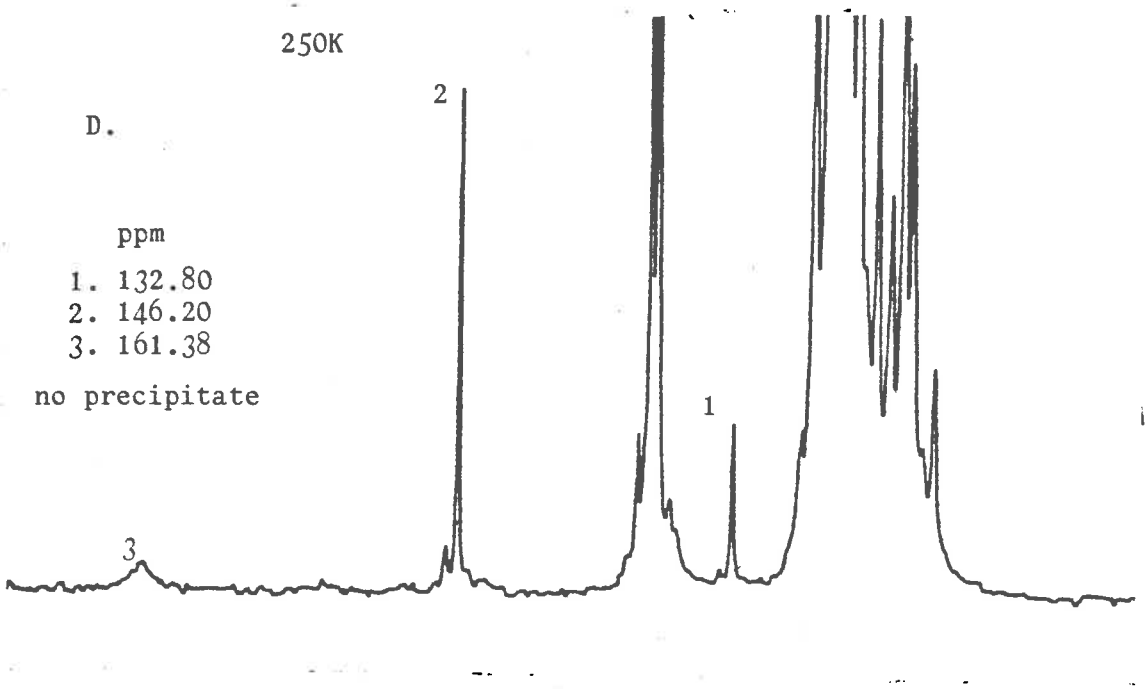


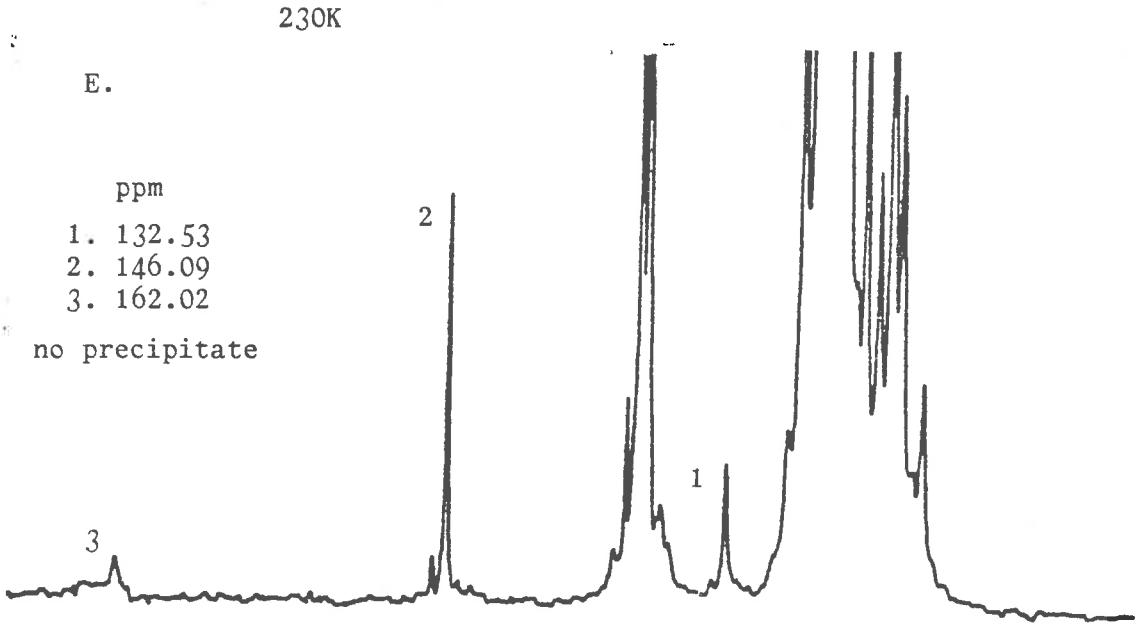
ppm

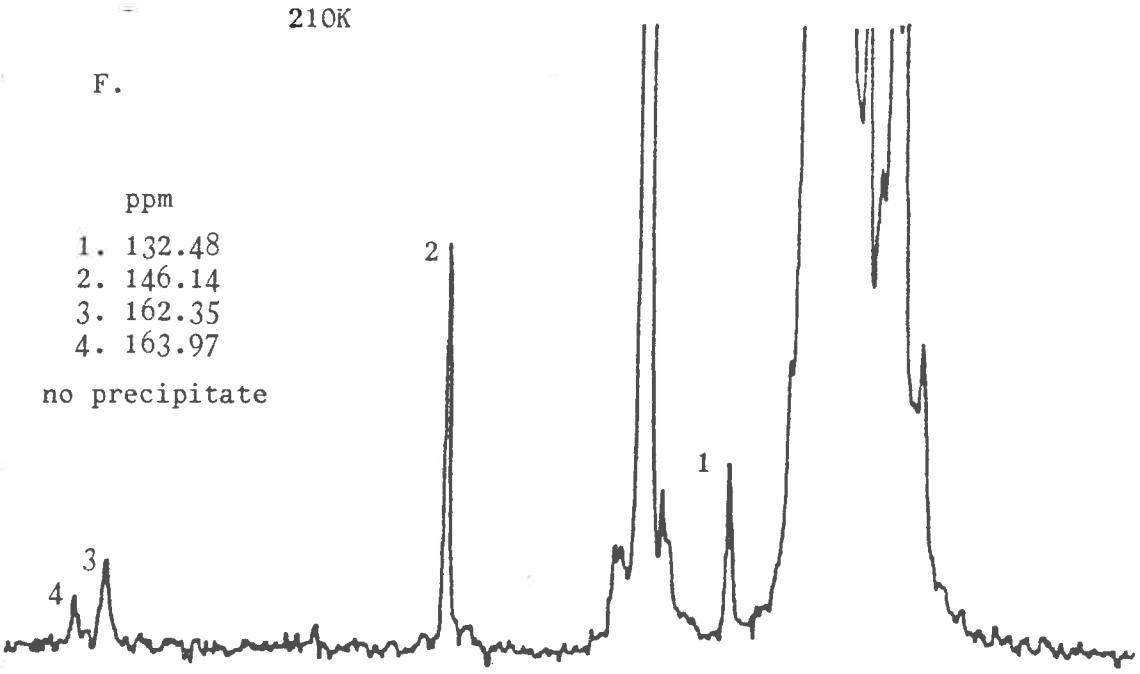
1. 132.86
2. 146.20
3. 161.21

no precipitate

Fig. 3.13 (cont'd): ^{13}C (22.62MHz) Broad Band Decoupled of MsMgBr/Schlenk/Tol/d_8Tol cont'd:







MsMgBr in toluene has a coalescence temperature significantly below that of the same species in THF at similar active bond and bromide contents (at about 240K compared to 290K in THF). Fig. 3.14 confirms the presence of the equilibrium process, in a comparison between the behaviour of C(1)-Mg and o-methyl carbons as a function of temperature. Significantly, however, and in contrast to the system in THF, the effects of exchange are not transmitted to other aromatic ring carbons as a splitting of these peaks (Fig. 3.13; peaks 1 and 2); merely a broadening of these resonances as a function of temperature. This effect remains unexplained.

Fig. 3.15 represents a variable temperature study of a mixed solvent system (41 mole per cent d_8-toluene in THF) and its characteristics relative to other mesitylene magnesium systems is indicated below:

Table 3.3:

Active Bond Content	Br/MsMg	Approx Mole % THF	Approx Coalescence Temp
.53	.94	100	∿ 290K
.52	.98	59	∿ 290K
.50	.88	10	∿ 240K

The coalescence temperature in mixed solvent (59 mole % THF) appears to be not significantly different to that in pure THF, but in the case of a more extensive de-etheration leaving ca. 10 mole per cent THF, the exchange process is much more rapid. Again, such correlations between coalescent temperatures require the equilibrium concentrations to be the same before any comment about the

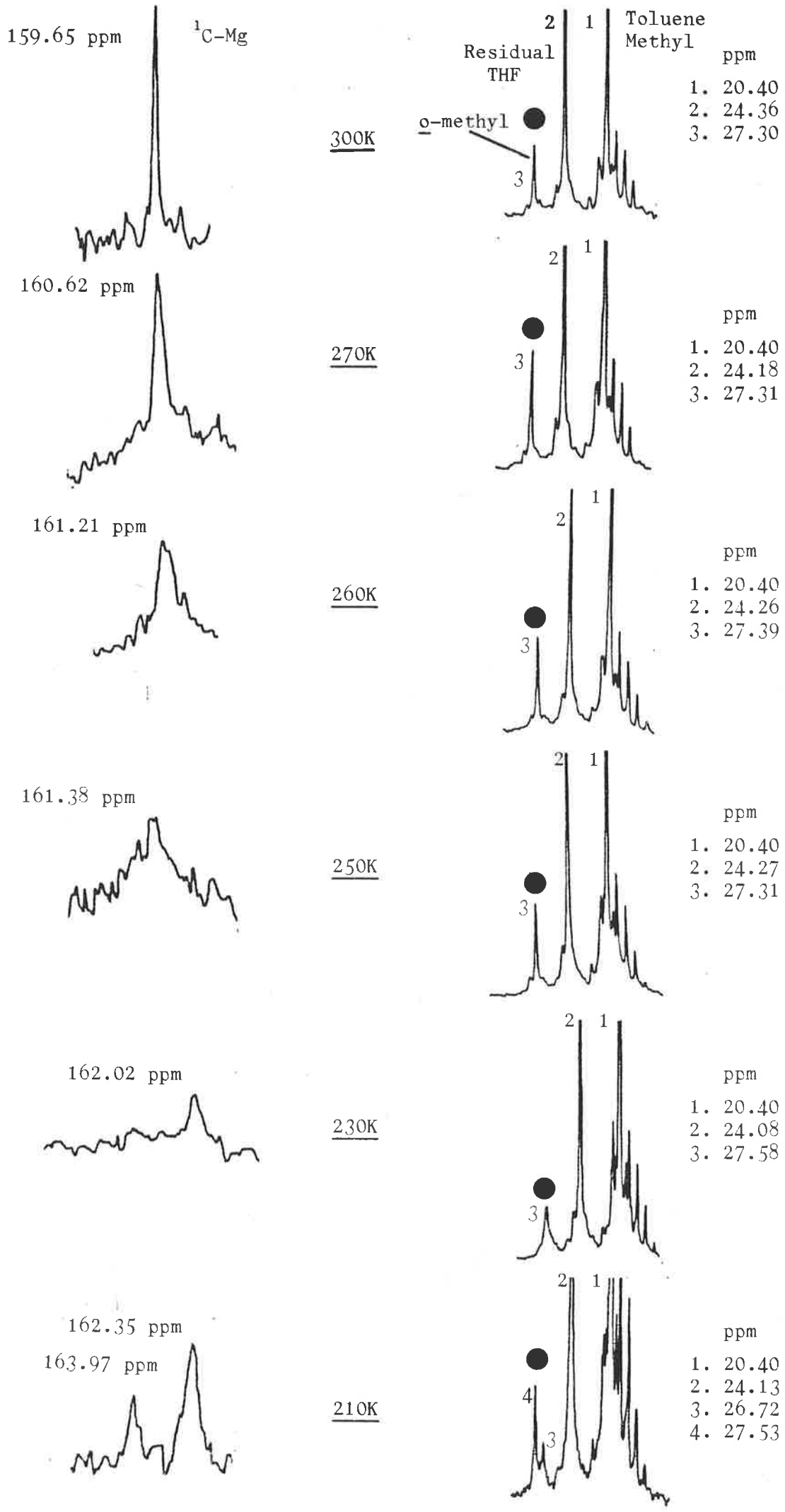
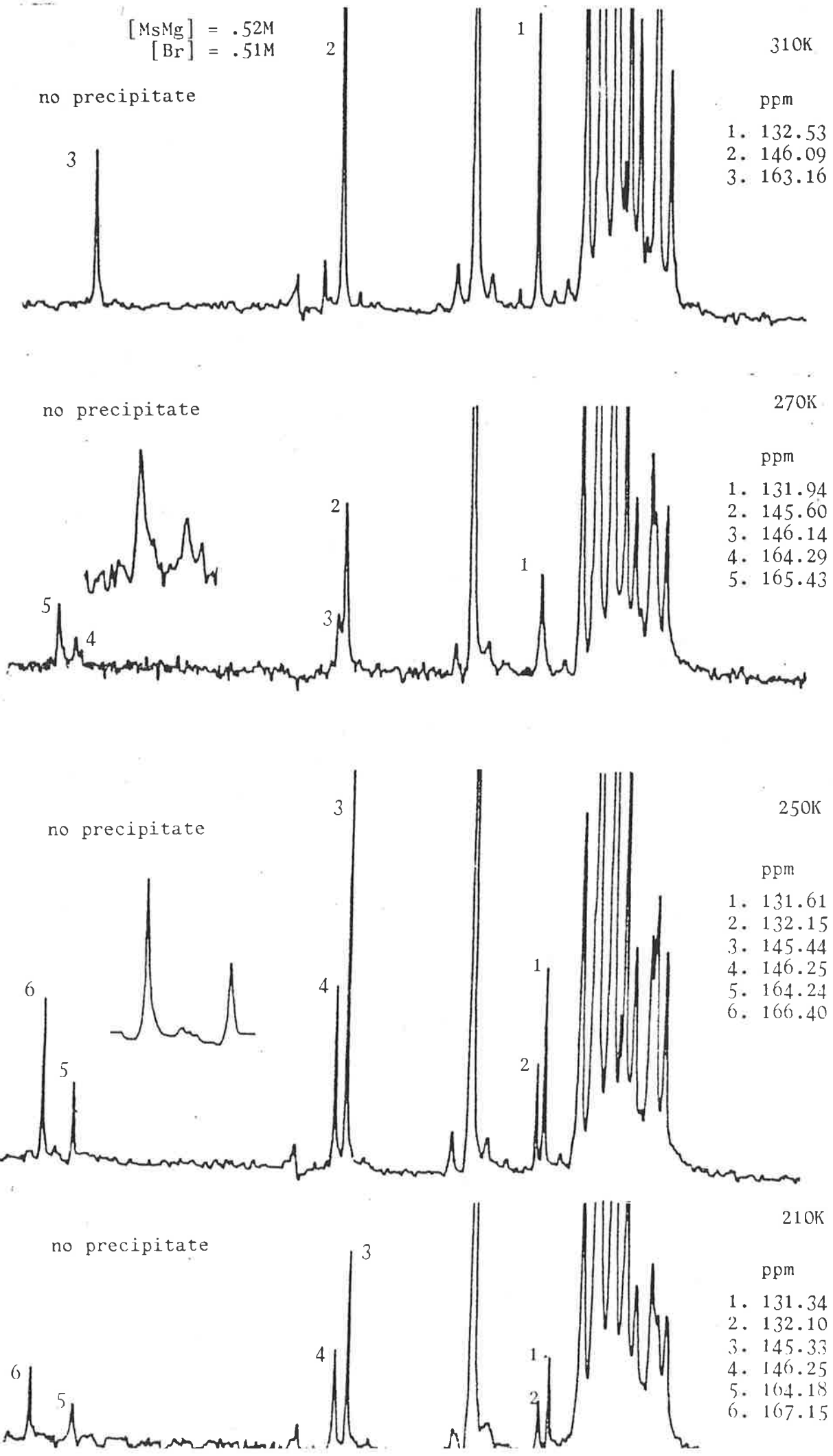


Fig3-14 Comparison between C(1)-Mg and o-methyls; MsMgBr/Tol/d_8Tol

Fig. 3.15: ^{13}C (22.62MHz) Broad Band Decoupled Spectrum of MsMgBr/Schlenk/THF/d_8Toluene $X_{THF/Tol}$ = .59



effect of solvent can be inferred. However, House and co-workers[25] have observed that the stronger the Lewis base character of the solvent, the slower the exchange rate, which is in general agreement with the data of Table 3.3, although this appears to be so only when de-etheration is more extensive. This solvent effect is explained by these workers in terms of a shift in a rapid pre-equilibrium between an unreactive disolvated organomagnesium and a reactive monosolvate.

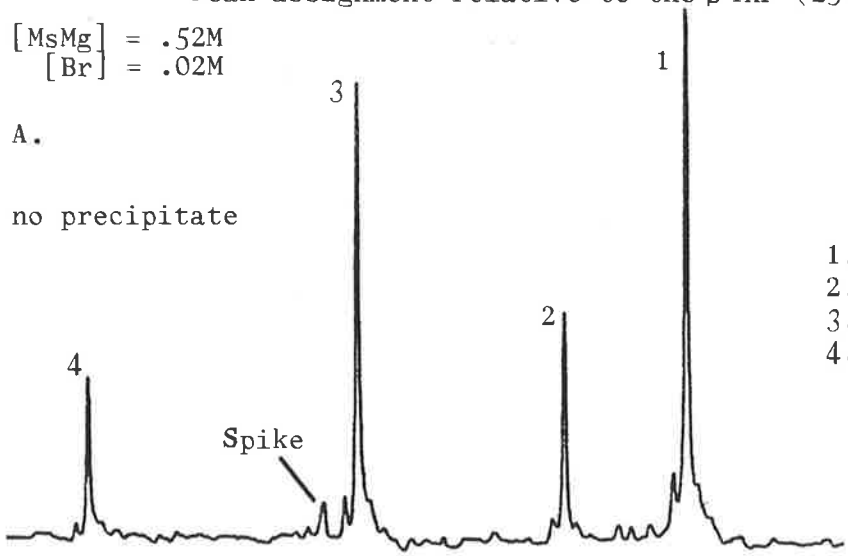
3.3.4.3 Variable Temperature Study of $Ms_2Mg/THF/d_8$-THF

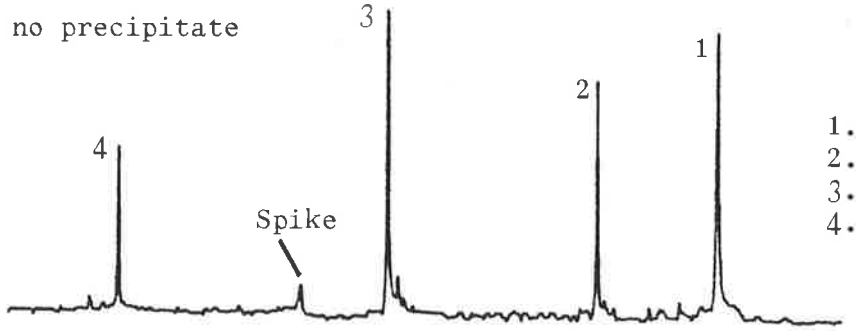
Variable temperature spectra for this system appear in Fig. 3.16A-E, and are of interest for two reasons:

(1) Imperfect removal of bromide presents the possibility of small amounts of MsMgBr appearing in solution. As mentioned previously, the MsMgBr resonances can be observed at 250K (Fig. 3.16C, indicated by dots).

(2) Fig 3.16D shows that at 235K each of the major peaks possesses a downfield shoulder (indicated by dots), possibily due to deshielded bridging mesitylene groups of associates. However, these peaks are not observed in the 210K spectrum (Fig. 3.16E) and may be related to the past history of the NMR tube sample. Due to intermittent spectrometer usage, tubes were often refrigerated at 260K for extended periods of time. Any precipitation noted just prior to usage was removed by slight warming of the tube - a condition which may not totally preclude the presence of associates. Such anomalies were noted infrequently.

Fig. 3.16: ^{13}C (22.62MHz) Broad Band Decoupled Spectra of $Ms_2Mg/THF/d_8THF$
Peak assignment relative to the β THF (25.30ppm)





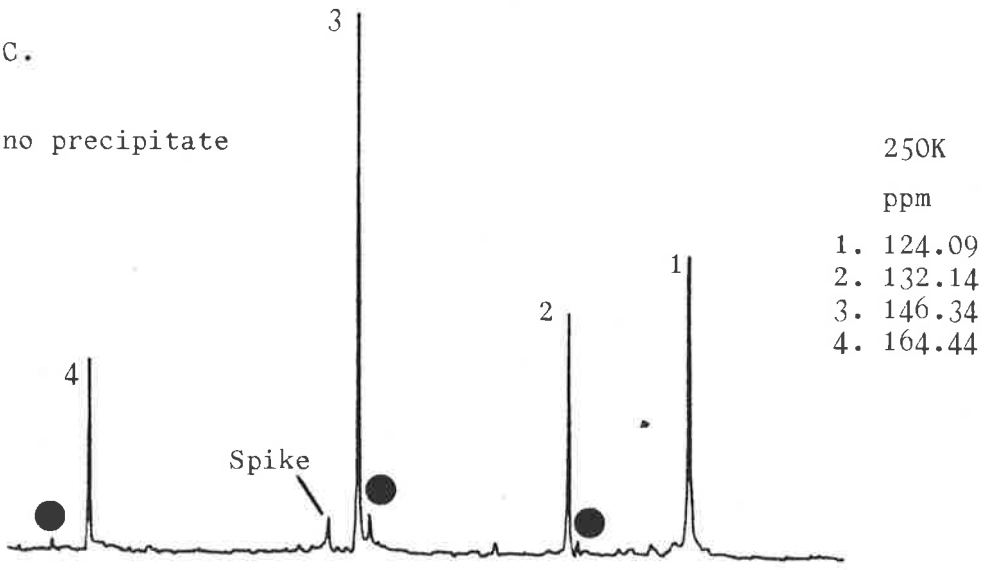
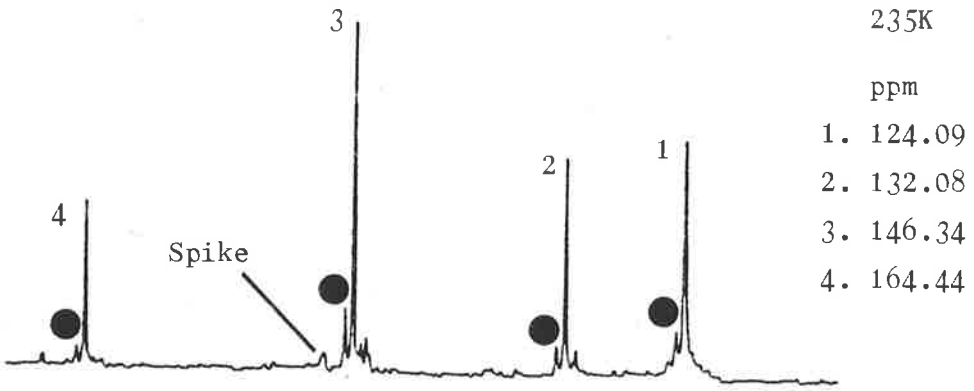


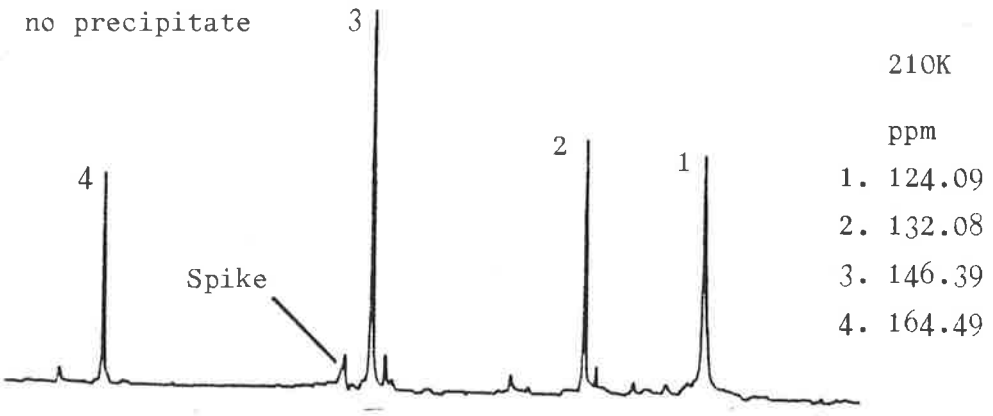
Fig. 3.16 (cont'd): ^{13}C (22.62MHz) Broad Band Decoupled Spectra of $Ms_2Mg/THF/d_8THF$
Peak assignment relative to β THF (at 25.30ppm)

D.

no precipitate



E.



3.3.5 Studies of the Cyclohexyl Magnesium Bromide System

Since this organomagnesium system was not used extensively as a polymerisation initiator, detailed studies of this system were not undertaken.

3.3.5.1 A ^{13}C Variable Temperature Study of chexMgBr/THF/d_8-THF

Broad band and off-resonance decoupled spectra are indicated in Fig. 3.17. A reliable assignment of resonances is made difficult by the presence of the β THF signal which is obscuring the remaining chexMgBr resonance (probably the C(1)-Mg); the triplet nature of peaks 2 and 3 reveal that they are not directly attached to the magnesium atom.

A variable temperature study of this system featured in Fig. 3.18, reveals the following:

(1) Coalescence temperature for the given bromide and active bond contents is in the range of 290-300K.

(2) The sensitivity of the downfield cyclohexyl peak (Fig. 3.18A; peak 3) to splitting, in comparison to broadening at other sites, probably indicates that this resonance corresponds to the C(2,6) carbons.

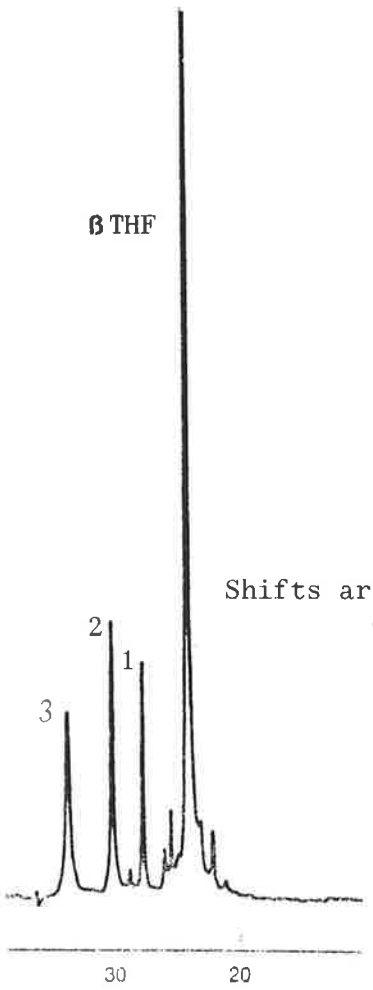
(3) In contrast to aryl systems where the C(1)-Mg resonance moves downfield with respect to C(1)-Br by approximately 40ppm, alkyl magnesium bromides show[19] upfield shifts with respect to alkyl bromides, for C(1)-Mg, of about 40ppm (e.g., secBuBr ⟶ secBuMgBr). In this case the C(1) resonance moves from

Fig. 3.17: ^{13}C (20.1MHz) Broad Band Decoupled and Off resonance.
Spectra of cyclohexyl Magnesium Bromide/Schlenk/THF/d_8THF

[chex Mg] = .57M
[Br] = .40M

300K

Broad Band
Decoupled



ppm

1. 29.03
2. 31.65
3. 35.29

Shifts are relative to the β carbon of THF (25.30ppm)

Off Resonance
Decoupled

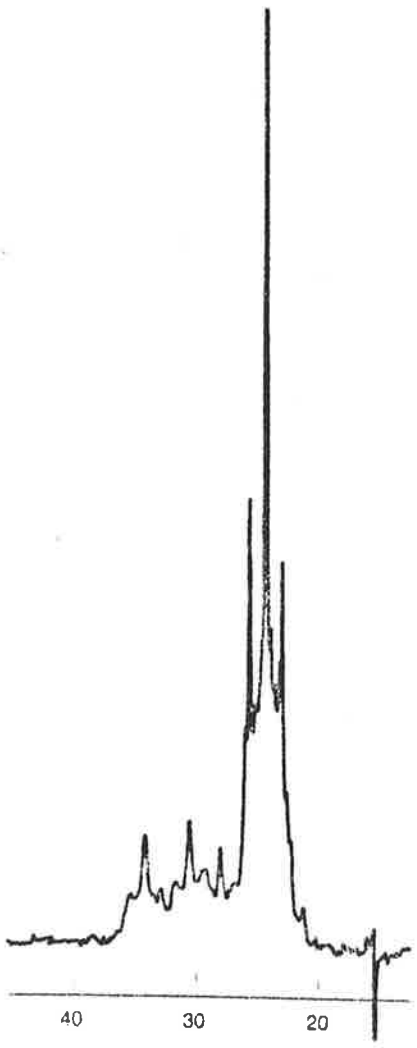
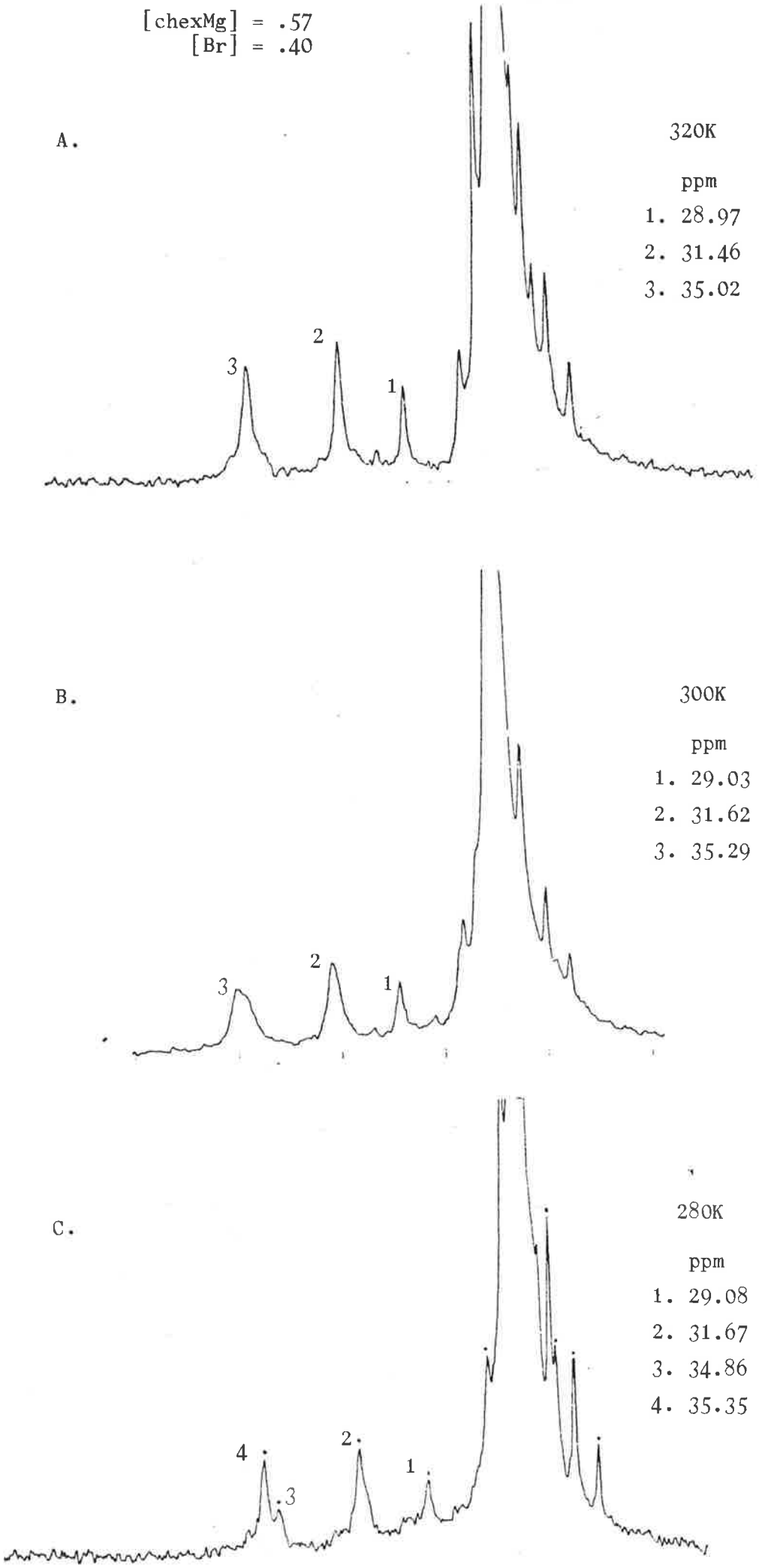


Fig. 3.18: ^{13}C (22.62MHz) Broad Band Decoupled Spectra of chexMgBr/Schlenk/THF/d_8THF



approximately 52ppm (chexBr) to, presumably, a position under the β THF peak at approximately 25ppm (chexMgBr).

3.3.5.2 A Variable Temperature ^{1}H Study of chexMgBr/d_8-toluene/residual THF

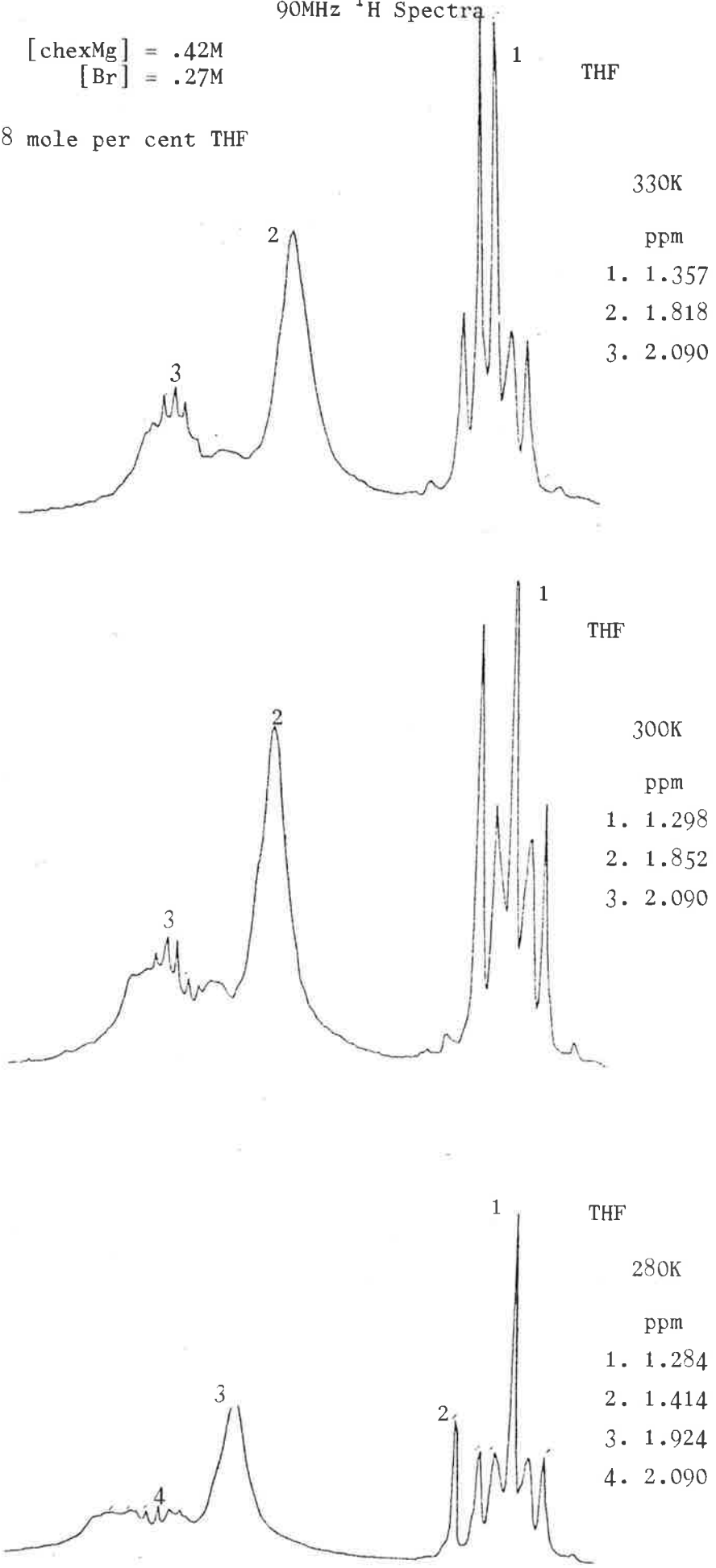
Fig. 3.19 shows a variable temperature examination of this system, revealing broadening and coalescence at low temperature (coalescence being observed at about 210K). Although this lower coalescence temperature is in keeping with results obtained in non-polar solvent, the result here is not entirely unambiguous. It is possible that a ring flip procedure:

also undergoes slow exchange concurrent with slow exchange in the Schlenk equilibrium process.

3.4 Summary

Studies of the constitution of Grignard reagents in solution have been made necessary because the definition of eneidic polymerisations, thought to be operating in organomagnesium initiated reactions with MMA,[42] suggests that discrete different active centres may be related to the presence of RMgX, R_2Mg and just as importantly, the presence of monomeric and extended forms of the initiator.

Fig. 3.19: Cyclo hexyl Magnesium Bromide/d_8Toluene/residual THF
90MHz ^{1}H Spectra

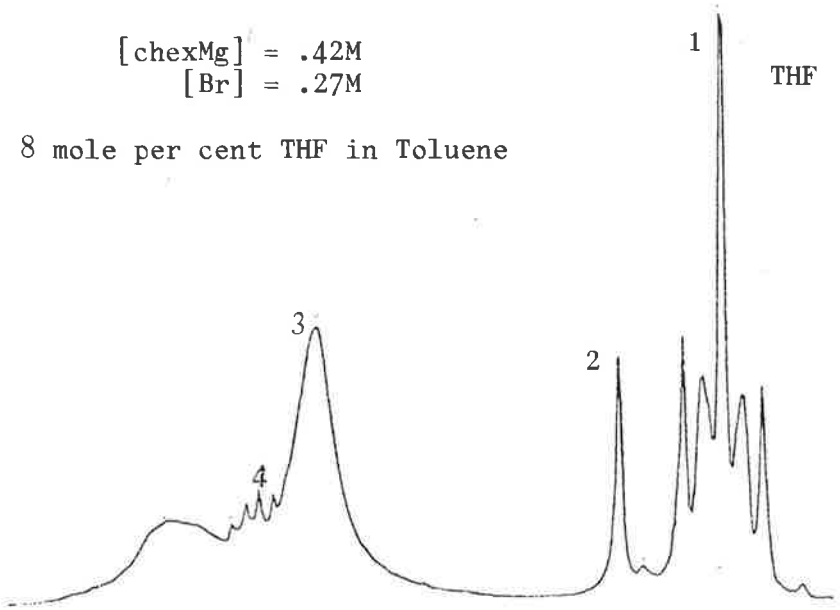


n.b. Residual proton resonance for the methyl group of d_8 Toluene appears as a multiplet overlapping the cyclo hexyl magnesium resonance.

Fig. 3.19 (cont'd): Cyclo hexyl Magnesium Bromide/d_8Toluene/residual THF

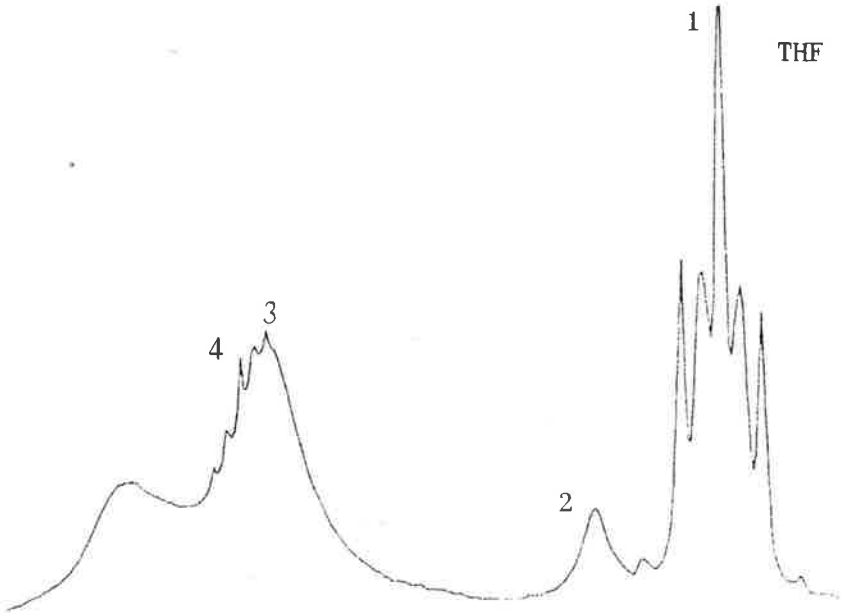
[chexMg] = .42M
[Br] = .27M

8 mole per cent THF in Toluene



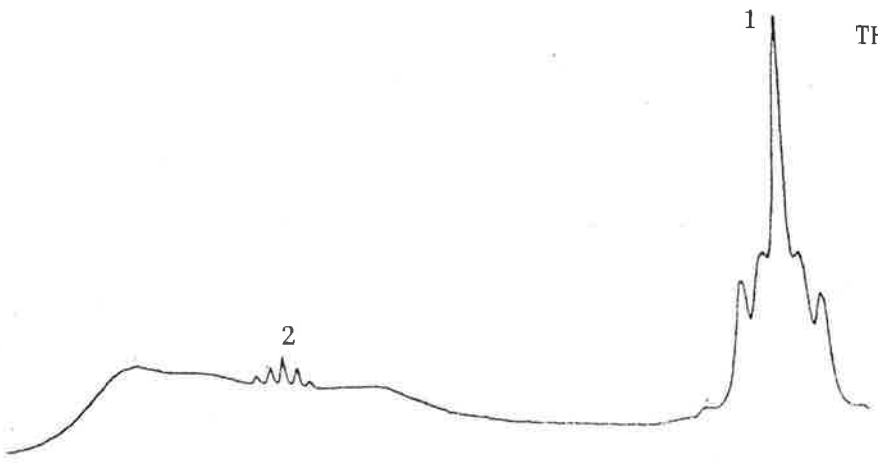
250K

ppm
1. 1.234
2. 1.423
3. 1.982
4. 2.090



230K

ppm
1. 1.232
2. 1.433
3. 2.040
4. 2.090



210K

ppm
1. 1.198
2. 2.090

Work carried out on the phenyl, mesitylene and cyclohexyl magnesium bromide systems supports the presence of the Schlenk equilibrium at the given active bond concentrations and active bond to bromide ratios. A comparison between PhMgBr and MsMgBr systems reveals that, provided equilibrium concentrations are the same, slower exchange is evident for the bulkier mesitylene entity. For the MsMgBr system, the nature of the solvent (THF/toluene) becomes important at more extensive de-etheration; the rate of exchange between R_2Mg and RMgX sites increasing in more extensively de-etherated systems.

The observation of associates has been noted in the Ph_2Mg/toluene/d_8-toluene system as a precursor to precipitation and, in certain circumstances, broadening of the upfield C(1)-Mg peak (in the case of PhMgBr/THF/d_8-THF and MsMgBr/THF/d_8-THF) may be associated with the onset of slow exchange between monomeric and extended forms of Ms_2Mg and Ph_2Mg. No apparent observation of such a process was noted for the C(1) resonance of the PhMgBr/MsMgBr entity, probably because terminal aryl groups of these halo bridged associates are not at chemical shifts sufficiently different from the aryl entity of monomeric PhMgBr/MsMgBr, at 22.62MHz resolving power.

Finally, the concentration of active species was necessarily high for ^{13}C analysis, since reasonable signal to noise was required over a five to six hour accumulation period. In the polymerisation process, however, the active bond concentration is significantly lower and observations

noted in this chapter may not necessarily apply under those circumstances. Likely differences may be the lower extent of association and slower bimolecular processes for the Schlenk equilibrium.

CHAPTER 4

4. POLYMER PRODUCTS

4.1 Introduction

In this chapter a discussion of molar mass, molar mass distribution and steric triad distribution of pMMAs formed by PhMgBr, MsMgBr and chexMgBr initiators and the corresponding diaryl magnesiums will be examined as a function of temperature, solvent (THF/toluene) constitution and bromide to active bond ratio. It is envisaged that a thorough examination of these parameters will provide information on the mechanism of monomer addition at active chain sites.

Molar mass and molar mass distributions were studied using Gel Permeation Chromatography (GPC), while microstructure was determined with the aid of NMR spectroscopy.

4.2 Outline of Theory for Techniques Used

4.2.1 GPC

This instrumental technique has long been acknowledged [1] as an extremely useful method for determination of molar mass distributions since other methods for evaluating $\bar{M}_w/\bar{M}_n$ by a combination of techniques such as osmometry ($\bar{M}_w$) and light scattering ($\bar{M}_n$) are "blind", i.e. a stated value for the heterodispersity index assumes a monodisperse distribution (Gaussian) of molecular weights. However, where polymer products arise from discrete non-exchanging active sites propagating at different rates, as has been observed in some systems,[2] such an assumption is

invalid. These conditions give rise to broad and polymodal distributions with molecular weight profiles representing the sum of component Gaussian distributions for each different type of active centre present in the reaction. GPC is the only tool capable of characterising such systems.

The GPC experiment involves the addition of a dilute polymer solution (in this thesis about 600µl of .3% w/w) into a system comprising:

(1) Injection Loop. A WATERS Model U6K Injector with a capacity for a 2ml injection was used.

(2) High pressure solvent pump to maintain solvent flow in the system (WATERS Model 6000A pump). Methylene chloride was routinely used as the carrier solvent in this work with the solvent being pumped at 1.5ml min^{-1}.

(3) A means of separating polymer molecules according to their size in solution. For this purpose a series of four columns containing cross-linked styrene/divinyl-benzene copolymer (WATERS µ-Styragel) were used with porosities 10^6 A°, 10^5 A°, 10^4 A° and 10^3 A°, respectively.

(4) An in-series detector to register the separation procedure occurring on the µ-Styragel columns. In this work a WATERS R401 differential refractometer was used, which monitored the difference in refractive index between pure solvent and polymer solution.

(5) Volume Counter. Elution volumes were measured by means of a constant volume delivery siphon attached

to the refractometer outlet. This volume count was electronically and simultaneously superimposed on the recorder profile of molar mass, received as an amplified signal from the differential refractometer.

The mechanism for the separation process occurring on the columns is still not unequivocally known,[3] although Moore[1] and Laurent and Killander[4] suggest that as the polymer solution passes through the columns, small molecules are retarded by entrapment in the pores of the gel, more so than large molecules which pass through more rapidly.

The quantitative determination of molar mass and heterodispersity index using this method is where problems arise, since the technique is not absolute; it relies upon the accurate calibration of the system, in the absence of suitable pMMA standards, with polystyrene standards of known molar mass and narrow molecular weight distribution. The calibration techniques most frequently used involve the plotting of elution volumes for these standards against $\log\bar{M}_w$ or $\log R_e$[5] (where R_e is the radius of an impenetrable equivalent hydrodynamic sphere). The $\log\bar{M}_w$ vs V_e curve is not linear, with deviations from linearity notable in the very high and very low molar mass ranges. At very high molecular weights the polymer chains may be envisaged as being totally excluded from the pore spaces of the μStyragel columns, thus having shorter retention times than predicted. For small molecules all pore sizes may be accessible to the polymer chain, so that retention

is longer than predicted. In these ranges GPC is an ineffective tool for estimating molar mass. In this thesis the working range of molecular weights that could be evaluated with respect to polystyrene was of the order 10^4 -10^6. Implicit in the interpolation of molar mass of pMMA from this calibration curve is the assumption that the solution properties of a polymer with polar side groups are coincident with that of polystyrene, which is probably not the case. Present research in the field of GPC has been directed toward the establishment of a universal calibration curve, independent of the type of polymer investigated, by inclusion of such parameters as root-mean-square radius of gyration, unperturbed mean end-to-end distance or intrinisic viscosity [6-10] into the expression relating molar mass to peak elution volume. The solution to a universal calibration curve has, however, yet to be fully resolved.

Another aspect of the GPC technique which requires consideration is whether detector response is independent of microstructure. Jenkins and Porter,[11] studying the unperturbed chain dimensions of isotactic and syndiotactic pMMA in a thermodynamically good solvent, THF, have shown that isotactic pMMA is 30% more extended than syndiotactic pMMA, with the former showing a lesser degree of polymer-solvent interaction. Refractive index (as well as peak elution count) may well differ as a consequence, giving, for example, erroneous estimates of the relative proportions of polymer produced at isotactic and syndiotactic sites in a reaction where both centres coexist. However,

work done in this thesis tends to indicate that, when isotactic-like and syndiotactic-like polymers were run under normalised conditions the variation in area under each chromatogram was about ± 15-20%, an error which is not unusual for a chromatographic technique. In this thesis it will be assumed that recorder response is independent of microstructure.

4.2.1.1 Treatment of Results

(a) Estimation of Molar Mass

Despite the fact that attempts to provide universal calibration curves for molar mass evaluation have been partially successful, these methods are totally unsuitable for broad molecular weight distributions encountered in this thesis. At present, one of the more accurate theories for molar mass determination utilises the relationship log $([\eta]\bar{M}_w)$ vs V_e [6] (the elution volume) for all polymers, necessitating the determination of $[\eta]$ at the GPC operating temperature (30° C) in the operating solvent to derive molecular weight. Given the difficulty of broad distributions present here, the plot of $\log\bar{M}_w$(pSty) vs V_e has been persevered with, despite its limitations, and values for the molar mass of pMMA appearing at a given V_e were interpolated from this plot. These molar masses should be viewed with caution. Hagias,[12] using an isotactic sample of pMMA with an interpolated $\bar{M}_w$ of 2×10^6 and an $\bar{M}_w/\bar{M}_n$ =1.8, obtained a viscosity average molecular weight of $8.\times10^6$ for the same sample (however, in the absence of data for K and α in the Mark-Houwink relationship for isotactic pMMA, values appropriate to atactic pMMA were used).

(b) Estimation of Molar Mass Distribution

As mentioned previously the evaluation of $\overline{M}_w/\overline{M}_n$ attains significance when the nature of the GPC is Gaussian in form. If this is so then two methods available for the evaluation of polydispersity index are:

(1) Using the method of Herdan,[13] a plot of elution volume versus cumulative weight per cent is produced, which under Gaussian conditions is linear, with standard deviation determinable from the difference in counts between the 50% and 16% mark. The molecular weight at the 50% mark, $\overline{M}_g$, representing the geometric mean, is evaluated and $\overline{M}_w$, $\overline{M}_n$ obtained from the relations:

$$\sigma_{MW} = \sigma_c \cdot k$$

$$\overline{M}_w = \overline{M}_g \exp(\sigma^2_{MW}/2) \qquad \text{Equn 4.1}$$

$$\overline{M}_w/\overline{M}_n = \exp(\sigma^2_{MW}) \qquad \text{Equn 4.2}$$

where k = slope of the calibration curve.

(2) Using the method of Waters Associates[14]

$$\overline{M}_n = \sum_{i=1}^{\infty} h_i \Big/ \sum_{i=1}^{\infty} (h_i/M_i) \qquad \text{Equn 4.3}$$

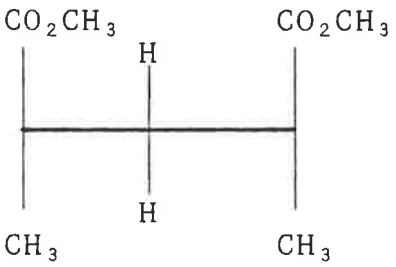
$$\overline{M}_w = \sum_{i=1}^{\infty} (h_i M_i) \Big/ \sum_{i=1}^{\infty} h_i \qquad \text{Equn 4.4}$$

where h_i is the height of the chromatogram above a theoretical baseline at the ith volume count; M_i is the interpolated molar mass from a polystyrene calibration curve at the ith volume count.

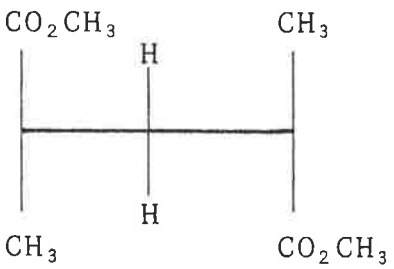
4.2.2 NMR

Before the inception of NMR spectroscopy as a means of evaluating polymer backbone stereochemistry, its determination was difficult. Goode and co-workers[15] utilised the concept of an infrared J value in conjunction with glass transition temperature measurements to determine whether the polymer was syndiotactic, isotactic or isotactic-syndiotactic. The problem with this method was its lack of sensitivity.

Bovey and Tiers[16,17,18] were responsible for development of the more sensitive NMR technique, whereby the variations in configuration and the relative population of those configurations could be evaluated about a site of interest, by virtue of the different chemical shifts imparted by configurational variation at that site. ^{1}H NMR resonances of the main chain methylene group of pMMA depend on whether these protons reside in a racemic (r) or meso (m) dyad:



m

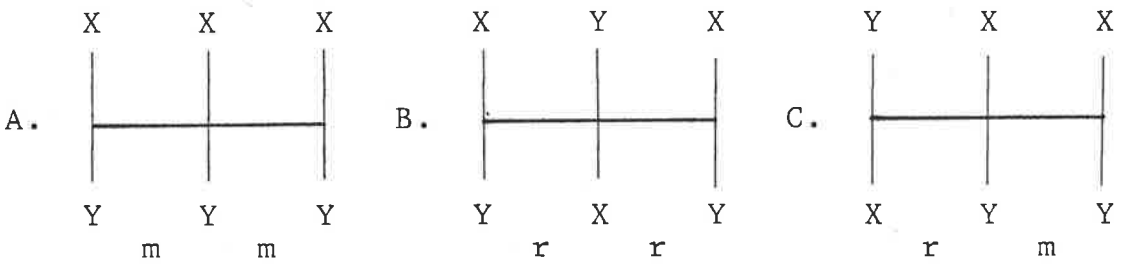


r

In the case of a racemic dyad, both methylene protons are in identical environments and thus a single ^{1}H peak arises. The two methylene protons of the meso dyad are not identical and mutually split each other to give an AB

quartet. Symmetrical additions of two monomer units to either end of the dyad generate tetrad, hexad etc. configurations. At 90MHz resolving power used in this thesis, however, tetrad configurations are only partially resolved and not of great help in statistical arguments concerned with mode of monomer addition.

By examination of α-methyl signals of pMMA using ^{1}H NMR, Bovey and Tiers[16,17,18] were able to distinguish the following triad configurations:



i = mm s = rr h = mr

where X = α-methyl Y = CO_2CH_3

and m,r denote meso and racemic dyads, respectively

Configuration A, above, represents the isotactic contribution to the triad, B the syndiotactic content and C the heterotactic contribution (effectively indicating the number of sequence changeovers in the system; occurring when an isotactic sequence changes to syndiotactic or at sites of isotactic inversion). At 90MHz resolving power used in this thesis A, B and C are clearly resolved. Further configurational resolution yields pentads, heptad etc., which are invaluable in mechanistic studies but beyond the capability of a 90MHz ^{1}H spectrometer. Chemical shift data for ^{1}H resonances, measured at 400K in a solvent

comprising 30% d_6-dimethyl sulphoxide (DMSO)/o-dichlorobenzene (ODCB), are indicated in Table 4.1 below:

Table 4.1:

Proton Environment	90 MHz Resolution		Chemical Shift
α - CH_3	Triads:	i	1.24 ppm
		h	1.11
		s	0.99
Backbone Methylene	Dyads:		
	AB signals (for m dyad)		2.20
			2.15
			1.67
			1.50
	r dyad		centred at 1.96 ppm

In our experiments the methoxy, OCH_3, protons do not appear to be influenced by the effects of stereochemistry. Spevácek and Schneider[19] propose that this may be due to free rotation about the C-O bond. Ramey and Messick[20] have shown, however, that the methoxy protons split into triad and higher placements if spectra are collected from pMMA in aromatic solvent. This solvent effect has not yet been explained.

The utilisation of ^{13}C NMR spectroscopy as a means for the determination of microstructure provides the most effective means yet to gain access to higher order chain placements (pentads etc.). Inoue et al.[21] have shown that the Nuclear Overhauser Effect due to proton decoupling has no influence on the estimation of microtacticity. This factor has particular significance in the resolution of the carbonyl carbon of pMMA, where Johnson et al.[22] have

noted that in comparison with the α-methyl carbons (both of which are sensitive to triad and pentad configurations), the carbonyl chemical shift range is approximately ten times greater than that of the α-methyl carbon. This implies that the ten pentad placements (mmmm, mmmr, mmrm, mmrr, mrrm, mrmr, rmmr, rrrm, rrmr, rrrr) incur less overlap than at the α-methyl carbon. However, even so, at 20.1MHz resolution used in this study all of these peaks in the carbonyl region were not clearly distinguishable. Numerous authors[23,24,25] have speculated on the assignment of carbonyl pentads, but absolute assignment awaits higher resolution spectrometers. Assignments of the various carbon environments of pMMA are listed in Table 4.2 below:

Table 4.2:

Carbon Environment	20.1 MHz Resolution		*Chemical Shift
α-CH_3	Triads (Distinct)	i	22.0 ppm
		h	18.8
		s	16.6
Quaternary Backbone	Triads (Partial Overlap)	i	45.5
		h	44.9
		s	44.6
Methoxy Carbon	Single unresolved peak		51.8
Methylene Carbon	Dyad ; broad overlapping		
		m	52.1
		r	55.0

Table 4.2: (continued)

Carbon Environment	20.1 MHz Resolution		*Chemical Shift
Carbonyl	Triads, Pentads (All pentads not resolved)		
	i		centred at 176.4
	h		centred at 177.1
	s	mrrm	178.2
		mrrr	178.0
		rrrr	177.7

*Chemical Shifts were recorded at 300K in $CDCl_3$-3% TMS.

Attempts by Mair[26] to use lanthanide shift reagents to improve signal resolution tended either not to shift the carbonyl peaks or decreased pentad resolution, when $Eufod_3$ or $Ybfod_3$ were used.

4.2.2.1 Statistical Arguments based upon the Assignment of Microstructure

As mentioned previously, the evaluation of tacticity is of great importance in the determination of the growth mechanism occurring at an active site. Statistics occurring at a growth centre may be described by Bernoullian, first (or higher) order Markov[27] or Coleman-Fox[28] behaviour.

The simplest of these is Bernoullian trial statistics, where the addition of successive monomer units is independent (in terms of addition of the next dyad) of any prior additions to the growing chain. These statistics are fully tested when data concerning triads is available. Given that P_m and P_r $(=1-P_m)$ are the probabilities that meso and racemic additions, respectively, occur for the adding monomer unit, then the following triad relations follow from this condition under Bernoullian statistics:

$$i = (mm) = P_m^2 \qquad \text{Equn 4.5}$$

$$h = (rm + mr) = (1-P_m)2P_m \qquad \text{Equn 4.6}$$

$$s = (rr) = (1-P_m)^2 \qquad \text{Equn 4.7}$$

$$i + h + s = 1 \qquad \text{Equn 4.8}$$

First order Markov statistics apply when the configuration of one unit, most probably the chain end, affects the mode of addition. This system is characterised by four probabilities P_{mm}, P_{mr}, P_{rm} and P_{rr} (where, for example, P_{rm} is the probability of a meso dyad placement following a racemic dyad). If:

(1) $P_{mr} \rightarrow 0$; $P_{rm} \rightarrow 1$; isotactic polymer is formed

(2) $P_{mr} \rightarrow 1$; $P_{rm} \rightarrow 0$; syndiotactic polymer

(3) $P_{mr} > 0$; $P_{rm} > 0.5$; heterotactic polymer

(4) P_{rm}, P_{mr} small but finite : stereoblock polymer

From triad data Markov models can be fitted but not distinguished. Confirmation of first order Markov statistics require a knowledge of tetrads in order to establish the validating relationships:[29]

$$4(mmm)(rmr)/(mmr)^2 = 1 \qquad \text{Equn 4. 9}$$

$$4(mrm)(rrr)/(mrr)^2 = 1 \qquad \text{Equn 4.10}$$

Similarly, for systems following second order Markov statistics, where the next to last completed dyad of the growing pMMA chain affects the mode of addition of the next dyad, full confirmation of these statistics is not tested until the following pentad relationships have been established:[29]

$$4(mmmm)(rmmr)/(mmmr)^2 = 1 \qquad \text{Equn 4.11}$$

$$(mmrm)(rmrr)/(mmrr)(rmrm) = 1 \qquad \text{Equn 4.12}$$

$$4(mrrm)(rrrr)/(mrrr)^2 = 1 \qquad \text{Equn 4.13}$$

If an active centre exists in two chemically different states of different reactivity and stereospecificity in equilibrium, then Coleman-Fox statistics[28] prevail if the lifetime in each state is longer than the time for monomer addition. The mode of addition here is dependent upon the state occupied by the reactive centre and not upon previous additions to the polymer chain. Pentad assignments are required to test the validity of these statistics.

Chain statistics give a good indication as to the nature of the active centre and how the next monomer unit is incorporated into the growing chain:

(1) Typically, radical polymerisations, ionic polymerisations (propagating via free ions or loose ion pairs at planar sp^2 hybridised chain ends) and rapidly inverting tetrahedral centres, are disposed to Bernoullian statistics. Under these circumstances the asymmetric carbon in the chain attains its configuration only after addition of the next unit.

(2) Under conditions where the active chain end is associated with a covalent carbon-metal bond at a site of non-inverting tetrahedral symmetry, with the mode of addition being via insertion into the carbon-metal bond,[30] or alternatively, associated with a tight ion pair, the stericity of neighbouring groups may impart

a persistent mode of monomer approach and addition. Such behaviour would be enhanced if penultimate or antepenultimate monomer residues were co-ordinated to the metal counter ion at the active centre. In the case of pMMA this co-ordination would be most probably through carbonyl groups. First or second order Markov behaviour would thus be evident.

Complicated non-Bernoullian systems have been observed in alkyl magnesium/MMA systems by Bateup and Allen[31] in non-polar solvents and by Müller[32] for the cumyl caesium/MMA/THF system, the latter showing first order Markov behaviour.

4.3 Experimental

4.3.1 Production of Polymer

Reaction vessels of the type shown in Fig. 2.8(b) and Fig. 2.9 were used to prepare samples of pMMA. In particular, the reaction vessel of Fig. 2.9 was useful since it gave the opportunity to examine samples of pMMA taken from the same reaction, without variation in the initial reaction conditions. The study of the mesitylene, phenyl and cyclohexyl magnesium systems as a function of solvent composition were routinely studied by using the reaction vessel of Fig. 2.8(b).

Studies to date on the reactions of MMA with organomagnesium compounds have shown considerable variability in the mode of mixing of the initiator with MMA. If the conditions at the instant of initiation are critical in

the determination of final polymer products, as predicted by Yoshino[33] and Allen,[31] then the mode of mixing can be critical.

Bateup[34] used a method whereby frozen monomer and frozen initiator were melted to the required polymerisation temperature. This method, in the case of Grignard reagents, has the disadvantage that often $MgBr_2$ is left as a precipitate following melting; a component which is critical in the determination of active centres produced and hence polymer resultant.

Mair,[26] utilising reaction vessels identical to Fig. 2.8(b), added terBuMgBr and $terBu_2Mg$ to the upper half of these reaction vessels in solvent (THF/toluene) which was of the same mole fraction THF in toluene as the MMA/solvent mixture in the bottom half of the reaction vessel. Following equilibration at the reaction temperature, the initiator was run on to the monomer solvent with shaking, and then left unstirred for the duration of the reaction. The advantage of this technique is that it partially relieves the discontinuity in the nature of the solvent at the instant of mixing (although monomer still imparts substantially different character to the lower part of the reaction vessel). The disadvantage of the technique lies in the fact that if a series of reactions is studied over the whole solvent range from total toluene to total THF, then the mole fraction THF/toluene in the upper half of the reaction vessel must change over the series of reactions as the total amount of THF in the reaction is increased. This may alter the nature of the Schlenk equil-

ibrium and association equilibria (Chapter 3), in addition to the desirous effect of altering the final mole fraction of THF.

Matsuzaki et al.,[35] in a study of the phenyl magnesium system, added the initiator in THF or THF/toluene mixtures to neat MMA as a variation to the approach by Mair.

The mode of initiation in organomagnesium/MMA systems is important and can be compared with other systems, most notably in the nBuLi/MMA/THF system examined by Hatada,[36] where, using a slow growth initiation technique, polymer with a 75% meso content has been produced (in contrast to 41% when initiator and monomer are mixed together in the usual fashion).

The method of initiation in this thesis entails the addition, with vigorous shaking, of the alkyl/aryl magnesium compound in either THF or toluene, initially thermostatted in the upper part of the reaction vessel, to monomer in THF and/or toluene, thermostatted in the lower part of the reaction vessel. Following this the reaction was allowed to stand without stirring for the given reaction time before termination by the addition of methanol. Polymer was then collected by precipitation in excess methanol. Low molecular weight material, when present, was obtained by the addition of H_2O subsequent to collection of methanol insoluble material. All polymeric material was dried in a vacuum oven prior to characterisation.

Some conventions require explanation for an understanding of diagrams in this chapter:

(1) All reactions have been defined on a mole fraction scale rather than in terms of temperature dependent molarities, and these mole fractions are expressed on diagrams as:

$x/y/z$ where $x = \chi_{RMg/MMA}$

$y = \chi_{MMA/Solvent}$

$z = \chi_{THF/toluene}$

(2) The concentration of active bonds mentioned in the diagrams refer to the initiator solution prior to its addition to the monomer in the lower part of the reaction vessel. In all instances, unless otherwise stated, $11.0cm^3$ ($\pm 3\%$, $25^\circ C$) of this initiator in THF or toluene were added, for the cited bromide to active bond ratios. Given this data and the reaction parameters x/y/z, actual molarities can be evaluated, at least in pure THF and toluene, if the following density-mole fraction equations by Mair[37] are employed:

(a) Toluene

$$\rho^{T}_{MMA/Tol} = 1.1287 + .1119\,\chi_{MMA/Tol} - (.8942 + .1280\,\chi_{MMA/Tol})T.10^{-3}$$

Equn 4.14

(b) THF

$$\rho^{T}_{MMA/THF} = 1.1945_{o} + .0919\,\chi_{MMA/THF} - (1.0332 + .0653\,\chi_{MMA/THF})T.10^{-3}$$

Equn 4.15

where T is the reaction temperature.

(3) For diagrammatic simplicity in this chapter, reactions carried out in "total" toluene are cited as

having $\chi_{THF/Tol}$ (=z) of zero. However, under these circumstances the initiator has been prepared in toluene by the solvent replacement of THF, leaving residual ether. This residual material in the initiator solution is extremely difficult to govern and is crucial in the determination of bromide to active bond ratios and could be important in determining the extent of initiator association, both of which may decide the nature of active centres produced. An attempt has been made to maintain consistent amounts of residual THF in any toluene initiator solution produced and is summarised below:

(a) Mesitylene magnesium initiators prepared in toluene contain between 1.0-2.3(±10%; GLC) mole per cent THF in toluene.

(b) Phenyl magnesium initiators contain 1.1-5.0(±10%; GLC) mole per cent residual THF in toluene.

(c) Cyclohexyl magnesium bromide prepared in toluene contains 7.0(± 10%; GLC) mole per cent THF in toluene.

4.3.2 GPC Operating Conditions

A summary of the operating conditions applying for this instrumentation is as follows:

(1) Solvent: Methylene Chloride

(2) Solvent Flow Rate: 1.5ml $min.^{-1}$

(3) Columns: μ-Styragel; 10^3, 10^4, 10^5, $10^6 A^{O}$ in series

(4) Column Temperature: 30°C

(5) Detector: Differential Refractometer (WATERS 401)

(6) Normalised Traces: when attempted, 20(±1%)mg. of polymer was dissolved in 6.80(±1%)gm. of methylene chloride. For the refractometer attenuated at x8, and a pen recorder full scale deflection of 0.1 volt, 600 µl of this polymer solution was injected.

Superimposed on all GPC traces was a volume count. For a meaningful correlation between traces, the volume count at the appearance of the solvent peak should be the same. However, during the course of this thesis the solvent count did vary on occasions due to instrumental difficulties. This was remedied by ensuring that polystyrene standards were run, so that a $\log\bar{M}_w$(pSty) vs elution count calibration curve was evaluated for each varying solvent elution volume.

4.3.3 NMR Operating Conditions

The following instrumental conditions applied for the determination of tacticity.

(1) ^{1}H NMR

(a) Resolution: 90MHz

(b) Solvent: 30% d_6DMSO/o-dichlorobenzene

(c) Temperature: 400K

(d) Concentration: due to the possibility of viscosity broadening of ^{1}H NMR signals, the concentration was maintained so that the contents of the 5mm tube were always non-viscous and freely flowing.

(e) Tacticity determinations: Triads were measured at the α-CH_3 ^1H resonance. Integrated intensities were used for triad evaluations.

(2) ^{13}C NMR

(a) Resolution: 20.1MHz

(b) Solvent: d_1-chloroform-3% TMS

(c) Temperature: 300K

(d) Concentrations: Due to low sensitivity, concentrations used were about 20%(w/w), with 5000-6000 scans (8K data) being sufficient to produce good signal to noise. ^{13}C linewidths are less affected by viscosity.

(e) Tacticity determinations: Triads were measured at the α-CH_3 resonance and confirmed at the quaternary backbone carbon. Partial pentad resolution could be made at the carbonyl carbon. Integrated intensities were used for triad evaluation.

4.4 Results and Discussion

4.4.1 Observation of Colour Change on Mixing of Reactants

Colour changes on mixing of reactants are characteristic of reactions of organometallic compounds of Groups IA, IIA and IIIA with MMA.

In the anionic polymerisation of MMA by alkyl sodium[38] and lithium[39,40] compounds the colour change has been assigned to the living anion, with an absorption maximum at λ_{max} ~300-330nm., trailing into the visible spectrum.

Observation of the colour change in the Et_3Al/MMA system is much more complex,[41] although the absorption maximum appears at a similar position, $\lambda_{max} \sim 300nm.$, and trails into the visible region. A 1:1 complex formed between MMA and Et_3Al produces an orange coloration at high concentration, but at low concentration appears yellow. In addition, a 2:1 (MMA: Et_3Al) adduct forms which is also yellow and a transient red flash is apparent and is believed to be due to the formation of a 1:2 complex.

In the reaction of cyclopentyl magnesium bromide with the ketone, 4-methylmercaptoacetophenone in diethyl ether, studied by Smith et al.,[42] the reaction was first order in ketone. The kinetic order with respect to organomagnesium was one in dilute solution and zero at high concentration, corresponding to a mechanism involving complex formation. Spectroscopic evidence for the presence of this complex came with the observance of a new absorbance maximum at 343nm. This is in agreement with other researchers[43,44] who postulated:

$$\text{ketone} + \text{Grignard} \underset{}{\overset{K}{\rightleftharpoons}} \text{complex} \xrightarrow{k} \text{products} \qquad \text{Equn 4.16}$$

Observation of colour changes in the chexMgBr/MMA reaction system noted in this thesis are as follows:

1) When the initiator was added as a toluene solution (upper part of the reaction vessel, Fig. 2.8(b)) to MMA in THF and/or toluene, the colour change ranged from an intense orange for the reaction in toluene (spontaneous and with a duration of 60-80 sec.) to a situation where no obvious change developed at $(\chi_{THF/Tol} = .8_o)_{final}$.

Pale yellow colorations were noted between ($\chi_{THF/Tol}$=.4-.8)$_{final}$. For the reaction with ($\chi_{THF/Tol}$)$_{final}$=.2$_1$, an orange coloration was noted, similar to the reaction carried out in pure toluene, except that the attainment of this colour was less spontaneous and less intense.

2) When the initiator was added in THF (upper part of the reaction vessel) to MMA in THF and/or toluene, colour changes ranged from undetectable for the reaction in THF to yellow when the final proportion of toluene in the reaction was at its highest ($\chi_{THF/Tol}$)$_{final}$=.4$_o$.

3) No correlation existed between the presence or absence of coloration and the yield of methanol-insoluble polymeric material (20% and 22% yields after 3 hours for reactions in THF and toluene, respectively), although the reaction in toluene yielded a more isotactic polymer with a higher molar mass component (see later). Reactions carried out in systems where THF was present did give significant yields of low molecular weight material after 3 hour reaction times, whereas in toluene this was not so.

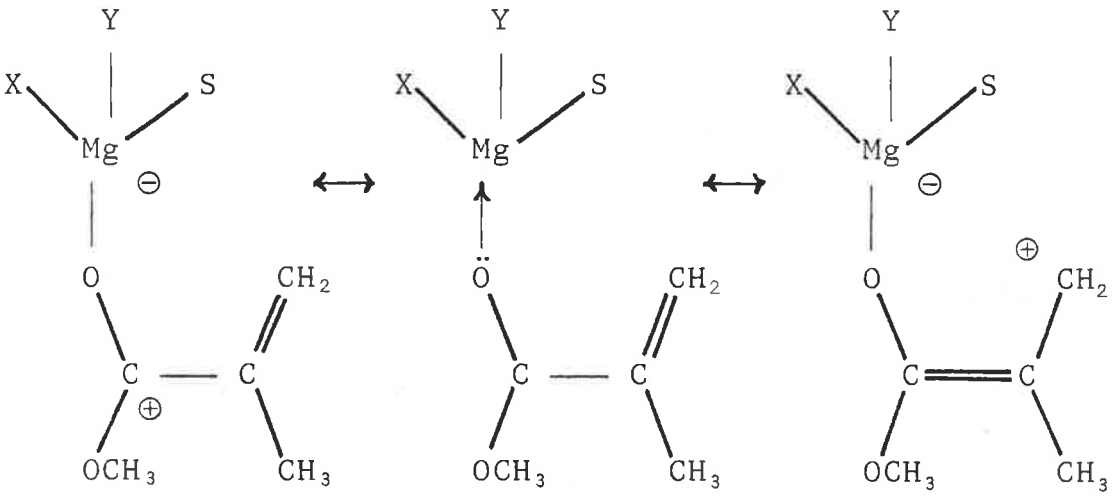
Colour changes for this system are similar to those observed by Mair[26] in the terBuMgBr system. The origin of this colour change may arise from several possibilities:

(1) Growth centres similar in character to those formed using alkylsodium/lithium initiators with MMA, where the intense orange or yellow colours could be due to the presence of two different types of active centre, one producing a yellow colour in the presence of THF

and the other giving an intense orange colour in toluene.

This option can be discounted by the fact that the concentration of active centres in Grignard/MMA systems is known[31] to be in the μmolar to mmolar range, with such concentrations being incapable of producing the intensity of colour change observed here.

(2) The formation of a complex between monomer and the alkyl magnesium centre as has been postulated[41,45] in the MMA/Et_3 Al system. This complex, as suggested by Mair,[26] would take the form:

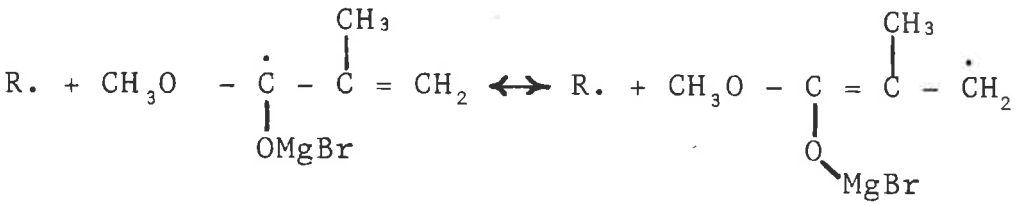


I

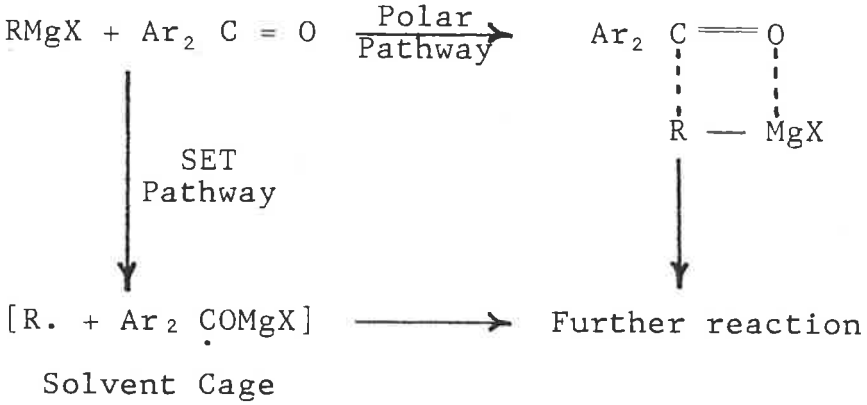
where a charge transfer band would arise from I→I* transitions, with the I* state being more polar than I, implying that the charge separated canonical forms make a greater contribution to the nature of the complex than the ground state. The entities X, Y and S are indeterminate, but S=THF or co-ordinated

polymer carbonyl and X, Y represent any two of: alkyl group, halogen or growing chain.

(3) A third possibility lies with the presence of ketyl radicals:



Okubo,[46] in the reactions of terBuMgCl, benzylMgCl and PhMgBr with substituted benzophenones, noted their ESR sensitivity and ascribed the transient pink coloration of the reaction as being due to the ketyl radical. ESR observations by Fauvarque et al.[47] in the reaction of R_2Mg compounds with benzophenone indicate the formation of intermediate ketyls, with their concentration dependent on solvent polarity as well as the ability of the R group to stabilise the radical. Fauvarque et al.[47] and Blomberg and Mosher,[48] presumed that the initial reaction between Grignard reagent and ketone proceeded via two reaction pathways:



Ashby and Wiesemann,[49] however, noted that when a single electron transfer occurred to provide the ketyl radical, the transfer was enhanced by an increase in solvent polarity. Provided it is assumed that the difference between orange and yellow colorations in the chexMgBr/MMA system, studied in this thesis, reflects concentration effects and not different chemical entities, then observations by Ashby and Wiesemann[49] tend to contradict the observed effect of greatest intensity coloration in toluene (orange) and the least in THF (no coloration or a very pale yellow).

In contrast to the chexMgBr system, the reactions of PhMgBr and MsMgBr and their corresponding dialkyls showed no colour change whatsoever, over the whole solvent range, at similar $\chi_{RMg/MMA}$ and comparable bromide to active bond ratios.

The most likely origin of the coloration in Grignard/MMA reactions appears to be via the charge transfer band of hypothesis (2) above. Lack of coloration for the PhMg and MsMg systems would imply that the charged canonical forms do not make a significant contribution to the nature of the aryl magnesium/MMA adduct. A possible explanation for this observation is that p orbitals of the π aromatic system are involved in overlap with the orbital of magnesium responsible for accepting electrons from the carbonyl group of a potential MMA donor, thus making charge transfer a less likely process.

4.4.2 Examination of Molecular Weight Distribution and Tacticity : MsMgBr

Since microstructure shows a strong correlation with the appearance and disappearance of peaks in the GPC molecular weight profile, these two aspects will be discussed together.

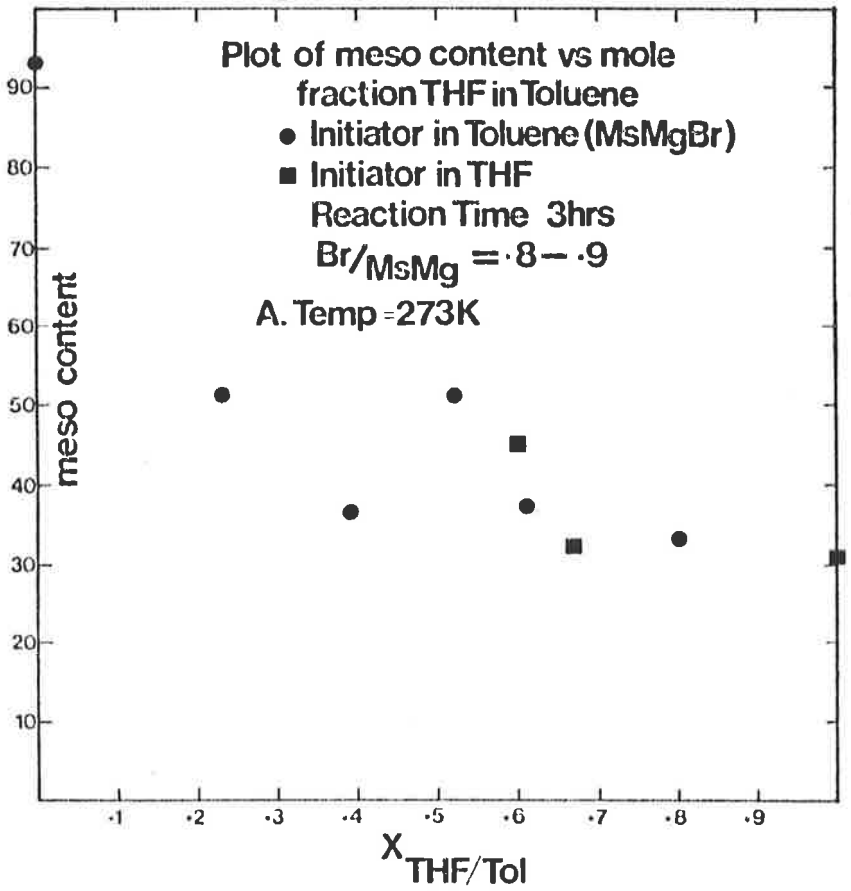
Fig. 4.1A-D and Fig. 4.2A-D show the NMR evaluated meso placement frequency and triad distributions, respectively, as a function of mole fraction THF in toluene, for a 3 hour reaction time and a bromide to active bond ratio of .8-.9. Temperatures range from 200K to 273K. Figs 4.3-4.6 show the corresponding GPC traces for those temperatures and include data concerning gravimetric yield, as well as defining the exact reaction parameters, x/y/z (described earlier). Low molecular weight, methanol soluble polymer/oligomer was not found when MsMg compounds were used as initiators, so discussion deals with high molar mass, methanol insoluble material.

Analysis of tacticity data shows:

(1) Polymers produced from reactions in toluene have a high meso content (approximately 90%) at 273K and 250K. The meso content of polymers formed at other temperatures diminishes with decreasing temperature.

(2) The addition of THF leads to a marked dimunition in the meso content, particularly at 200K where, by the time a value of $\chi_{THF/Tol} \sim 0.2$ has been reached, a minimum value of the meso content is attained, which persists over the remaining solvent range.

Fig4·1


Plot of meso content vs mole fraction THF in Toluene
● Initiator in Toluene (MsMgBr)
■ Initiator in THF
Reaction Time 3hrs
Br/MsMg = ·8 – ·9
A. Temp = 273K
meso content
90
80
70
60
50
40
30
20
10
·1
·2
·3
·4
·5
·6
·7
·8
·9
X THF/Tol

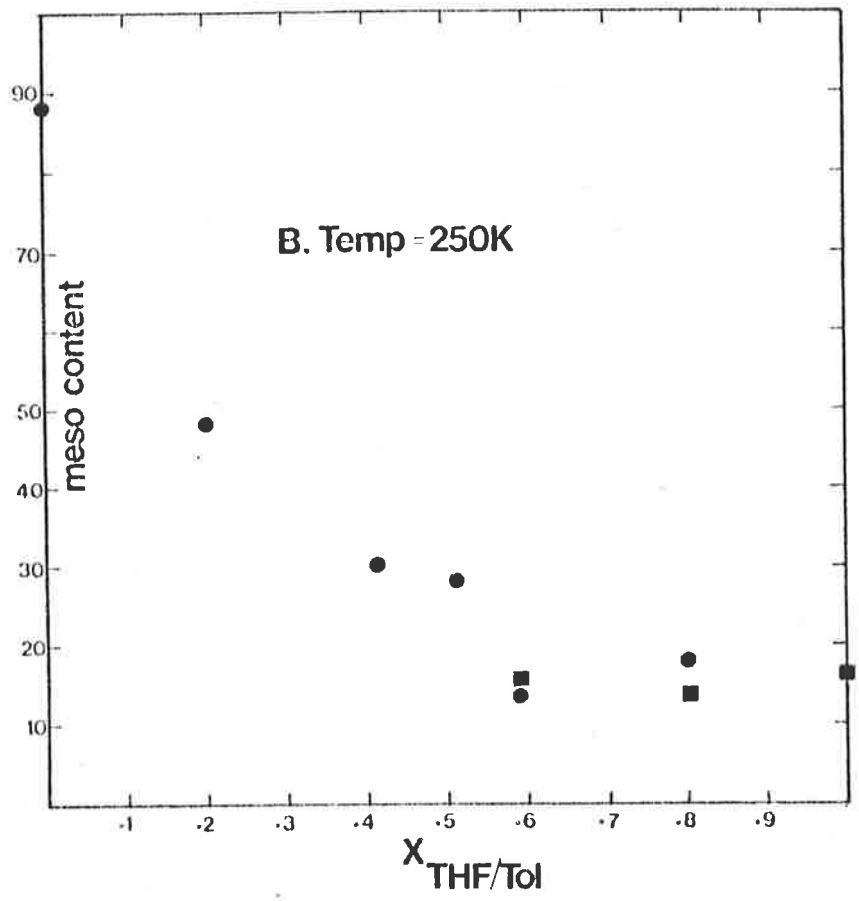
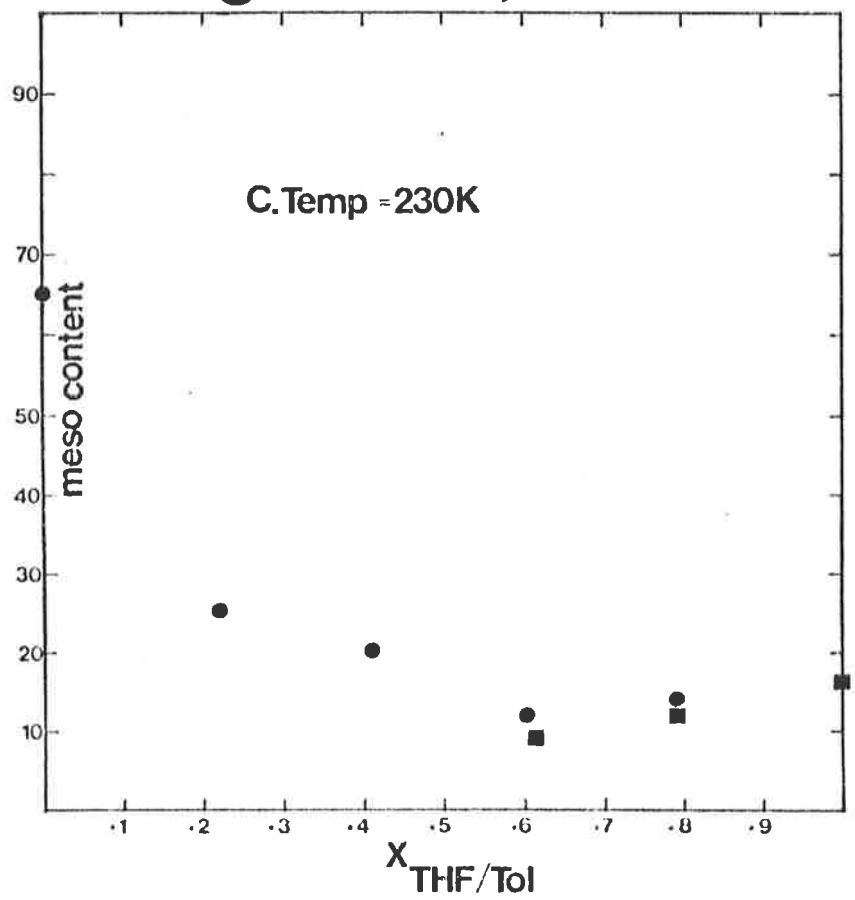

B. Temp = 250K
meso content
90
70
50
40
30
20
10
·1
·2
·3
·4
·5
·6
·7
·8
·9
X THF/Tol

Fig4·1cont;


C. Temp = 230K
meso content
90
70
50
40
30
20
10
·1
·2
·3
·4
·5
·6
·7
·8
·9
X THF/Tol

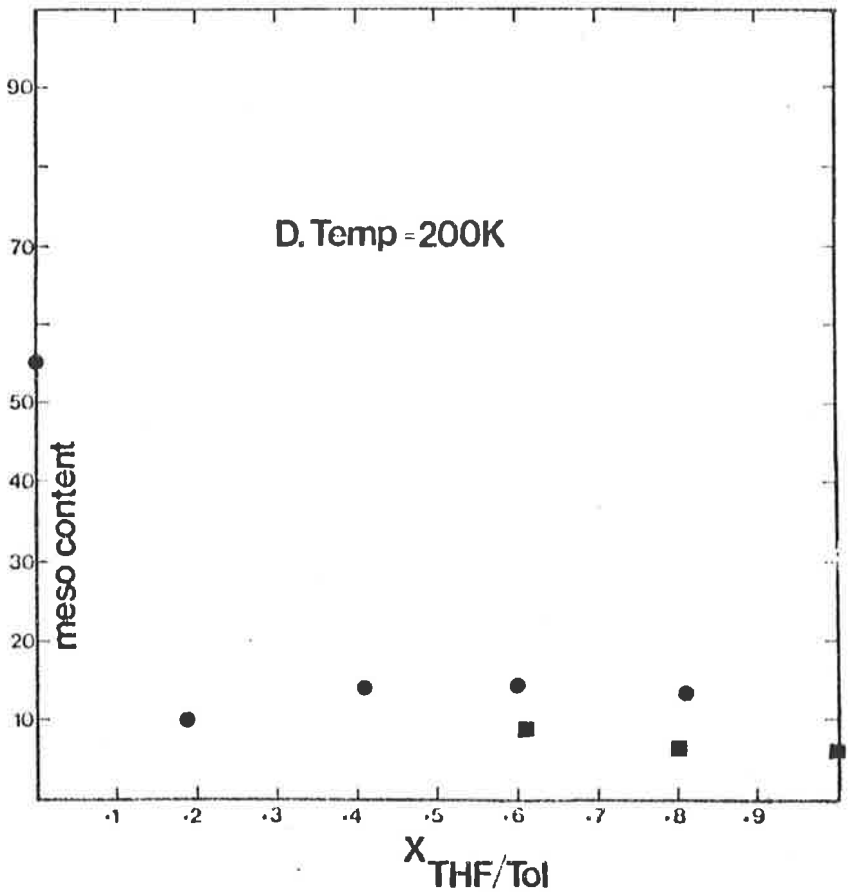
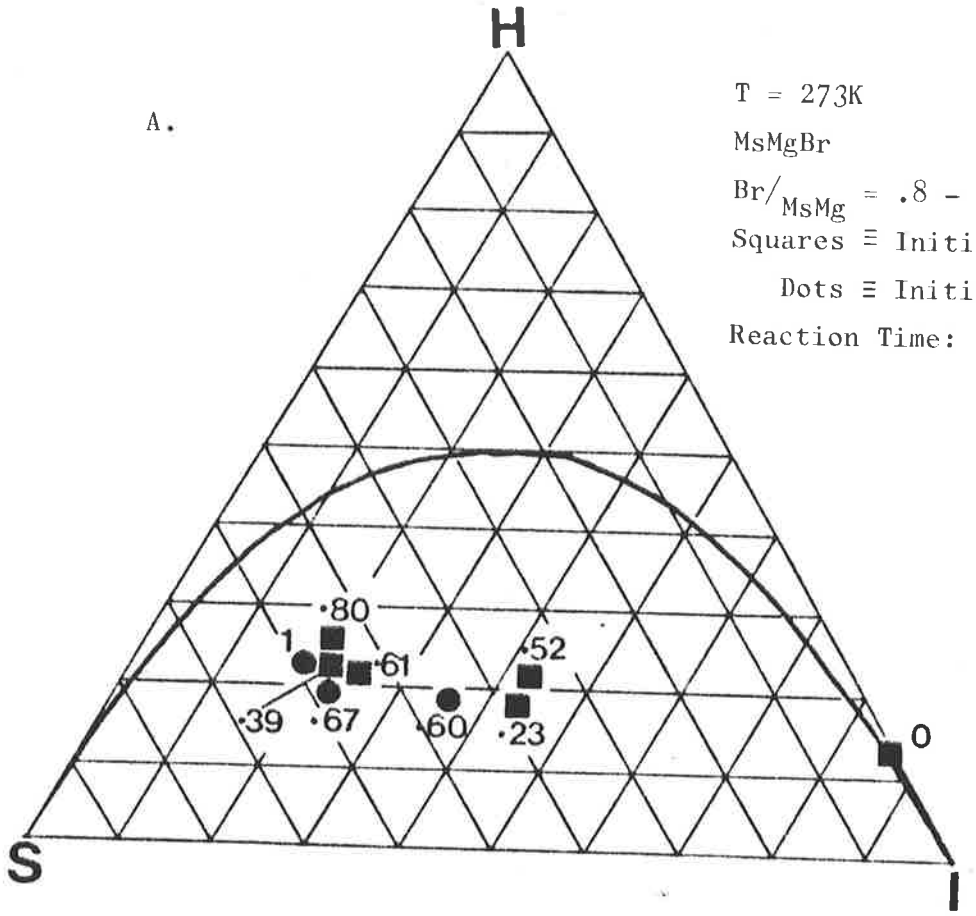

D. Temp = 200K
meso content
90
70
50
40
30
20
10
·1
·2
·3
·4
·5
·6
·7
·8
·9
X THF/Tol

Fig. 4.2: Tacticity Triangles of the Triad Distribution as a Function of Solvent Composition and Temperature. Numbers on the plots refer to mole fractions of THF.

A.



T = 273K

MsMgBr

$Br/_{MsMg}$ = .8 - .9

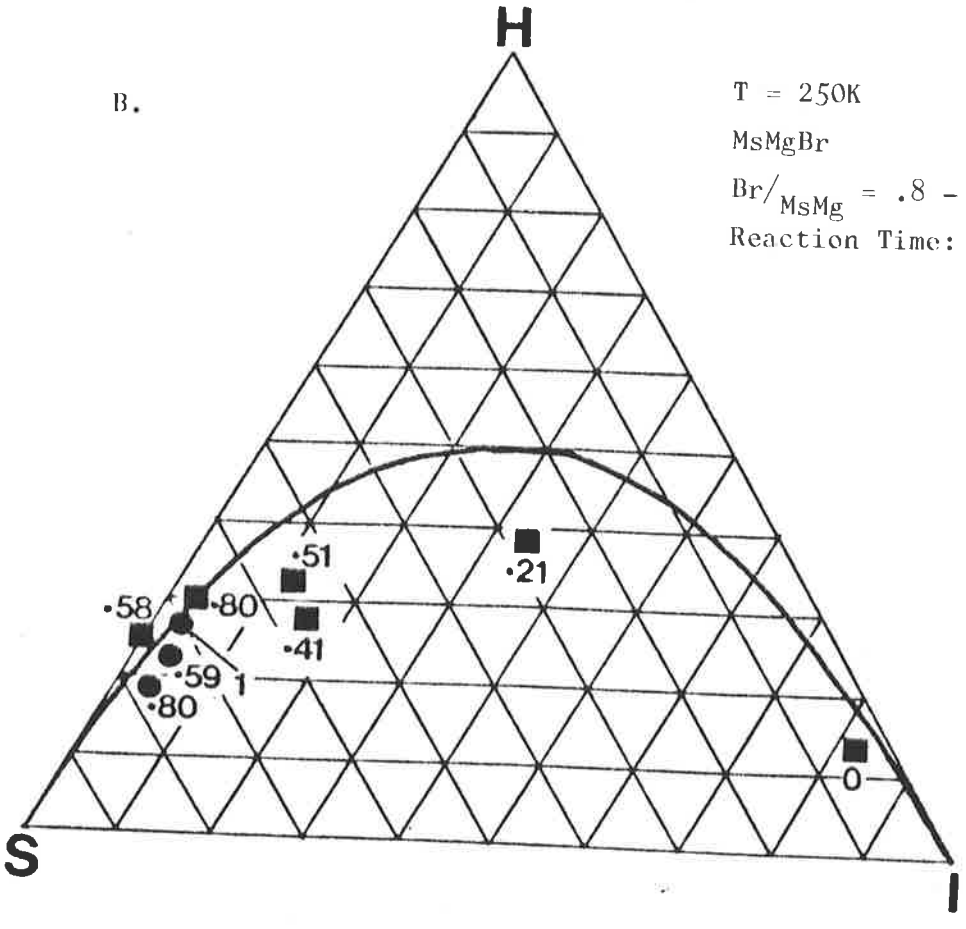
Squares ≡ Initiator in Toluene

Dots ≡ Initiator in THF

Reaction Time: 3hrs

Curved line indicates a Bernoullian Distribution

B.



T = 250K

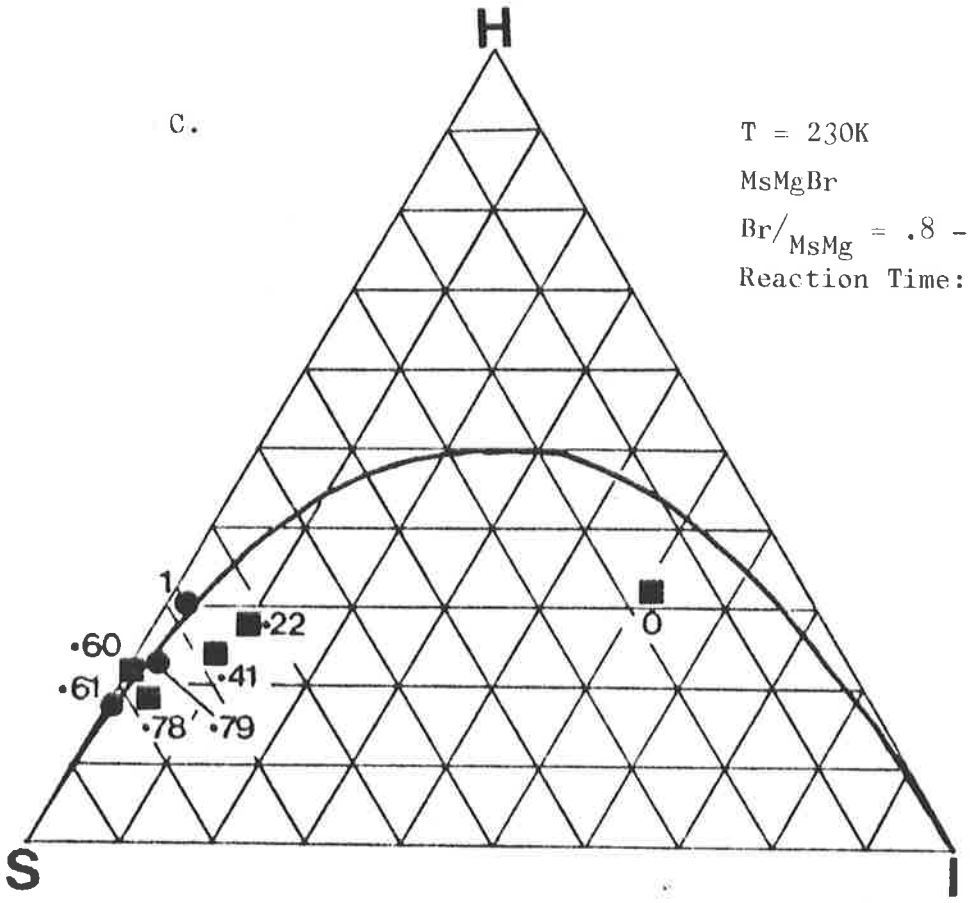
MsMgBr

$Br/_{MsMg}$ = .8 - .9

Reaction Time: 3hrs

Fig. 4.2 (cont'd):

C.



T = 230K

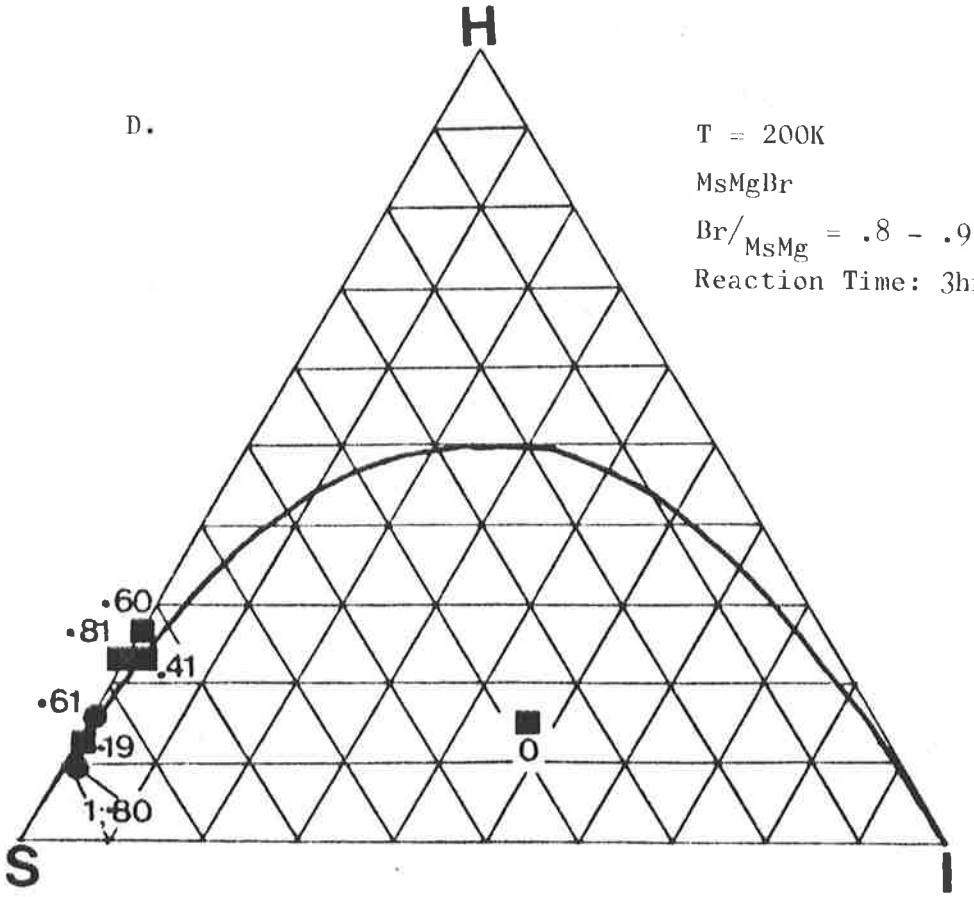
MsMgBr

$Br/_{MsMg}$ = .8 - .9

Reaction Time: 3hrs

Curved line indicates Bernoullian Distribution

D.



T = 200K

MsMgBr

$Br/_{MsMg}$ = .8 - .9

Reaction Time: 3hrs

(3) Apart from polymer products observed at 273K (Fig. 4.1A), where yields were low and molecular weight distributions erratic (Fig. 4.3), it is apparent that if the initiator is added in either THF or toluene for similar reaction parameters x/y/z, the meso content is independent of the nature of the initiator solvent. At 273K, in the presence of THF, yields are less than 1%, probably indicating reduced initiator efficiency due to side reactions in the system (i.e., carbonyl addition to monomer). It is uncertain how the effect of side products affect the mode of monomer addition, but they may be responsible for the erratic behaviour both with regard to tacticity and the nature of GPC traces (Fig. 4.3).

(4) The triad distribution triangles (Fig. 4.2) confirm the unique behaviour of the reaction in toluene, with the high meso placement manifest in isotactic sequences. Once THF has been added the syndiotactic content increases markedly.

(5) Below 250K, and particularly at 200K, the polymers produced in reactions where some THF is present have triad distributions which are very close to Bernoullian, where monomer addition is independent of prior additions to the chain. Tacticity evaluations lying on the Bernoullian curve (Fig. 4.2) do not have significance if the polymer formed is as a result of independent centres which propagate at different rates and with different stereospecificity, giving rise to broad molar mass distributions (i.e., if they

follow eneidic pathways). Many polymers which are formed with the MsMg initiator system are, however, monodisperse, particularly for reactions where THF is present, and hence can be classified as strictly Bernoullian.

A summary of observations from GPC data (Figs 4.3-4.7) is given below:

(1) For reactions carried out in toluene the molar mass distribution appears as a complex multimodal system. Fig. 4.7 shows a comparison of runs carried out in toluene over a 3 hour reaction period. These traces are at least trimodal in character (at 248K the peak molar mass maxima are at ca. $1x10^4$, $2x10^5$ and $2x10^6$gm mol^{-1}), while the relative proportions of material under each peak vary in a regular manner with temperature; the high molar mass component diminishing with decreasing temperature. The triad components of the polymers formed in toluene at 273K and 250K (Fig. 4.2A,B) indicate an almost identical microstructure (i:h:s = 87:13:0 and 81:14:5), indicating that the decrease in the high molar mass component (Fig. 4.7) at these temperatures does not exactly parallel tacticity changes. At 230K and 200K, polymers formed in toluene have isotactic contents that are similar (Fig. 4.2C,D) but considerably lower than polymer formed at 273K and 250K, with the low molar mass components ($1x10^4$; Fig 4.7) beginning to dominate the chromatograms at these lower temperatures. Although isotactic contents are similar at 230K and 200K, the

Non-normalised GPC Traces at 273K for the MsMgBr System (Br/MsMg = ·8–·9)

Fig 4·3 Molar Mass x 10^{-5} under each Trace

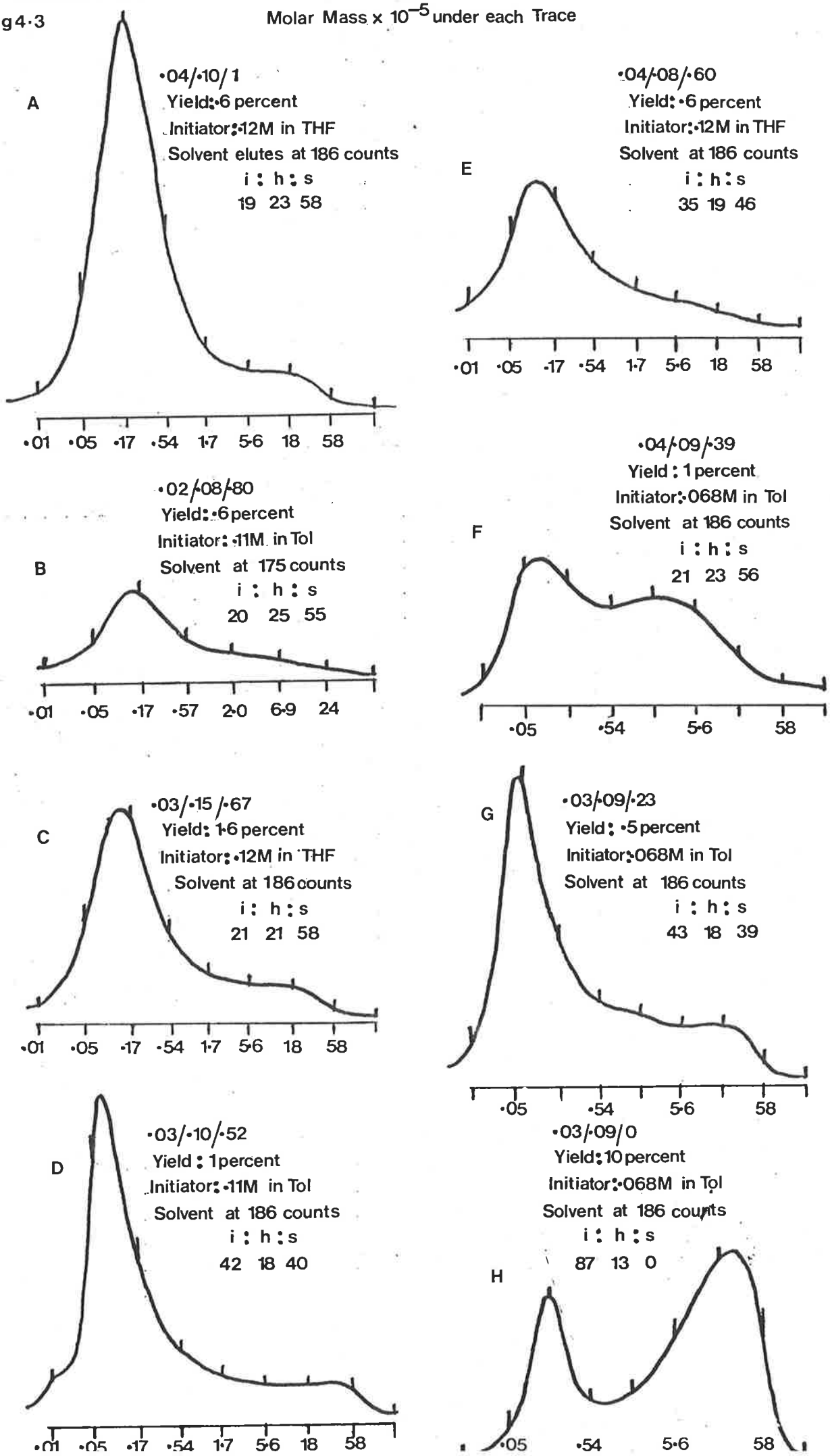


Fig4·4 Non-normalised GPC Traces at 250K for the MsMgBr System (Br/MsMg = ·8 – ·9)
Molar Mass $\times 10^{-5}$ under each Trace Reaction Time: 3 hrs

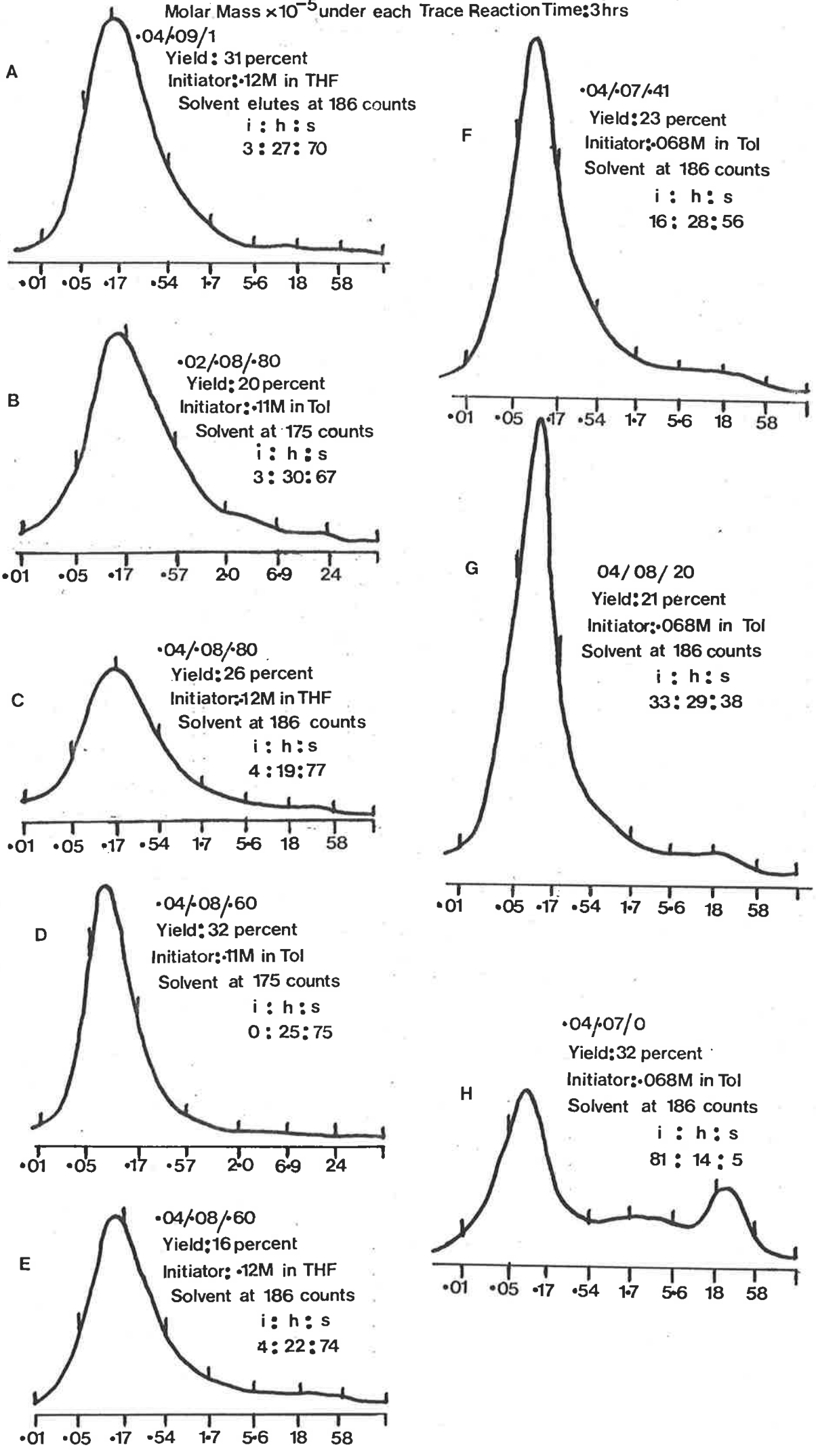
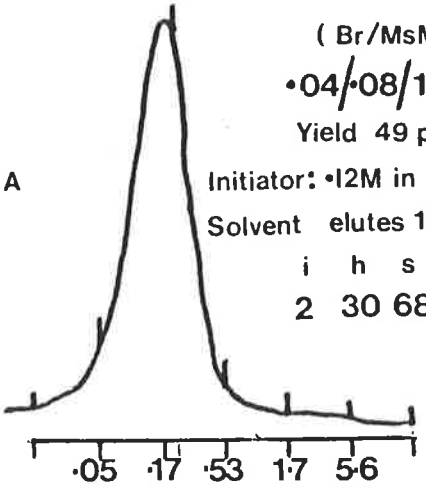


Fig 4·5 Non Normalised GPC Traces at 230K for the MsMgBr System ; Reaction Time : 3hrs

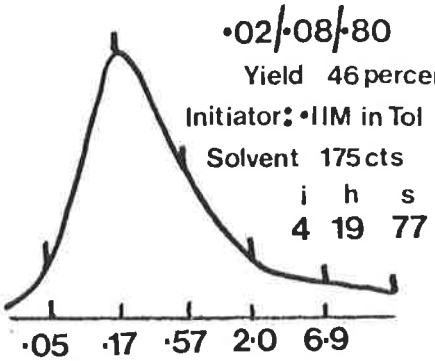
(Br/MsMg = •8 – •9)

A



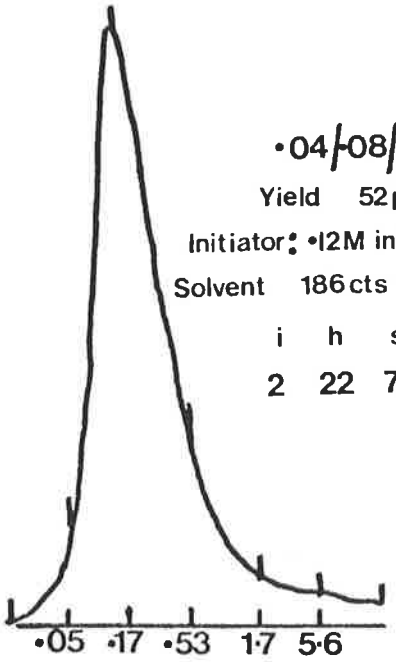
•04/•08/1
Yield 49 percent
Initiator: •12M in THF
Solvent elutes 186 counts
i h s
2 30 68

B



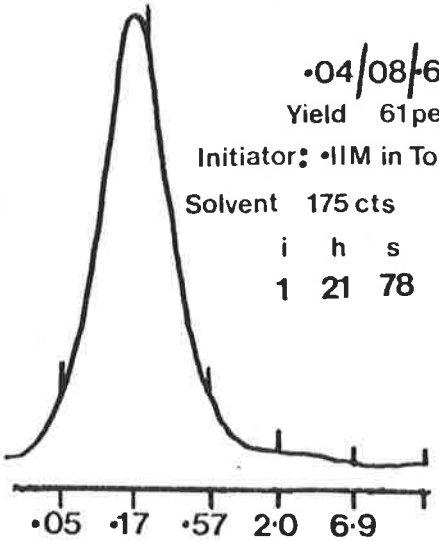
•02/•08/•80
Yield 46 percent
Initiator: •11M in Tol
Solvent 175 cts
i h s
4 19 77

C



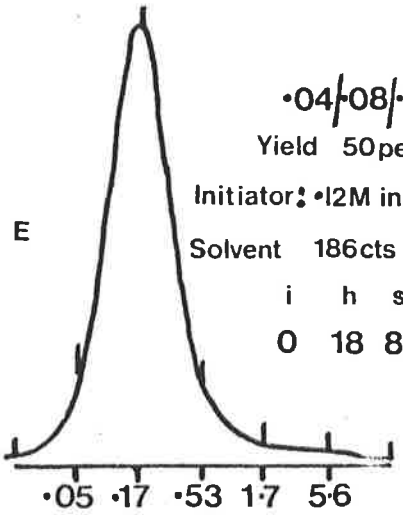
•04/•08/•80
Yield 52 percent
Initiator: •12M in THF
Solvent 186 cts
i h s
2 22 76

D



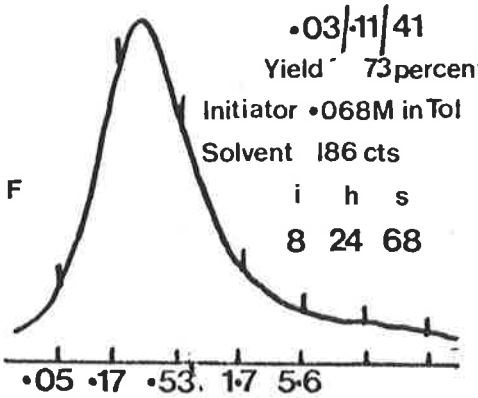
•04/08/60
Yield 61 percent
Initiator: •11M in Tol
Solvent 175 cts
i h s
1 21 78

E



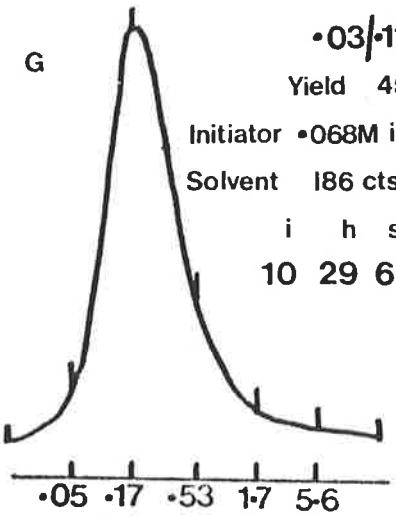
•04/08/60
Yield 50 percent
Initiator: •12M in THF
Solvent 186 cts
i h s
0 18 82

F



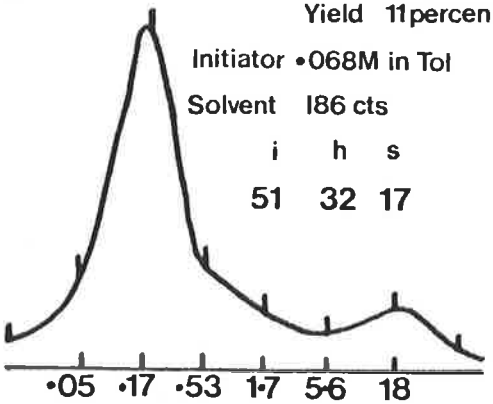
•03/•11/41
Yield 73 percent
Initiator •068M in Tol
Solvent 186 cts
i h s
8 24 68

G



•03/•11/•22
Yield 45 pe
Initiator •068M in Tol
Solvent 186 cts
i h s
10 29 61

H

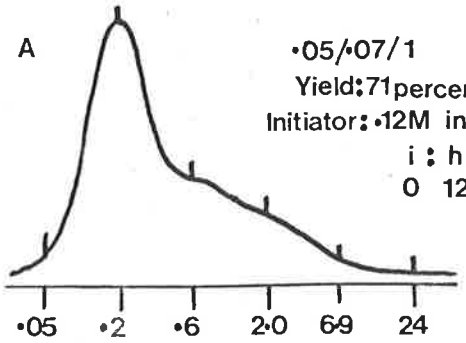


•04/08/0
Yield 11 percent
Initiator •068M in Tol
Solvent 186 cts
i h s
51 32 17

Molar Mass x 10^{-5}

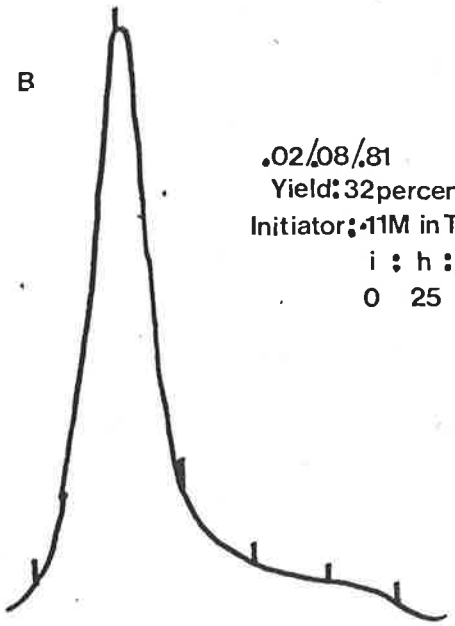
Fig4·6Non-normalised GPC Traces at 200K for the MsMgBr System
Solvent elutes at 175 counts
Br/MsMg =·8 −·9
Reaction Time: 3hrs

A



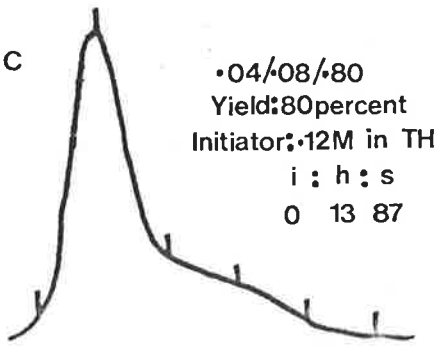
·05/·07/1
Yield: 71 percent
Initiator: ·12M in THF
i : h : s
0 12 88

B



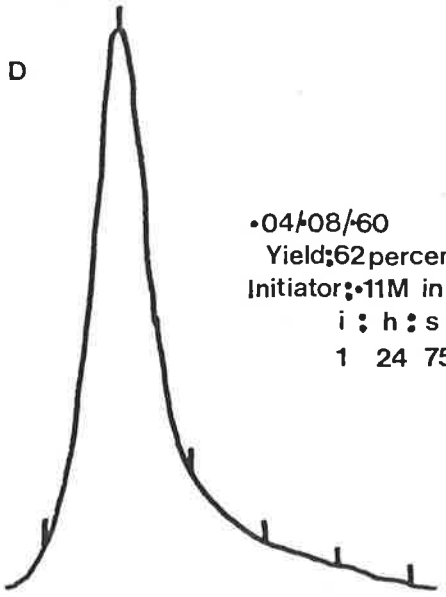
·02/·08/·81
Yield: 32 percent
Initiator: ·11M in Toluene
i : h : s
0 25 75

C



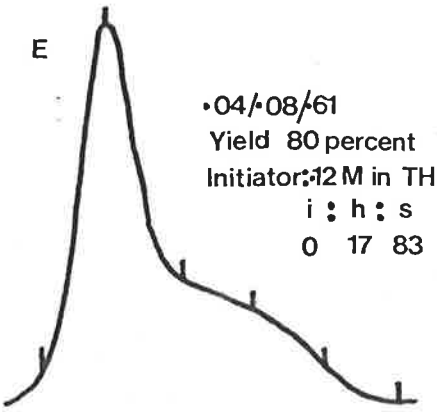
·04/·08/·80
Yield: 80 percent
Initiator: ·12M in THF
i : h : s
0 13 87

D



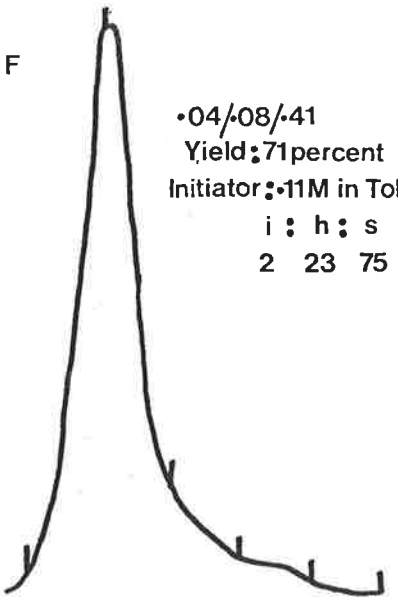
·04/·08/·60
Yield: 62 percent
Initiator: ·11M in Toluene
i : h : s
1 24 75

E



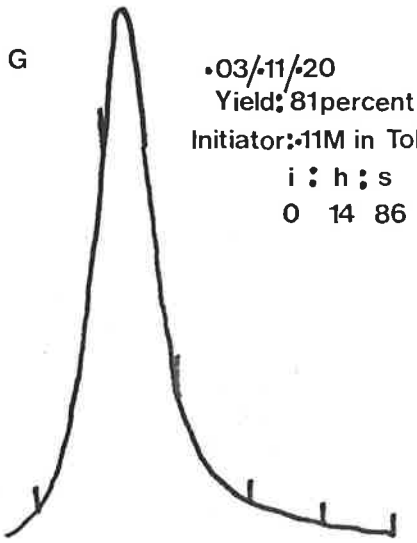
·04/·08/·61
Yield 80 percent
Initiator: ·12 M in THF
i : h : s
0 17 83

F



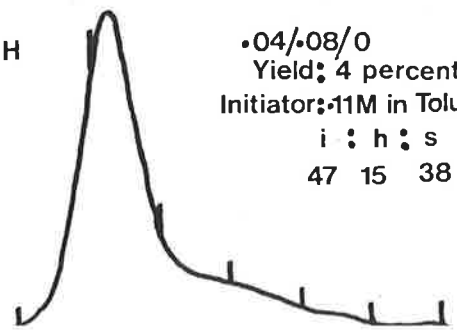
·04/·08/·41
Yield: 71 percent
Initiator: ·11M in Toluene
i : h : s
2 23 75

G



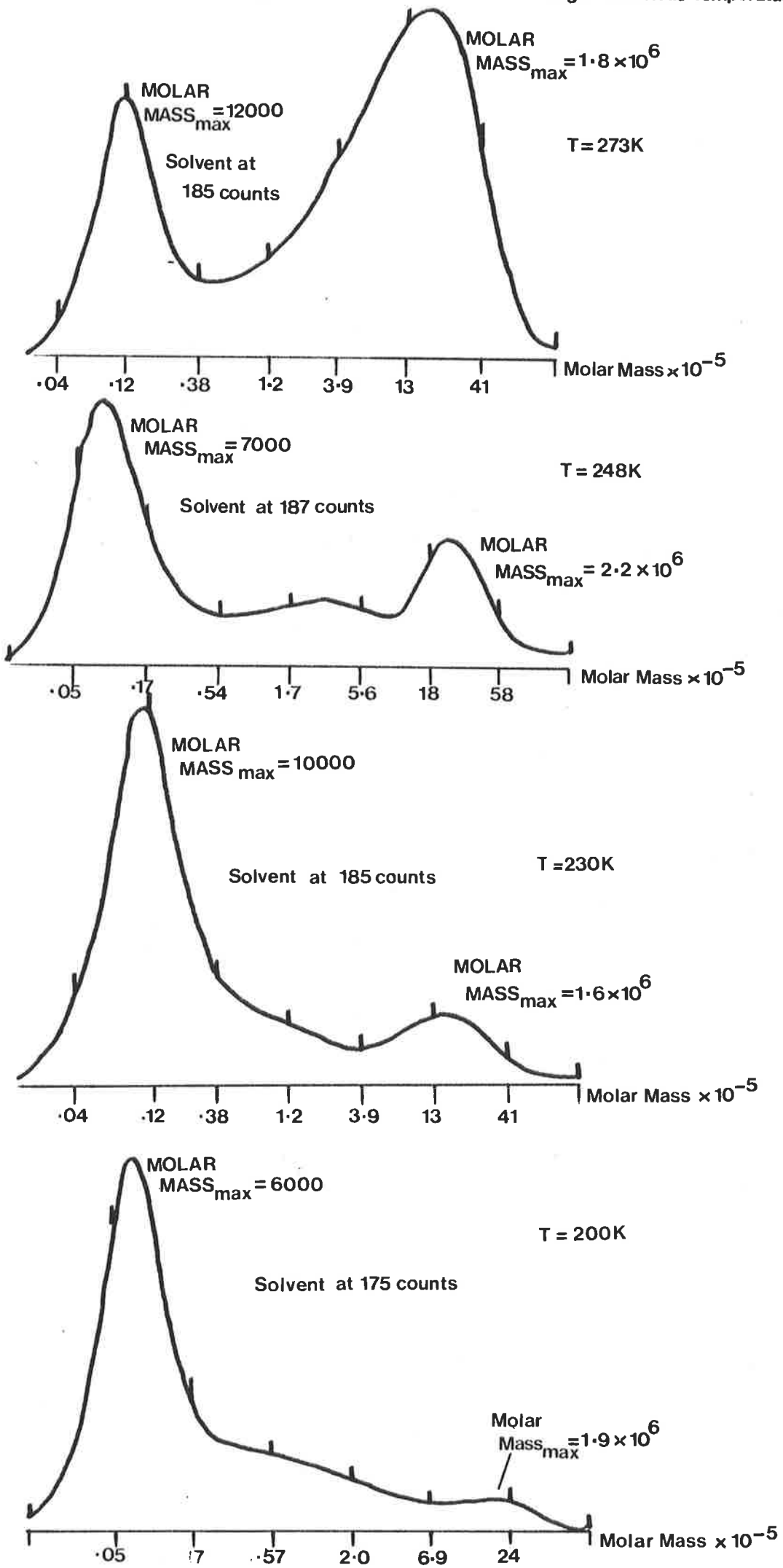
·03/·11/·20
Yield: 81 percent
Initiator: ·11M in Toluene
i : h : s
0 14 86

H



·04/·08/0
Yield: 4 percent
Initiator: ·11M in Toluene
i : h : s
47 15 38

Fig 4·7 GPC of Methanol Insoluble Polymer formed in Toluene with MsMgBr at various Temperatures



heterotacticity, reflective of the frequency of sequence changeovers, differs significantly (i:h:s = 51:31:18 and 48:15:37 at 230K and 200K, respectively).

(2) The addition of THF to the reaction mixture causes the proportion of high molar mass polymer to drop markedly, so that low molar mass material dominates. The effect of THF addition appears to mimic the behaviour of decreasing temperature in its effect on high molar mass peaks ($2x10^6$ gm mol^{-1}). Reactions carried out at 273K suffered from extremely low yields in the presence of THF and showed erratic behaviour in the nature of molecular weight distributions (Fig. 4.3). At this temperature some high molecular weight material does appear to persist to various degrees over the whole range of solvent compositions.

(3) At 250K (Fig. 4.4), the collapse of multimodal character as the mole fraction of THF increases, is accompanied by a relative broadening of the low molar mass peak. Higher molar mass polymer does persist to some degree in the presence of THF and reflects the possibility that those centres responsible for the production of high molecular weight polymer ($2x10^5$, $2x10^6$) for the reaction in toluene (Fig. 4.4H) may still persist, but at much lower concentration. At $\chi_{THF/Tol} = .2_o$ (Fig. 4.4G) the heterodispersity index of the low molecular weight peak is $1.4(\pm.2)$ as calculated by the Waters Associate method,[14] whereas at $\chi_{THF/Tol} = 1$ and $.8_o$ the heterodispersity index is $2.0(\pm.2)$.

(4) At 230K (Fig. 4.5), the estimate of $\bar{M}_w/\bar{M}_n$ for the low molecular weight peak formed when THF is present vary in a less definite manner. In total THF, in contrast to the reaction carried out at 250K, the distribution is narrow, $\bar{M}_w/\bar{M}_n$ = 1.4(± .2) (Fig. 4.5A). Reactions indicated in Figs 4.5B,F, where the initiator has been added in toluene, have broader distributions ($\bar{M}_w/\bar{M}_n$ = 2.1± .2), indicating that the nature of the initiator solvent may be important. However, this is inconsistent with Fig. 4.5D, where the initiator in toluene produces a narrower distribution ($\bar{M}_w/\bar{M}_n$ = 1.4(±.2).

(5) At 200K the small proportions of intermediate and high molar mass polymer formed in toluene (Fig. 4.6H) disappear completely on addition of THF to the system (Fig. 4.6G). The molar mass profiles are complex and directly related to the nature of the solvent in the initiator solution, and to a lesser extent on the final mole fraction of THF in the reaction mixture. When MsMgBr is added in THF solution at high $(\chi_{THF/Tol})_{final}$, intermediate molecular weight species represent a significant proportion of the polymer produced. If MsMgBr is added in toluene this intermediate molecular weight material comprises a smaller proportion of the polymer produced. Fig. 4.6G indicates that the final $\chi_{THF/Tol}$ has some bearing on the presence of intermediate molecular weight polymer, since at $\chi_{THF/Tol}=.2_o$ none of this material is evident.

4.4.3 Examination of Molecular Weight Distribution and Tacticity : Ms_2Mg

Figs 4.8A-D and 4.9A-D display the variations in meso content and triad distribution as a function of solvent and temperature, while Figs 4.10-4.13 show GPC traces at the corresponding temperatures.

Major conclusions to be made from tacticity data of pMMA produced with Ms_2Mg are:

(1) The tendency for fewer meso placements for reactions in toluene compared to the MsMgBr/toluene system (Figs 4.1 and 4.8).

(2) The meso content of pMMA is much lower when THF is added.

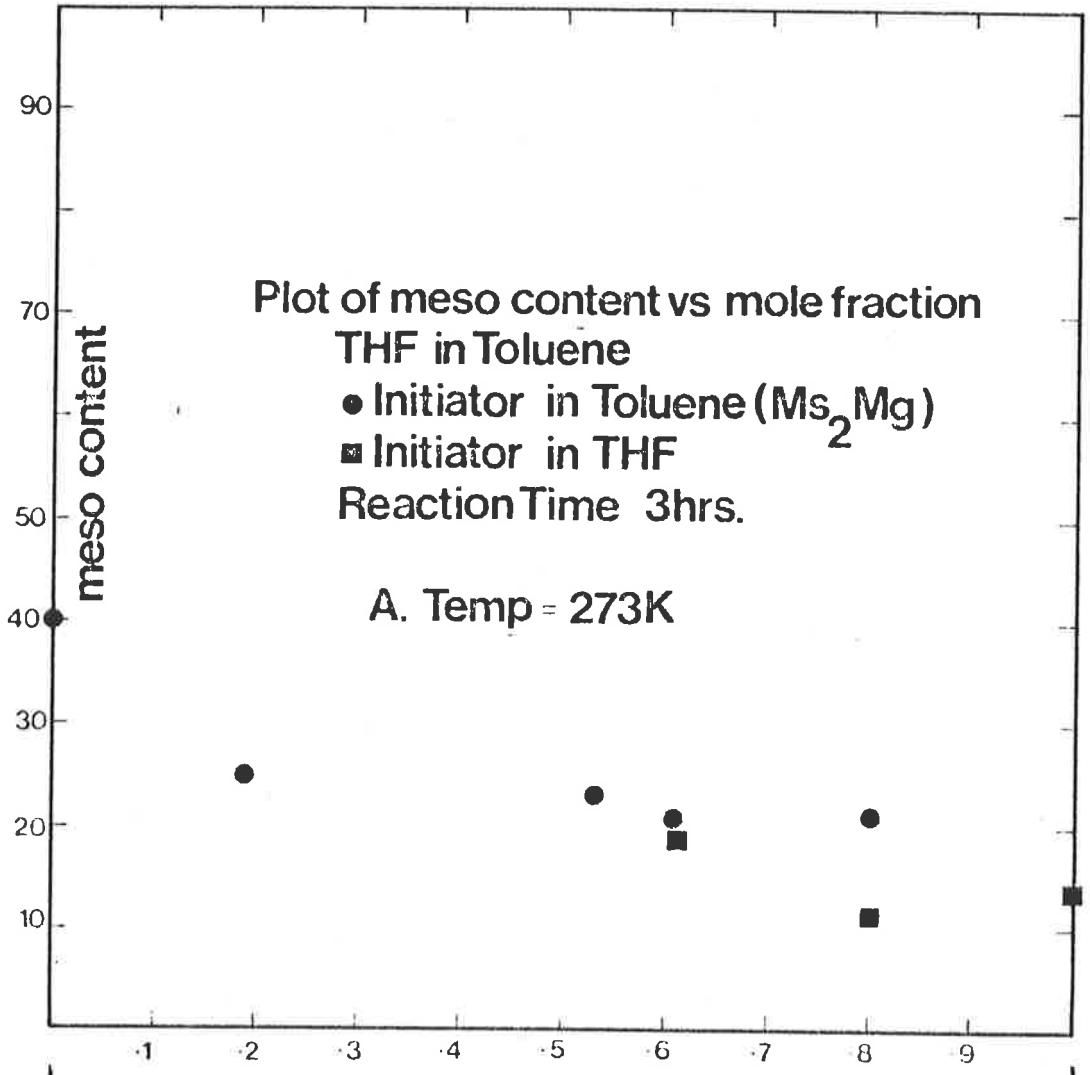
(3) The reaction carried out in toluene obeys non-Bernoullian statistics at 273K, whereas at other temperatures polymer formed lies close to the Bernoullian distribution (Fig. 4.9).

(4) In the presence of THF all pMMA products approach Bernoullian behaviour which is generally independent of the nature of the initiator solvent.

Important aspects of GPC eluograms obtained from Ms_2Mg initiated systems are:

(1) At 273K (Fig. 4.10), the reaction in toluene tends to produce significant amounts of intermediate and high molar mass pMMA (Fig. 4.10H) which is absent in similar reactions at lower temperature (Figs 4.11G, 4.12H, 4.13H). This correlates with the higher meso/isotactic content noted for the same reaction at 273K

Fig4·8


Plot of meso content vs mole fraction
THF in Toluene
● Initiator in Toluene (Ms_2Mg)
■ Initiator in THF
Reaction Time 3hrs.
A. Temp = 273K
meso content
90
70
50
40
30
20
10
·1
·2
·3
·4
·5
·6
·7
·8
·9

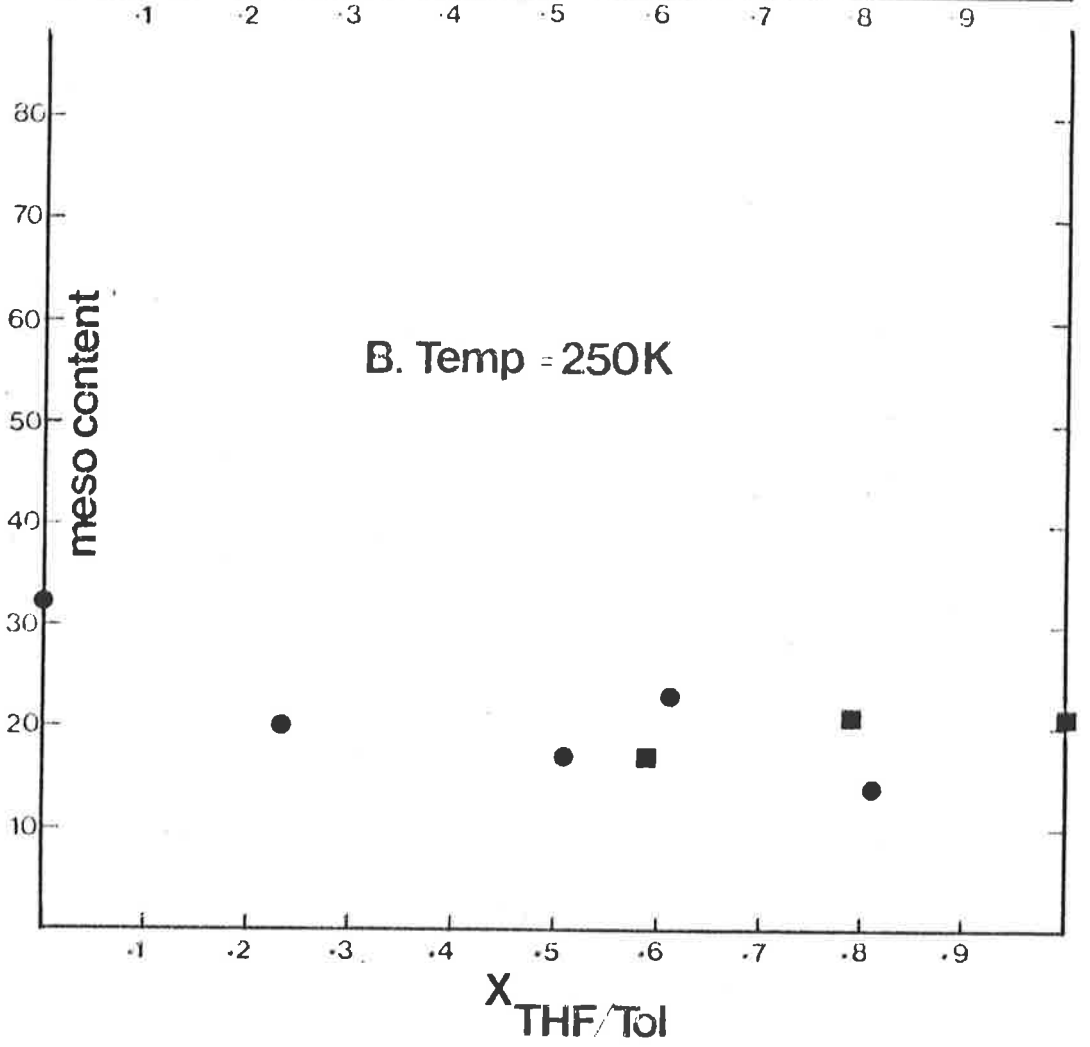
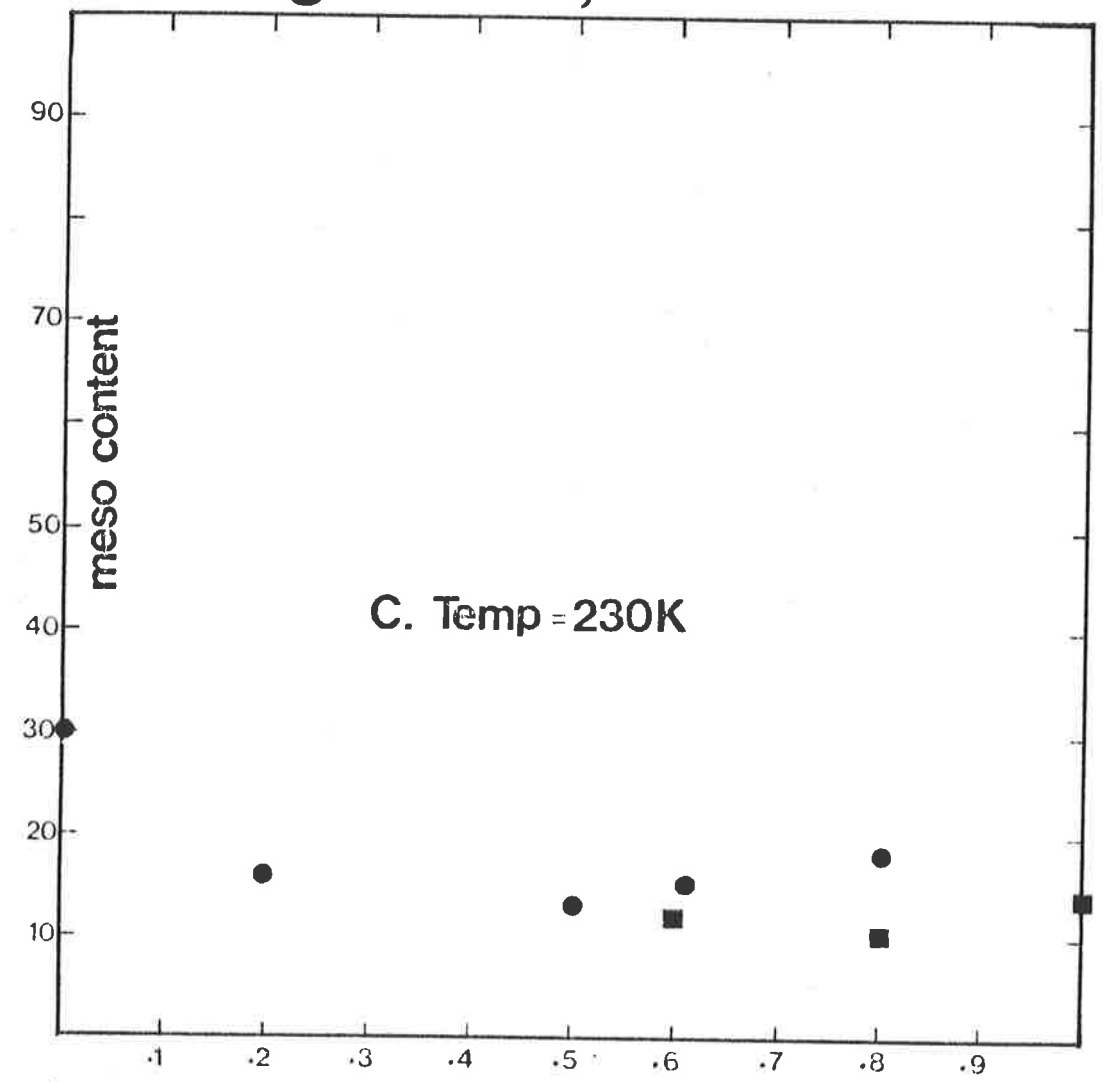

B. Temp = 250K
meso content
80
70
60
50
40
30
20
10
·1
·2
·3
·4
·5
·6
·7
·8
·9
$X_{THF/Tol}$

Fig4·8cont;


meso content
90
70
50
40
30
20
10
C. Temp = 230K
·1
·2
·3
·4
·5
·6
·7
·8
·9

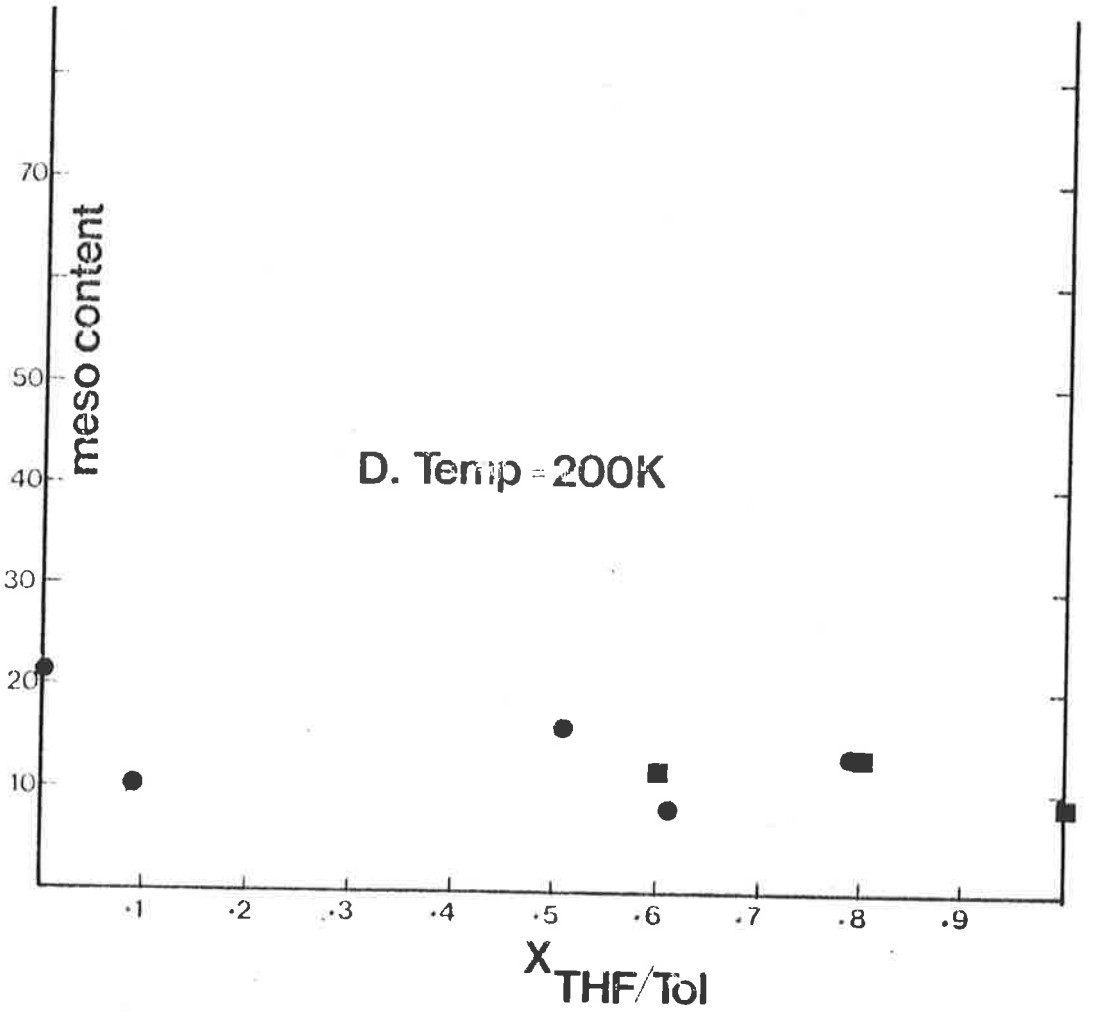
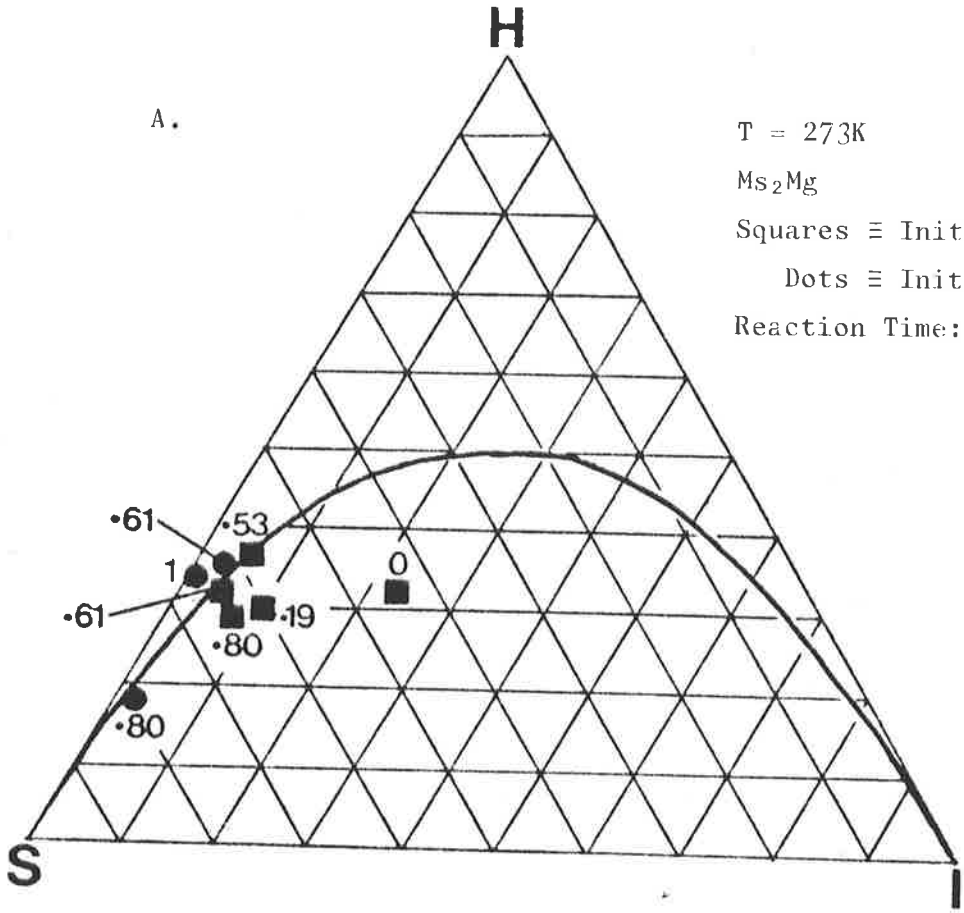

meso content
70
50
40
30
20
10
D. Temp = 200K
·1
·2
·3
·4
·5
·6
·7
·8
·9
X THF/Tol

Fig. 4.9: Triangular Plots of the Triad Distribution as a function of Solvent Composition at the given Temperature. Numbers on the plots refer to mole fractions of THF.



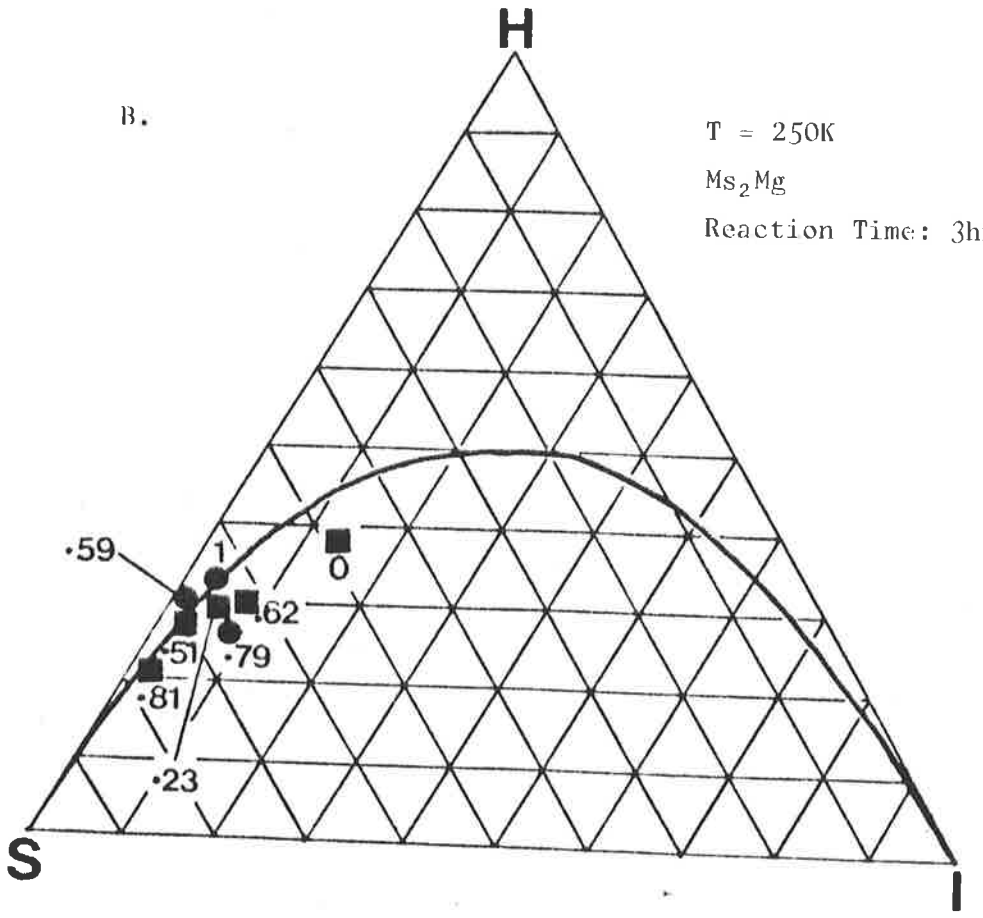
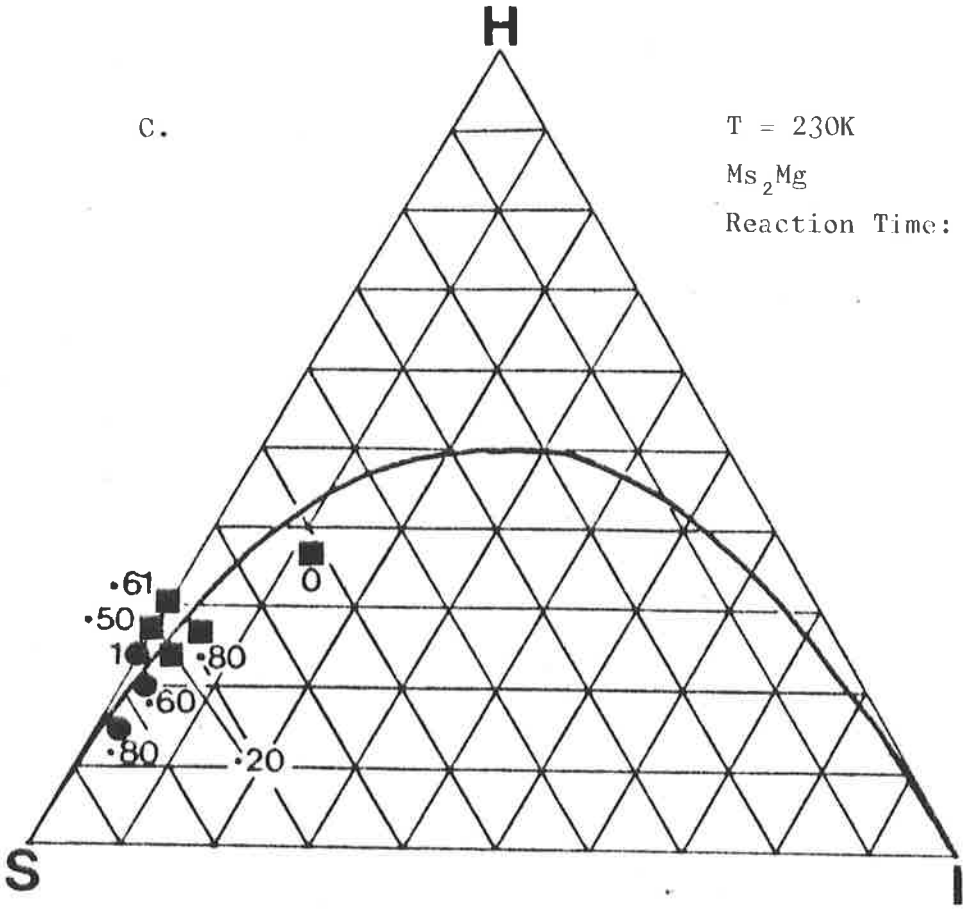


Fig. 4.9 (cont'd):

C.

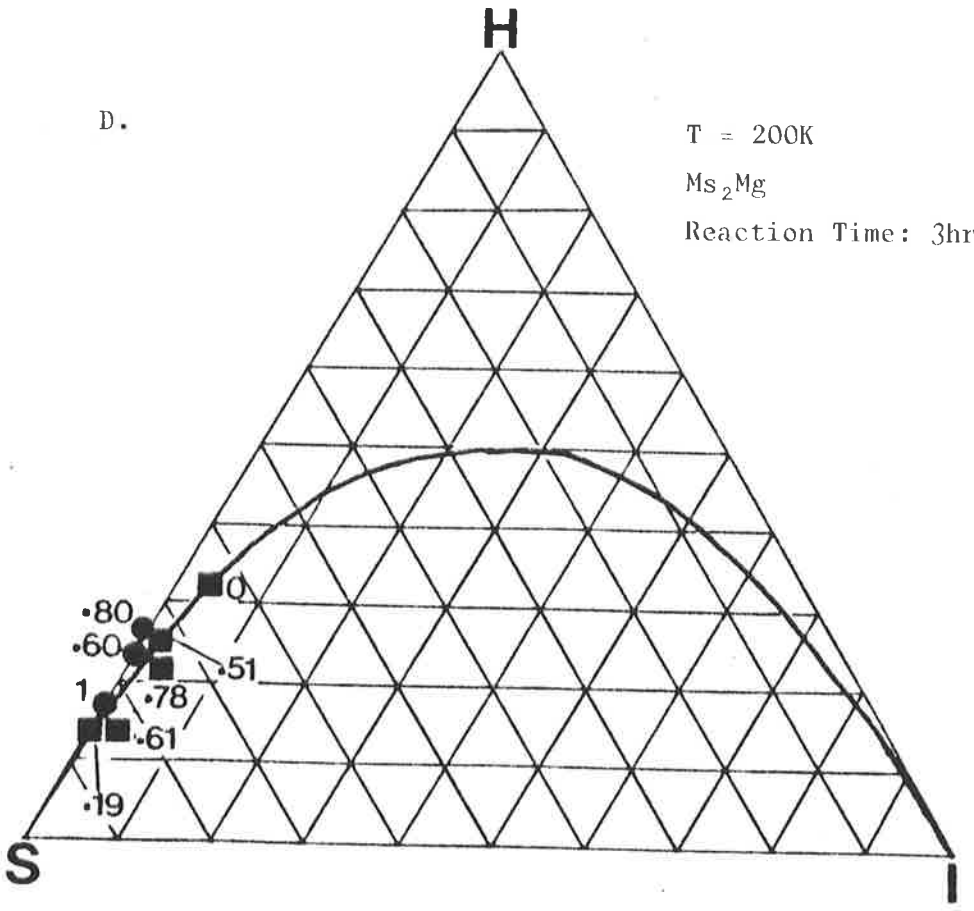


T = 230K

Ms_2Mg

Reaction Time: 3hrs

D.



T = 200K

Ms_2Mg

Reaction Time: 3hrs

Fig. 4.10: Non-Normalised GPC Traces at 273K for the Ms_2Mg System.

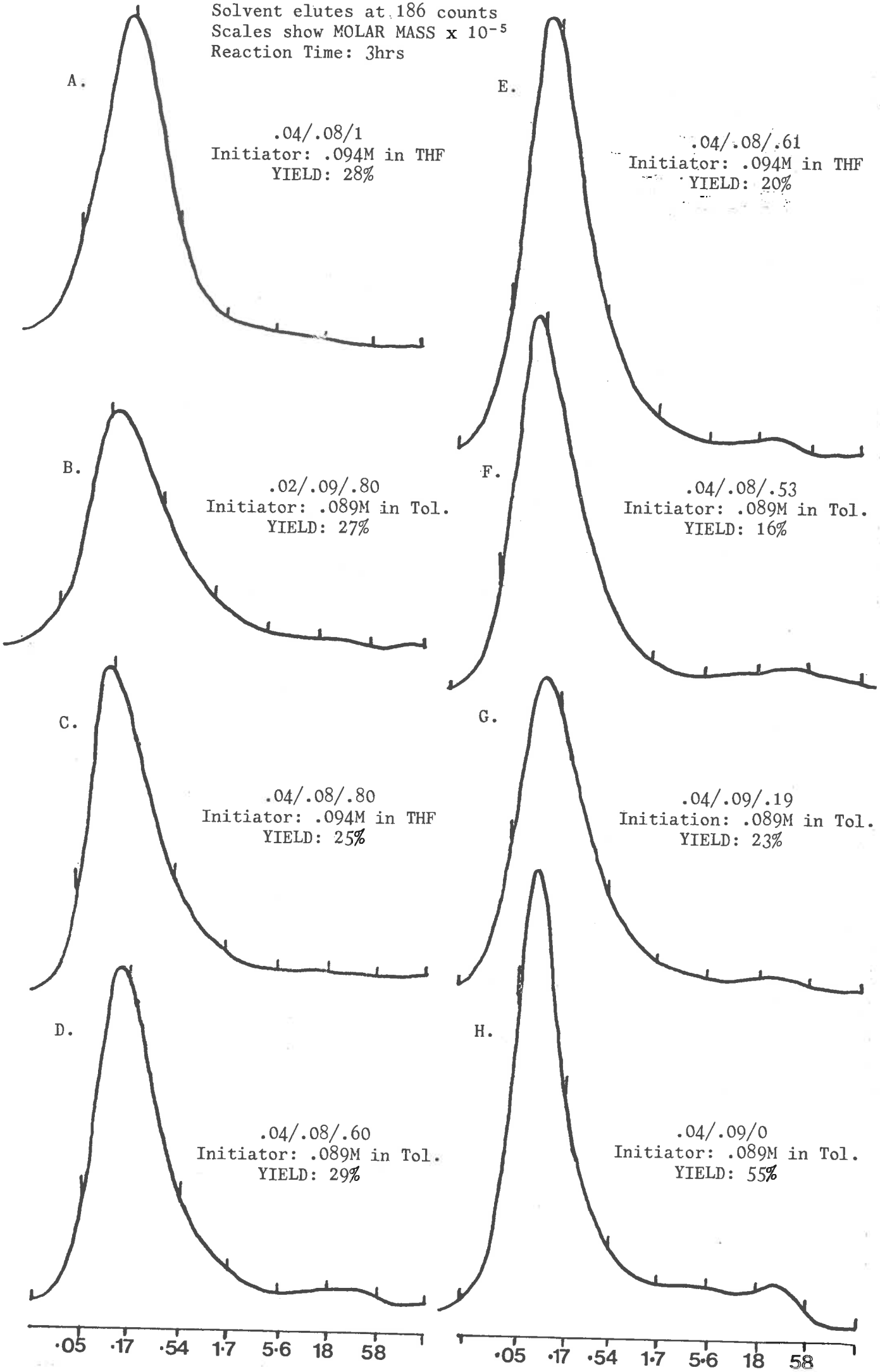


Fig. 4.11: Non-Normalised GPC Traces at 250K for the Ms_2Mg System

Solvent elutes at 186 counts in all cases
Scales show MOLAR MASS x 10^{-5}
Reaction Time: 3hrs

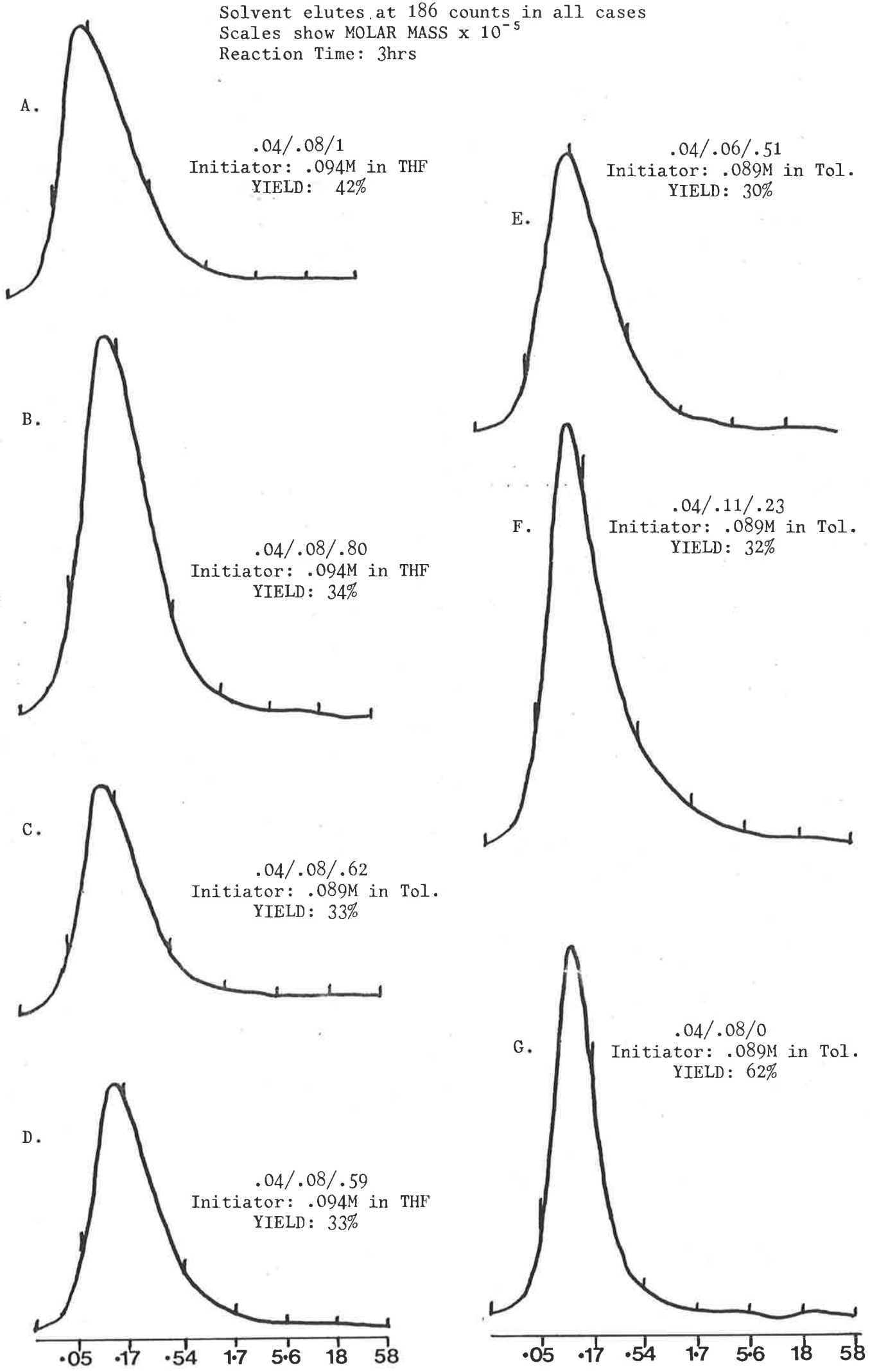


Fig. 4.12: Non-Normalised GPC Traces for the Ms_2Mg System at 230K
Solvent elutes at 186 volume counts
MOLAR MASS x 10^{-5} stated under A. applies to all traces
Reaction Time: 3hrs

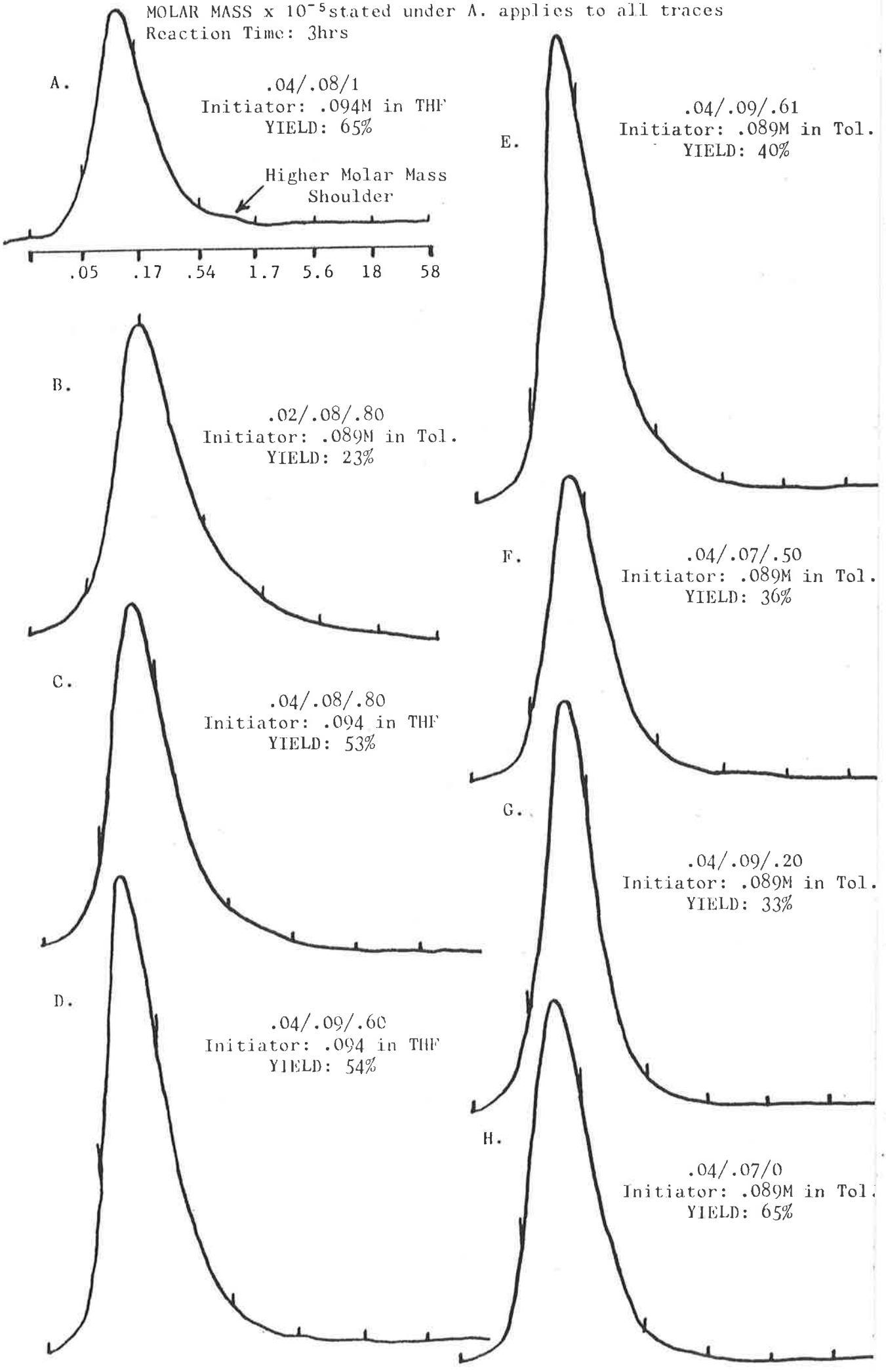
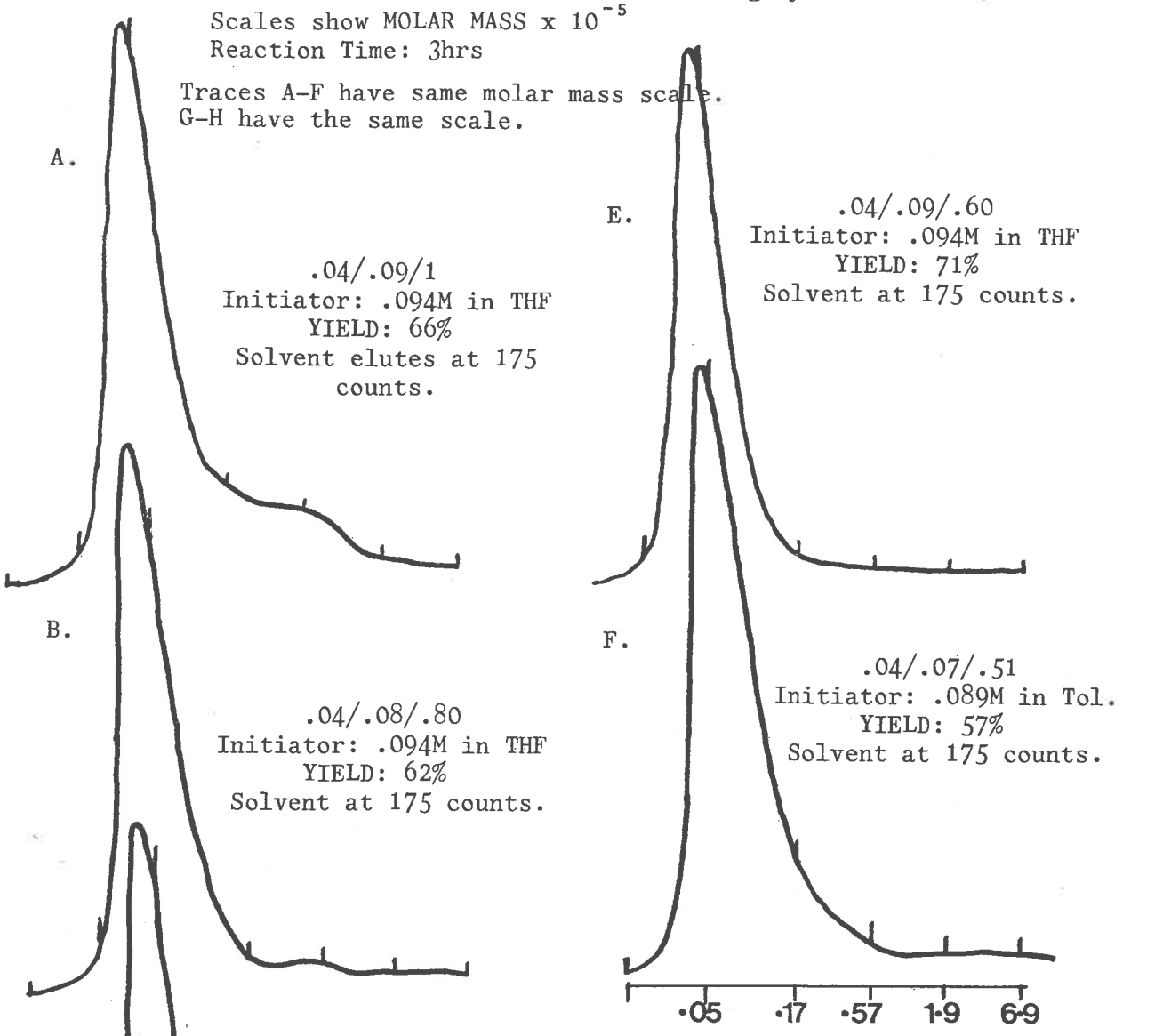


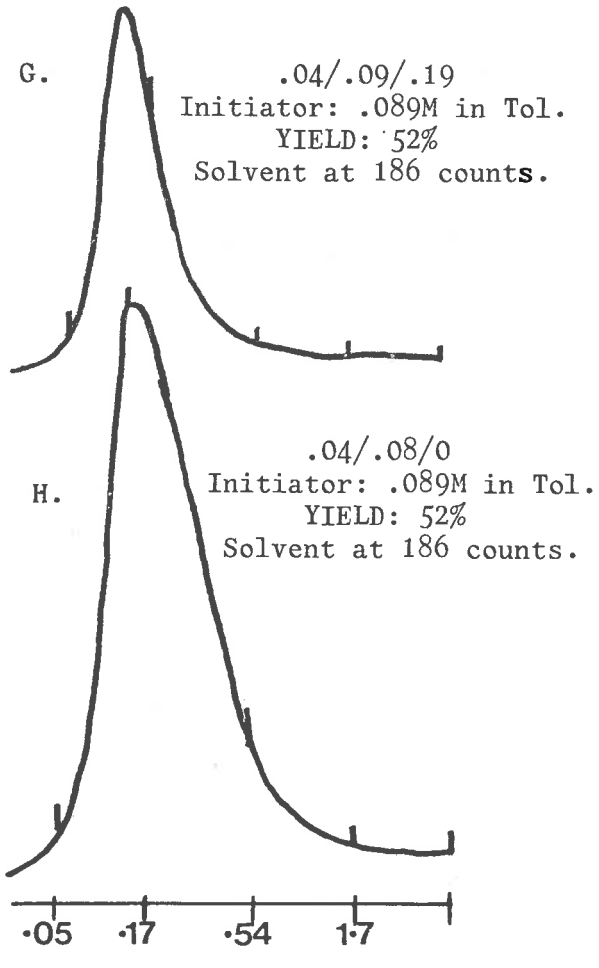
Fig. 4.13: Non-Normalised GPC Traces for the Ms_2Mg System at 200K.

Scales show MOLAR MASS x 10^{-5}

Reaction Time: 3hrs

Traces A-F have same molar mass scale.
G-H have the same scale.





in toluene (Figs 4.8A, 4.9A). However, the presence of intermediate/high molar mass polymer cannot unequivocally be assigned to the Ms_2Mg entity. Discussion in Chapter 3 suggested that difficulty was encountered in the complete removal of $MgBr_2$ by the addition of dioxane to the MsMgBr system. The initiator Ms_2Mg used here had Br/MsMg∿.05, so that it can be assumed that some MsMgBr exists and is capable of initiation, although the proportion of intermediate/high molar mass material appears high for MsMgBr to be responsible, given the small bromide to active bond quotient. Intermediate/high molar mass material persists until the final mole fraction of THF reaches about $.6_0$.

(2) Whereas MsMgBr polymerisations at 273K produced characteristically low yields (Fig. 4.3; less than 1% in THF), in particular when THF was present, reactions using Ms_2Mg produced much higher yields (Fig. 4.10; 20-30% in THF) at the same temperature, possibly implying greater initiation efficiency due to fewer side reactions.

(3) At 250K and 230K (Figs 4.11 and 4.12), and with the exception of the reaction in total THF at 230K (Fig. 4.12A) where an intermediate molar mass shoulder appears between $.54\text{-}1.7\times10^5$ gm.mol.$^{-1}$, GPC curves are basically unimodal. In a manner similar to the low molar mass peak produced in the MsMgBr system at 250K (Fig. 4.4), there is a distinct broadening of this peak in the presence of THF. At 250K, the value of

$\bar{M}_w/\bar{M}_n$, using Waters Associates method, for the unimodal peaks produced in toluene and THF (Figs 4.11G and 4.11A) are 1.4(±.2) and 2.8(±.2), respectively.

(4) At 200K (Fig. 4.13), the heterodispersity index of the dominant low molecular weight peak appears invariant across the range of solvents. In toluene (Fig. 4.13H) $\bar{M}_w/\bar{M}_n$ = 1.4(±.2) and in THF (Fig. 4.13A) $\bar{M}_w/\bar{M}_n$ = 1.3(±.2). However, at high $(\chi_{THF/Tol})_{final}$ and when initiator has been added in THF, a distinct intermediate molecular weight shoulder develops (.57-1.9x10^5; Figs 4.13A,B). This shoulder is also present at 230K, although less obviously, for the reaction in THF (Fig. 4.12A). Temperature and solvent conditions also correspond to the occurrence of intermediate molar mass material in the MsMgBr system (Fig. 4.6; 200K), although here it persists to much lower $(\chi_{THF/Tol})_{final}$.

4.4.4 Discussion of Mesitylene Magnesium Initiated Systems

Current literature[2,26,30,34,35] concerning alkyl/aryl magnesium/MMA systems strongly indicates that these polymerisations follow eneidic pathways, with discrete independent active centres propagating at different rates producing characteristically broad molar mass distributions. The mode of monomer addition need not be the same at these independent sites and thus a complicated tacticity/GPC picture develops with these parameters determined by such things as the number of different types of active centres present, the relative populations of these centres, relat-

ive rates of propagation and/or termination and the presence or absence of side reactions, providing by-products which may change the nature of active sites. The situation is further complicated in the case of Grignard systems because of the presence of at least two types of active bonds (Schlenk equilibrium, Chapter 3):

$$\underline{R}_2Mg + MgX_2 \rightleftharpoons 2\underline{R}MgX \qquad \text{Equn 1.1}$$

whose equilibrium concentrations are dependent upon temperature, solvent, nature of R group and nature of halide (=X). Evidence suggests[50,51] that the RMgX species is favoured by high temperatures and non-polar solvent while the equilibrium favours R_2Mg at low temperature. Further sites for eneidic polymerisations may arise from the formation of associates of R_2Mg and RMgX. The NMR presence of associates of Ph_2Mg (see Chapter 3) was shown to be a precursor of precipitation, and while no precipitation was noted in any initiator solutions used for polymerisation, it is conceivable that associated Ms_2Mg exists, particularly at low temperature in non-polar solvent. No NMR evidence of associated RMgX was observed, but if they exist in R_2Mg rich systems, they are almost certain to exist due to the enhanced bridging ability of the electron rich halide.

High isotacticity and high proportions of high molar mass polymer (2×10^6 gm. mol^{-1}) are observed at high temperatures in non-polar solvents when MsMgBr is used (Fig. 4.2A,B and Fig. 4.7), but lower isotacticity and low yields of high molecular weight polymer are evident when Ms_2Mg is used as initiator under the same temperature and

solvent conditions (Fig. 4.9A,B and Fig. 4.10H, Fig. 4.11G). This supports the postulate of other workers[26,35] that halide is required in toluene for the generation of isotactic growth centres, and the generation of high proportions of high molar mass material is favoured under such conditions. Coupled with evidence[50,51] for RMgX at high temperatures, it suggests that "RMgX-like" active sites may be responsible for high molar mass, isotactic pMMA.

A comparison between the low molar mass components of MsMgBr and Ms_2Mg initiated systems at 250K (Figs 4.4 and 4.11), as a function of solvent composition, suggests that they arise from the same type of active centre; one based upon Ms_2Mg. This hypothesis is supported by the following:

(1) In both systems the low molar mass component is centred at 2×10^4 gm. mol^{-1}.

(2) In both systems the estimate of $\bar{M}_w/\bar{M}_n$ varies from 1.4 ($\pm$.2) for reactions where toluene is the predominant solvent, to values of 2-2.8 for reactions in THF.

(3) The Br/MsMg quotient for MsMgBr initiated systems is .8-.9, indicating that some Ms_2Mg must be present, and capable of initiating polymerisation, even if all bromide is present as MsMgBr.

The presence, in toluene at 250K, of a similar low molar mass peak arising from MsMgBr initiation (Fig. 4.4H, where it comprises ca. 50% of the polymer produced) implies that if Ms_2Mg is responsible for its production, then these sites must add monomer in a more isotactic fashion than that produced when Ms_2Mg solely is used in toluene at 250K

(Fig. 4.11G). Using Ms_2Mg in toluene as initiator at 250K (Fig. 4.11G), the unimodal low molecular weight polymer formed is predominantly syndiotactic (i:h:s=12:38:50). Given that the low molar mass peak of the MsMgBr initiated system (Fig. 4.4H) comprises about 50% of the polymer produced it is unlikely that such a low meso placement frequency could persist and still produce a triad evaluation of 81:14:5(=i:h:s), as noted in Fig. 4.4H. Matsuzaki et al.,[35] examining stereoregularity and GPC character of the PhMgBr system with Br/PhMg=1, fractionated the product (trimodal in character) and concluded that the low molar mass isotactic-like component was probably due to Ph_2Mg.

Broadening of the low molar mass peak as the mole fraction of THF increases at 250K, in both the MsMgBr and Ms_2Mg systems, requires consideration. Since broadening at this temperature is most pronounced at high solvent polarity, the possibility of associated forms of the active centre (most probably based upon Ms_2Mg if the postulated origins of low molar mass material, $2x10^4$ gm. mol^{-1}, are correct), capable of providing independent, alternative sites for polymerisation, can be discounted as the reason for broadening. Tsvetanov,[52] studying infra-red data for the reaction of methacrylonitrile with alkyl magnesium compounds, suggested the presence of two different types of active centre:

AC I AC II

where the entity X in AC I is probably another mesitylene group (assuming that the low molar mass polymer is associated with "Ms_2Mg-like" active centres). Tsvetanov[52] considered that AC I was predominant in ether solvents, while both AC I and AC II were present in toluene. Assuming that this is so, broader distributions would be more likely in a paucity of THF, contrary to observations here at 250K (Fig. 4.4), where the low molar mass component is broadest in THF. The likely reasons for broadening appear to the subtle (e.g., changes in solvation at the active site), and, if the erratic behaviour of the heterodispersity index as a function of THF content at 230K for the MsMgBr system is an indicator (Fig. 4.5), subject to little control. Broadening of the low molar mass peak with increasing THF content may be an artefact of the increase in proportion of intermediate molecular weight polymer noted for the MsMgBr and Ms_2Mg initiator systems at 200K in high mole fractions of THF (Figs 4.6 and 4.13).

In Chapter 3 it was argued, mainly on the evidence of crystal structure, that organomagnesium compounds in solution were of tetrahedral geometry. There is no NMR evidence to suggest the appearance of magnesium with higher coordination numbers, although the MsMgBr system studied in THF (Fig. 3.11; [MsMg] = .53M; Br/MsMg = $.9_4$) indicated distinct low temperature broadening (200K and 190K) for the C(1)-Mg resonance associated with Ms_2Mg, denoting the onset of a slow exchange process which was thought to be due to an equilibrium between monomeric and associated forms. However, evidence for this was not conclusive.

An examination of GPC traces at 200K for the MsMgBr and Ms_2Mg initiator systems (Figs 4.6 and 4.13) has shown the appearance, at high mole fractions of THF, of intermediate molar mass polymer ($.6-6.9x10^5$ gm. mol^{-1}), with its contribution to the total polymer formed being dependent on the nature of the initiator solvent. If the initiator was added in THF the proportion of this material was high compared to addition of initiator in toluene. This observation tends to indicate that change in co-ordination number may be responsible. Addition of initiator in THF may present potential organomagnesium active sites with varying THF solvation, which are not present, but which may be subsequently formed, for the initiator in toluene, provided THF is present in the reaction mixture. Development of the intermediate molecular weight material is then envisaged as forming from these more highly solvated magnesium sites. If this argument is feasible, then the line broadening observed at low temperature in the ^{13}C spectra of MsMgBr/THF (Fig. 3.11) may indicate exchange between sites of different co-ordination number rather than between species of different association.

An important point for consideration in any anionic/pseudo-anionic system is whether the centre(s) produced represent "living" or terminationless systems. If such centres exist in mesitylene magnesium initiated reactions then there should be a correlation between molar mass and conversion, which should be manifest in GPC traces as the "shifting" of peaks to higher molar mass with conversion. Fig. 4.14 shows normalised (defined in the Experimental

section) traces of methanol insoluble polymer formed in the same reaction vessel as a function of time at 250K for reaction parameters .02/.10/0 ($60cm^3$ of .15M MsMgBr were added to the upper part of the reaction vessel; and with $Br/MsMg=.7_4$). Tacticities of polymer products formed after termination at the prescribed time intervals are:

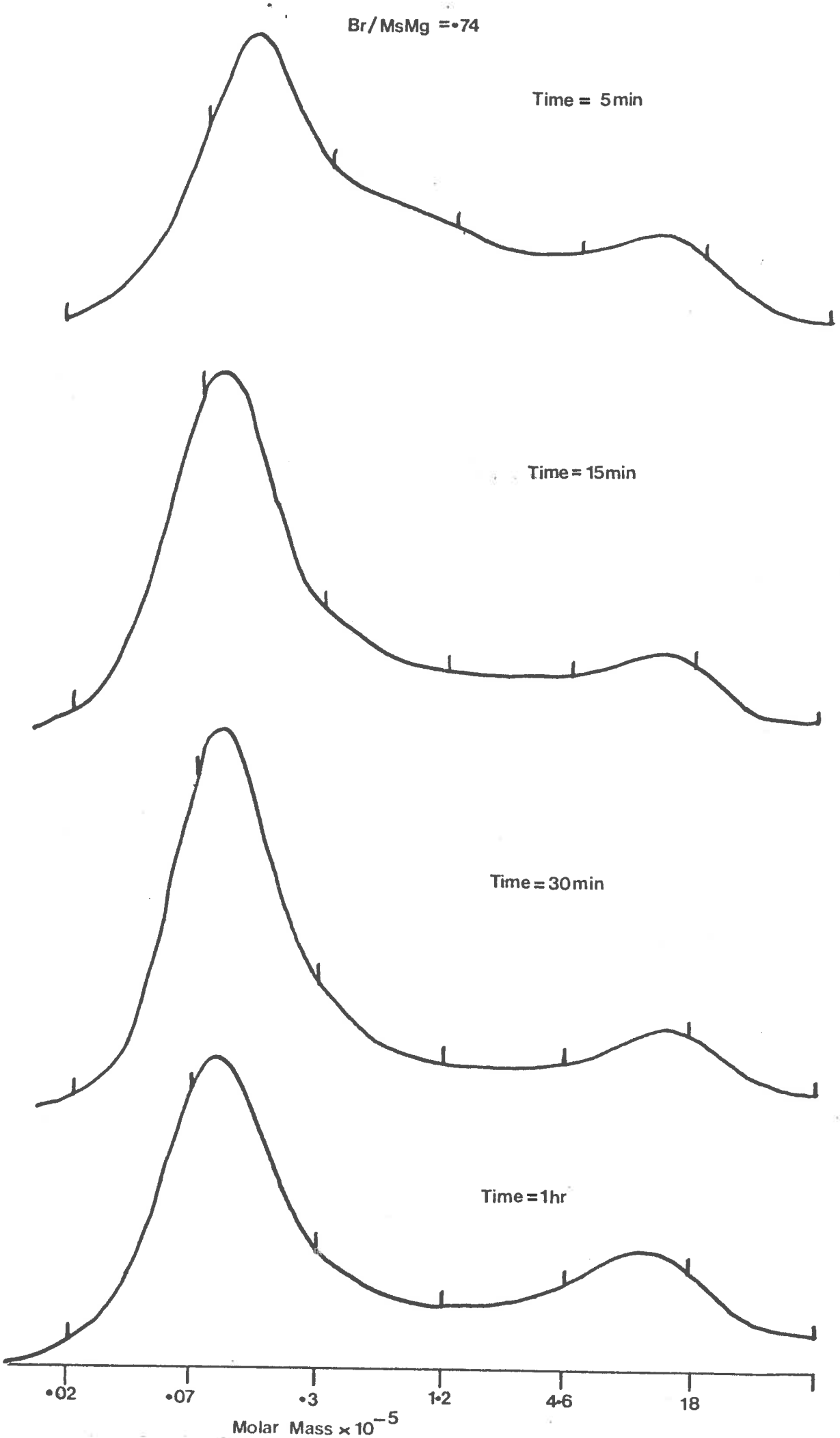
Table 4.3:

	i	h	s	m	r
5 min	93	7	0	97	3
15 min	89	11	0	95	5
30 min	91	9	0	96	4
60 min	89	11	0	95	5

indicating the relative invariance of these parameters over the examined time interval. Conversion could not be measured for samples withdrawn from the same reaction vessel, but increasing viscosity was noted with time, indicative of an increasing conversion. Conclusions from the GPC eluograms of Fig. 4.14 are:

(1) No new peaks appear after the time of the first sampling. Intermediate molecular weight pMMA (.3-$1.2x10^5$) present at a reaction time of 5 minutes is less evident at longer reaction times, where the eluograms are essentially invariant with both time and conversion. It is questionable whether the intermediate molar mass material present after 5 minutes represent products of living sites which continue propagation to produce the high molecular weight peak. An alternative is that those sites producing intermediate molecular weight polymer are all formed quickly after reaction initiation but are subject to termination. If the proportions of low ($\sim.07x10^5$ gm.

Fig 4·14 GPC of Methanol Insoluble Polymer formed at 250K from the same Reaction in Toluene as a Function of Time. Initiator MsMgBr



mol^{-1}) and high molar mass ($\sim 1.8 \times 10^6$ gm. mol^{-1}) were then to increase with time/conversion, the amount of intermediate molar mass material would appear to decrease with increasing time.

(2) The relative invariance of GPC curves at longer reaction times and increased conversion indicates that chain termination is important in a kinetic description of the system.

(3) After 5 minutes reaction time high molar mass material ($\sim 1.8 \times 10^6$ gm. mol^{-1}) is already present, although it constitutes a relatively small proportion of the polymer produced. This is consistent with the work of Bateup and Allen,[2] who ascribed the isotactic high molar mass material formed in terBuMgBr initiated systems as arising from active centres involving bromide at μM concentration and high reactivity. The concurrent appearance of high and low molar mass pMMA at short reaction times, coupled with possible termination processes for intermediate molecular weight pMMA, is suggestive of independent active centres propagating at different rates.

4.4.5 Examination of Molecular Weight Distribution and Tacticity : PhMgBr

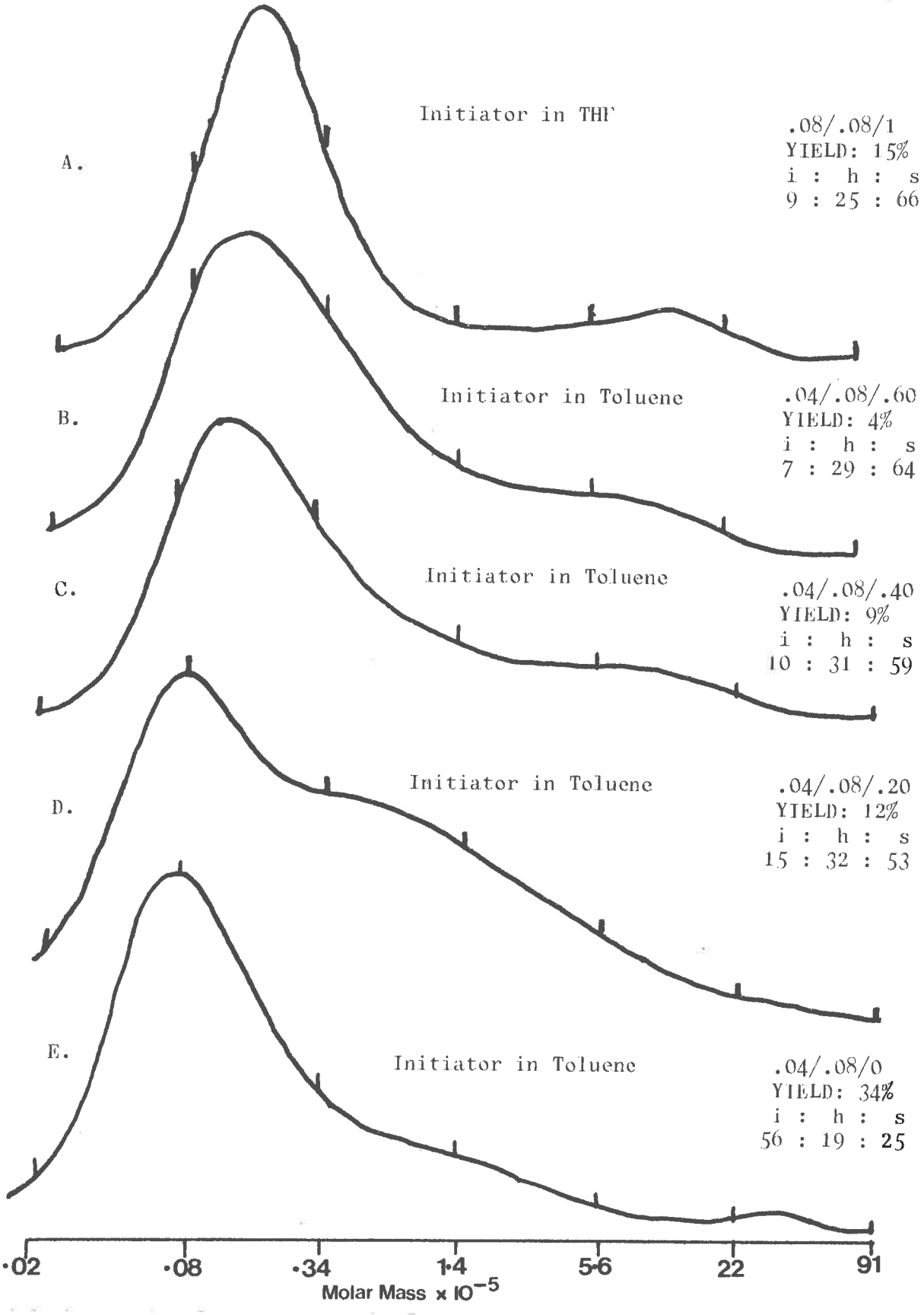
A strong correlation has been observed between the behaviour of this initiator system and the MsMgBr and terBuMgBr[26] systems, most notably:

(1) Increased tendency to form isotactic polymer in non-polar solvent when bromide is present in solution (Fig. 4.15).

Fig. 4.15: GPC of Methanol Insoluble polymer formed at 250K after 3hr Reaction Time as a function of Solvent Composition

Initiator in Toluene: [PhMg] = .099M ; Br/PhMg = .71

Initiator in THF : [PhMg] = .12M ; Br/PhMg = .67



(2) The absence of isotactic directing centres when THF is present, together with the absence of high molar mass pMMA (Fig. 4.15E; $\sim 2 \times 10^6$ gm. mol^{-1}). The formation of this high molecular weight isotactic polymer in the presence of bromide in non-polar solvent suggests the active centre involves RMgX, possibly as an associated halo-bridged form, which is disrupted on addition of THF.

(3) The relative decrease in yield of polymer product as the mole fraction of THF increases (Fig. 4.15). Decreased yields of polymer in THF may be explained by competition between monomer and THF for the available co-ordination site at a potentially active magnesium centre, if it is assumed that polymerisation occurs through the prior formation of such an adduct.[53] In total THF (Fig. 4.15A), the mole fraction of active bonds with respect to monomer had to be increased to produce polymer.

(4) An absence of methanol soluble pMMA was generally noted across the whole range of solvent compositions.

Differences do exist however, in the behaviour of PhMgBr and MsMgBr systems. Under comparable reaction conditions, the PhMgBr system produces a less isotactic polymer than MsMgBr (e.g., when Br/RMg $\sim$ .7 for a 3 hour reaction period in toluene, i:h:s=56:19:25 for PhMgBr and 90:10:0 for MsMgBr at 250K). Further variations in behaviour will be discussed as they arise.

4.4.5.1 Effect of Variation of Initial Monomer Concentration : PhMgBr

Fig. 4.16 shows the effect of initial monomer concentration on the nature of GPC eluograms and tacticity, for the initiator solution defined by the indicated bromide and active bond concentrations. From these data the following points are noted:

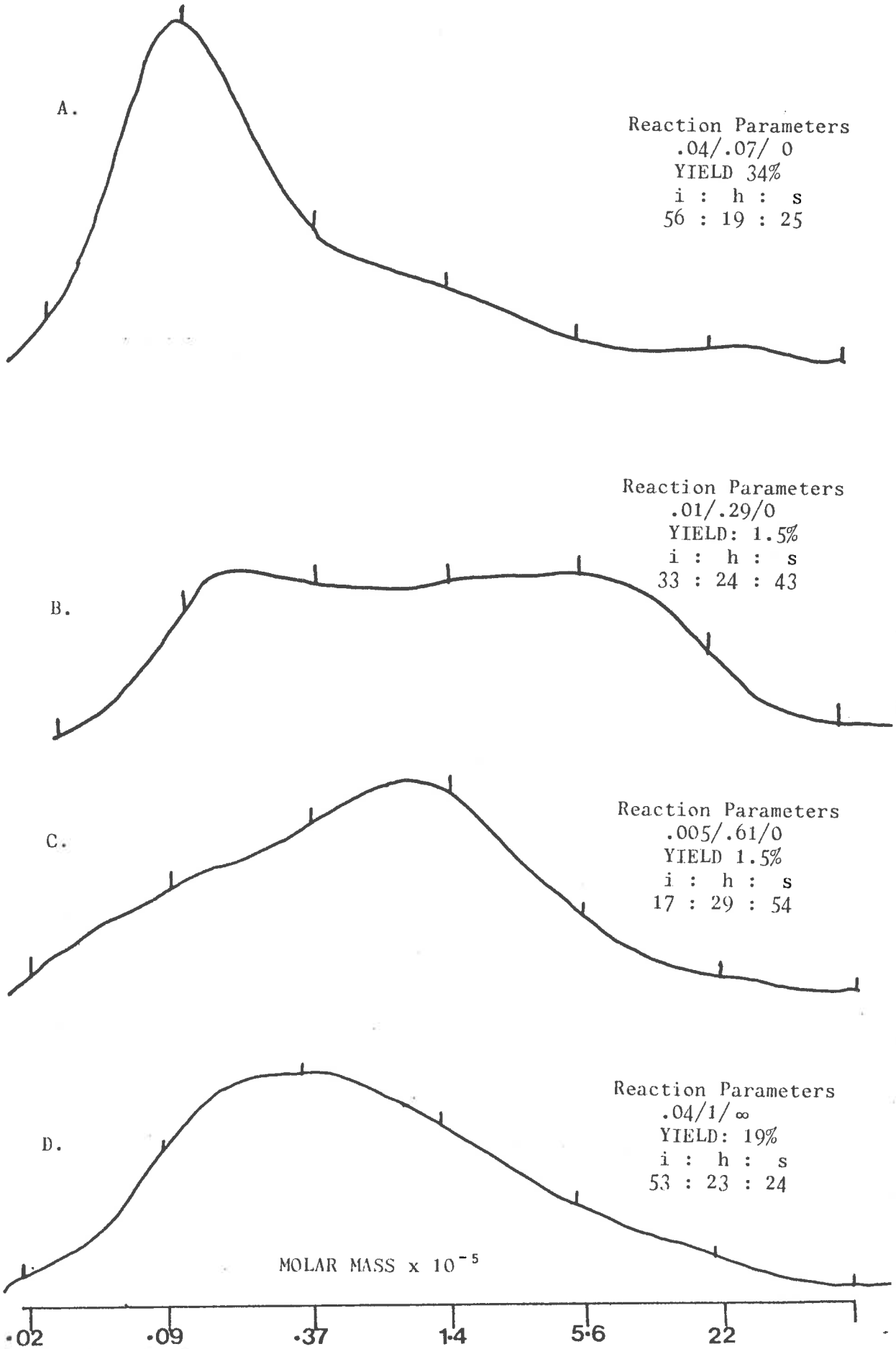
(1) As the concentration of monomer at the moment of initiation increases, the isotactic content diminishes, for the reaction carried out in toluene. This can be explained by acknowledging that as the initial polar monomer content is increased, it mimics polar THF in its effect upon stereoregularity. This is also reflected in the greatly diminished yields (Fig. 4.16B,C) which is also typical of THF addition for aryl magnesium bromide initiator systems. Fig. 4.16D, an heterogeneous polymerisation, was achieved by evaporation of toluene from the initiator in the lower compartment of the reaction vessel (Fig.2.8(b)), with monomer added from the upper compartment. Its enhanced stereoregularity is probably due to a Ziegler-Natta stereoregulating effect on the solid initiator surface, but is possibly more complex due to some dissolution of the initiator into the neat monomer before initiation, reducing stereoregularity.

(2) High initial monomer concentrations tend to increase the proportion of intermediate molar mass material ($.34\text{-}5.6\times10^{5}$ gm. mol^{-1}) and decrease the amount of low molecular weight pMMA. The reasons for this are

Fig. 4.16: GPC of Methanol Insoluble Products formed at 250K after 3 hours reaction time.

[PhMg] = .099M
[Br] = .070M
} in Toluene

The traces A,B,C were from reactions carried out at constant volume and constant [PhMg] at time = 0. Trace D is for an heterogeneous reaction.



difficult to determine, especially since GPC character does not parallel the behaviour of THF addition (Fig. 4.15), suggesting other variables beside solvent polarity govern molar mass polydispersity. Final $\chi_{MMA/Solvent}$ values used in this thesis were usually less than .10, to ensure that monomer did not contribute greatly to the nature of the solvent.

4.4.5.2 Variation of Tacticity and Molar Mass with Conversion : PhMgBr

Figs 4.17A-E and 4.18A-E show tacticity and GPC data at 230K, 250K for the PhMgBr system, with Br/PhMg=1 and .6, respectively. Fig. 4.17 traces were produced from five different reaction vessels while those of Fig. 4.18 arise from products obtained from the same reaction, using the reaction vessel of Fig. 2.9.

Fig. 4.17A shows that after a reaction period of one hour under the specified conditions no methanol insoluble material was found, and only trace amounts of methanol soluble material were produced. This methanol soluble pMMA is absent in other reaction products, with its formation probably occurring at a different type of active centre which is at very low concentration. A similar explanation for the presence of methanol soluble and methanol insoluble polymer in nBuMgBr initiated systems has been suggested by Bateup and Allen.[54] The trend in behaviour for methanol insoluble polymer (Fig. 4.17B-E) reveals the following:

(1) An increase in isotactic content from i=33% after 2 hours to i=50% after 42.6 hours.

Fig. 4.17: GPC Traces of Polymer formed at 230K with PhMgBr as a function of Time (Normalised).

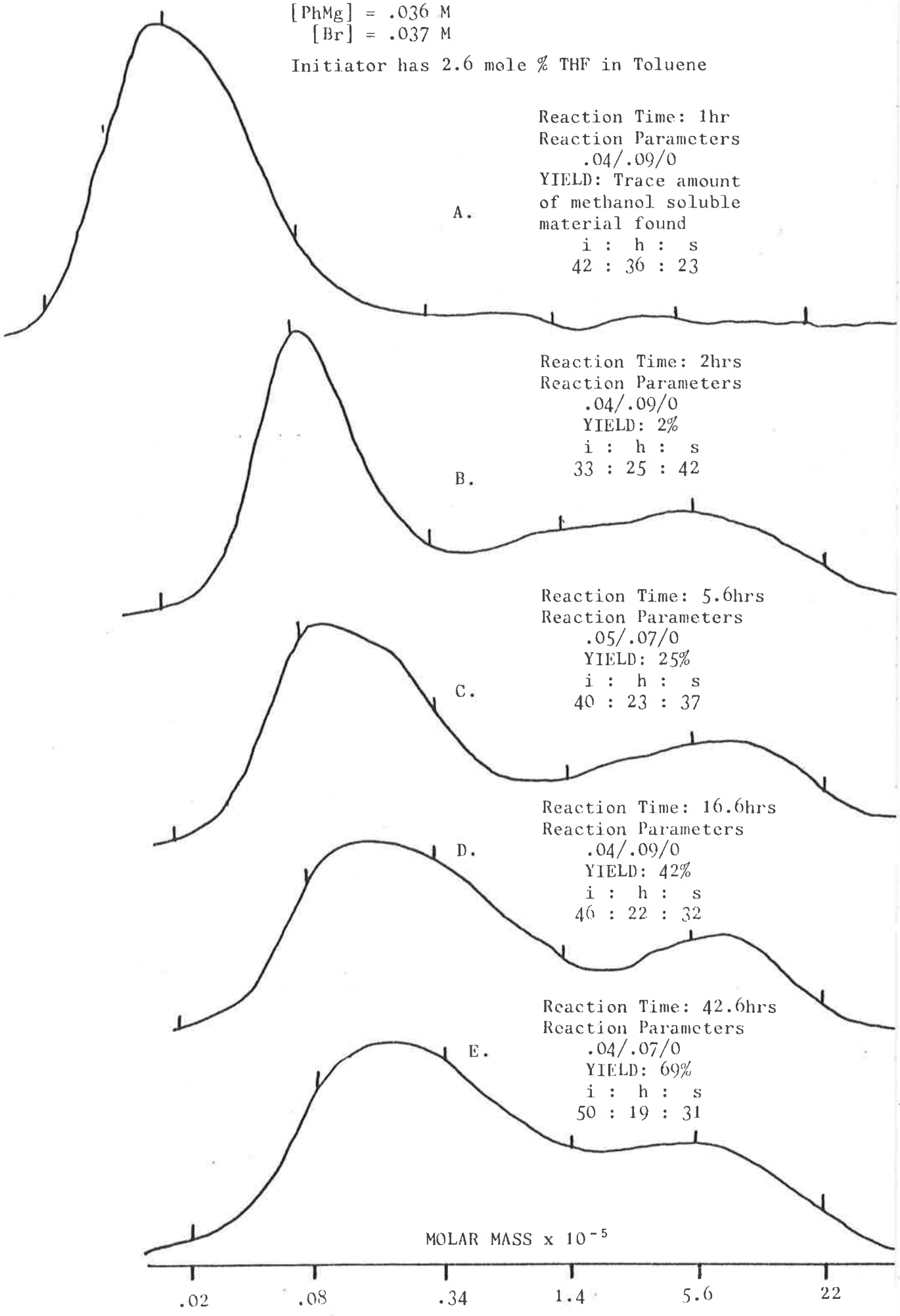
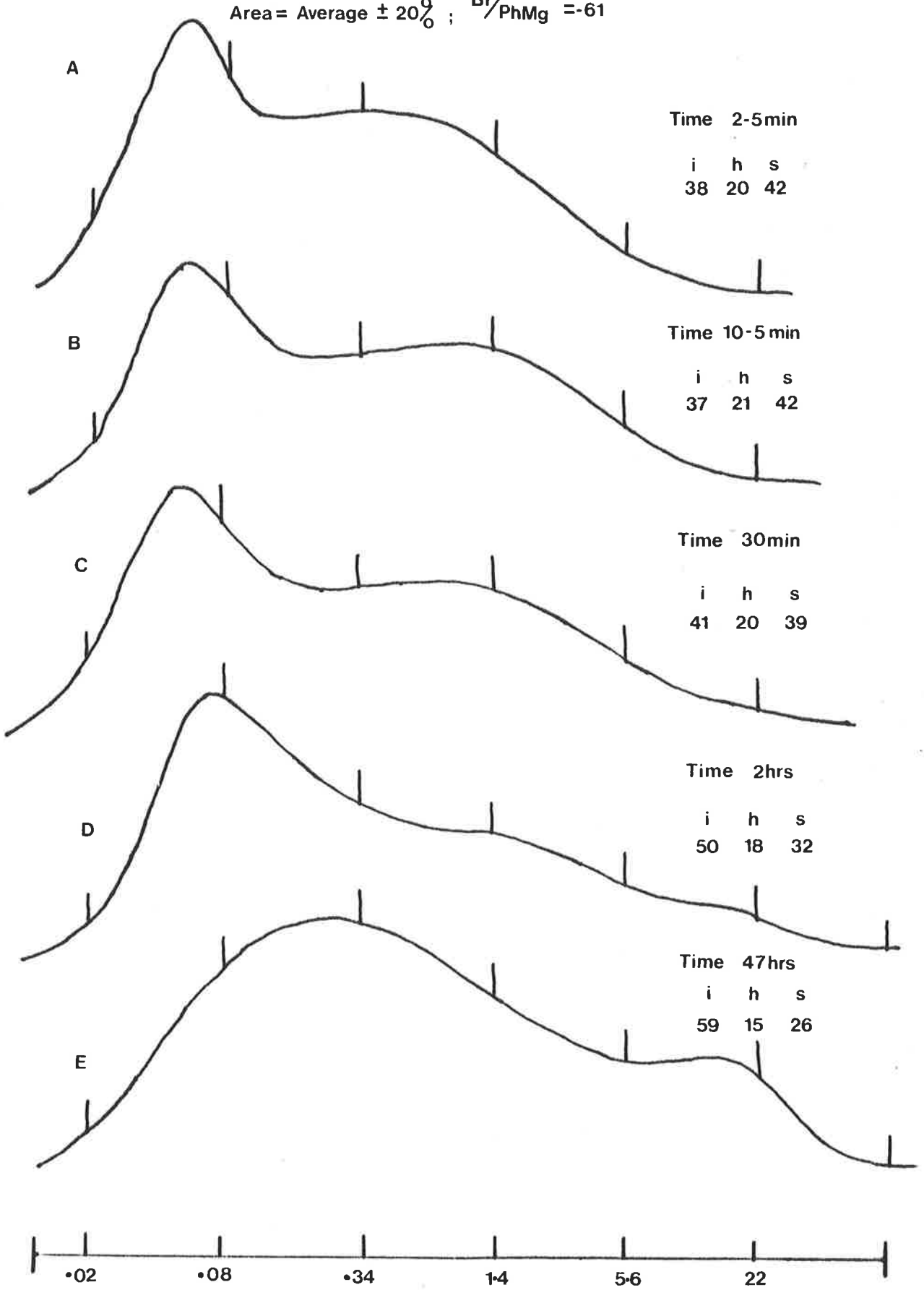


Fig4·18 Phenyl Magnesium Bromide - MMA - Tol ; 250K ; GPC & Tacticity Study

as a Function of Time ; Same Reaction Vessel; Normalised curves –

Area = Average ± 20% ; $^{Br}/_{PhMg}$ =·61



Molar Mass × 10^{-5}

(2) An increase in yield as a function of reaction time.

(3) Apparent broadening of the low molar mass peak, most evident in Fig. 4.17C, such that pMMA in the molar mass range .34-1.4x10^5 gm. mol^{-1} represents a greater proportion of the polymer product at extended reaction times. This indicates that those centres producing this "shifting" to higher molar mass may, over the time of examination, constitute "living" sites. However, it is uncertain whether these sites continue growth past the .34-1.4x10^5 gm. mol^{-1} molecular weight stage.

(4) The peak centred at about 5.6x10^5 gm. mol^{-1}, does not appear to shift to higher molar mass as a function of conversion, so it appears that termination/pseudo-termination has occurred at these chain ends.

In accordance with an increased isotactic content with time, the following possibilities may be considered:

(1) The peaks produced at 1x10^4 and 5.6x10^5 gm. mol^{-1} (Fig. 4.17B) arise from different, independent centres which produce polymer of the same tacticity as the unfractionated blend, but add monomer at different rates. The consequences of termination/pseudo-termination of active sites producing the peak at 5.6x10^5 gm. mol^{-1} then imply that if the low molar mass peak is broadening/shifting to higher molecular weight via centres which are "living", then those centres would have to change their mode of monomer addition to accommodate enhanced isotacticity as a

function of conversion. Such behaviour is unlikely, even though the polarity of the medium is changing slightly due to consumption of monomer.

(2) The low molar mass ($1x10^4$ gm. mol^{-1}) producing centres of Fig. 4.17B are living centres, producing more isotactic pMMA than those responsible for terminating chains at $5.6x10^5$ gm. mol^{-1} (these centres being discrete and independent of those producing low molar mass pMMA). These growing, istotactic-like chain ends would then cause a shift to higher molar mass as well as a drift to higher isotacticity. No fractionation of polymer obtained in Fig. 4.17 was attempted, but results by Matsuzaki and co-workers[35] indicate for Br/PhMg=1, at THF concentrations less than .06M and at temperatures between 273-223K (conditions applying in our case), the molar mass peak centred at $1x10^4$ (Fig. 4.17B) is isotactic-rich. These workers noted, however, that conversion did not affect molecular weight distribution and that polydispersity arose as a result of at least three different active centres producing polymer of the following types:

(a) Isotactic-rich (MW=$1x10^4$gm. mol^{-1})

(b) Syndiotactic-rich (MW=$1x10^5$)

(c) Highly isotactic (MW $>10^6$gm. mol^{-1})

This highly isotactic, high molecular weight pMMA is absent at 230K for Br/PhMg=1, but is present at 250K for Br/PhMg=$.6_1$ (Fig. 4.18D), indicating that temperature increment, forcing the Schlenk equilibrium toward PhMgBr (thought[26] to be required for production

of this type of polymer), is more important than decrement in bromide.

(3) Increased isotactic content with conversion could be due to a highly isotactic centre which propagates slowly and independently of those terminating centres which produce pMMA with molar masses $1x10^4$, $5.6x10^5$ gm. mol^{-1} in Fig. 4.17B, thus producing a shoulder on the peak at $1x10^4$ gm. mol^{-1} which continues to grow, causing peak broadening with increasing conversion.

Fig. 4.18 shows similar behaviour at 250K, although several reaction conditions have been changed. The initial concentration of initiator was .094M with $Br/PhMg=.6_1$ ($50cm^3$ added), and the final reaction parameters were .01/.10/0. Broadening/shifting to higher molar mass of the low molecular weight peak is again apparent with an increased isotactic content at longer reaction times, but at this higher temperature a new peak exists at longer reaction times ($2x10^6$gm. mol^{-1}), which is not present at 230K. Matsuzaki et al.[35] have shown that polymer formed with molecular weight of $1x10^6$ gm. mol^{-1} in their distributions is highly isotactic, whereas material formed at $1x10^4$ is only isotactic-like, so it is unlikely that the high molecular weight peak is resultant from continued growth of the low molar mass peak. Growth from different active centres seems more likely. This tends to be supported in this thesis by the presence of the high molecular weight peak at 250K and its absence at 230K, indicating temperature sensitivity of this type of active centre, probably an

"RMgBr type", since the Schlenk equilibrium favours RMgX at elevated temperature.

4.4.6 Examination of Molecular Weight Distribution and Tacticity: Ph_2Mg

Fig 4.19 shows GPC traces for Ph_2Mg initiated systems in toluene at 250K as a function of solvent composition. In toluene, as has been observed in the Ms_2Mg system, isotactic content of the polymer formed is relatively high but diminishes greatly in THF. It is apparent that at intermediate solvent polarity a higher molecular weight species develops but becomes less prevalent for reactions in total THF. If associated forms of Ph_2Mg were responsible for the production of different types of active centres, then greatest GPC complexity would be expected for reactions undertaken in toluene, which is not the case here. The solvent effect for the Ms_2Mg system is completely different at 250K (Fig. 4.11), where a unimodal low molar mass peak was noted which broadened with increasing amounts of THF in the final reaction mixture. Increased complexity at intermediate solvent composition has been noted by Mair[26] for the $secBu_2Mg$ initiated system.

Fig. 4.20 shows the variation in the nature of GPC traces as a function of time for Ph_2Mg initiated runs in toluene at 250K. Tacticity data indicates that polymer produced at longer reaction times is only slightly more syndiotactic than after 3 hours, but a greater proportion of pMMA appears to trail to higher molecular weight. More than one active centre may be operating, or alternatively pseudotermination (discussed in Chapter 5) of pMMA formed

Fig. 4.19: GPC Traces of Methanol Insoluble polymer formed with Ph_2Mg under varying solvent conditions at 250K.

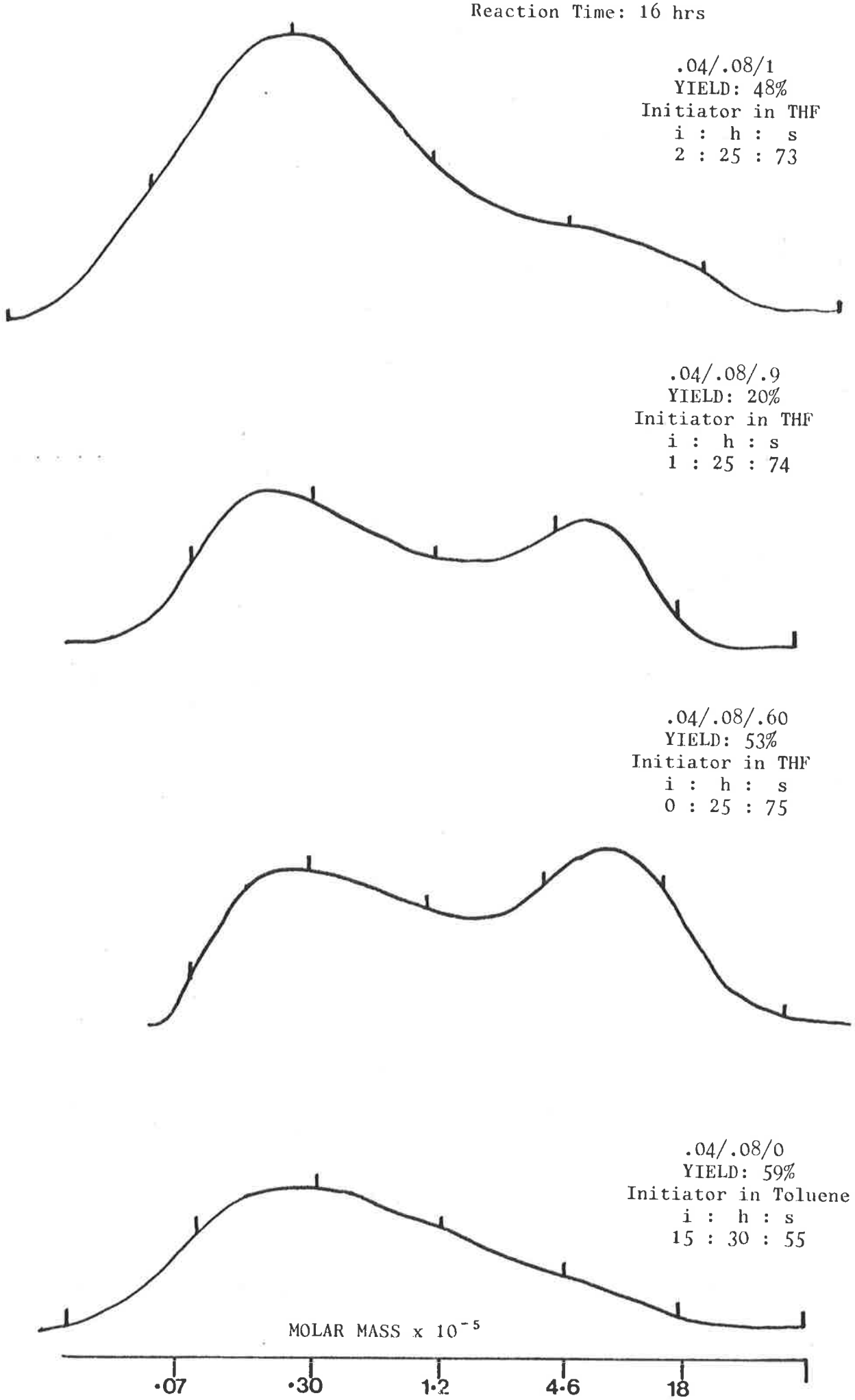
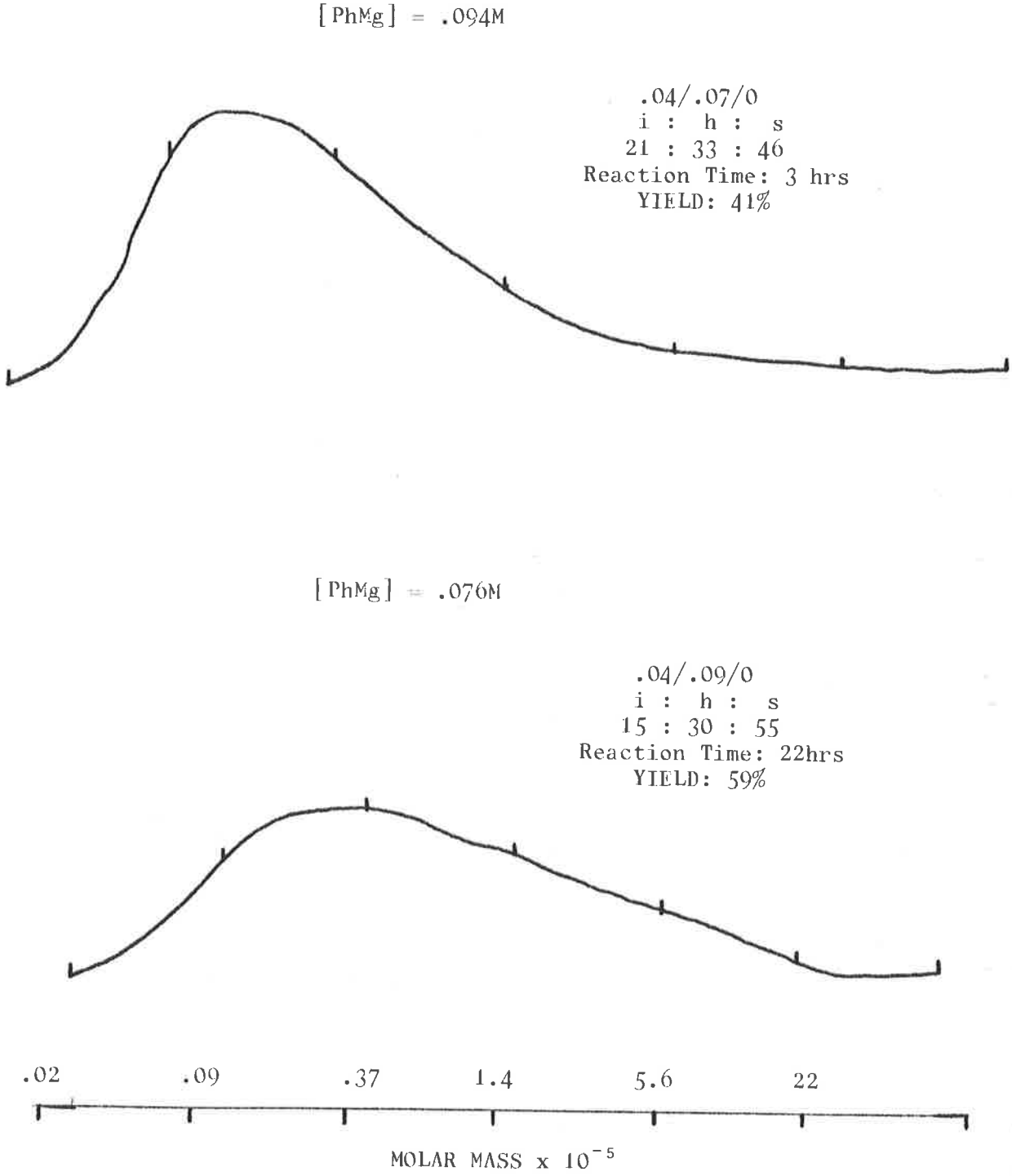


Fig. 4.20: Variation of the nature of Methanol Insoluble Product as a function of Reaction Time for Ph_2Mg/MMA/Tol at 250K.



Active bond concentrations referred to are those of the initiator in the upper compartment of the reaction vessel prior to addition to the monomer/toluene.

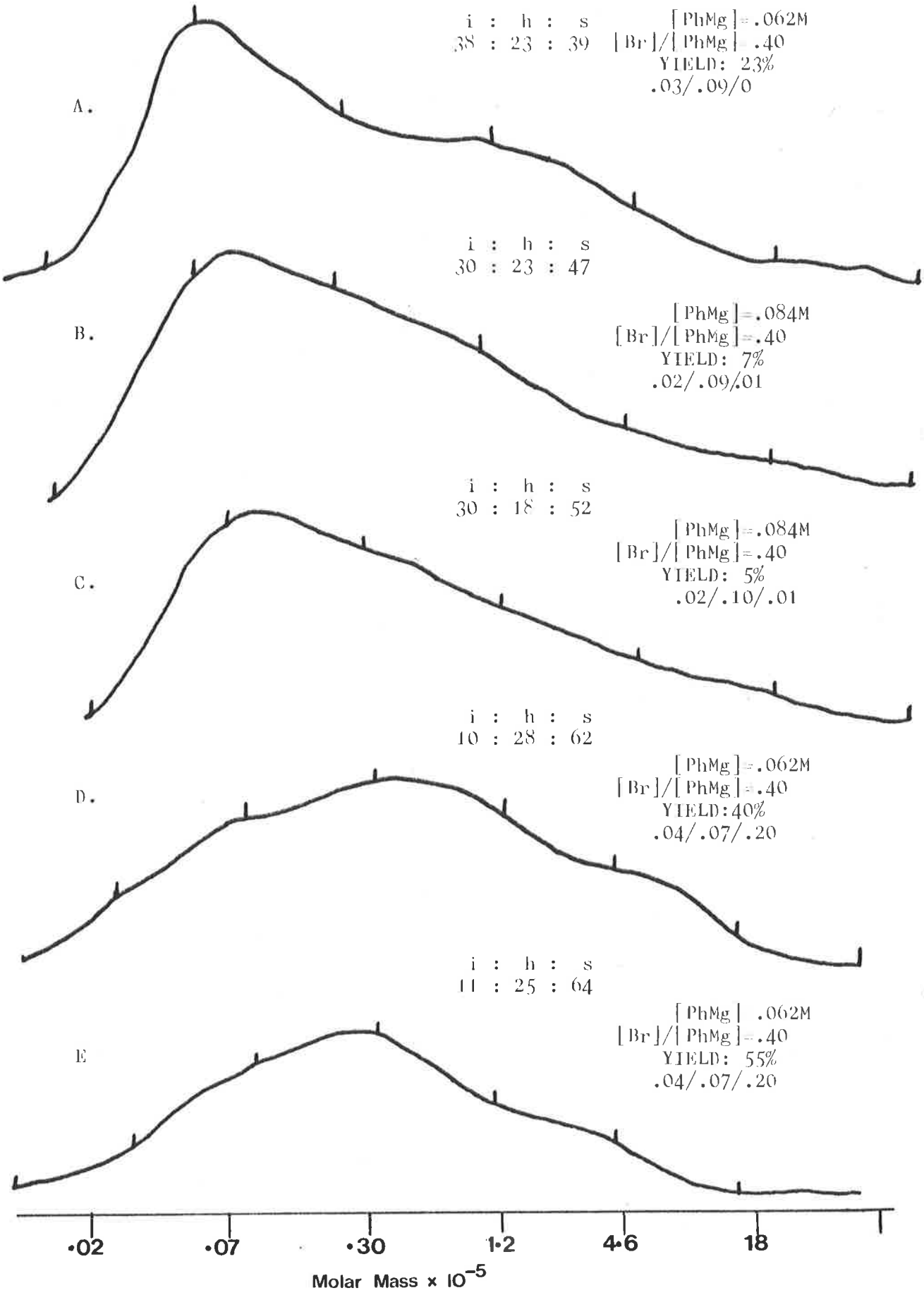
after 3 hours (centred at $1\text{-}2\times10^{4}$ gm. mol^{-1}) with subsequent reactivation of some of these sites at a later stage may be responsible for development of higher molar mass material. Bimodal distributions have been noted for $sec Bu_2 Mg$ initiated runs in toluene at 250K by Mair,[26] and in diethyl magnesium/methacrylonitrile/toluene systems by Joch and co-workers.[55,56]

4.4.7 Miscellaneous Experiments : PhMgBr, Ph_2Mg Initiated Systems

4.4.7.1 Reactions using Extensively De-etherated PhMgBr

Fig. 4.21A-E shows GPC, tacticity and gravimetric data for pMMA obtained under various reaction conditions at 250K, with stated initiator concentrations applying before addition to the monomer/solvent in the lower compartment of the reaction vessel. Preparation of extensively de-etherated PhMgBr has been described in Chapter 2, and NMR data (Chapter 3) indicates that the THF:PhMg ratio is about 0.8:1, with $Br/PhMg=.4_0$. The isotactic content of the polymer formed with this initiator (Fig. 4.21A) is much lower than that of pMMA formed from less extensively de-etherated initiators. If $MgBr_2$ is added to the extensively de-etherated PhMgBr to produce $Br/PhMg = 1._3$, a trend to higher isotacticity is noted (i:h:s = 53:22:25), providing values identical with, and GPC traces similar to, the polymer produced in Fig. 4.15E, under similar reaction conditions, except that $Br/PhMg=.7_1$. Extensively de-etherated PhMgBr produces polymer with a greater proportion of intermediate molecular weight molar mass material (Fig. 4.21A), which for a Ph_2Mg rich system

Fig. 4.21: GPC Traces for Methanol Insoluble Polymer formed by Variation of Extensively de-etherated PhMgBr Systems at 250K over a 3 hour reaction time.



is consistent with Matsuzaki,[35] who suggests, on the basis of fractionation studies, with Br/PhMg=1, that intermediate molar mass pMMA arises from a "Ph_2Mg-like" active centre with syndiotactic-like addition. Crude fractionation studies of the pMMA product of Fig. 4.21A were achieved by placing a sample in THF overnight. Supernatant THF was separated from swollen pMMA in the bottom of the container, and found to contain predominantly the low molecular weight component (ca. $1x10^4$) with tacticity i:h:s=55:22:23; of much higher isotacticity than the overall blend (Fig. 4.21A; i:h:s=38:23:39). This is in agreement with Matsuzaki and implies the intermediate molar mass material is more syndiotactic-like.

Fig. 4.21B,C show GPC traces of polymer formed when small, identical amounts of THF are added to either:

(1) the lower compartment of the reaction vessel (Fig. 2.8(b)) along with monomer/toluene (Fig. 4.21B), or

(2) the extensively de-etherated PhMgBr/toluene prior to its addition to monomer/toluene (Fig. 4.21C).

The polymer produced appears independent of the mode of THF addition, with the syndiotacticity of the polymer enhanced and yield decreased in comparison with the reaction in toluene (Fig. 4.21A; this behaviour is typical for PhMgBr-like systems). This generally correlates with the MsMgBr system where the initiator solvent only became important at low temperatures (Fig. 4.6).

Fig. 4.21D shows data for polymer formed when a supernatant solution from saturated $Mg(OMe)_2$/THF was added

to a reaction identical to Fig. 4.21A, one minute after initiation using the double initiation vessel in Fig. 2.10. The experiment was primarily concerned with the effect that methoxide, formed as a result of carbonyl addition to MMA by RMgX (X=Br,R), may have upon the polymerisation. Hatada and co-workers,[57] examining the polymerisation of ethyl methacrylate with n-butyl lithium, indicate that the multiplicity of active species for the reaction in toluene is strongly related to the lithium ethoxide formed at -78°C. Three different active species for isotactic polymer, syndiotactic polymer and isotactic oligomer were noted, but when the polymerisation was initiated with 1,1diphenylhexyl lithium, where no ethoxide was formed, only an isotactic polymer was obtained.

To most successfully dope the reaction with $Mg(OMe)_2$ in order to mimic a possible reaction, the methoxide should ideally be added in toluene, but $Mg(OMe)_2$ is insoluble in this medium.[58] As such it was added in THF with a one minute delay after mixing, since side products are not present at the moment of initiation, but may be so soon after. It has been shown[59] that individual magnesium alkoxides are inactive toward polymerisation of MMA in toluene (although Müller et al.[60] have shown that in THF methoxide ion is capable of initiating polymerisation), so that any effect observed may be as a result of:

(1) modification by co-ordination of methoxide to already polymerising active sites.

(2) the formation of associated alkyl magnesium species due to the enhanced bridging ability of methoxide, prior to the formation of an active centre.

(3) the association of methoxide with an incoming monomer unit before addition to the polymer chain.

Okamoto et al.[61] have noted that EtMgOMe, used to initiate polymerisations of MMA in toluene at 198K, gave polymer that was not greatly different from Et_2Mg initiated polymerisations under the same conditions. The effect of the alkoxide group was found to be important only when its stericity became greater. Under these conditions isotactic polymer was produced.

A comparison between Fig. 4.21A and Fig. 4.21D (where $Mg(OMe)_2$/THF has been added one minute after mixing), does reveal extensive changes. However, these changes are indistinguishable from an addition of THF one minute after mixing (Fig. 4.21E), so results appear inconclusive and reflect the experimental difficulties observed in introducing $Mg(OMe)_2$ into the system homogeneously.

The effect of introduction of THF subsequent to mixing (Fig. 4.21D,E) is much different, in terms of polymer products, to the situation where THF is present during the mixing procedure. Generally, in the latter case the presence of THF implies drastic reduction in yield and increased syndiotacticity as is typified by Fig. 4.21B,C, but in the former case addition of THF promotes the formation of pMMA (Fig. 4.21D,E). In all cases (Fig. 4.21B-E), when THF has been added the production of inter-

mediate molar mass polymer ($3x10^4$ gm. mol^{-1}) is favoured. Since it has been shown (see above) that the low molar mass component of Fig. 4.21A ($1x10^4$gm. mol^{-1}) is isotactic-like (i:h:s=55:22:23), one of two conclusions may be inferred from the increased yields and increased syndiotacticity noted in Fig. 4.21D,E:

(1) If addition of THF after reaction initiation enhances the growth of the low molecular weight peak, so that it continues its growth to form the greater proportions of pMMA at ca. $3x10^4$ gm. mol^{-1}, then those centres must change their mode of monomer addition to promote syndiotactic growth.

(2) Addition of THF after mixing may produce totally different centres which add monomer in a syndiotactic fashion to produce the pMMA centred at $3x10^4$gm. mol^{-1}. Intrinisic to this conclusion is the assumption that all active bonds are not consumed at the time of mixing. This assumption is consistent with the results of Mair[26] and Bateup,[34] who noted the persistence of organomagesium bonds throughout the course of a reaction with MMA.

Conclusion (2) above seems least likely, since it has already been noted that reactivity is diminished by addition of THF, which may effectively block the formation of a monomer-initiator adduct at the initiation stage.[2] Modification of already existing centres is more likely.

4.4.7.2 The Effect of Variation of Bromide : PhMgBr

Fig. 4.22 and Fig. 4.23 show the effect of variation in bromide content on the nature of polymer formed at 250K with termination after 30 minutes and 3 hours, respectively. The initiator solutions for each of the four runs were produced by equally dividing a stock initiator/toluene solution with $Br/PhMg=.6_2$ and adding to each of these solutions a small constant volume mixture of dioxane in toluene, where the mole fraction of dioxane in toluene was varied for each of the initiator solutions. In this way a constant active bond concentration but changing bromide content could be obtained by variable precipitation of $MgBr_2$.2dioxane. The results obtained for each of the two reaction times indicate:

(1) yield is fairly independent of the bromide content, given that all other reaction conditions are the same.

(2) that below $Br/PhMg = .1_2$ (and probably up to $Br/PhMg = .3_2$) the triad data does not vary greatly.

(3) that as Br/PhMg increases from zero there is a concurrent increase in intermediate molecular weight pMMA until $Br/PhMg=.3_2$. A discontinuity in behaviour is observed thereafter such that when $Br/PhMg=.6_2$, low molar mass material predominates with an increase in isotacticity.

Fig. 4.22A and Fig. 4.23A have had no dioxane added to them which might suggest that the increase in the intermediate molecular weight range noted in the remaining

Fig. 4.22: GPC Traces of Methanol Insoluble Polymer Terminated after 30 min (normalised curves) T = 250K ; Reaction Parameters: .04/.08/0
Trace amounts of Methanol Soluble polymer found

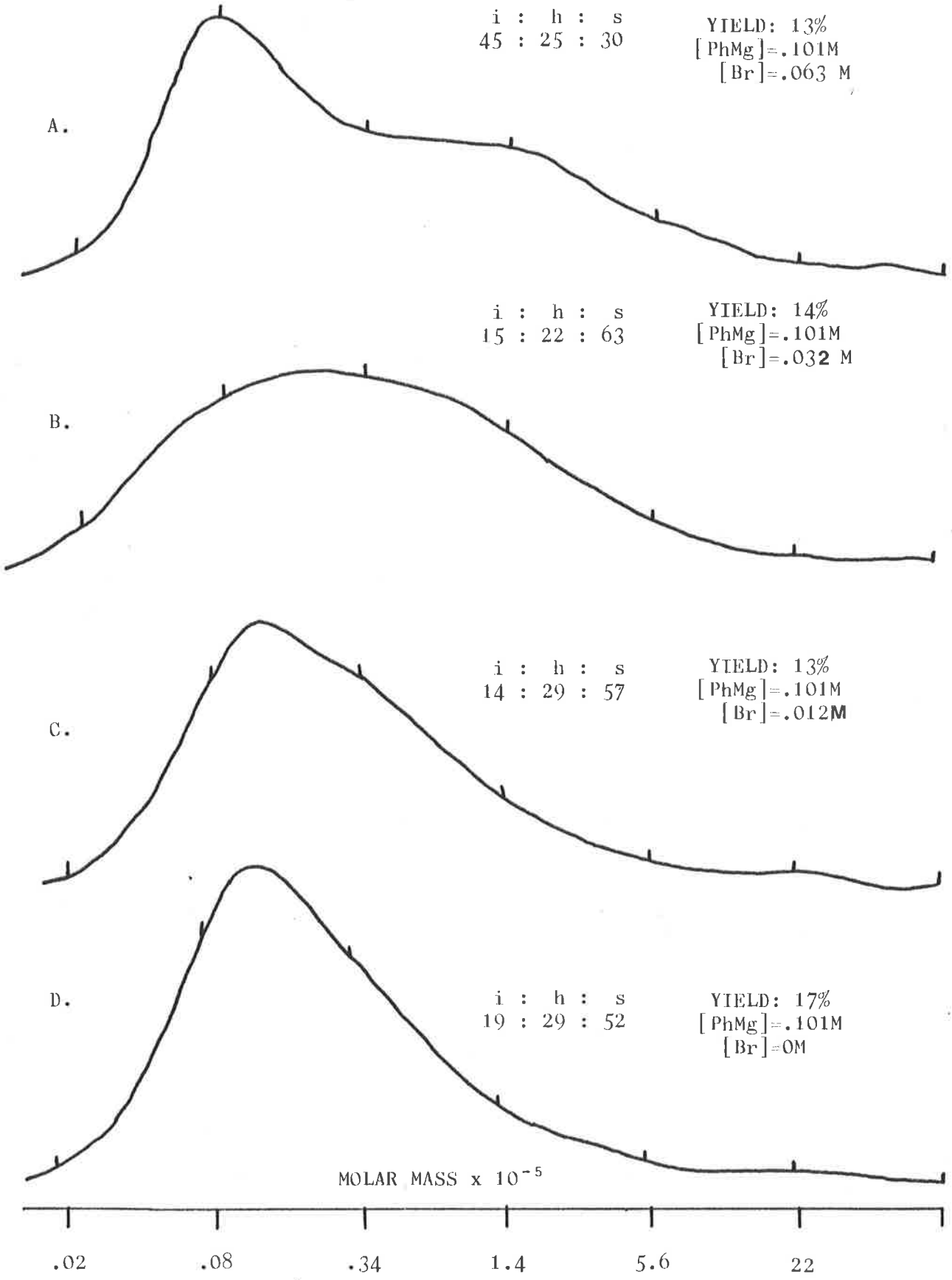
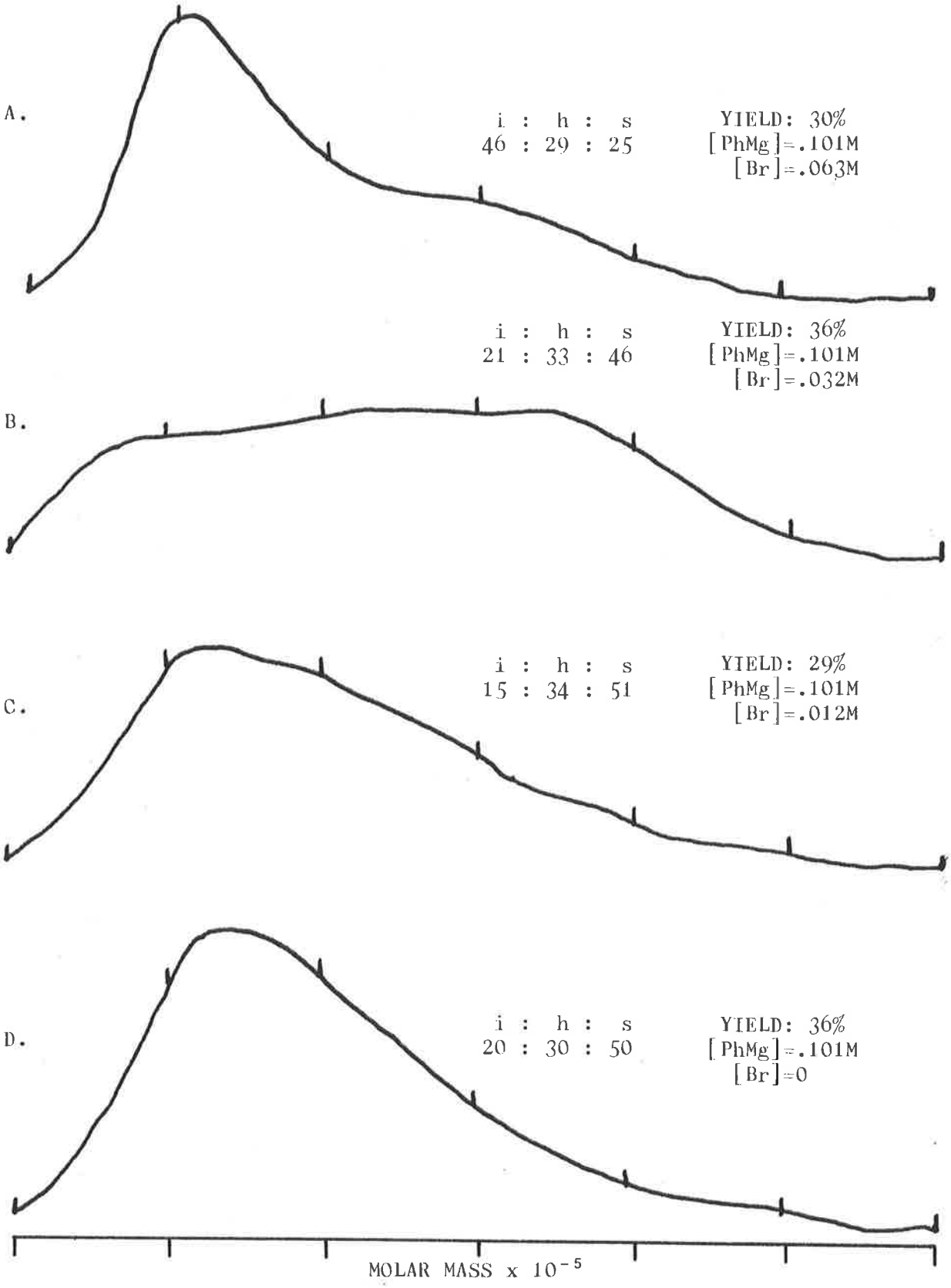


Fig. 4.23: GPC Traces of Methanol Insoluble Polymer Terminated After 3 hours (Normalised Curves) at 250K

Reaction Parameters: .04/.08/0



Very low yields of Methanol soluble polymer were recorded - present as trace amounts only.

distributions could arise due to trace amounts of dioxane present modifying or producing new types of active centres. This argument tends to be negated by the observation that in the PhMgBr system dioxane has appeared efficient in the removal of $MgBr_2$ and there is no reason to suggest that the corollary: that $MgBr_2$ is an efficient remover of dioxane, is not true. If dioxane is present, then it is most likely in evidence at Br/PhMg=0, due to a slight overestimate in the amount of dioxane required, but this is where the proportion of intermediate molecular weight polymer is at its lowest.

It is apparent that up to Br/PhMg=$.3_2$, the presence of bromide instigates a secondary effect on GPC eluograms, increasing the proportion of intermediate molecular weight pMMA but without significantly increasing the isotactic content. This implies that in Fig. 4.22A and Fig. 4.23A a critical bromide content has been reached where "RMgX-like" active centres are present, with a corresponding isotacticity increase.

The constancy of yield with variation in the Br/PhMg quotient is difficult to explain. For Br/PhMg < $.3_2$ in Figs 4.22, 4.23, the same centres present for the system where Br/PhMg=0 (Figs 4.22D, 4.23D) cannot be responsible for the development of the intermediate molar mass polymer present at increasing Br/PhMg quotients, otherwise yield would increase, which is not the case. If $MgBr_2$ modifies some of the centres present at Br/PhMg=0 so that they propagate at a faster rate then the increase in intermediate molecular weight material with increasing Br/PhMg

might be explained. But for constancy of yield to be maintained the population and rate of propagation of these $MgBr_2$ modified active centres must exactly compensate for the loss of centres evident when Br/PhMg=0, and their rate of propagation. This seems to be a very stringent condition. Intermediate molar mass material may increase with constancy of yield if chain grafting reactions were favoured by the presence of bromide, but Goode et al.[62] indicate that such a process is unlikely in organomagnesium systems. The answer to this problem remains unclear.

4.4.7.3 Variation of Initiation and Propagation Temperatures on Polymer Formed

Fig. 4.24 shows the effect of variation of initiation and propagation temperature on gravimetric, molar mass and tacticity data. Yoshino et al.,[33] studying the mode of double bond opening at the β carbon in the polymerisation of isopropyl acrylate with PhMgBr, determined that this mode of opening is set in the initial very short period and persists against temperature change.

A comparison between Figs. 4.24A,B shows that initiation for one minute at -73°C before transfer to a bath at 0°C for 3 hours, has little effect on the nature of polymer formed, producing similar polymer in terms of yield, tacticity and molar mass as initiation and propagation at 0°C. Fig. 4.24C was initiated at 0°C for one minute and propagated for one hour at -70°C to give a low yield of polymer similar in tacticity and molar mass distribution to Fig. 4.24A,B. A comparative run (not shown in

Fig. 4.24: GPC Traces of Methanol insoluble polymer as a function of varying initiation and propagation conditions.

[PhMg] = .099M
[Br] = .070M

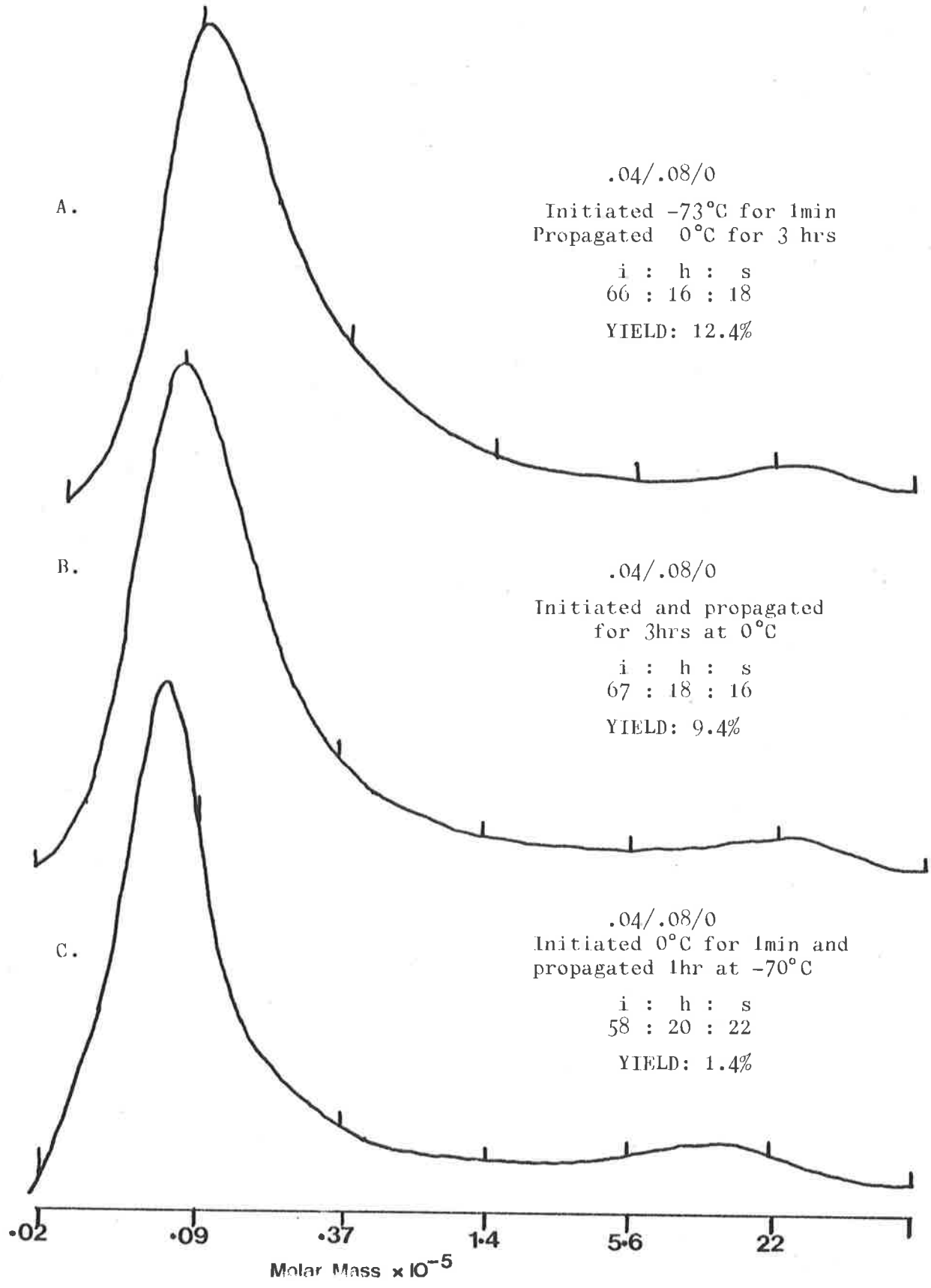


Fig. 4.24), with initiation and propagation carried out at -70°C for one hour produced only trace amounts of polymer, determined to have a high racemic dyad content.

Rather than indicating that the symmetry at the α-carbon atom is determined at initiation, similar to Yoshino's observation at the β-carbon site, results tend to imply a deactivation of active centres for reactions at -70° C. Figs 4.24A,B, however, reveal that this deactivation can be reversed by elevating the temperature, so inactivity at -70° C is not due to consumption of active bonds in side reactions. Active bonds must become inaccessible to the approach of monomer units at low temperature. Similar organomagesium bond inactivity has been noted by Hagias,[12] using the Grignard reagent synthesised from 1,4dibromobenzene, while the inactivity of $PhMgBr/Ph_2Mg$ systems with MMA in toluene at low temperature has also been acknowledged by Matsuzaki.[35]

4.4.8 Variation of Tacticity and Molar Mass : chexMgBr

As mentioned previously this system was the only one examined where colour change, so prominent in alkyl magnesium bromide systems,[26,34] was observed over the range of solvent compositions. The presence or absence of coloration was not indicative of polymeric yields. A deep orange colour characterised reactions in toluene, and pale yellow for reactions in THF, diminishing in intensity as the amount of THF increased. This system yielded methanol soluble polymer, especially in reactions where THF was present. Yields of this material were erratic, showing no

correlation with the final mole fraction of THF or the nature of the initiator solvent, indicating a lack of control with regard to active centres producing this material. The tacticity of this methanol soluble material was similar to that of methanol insoluble material, shown in Fig. 4.25. The tacticity trend shown here is typical of the behaviour for Grignard reagents under varying solvent conditions.

Fig. 4.26 shows GPC eluograms as a function of solvent composition. Behaviour is quite consistent with the trends noted in the MsMgBr system at 250K: the loss of the high molecular weight peak on addition of THF and a broadening of the low molar mass peak.

Fig. 4.27 shows GPC traces for the chexMgBr/MMA/ toluene system as a function of time. Syndiotactic content of polymer formed decreases with increased conversion and is associated with the development of a high molar mass peak ($2x10^6$ gm. mol^{-1}). This high molar mass peak is evident at short reaction times, similar to the MsMgBr system (Fig. 4.14; Br/MsMg=.7_4) but in contrast to the PhMgBr system (Fig. 4.18; Br/PhMg=.6_1). At short reaction times a shoulder is apparent at a molar mass of about $3x10^4$gm. mol^{-1} which becomes less evident with increasing conversion, similar to the shoulder present in the PhMgBr system at 230K (Fig. 4.17; Br/PhMg=1). This may indicate an active, "living" centre, propagating to produce higher molecular weight material with time or, alternatively, a product of very reactive centres, all of which are produced at init-

Fig. 4.25: Tacticity Triangle for thechexMgBr System at 250K

Reaction Time: 3hrs

Br/ChexMg = .65 - .69

Curved line indicates Bernoullian statistics.

Numbers indicate the mole fraction of THF in Toluene.

Dots ≡ Initiator in THF

Squares ≡ Initiator in Tol.

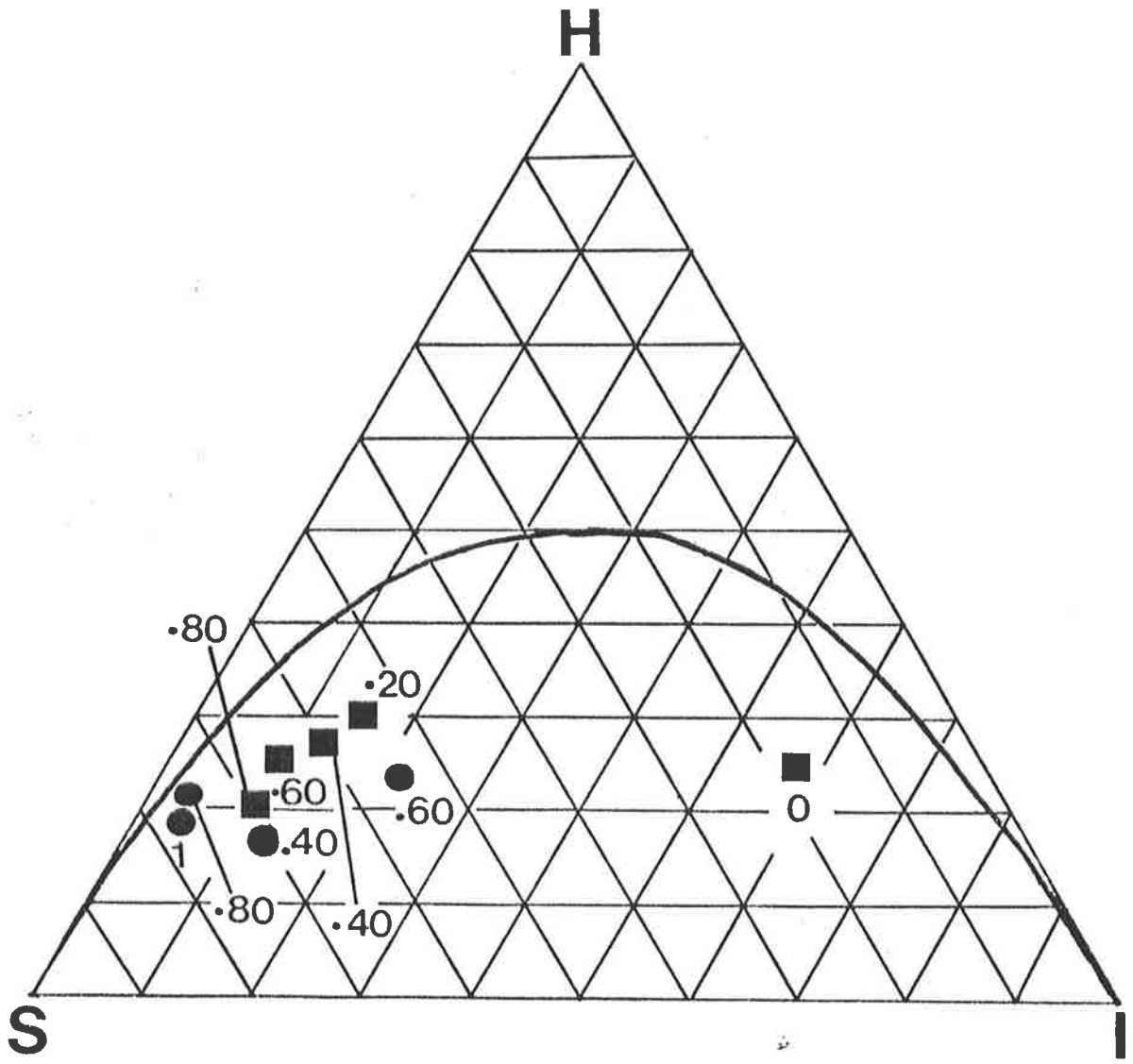


Fig. 4.26: Normalised GPC Traces at 250K for the ChexMgBr System.

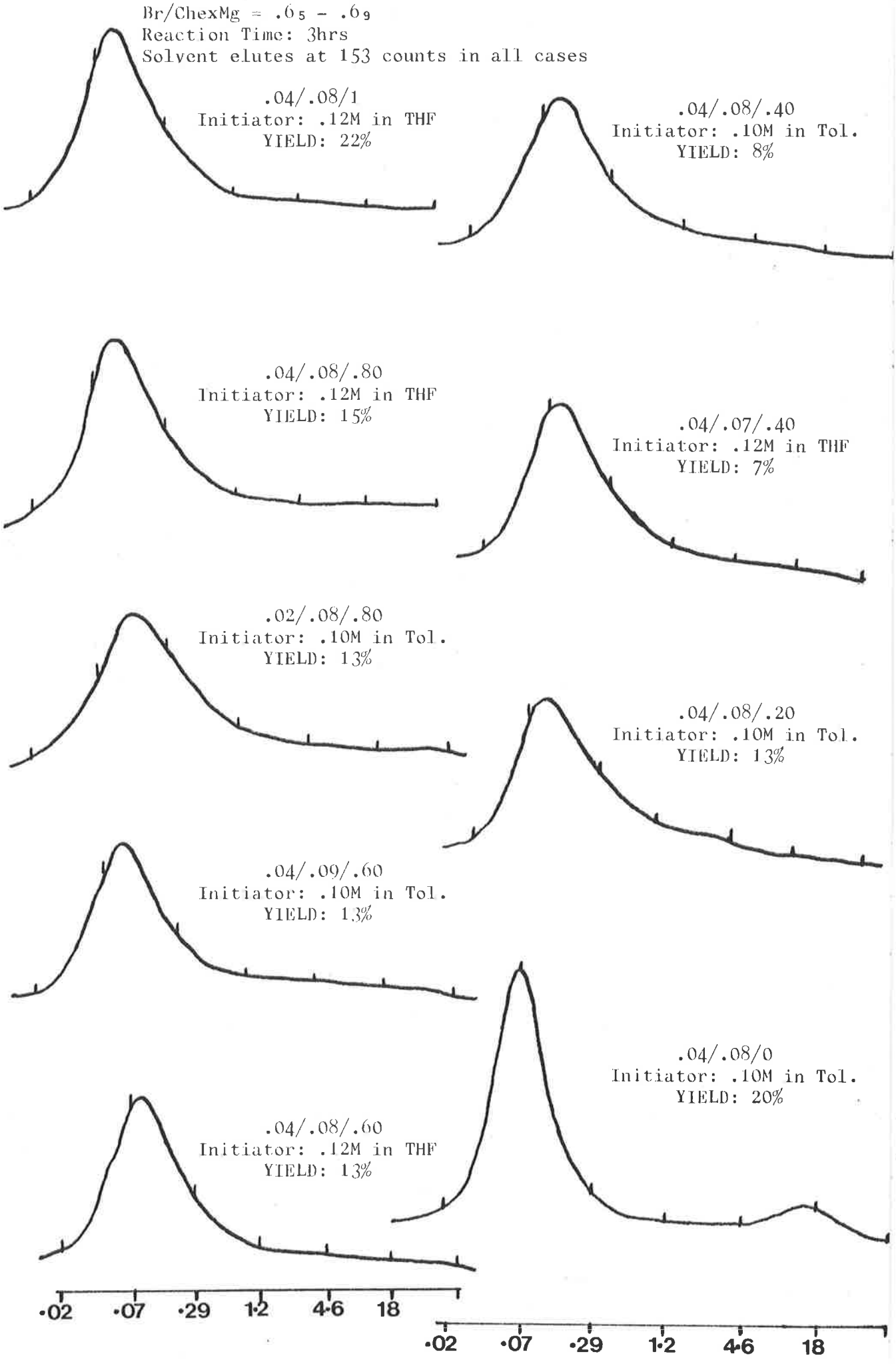
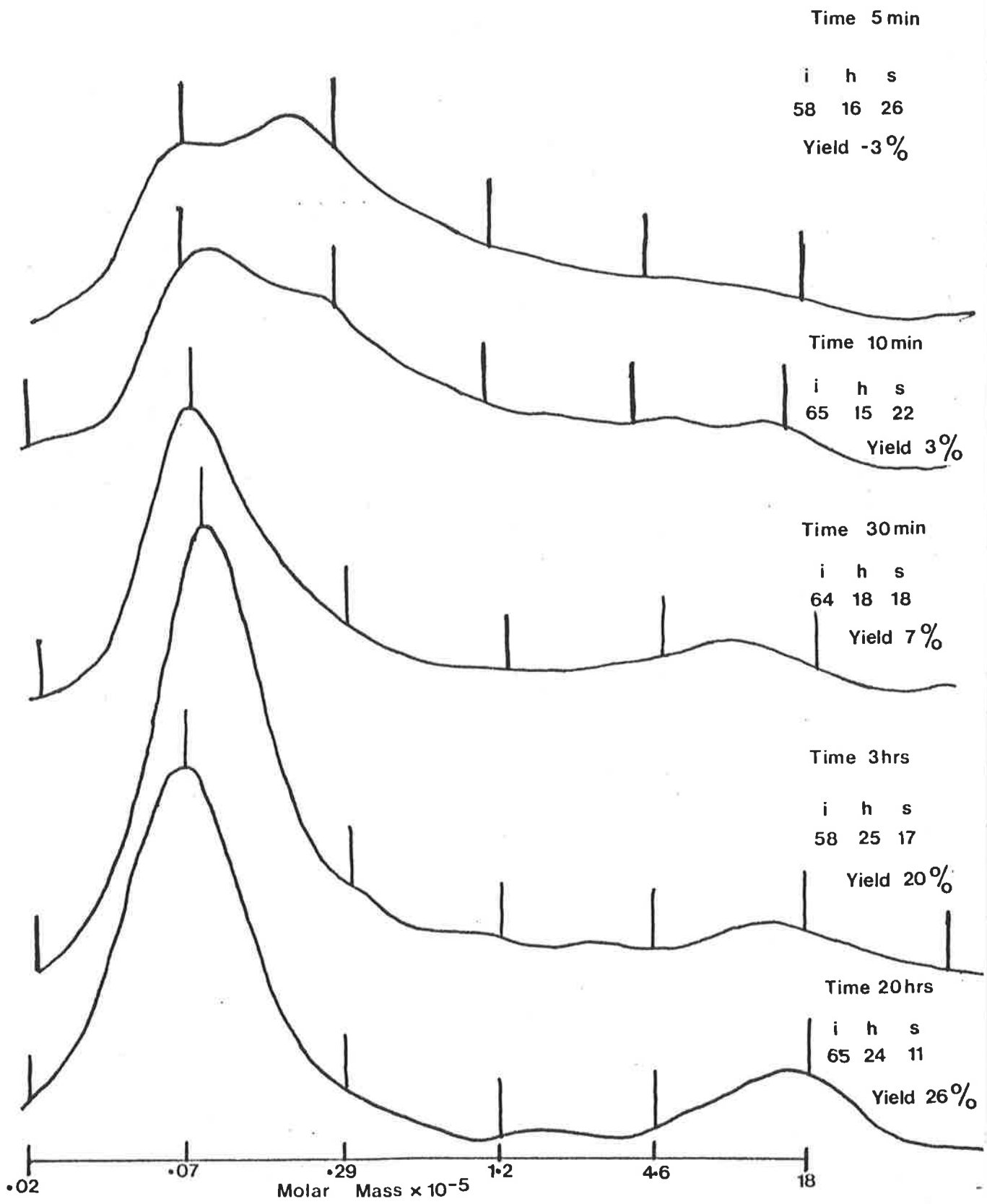


Fig4·27 Cyclo-hexyl Magnesium Bromide - MMA - Tol; GPC & Tacticity Study

as a Function of Time; Different Reaction Vessels; 250K;

Normalised curves - Area = Average ± 15% ; $^{Br}/_{PhMg} = \cdot 65$



iation but which terminate and represent progressively smaller proportions of the polymer product as conversion increases.

4.5 Summary

Polymer products have been shown to be quite dependent on the nature of the initiator used and the differing sensitivity of these alkyl/aryl magnesium compounds toward the presence of bromide.

Preparation of initiator solutions in toluene, under the conditions of this thesis has provided, in general, bromide deficient systems with bromide content showing dependence on the final amount of THF remaining after solvent replacement.

Variable temperature studies of Grignard reagents (see Chapter 3) have indicated the presence of RMgX and R_2 Mg species which possess potential active sites for polymerisation, capable of acting independently of each other. Factors wich may vary the type of different active sites further are:

(1) the presence or absence of associated species RMgX and R_2Mg which are involved in the Schlenk equilibrium (Ph_2Mg in toluene has shown the presence of associates and should thus be more likely for RMgX species due to the enhanced bridging ability of the bromide).

(2) the presence of one or two growth sites associated with R_2Mg and whether or not these two different

active sites are kinetically and/or stereochemically different from each other.

(3) the presence or absence of potentially active magnesium centres with co-ordination numbers greater than the solid state-predicted tetrahedral, four co-ordinate geometry. Thermodynamically, any equilibrium between four and higher co-ordinate systems should be unfavourable in terms of entropy, but at low temperature the $T\Delta S$ term may be small, favouring significant equilibrium concentrations of higher co-ordination number magnesium.

The reactions of MsMgBr, PhMgBr and chexMgBr with MMA in toluene reveal the presence of broad molar mass distributions with a peak centred at $1\text{-}2\times10^{4}$ gm. mol^{-1}, a range of intermediate molecular weights, $.3\text{-}4.6\times10^{5}$ gm. mol^{-1}, and a high molar mass peak at about 2×10^{6} gm. mol^{-1}. At the bromide deficient active bond ratios studied at 250K, the chexMgBr and MsMgBr systems produce high molar mass pMMA after very short reaction times, but this is not so in the case of PhMgBr. In particular, for the chexMgBr, PhMgBr/MMA/toluene reaction systems (Figs 4.27, 4.17, 4.18) the nature of GPC traces varies with conversion, in contrast to the results of Matsuzaki.[35] However, Fig. 4.22A and Fig. 4.23A show that, for the PhMgBr system, GPC traces are invariant with conversion, which concurs with the results of Matsuzaki.[35] The issue of the invariance of GPC eluograms with conversion is contentious and may be dependent on the experimental conditions. Further discussion of this

aspect and its kinetic significance is examined in Chapter 5.

Tacticity data for the MsMgBr system in toluene is the least sensitive system to bromide deficiency, producing highly isotactic polymer which implies that all centres are at least isotactic-like in their mode of monomer addition. At similar bromide to active bond ratios, the PhMgBr and chexMgBr initiated reactions in toluene at the same temperature produce pMMA of lower isotactic content than MsMgBr initiated runs. Strong evidence for the presence of eneidic pathways in these systems (Figs 4.27, 4.17, 4.18) is the changing tacticity as a function of conversion, implying different centres operating with a different mode of monomer addition. This is confirmed by some fractionation work on polymer produced from extensively de-etherated PhMgBr and by results from other workers.[35]

Decrease in the polymerisation temperature causes a decrease in both the proportion of high molar mass material and the isotacticity of the system, for reactions in toluene (Figs 4.2, 4.7).

The presence of THF in the reactions of PhMgBr, MsMgBr and chexMgBr with MMA greatly reduces isotacticity of the pMMA formed and diminishes, or results in the absence of, high molar mass polymers (Figs 4.3-4.6, 4.15, 4.26). The disappearance of high molar mass material (ca. 2×10^6 gm. mol^{-1}) in THF possibly implies that its formation is due to the presence of active centre associates which

are destroyed in THF, while absence of this material with R_2Mg initiators implies that those associates are of the RMgX form. The yield of polymer is also greatly reduced for aryl magnesium bromide systems in the presence of THF, particularly at higher temperatures (Fig. 4.3). For initiator MsMgBr, the addition of THF caused low molar mass unimodal distributions to develop with apparent broadening of this peak at higher mole fractions of THF at 250K, but more erratically so at 230K, indicating some lack of control over this process. Broadening of the low molar mass peak in the presence of THF is also found in the chexMgBr system.

The nature of the initiator solvent appears as a variable in the MsMgBr system at low temperature, where the addition of initiator in THF, for reactions with high final $X_{THF/Toluene}$, afforded significant proportions of intermediate molar mass material. Such material was only present in smaller amounts when initiator was added in toluene at high final mole fractions of THF (Fig. 4.6). This may be explained by assuming an increase in co-ordination number at an active site (thermodynamically more favourable at low temperature) when the initiator is in THF, giving rise to centres producing intermediate molar mass material. Smaller proportions of this material were produced for the initiator in toluene since this initiator required solvation by THF after mixing reagents together, during which time most active centres may have been formed at lower co-ordination sites. If this argument is correct ^{13}C peak broadening observed in the study of the

MsMgBr/THF initiator system at low temperature (see Chapter 3) may be due to co-ordination number changes rather than associate formation. The Ms_2Mg initiator system in THF (Fig. 4.13A) also produced an intermediate molar mass peak at 200K in THF.

Striking differences were observed in polymers formed with Ms_2Mg and Ph_2Mg as a function of solvent composition at 250K (Figs 4.11 and 4.19), although lower isotactic contents were common to both. Whereas Ms_2Mg produced a single low molar mass peak ($1\text{-}2x10^4$ gm. mol^{-1}) which broadened in a manner analogous to that of the MsMgBr system at 250K, the Ph_2Mg initiator produced a low molar mass peak trailing to high molecular weight for the reaction in toluene. This then changed to a bimodal system at intermediate solvent polarity by development of an intermediate molar mass peak, which gradually diminished in proportion to the total polymer produced in THF. The reasons for this are not fully understood. Reactions of Ph_2Mg/MMA/ toluene at 250K show a slight increase in the syndiotacticity of polymer produced with time, associated with an increase in the proportion of material trailing to intermediate molar mass.

Finally, evidence exists, for PhMgBr initiated reactions in toluene at low temperature, to suggest that the initiator exists in an inert form at low temperature which is capable of being reactivated by increasing the reaction temperature. This may be a significant factor in any kinetic analysis in Chapter 5 and may be important in a

discussion of why PhMgBr initiated runs have recently[35] been defined as slow initiating.

CHAPTER 5

5. REACTION KINETICS

5.1 Introduction

The prospect of more than one different, independent active centre operating in the polymerising alkyl/aryl magnesium-MMA system, together with the possibility of side reactions occurring at the MMA carbonyl site with corresponding low initiator efficiency, renders kinetic studies of this system difficult. The unknown constitution of Grignard reagents in hydrocarbon and ether solvents, particularly as a function of temperature , provides a further major problem in the understanding of kinetic data. The aim of this chapter will be to resolve some of these problems, particularly with respect to polymerisations initiated by aromatic Grignard reagents in non-polar solvent where stereoregular polymers result, and to present some recent and novel techniques using NMR spectroscopy to follow the course of a polymerisation reaction.

Allen[1] has noted that organomagnesium/MMA polymerisations are awkward to follow since they are too slow for modern fast reaction techniques but reside at the fast end of the classical kinetic domain. Means of study in this field so far have relied upon classical dilatometry and gravimetric analysis. In the kinetic dilatometry experiment, as a result of the dilatometer filling procedure, the first ten minutes are rendered useless due to temperature re-equilibration problems, limiting its capacity in

studying faster reactions which may be occurring, particularly if retardation occurs by gelation of the reaction medium. Gravimetric studies are insensitive due to difficulties associated with quantitative isolation of products, in particular oligomeric material and non-polymeric side products.

Bateup,[2] using dilatometric studies to examine the nBuMgBr initiated polymerisation of MMA in mixed THF/toluene solvent, observed an external first order relationship with respect to initial active bond concentration at 223K, and similarly with respect to initial monomer concentration under the same reaction conditions. However, upward curvature of $\ln[M]_o/[M]$ vs time plots at high conversion and the linearity of the [M] vs time curve up to high conversion led to the conclusion that the reaction was internally zero order with respect to monomer. These observations were found to correlate with the results of Erusalimskii[3] for the Grignard/acrylonitrile system and was taken to infer that propagation proceeded via a monomer/active site complexation mechanism. Implications of these results will be expanded upon later in this chapter. Bateup[2] found no evidence to suggest that external order with respect to active bond and monomer concentration differed as a function of THF concentration, even though the initial rate of reaction was affected by this parameter. At $\chi_{THF} > .12$ the initial rate of polymerisation decreased linearly with THF mole fraction, but at $\chi_{THF} < .12$ the maximum initial rate of polymerisation was independent of χ_{THF}. This change in kinetic behaviour

correlated with a marked increase in the stereospecificity of polymer products formed. These kinetic results were consistent with the evaluation of Allen and Moody[4] using the diethyl ether/toluene system at 223K.

The nBu_2Mg/MMA system at 223K [2] showed similar behaviour to nBuMgBr/MMA with an external first order dependence with respect to both monomer and initiator active bond concentrations, but with initial rates of polymerisation slightly faster than for nBuMgBr initiation.

The results for nBuMg systems, using THF as the polar component of the solvent mixture, appear less complex than those obtained by Nishioka[5] using diethyl ether as the polar aspect of the solvent, where external second order active bond and first order monomer dependence were observed.

In a similar manner to the nBuMgBr/MMA system, secBuMgBr/MMA reactions showed[2] external first order dependence on the organomagnesium concentration in THF/toluene solvent at 223K.

Dilatometric studies of terBuMgBr/MMA systems by Mair[6] indicated extremely fast rates of reaction, with rapid gelation of the reaction mixture making measurement of initial rates of polymerisation impossible. However, for reactions carried out in total THF at 250K, polymerisations were retarded by the combined effects of dilution of initiator and the introduction of large excesses of bromide, via additions of magnesium bromide, to the init-

iator solution. Bateup[2] had earlier shown that this latter action had a drastic effect upon initiator efficiency. Under these circumstances the external order of reaction with respect to monomer and organomagnesium bonds was found to be one. For reactions of terBuMgBr/MMA in toluene the addition of $MgBr_2$ was prohibited due to solubility problems and reliable initial rates of reaction could not be achieved. This effect of $MgBr_2$ has been observed in some non-polymerisation reactions where the amount of conjugate addition to certain α, β-unsaturated esters decreases with increasing $MgBr_2$ concentration.[7] Complexation of $MgBr_2$ to the carbonyl entity may promote addition at this site, leading to side products in the polymerisation reaction. Gravimetric determinations of pMMA for the terBuMgBr initiator reveal[6] that yields across the THF/toluene solvent range are higher in toluene predominant solvents; an aspect reinforced in this work (refer to Chapter 4).

Most recent advances in the examination of kinetic relationships for Grignard reagent/MMA systems have arisen as a result of novel NMR techniques for the evaluation of internal orders of reaction, developed by Mair.[6] Using time dependent evaluations of monomer concentration, derived from ^1H NMR vinyl integrals of monomer in the absence of viscosity effects, decay curves could be generated to almost complete monomer conversion, thus enabling an estimate of internal order. For the terBuMgBr system in toluene, a variation in internal order from zero to one occurred for reactions carried out over the temperature

range 225-275K. The estimate of zero internal order at low temperature (200K) reinforced the previously proposed mechanism of Erusalimskii[3] for monomer/active centre complexation during propagation; zero orders implying that the rate determining step involved the insertion of a co-ordinated monomer unit into a growing chain attached at the same site by a covalent metal-carbon bond.

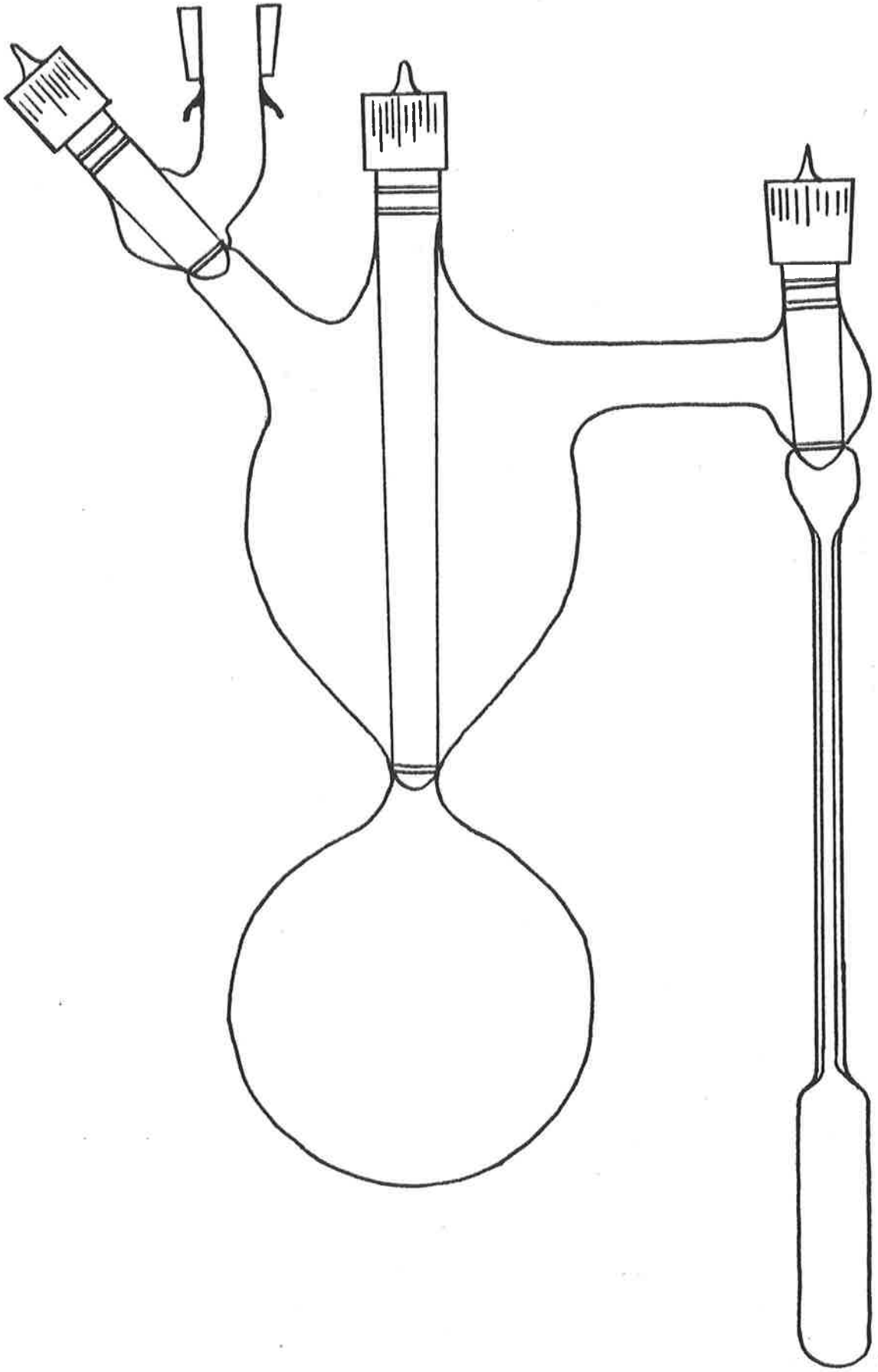
5.2 Experimental

The principal means for the assessment of kinetics in this thesis utilised the NMR techniques developed by Mair,[6] and to a lesser extent, classical dilatometry, for the evaluation of internal and external orders respectively.

5.2.1 Dilatometry

Studies undertaken in this work were achieved using a modified reaction vessel, depicted in Fig. 5.1. External orders of reaction were determined for the PhMgBr system at 250K for both monomer and active bond concentrations in predominantly toluene solvent and were unsuccessfully attempted for the Ph_2Mg system under similar reaction conditions. Reaction vessels were loaded in a manner identical to that used for the production of polymer in Chapter 4 and were equilibrated at bath temperatures of 250K for 15-20 min. prior to the mixing of reactants. A YOUNG tap, situated above the dilatometer arm (Fig. 5.1), prevented distillation of solvent from the initiator solution stored in the upper compartment of the reaction vessel into the dilatometer during the thermal equilibration period. On all occasions the weight of materials in the

Fig 5·1 Reaction Vessel – Kinetic Dilatometer



reaction vessel was recorded, and, together with equation 5.1 postulated by Mair[6] over the temperature range 188-275K:

$$\rho^{T}_{MMA/Tol} = 1.1287 + 0.119\ X_{MMA/Tol} - (.8942 + .1280\ X_{MMA/Tol}).T.10^{-3}$$

Equn 5.1

the volume of the reaction solution could be determined and maintained at a constant value for a series of runs. This procedure neglects the residual THF present in the initiator/toluene solution, but this component comprises about one mole per cent (GLC) of the initiator solvent, so that its omission does not represent a significant error in the above equation. Estimates of the cross-sectional area of the capillary were made using distilled water or alcohol and evaluation of meniscus contraction-time plots was made using a cathetometer capable of measuring to ± .001cm.

5.2.2 NMR Kinetic Experiments

5.2.2.1 NMR Tube Preparation

Sealed tube, kinetic NMR experiments were conducted in a similar manner to that adopted by Mair[6], with reagents added to 5mm NMR tubes <u>in vacuo</u> using the glassware depicted in Fig. 2.8(a). The addition of a small glass dumb-bell facilitated efficient mixing of reactants. On all occasions the initiator/d_8-toluene/toluene solution, with predetermined active bond and bromide concentrations, was decanted first into the lower section of the NMR tube and frozen with liquid nitrogen. Onto this was decanted the monomer/toluene solution which was also frozen. The

amounts of material placed in each tube were checked by weighing. Subsequent to the addition of all reagents, the tube was sealed at the constriction (Fig. 2.8(a)). Tubes were prepared immediately before use and stored in liquid nitrogen until initiation of reaction. Care was taken to ensure that the volume of the reaction solution did not exceed the volume capable of being thermostatted in the NMR probe; this volume always being in the range 1.0-1.2cm^3.

5.2.2.2 Reaction Initiation

The reactivity and stereochemistry of polymerisation have been shown[1,6] to be determined by conditions prevailing at the initiation stage, making it essential to define these conditions precisely.

Immediately before initiation a small alcohol bath was brought to the required reaction temperature i.e., the temperature of the NMR probe. The reaction tube was removed from the liquid nitrogen bath and melted and mixed in the alcohol bath with the aid of the small glass dumb-bell in the tube. This was then quickly interchanged with a dummy tube in the spectrometer probe which contained the same deutero-lock solvent as the reaction tube. In the interim period between insertion of the reaction tube in the probe and the first acquisition of data, the magnetic field was reshimmed to the optimum conditions for the reaction tube.

5.2.2.3 Choice of NMR Pulse

The choice of pulse angle, especially for ^{13}C kinetic studies, was critically dependent on the chemical site of observation. For ^{1}H NMR, where the chief source of information arose from observation of the vinyl proton environment of monomer, a pulse of 3-4 μsec was routinely used with an automatic recurrence pulse mode.

This parameter became critical in ^{13}C kinetic analysis. Mention has been made in Chapter 2 that the chosen site of enrichment was the carbonyl carbon of MMA. As a result, the absence of attached protons confers longer relaxation times on this carbon site, which must be compensated for by the use of either narrow pulse angles or delayed pulses, so that the magnetisation vector can fully relax before initiation of the next pulse. The former option was more favourable since a delayed pulse arrangement presented too many limitations on the kinetic experiment, particularly for fast reactions. Examination of all options available showed that a 2.9 μsec pulse under automatic pulse recurrence optimised conditions.

5.2.2.4 Acquisition of Data

A BRÜKER HX90E spectrometer was used at either 90MHz resolution for ^{1}H examination of kinetics, or at 22.62MHz for study of ^{13}C kinetics using enriched monomer. Coupled to the spectrometer was a BNC-12 computer, DIABLO disk system, a B-GD1 gated decoupling unit and a visual display unit/teletype. Kinetic data were obtained either by using the modified BNC-12 computer program, T1PRGM/11 (version

74), for single mode detection or more frequently by use of an updated form, QDPRGM, for quadrature detection. These programs were modified to wait for a hardware flag before acquisition of blocks of f.i.d. The hardware signal was generated by the modified B-GD1 gated decoupling unit and was appied to the SENSE1 input of the BNC-12. The predetermined time interval between blocks of f.i.d. could be varied from .1-9999 sec. At the appropriate time the hardware flag allowed accumulation of the first set of f.i.d., with this first block of accumulated scans being automatically stored on disk. Following this the spectrometer and computer remained in idle mode until the end of the next time interval when the acquisition process was repeated. Typically, for ^{1}H NMR kinetics, 40 blocks of f.i.d. were collected, with each block containing 10 f.i.d., while for ^{13}C enriched experiments 100 f.i.d. were collected for each of the 40 blocks. To minimise the time for accumulation a 4K data base was used, with the actual time of accumulation being taken as half-way through the collection of each block of f.i.d.

5.2.2.5 Choice of Nucleus for Examination of Extent of Reaction

Table 5.1 below lists all resonances for both ^{13}C and ^{1}H examinations of monomer/polymer systems.

Table 5.1

^{1}H - NMR Resonances - ppm (in the reaction mixture)

	Methoxy	Methyl	Vinyl Cis	Vinyl Trans	Methylene
MMA monomer	3.03	1.50	5.81	4.88 4.86 4.81	-
MMA polymer	3.0-3.02	1.13(broad)	-	-	1.7-1.8

^{13}C - NMR Resonances - ppm (in $CDCl_3$)

	Carbonyl	Methoxy	Methyl	Vinyl	Quaternary	Methylene
MMA monomer	167.3	51.5	18.3	124.7 137.0	-	-
MMA polymer	177	50	16-20	-	45	52

While ^{1}H NMR initially offered the possibility for examination at various resonances, the choice was restricted by the presence of solvent peaks and the overlap of monomer and polymer environments. The α-methyl resonances suffered due to overlap with the toluene methyl resonance. Using the terBuMgBr initiator in toluene, Mair [6] noted partial overlap of monomer and polymer methoxy groups which were not readily deconvoluted by automatic peak pick procedures used in the estimation of peak area. Using aromatic organomagnesium initiators in toluene gave rise to almost complete overlap of these peaks which rendered them useless for kinetic analysis. The most favourable resonances, and those used for evaluations in this work, were the two vinyl proton resonances lying in sparsely occupied field positions (Table 5.1).

The carbonyl monomer carbon was chosen to examine ^{13}C kinetics, despite relaxation problems, for three reasons:

(1) The chemical shift difference between monomer and polymer carbonyl resonances was sufficient to observe decrement and increment of these two peaks (Table 5.1).

(2) Room temperature examination of polymer products in chloroform, utilised in Chapter 4, indicated that the polymer carbonyl resonance was sensitive to stereochemistry. It was envisaged that a kinetic examination of polymerising systems would consequently give an indication of the reaction time dependence of microstructure.

(3) The carbonyl carbon also provides the site for possible side reaction in the system. Examination of kinetics at this site was therefore capable of giving an insight into all monomer consumed.

5.2.2.6 Quantitative Estimate of Peak Area for Internal Order Evaluation

Procedures adopted by Mair[6] for estimation of peak area in ^{1}H NMR kinetics employed automatic peak pick procedures available in software annexed to the BRÜKER HX90E. Under these conditions a peak was picked and integration was commenced when the signal departed by more than twice the r.m.s. error from the baseline. Integration ceased when the signal returned to the mean baseline or when it began to increase again by more than twice the r.m.s. error from the baseline. This procedure was used on occasions in this thesis, but problems often arose due to the inability of the peak picker to register all three peaks of the trans vinyl proton environment (Table 5.1).

This problem was corrected by using a line integral evaluation of peak area, this method being used on most occasions.

The presence of two vinyl protons provided a convenient method for estimation of error in the peak integral. The area recorded at any time was taken as the average of these two environments. The scatter about this value was never more than ± 8-13%. For convenience in interpretation of peak area vs time plots in this chapter, scatter range for each point has been omitted. On occasions, as a check for the validity of vinyl area decrement vs time plots, to ensure that spectrometer operating characteristics were not varying during collection of different blocks of f.i.d., the vinyl area was compared, as a ratio, with a suitably invariant peak (e.g., toluene methyl ^{1}H resonance) in each block, as a function of time. Parallel behaviour between this plot and the vinyl area vs time plot was always found, although scatter of points was greater in the former case due to compounding of errors.

5.2.2.7 Advantages and Limitations of the NMR Kinetic Experiment

Beside the advantages of determination of internal orders of reaction, NMR scale reactions, due to small reaction volumes, minimise the amount of heat released due to exothermic initiation and propagation reactions. That reaction mixture temperatures often lie significantly above the nominal bath or probe temperature was first noted by Nishioka[8] et al., although for large scale reaction volumes of about $20cm^3$ used in this thesis, the

maximum temperature did not exceed the bath temperature by more than 2-3K. For NMR scale reactions where smaller reaction volumes and lower initial monomer concentrations were used, the temperature rise is likely to be much less than this.

The other important advantage of small reaction volumes is the shorter thermal re-equilibration time required, which means shorter delays between reaction initiation and data acquisition. This is useful in the examination of faster reactions.

Disadvantages of the technique are summarised below:

(1) Initiation has been referred[1,6] to as the critical stage in the determination of the nature of potential active centres, their relative populations and the resultant pMMA stereochemistry, but little control in the initiation step seems to be invested by returning a reaction solution from the frozen state to the prescribed reaction temperature. This may be less important for the PhMgBr system where inactivity is evident at and below 200K (see Chapter 4), thus reducing the possible range of temperatures, between frozen state and the nominal reaction temperature, at which reaction could occur.

(2) Given the errors inherent in determination of peak areas as a function of time, unquestionable estimates of internal reaction orders can only be made for conversions greater than 50%, and preferably greater than 75%. Viscosity and gelation effects are prohib-

itive under such circumstances lest the reaction become diffusion controlled as a result of these medium effects. Consequently, the mole fraction of monomer was kept low ($X_{MMA/tol} \sim .02-.04$), and all runs indicated in this chapter provided final reaction solutions which were non-viscous and freely flowing.

(3) NMR reaction kinetics, determined from 5mm tubes, provided difficulty in the determination of exact concentration of monomer initially present. The method of loading the tube, described earlier, required the weighing, after addition of monomer, in the frozen state so as to prevent any possibility of reaction. Accurate weighing on a four figure balance was thus rendered difficult, and NMR tubes invariably cracked during such a weighing procedure. Tubes were therefore weighed quickly on a top-loading balance, but this, combined with the small weights introduced into the tube, produced errors of ± 20-25% in estimates of initial monomer concentration.

5.3 Theory

5.3.1 Dilatometry

The extent of reaction is defined by:

$$(M_o - M)/M_o \qquad \text{Equn 5.2}$$

where M_o = the initial mass of monomer present

M = mass of monomer remaining at time t.

This is related to the observed contraction in the polymerising system by:

Extent of reaction = $(V_o - V)/(V_o - V_{100})$ Equn 5.3

where V_o = volume at time zero

V = volume at time t

V_{100} = volume at 100% conversion

For a dilatometer capillary with cross-sectional radius, r:

$$\Delta V = (V_o - V) = \Pi r^2 \Delta h \qquad \text{Equn 5.4}$$

where Δh = the experimentally observed drop in meniscus height.

Extent of reaction may thus be expressed as:

$$(\Pi r^2 \Delta h)/(M_o(1/\rho_m - 1/\rho_p) = K\Delta h \qquad \text{Equn 5.5}$$

where ρ_m = density of monomer

ρ_p = density of polymer

and $(1/\rho_m - 1/\rho_p)$ = volume change when one gram of monomer is converted to one gram of polymer. Conventionally the value of ρ_p has been taken[2,6,9] as 1.19gm cm^{-3}, while ρ_m at the given temperature was evaluated by substituting $\chi_{MMA/tol} = 1$ into Equn 5.1.

5.4 Results and Discussion

5.4.1 Kinetic Dilatometry

Evaluation of initial rates of reaction was influenced by the following factors:

(1) In the determination of external order with respect to monomer at the initial active bond concentration cited below, initial monomer concentrations greater than about 1.3M at 250K showed no region of linearity in meniscus height-time plots, which were required

for the interpolation of meniscus height, and hence reaction volume, at zero time. This upward curvature of meniscus height-time plots at low conversion (2-3%) is also evident in dilatometric runs evaluated below for initial rates of reaction, but definite regions of linearity were observed in height-time plots for these experiments. Given the low conversion, viscosity is not responsible for the upward curvature in these plots, and it appears likely that termination of growing chains is responsible. No absolute correlation is apparent between conversion at the onset of curvature in these plots and the initial monomer concentration, which might imply predominant chain termination by reaction of the living end with the monomer carbonyl group. All height-time plots under these conditions showed the onset of upward curvature at 2-3% conversion.

(2) In the determination of external order with respect to active bond concentration at 250K for the initial monomer concentration cited below, a minimum phenyl magnesium concentration of about .004M was found, below which little or no polymerisation took place. Similar observations were noted by both Mair[6] and Bateup[2] for the terBuMgBr and nBuMgBr systems, respectively, with the effect being possibly attributable to side reactions of active bonds with monomer resulting in low initiator efficiency.

(3) An upper limit of about .03M with respect to initial active bond concentration was necessary due to the

difficulty in discernment of a linear meniscus height vs time region above this concentration. In contrast to the loss of linearity in mensiscus height-time plots at 2-3% conversion for the determination of external order with respect to monomer, the conversion at the point of deviation from linearity of these plots in external order determinations with regard to phenyl magnesium concentration monotonically increased from 1.8% (theoretical) at $[PhMg]_o$ = $6.4_9 \times 10^{-3}$ M to 7.2% (theoretical) at $25._o \times 10^{-3}$ M = $[PhMg]_o$.

5.4.1.1 Kinetic Dilatometry - PhMgBr/MMA/ Toluene/residual THF/250K

(a) External Order with respect to Monomer

Table 5.2 indicates the initial monomer concentrations and corresponding initial rates of reaction, R_{po}.

Table 5.2:

Initial Monomer Conc	$R_{po} \times 10^4$ mole dm^{-3} min^{-1}
$.37_7$M	3.1_9
$.59_5$M	4.2_2
$.75_9$M	5.3_o
1.1_5 M	8.7_o

These results were obtained using a stock initiator solution having the following characteristics: $[PhMg]_o$ = $.047_2$ M; Br/PhMg=$.6_o$ and mole per cent THF in toluene = 1.1%(GLC). On mixing of reactants at 250K this initiator solution provided an initial active bond concentration of $8.7_1 \times 10^{-3}$M, which was maintained for the four runs evaluated. A plot of $\log R_{po}$ vs $\log [MMA]_o$ produced a straight

line with slope .90(± .11 s.e. of slope), indicating that the reaction is conceivably externally first order in monomer. Fig. 5.2 shows a plot of R_{po} vs $[MMA]_o^1$ with 90% confidence intervals marked.

(b) External Order with respect to Active Bonds

Table 5.3 indicates initial active bond concentrations and corresponding initial rates of reaction, for an initial monomer concentration of $.78_8$M(250K).

Table 5.3:

Initial Active Bond Conc x 10^3	R_{po} x 10^4 mol dm^{-3} min^{-1}
6.4_9M	6.3_0
$11._4$ M	$11._6$
$15._2$ M	$14._2$
$25._0$ M	$26._1$

A plot of $\log R_{po}$ vs $\log[PhMg]_o$ produced a straight line with slope 1.04 (±.06 s.e. in slope), indicating that the reaction is probably externally first order with respect to active bonds. Fig. 5.3 shows a plot of R_{po} vs $[PhMg]_o^1$ assuming such a relationship (90% confidence limits marked).

5.4.1.2 Kinetic Dilatometry - Ph_2Mg/MMA/ Toluene/residual THF/250K

In contrast to the PhMgBr system studied at 250K, difficulties arose in the determination of external order with respect to monomer using Ph_2Mg as initiator.

Although regions of linearity in the meniscus height-time plots were found, calculations of the theoretical

Fig. 5.2 Plot of Initial Rate of Polymerisation vs. $[MMA]_o^1$
90% Confidence Limits Marked.

Line of best fit: Slope : 7.3×10^{-4} min^{-1}
Intercept : $.11 \times 10^{-4}$ mol dm^{-3} min^{-1}
S.E. in Slope : $.7 \times 10^{-4}$ min^{-1}
S.E. in Intercept : $.56 \times 10^{-4} \times 10^{-4}$ mol dm^{-3} min^{-1}

Temperature : 250K

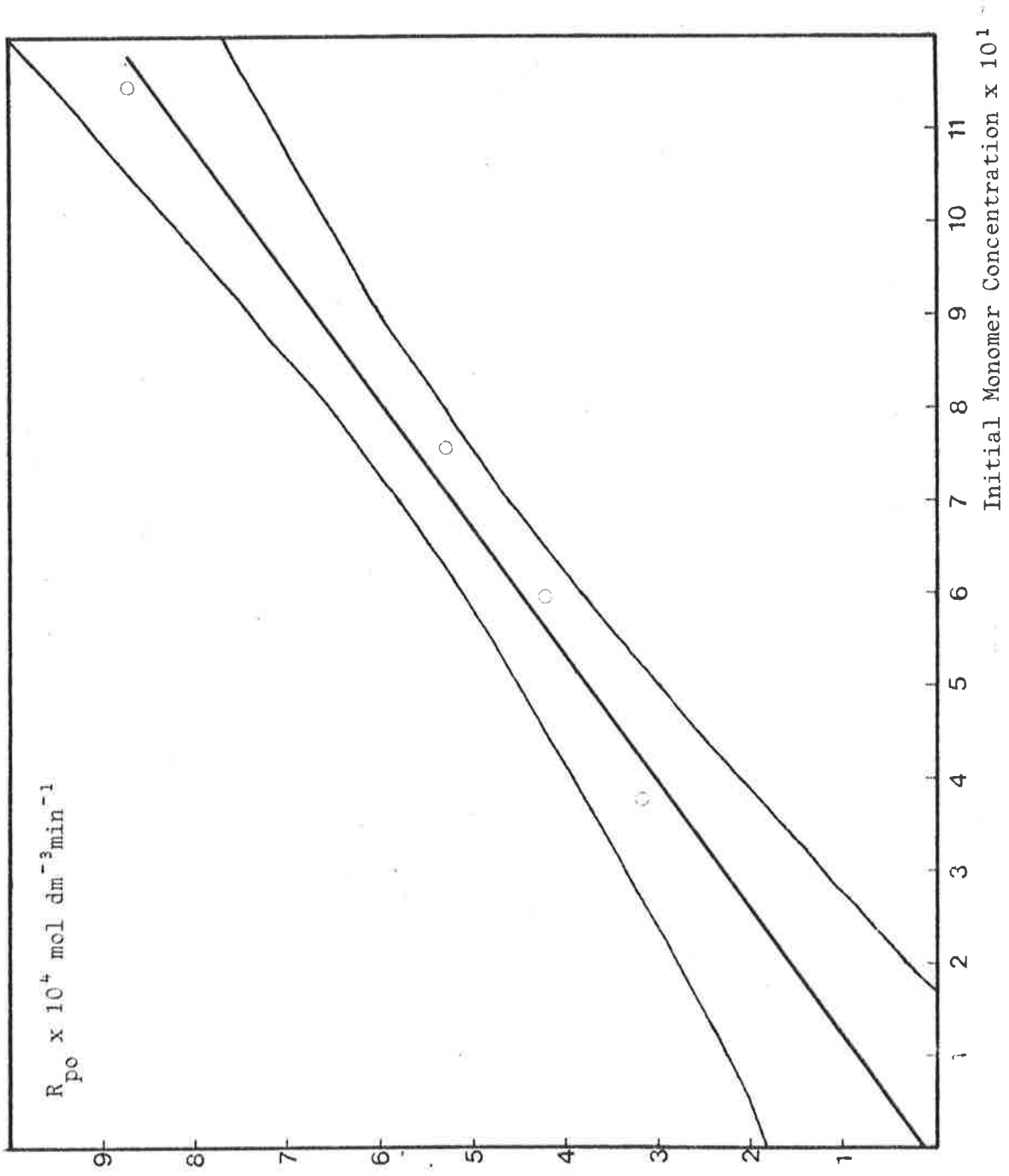
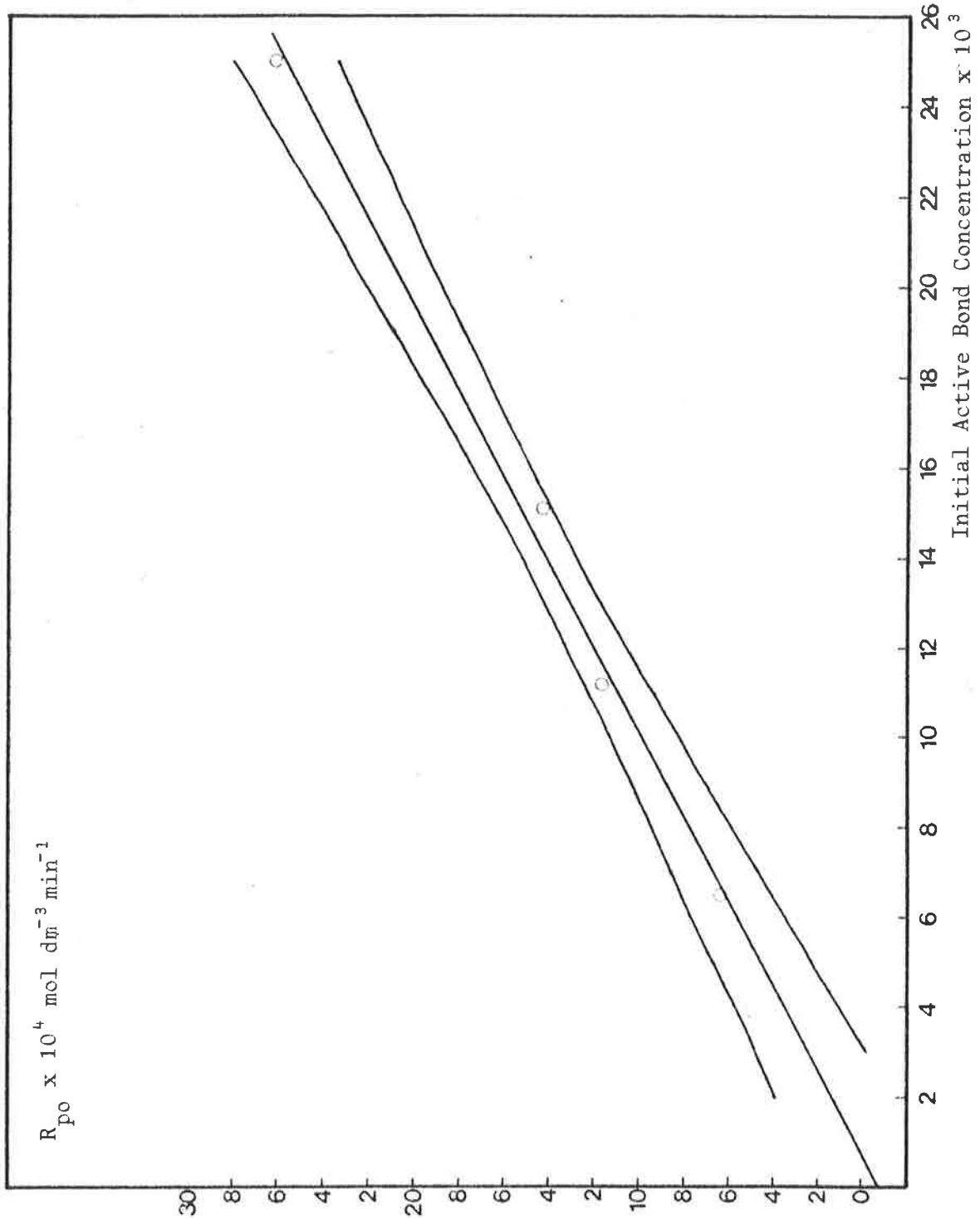


Fig. 5.3 Plot of Initial Rate of Polymerisation vs. $[PhMg]_o^1$
90% Confidence Limits Marked.

Line of best fit: Slope : 106×10^{-3} min^{-1}
Intercept : $-.89 \times 10^{-4}$ mol dm^{-3} min^{-1}
S.E. in Slope : 6×10^{-3} min^{-1}
S.E. in Intercept : 1.0×10^{-4} mol dm^{-3} min^{-1}

Temperature : 250K



yield produced conversions much lower than those found experimentally, in contrast to those experiments in section 5.4.1.1, which indicates fast reactions. A plot of log R_{po} vs log$[MMA]_o$ produced a gradient, α , such that when R_{po} vs $[MMA]_o^{\alpha}$ was plotted the origin did not lie within one standard error of the intercept.

NMR kinetic experiments (see later) with the Ph_2Mg system confirm that rapid consumption of monomer occurs in the first 5-10 minutes of reaction - a period which cannot be monitored due to re-equilibration problems in dilatometry - followed by significant retardation of reaction due to termination of growing chains at about 60% conversion. Such conditions render dilatometry ineffective.

The PhMgBr kinetic experiments were carried out using $Br/PhMg=.6_o$, implying that appreciable amounts of Ph_2Mg must exist. However, the disparity in behaviour observed between dilatometric studies of both initiator systems suggests that Ph_2Mg is not present in the PhMgBr initiator with $Br/PhMg=.6_o$, otherwise there would have also been discrepancies between theoretical and experimental yields for reactions with this latter initiator. It is possible that the presence of bromide, through its enhanced bridging ability, modifies Ph_2Mg by formation of associates to produce slower propagating active centres.

5.4.2 NMR Kinetic Studies

Obtaining the right conditions for reactions in NMR kinetic experiments was difficult and success was only

achieved by invoking the following experimental conditions, particularly for initiators containing bromide:

(1) Ensuring that the external bath was set to the temperature at which polymerisation in the NMR probe was to take place. Preliminary runs, where the NMR tube was taken from liquid nitrogen and melted in an acetone bath at room temperature invariably failed, probably because the tube contents are elevated to temperatures conducive to side reactions and a loss of initiator efficiency.

(2) The most critical factor, for the PhMgBr initiator system in particular, was the observation that successful polymerisations only occurred when $\chi_{PhMg/MMA}$ was set at values considerably higher ($\sim$.2-.3) than those described in the large scale polymerisations of Chapter 4 ($\sim$.04). Only small/negligible conversions of monomer were observed in NMR experiments when $\chi_{PhMg/MMA}$ was set to the value of these large scale experiments for the PhMgBr system. Mention has been made in Chapter 4 of the inability of this initiator to induce polymerisation at 200K for large scale runs, although subsequent transfer of the reaction to a bath at 250K produced the same polymer, and in similar yield, as that obtained when reaction was initiated and propagated at 250K. Inactivity of the initiator possibly arises from the formation of inert aggregates which are disrupted and activated at higher temperatures. Inactivity of the initiator in NMR kinetic experiments carried out at $\chi_{PhMg/MMA}$=.04,

especially where the tube contents are melted from the frozen state, may arise from the persistence of some of these inert aggregates. Increasing $\chi_{PhMg/MMA}$ was initially avoided on the basis that it might be conducive to excessive side reaction with the monomer carbonyl, but finally appeared as the only means of following PhMgBr initiated runs to high conversion. Possible reasons why variations exist between $\chi_{PhMg/MMA}$=.04 and $\chi_{PhMg/MMA}$=.2-.3 are discussed later in this chapter.

(3) Although kinetic experiments using the Ph_2Mg initiator in toluene were also examined at high $\chi_{PhMg/MMA}$ (for reasons of comparison with the PhMgBr system), this initiator appeared more robust than PhMgBr under similar initiation and propagation conditions. This is exemplified by two reactions carried out at 250K for the Ph_2Mg and PhMgBr initiators, where the reaction parameters were .03/.06/$\sim$.01-.02 ($=\chi_{PhMg/MMA}/\chi_{MMA/Tol}/\chi_{THF/Tol}$) and .03/.05/.01-.02, respectively, with the former initiator producing a significant conversion of monomer to polymer (50-60%) in contrast to the latter. If the proposition presented in (2) above is feasible; that inactivity of organomagnesium bonds is governed by the presence of inert aggregates (e.g., linear associates), then the proposition is strengthened by the comparison between Ph_2Mg and PhMgBr initiators. The tendency for enhanced association in the presence of halide has been noted by Ashby[10,11] in the formation of linear associates. This propensity to associate appears to parallel the reac-

tivity of the organomagnesium compound in NMR experiments carried out here.

(4) NMR scale reactions have been examined almost exclusively at low $\chi_{THF/Tol}$ due to the more interesting stereoregular polymerisations occurring under such conditions. NMR scale reactions using the PhMgBr initiator were attempted in THF, primarily at 250K, but invariably failed to produce anything but trace amounts of polymer. This observation seems in accord with large scale polymerisations examined in Chapter 4, where yields were also low at high mole fractions of THF.

5.4.2.1 NMR Kinetic Experiment - PhMgBr/MMA/ Toluene/d_8-Toluene/residual THF

Figs 5.4, 5.5 and 5.6 show plots of vinyl line integral as a function of time for the PhMgBr system at 250K, 240K and 230K while Figs 5.4(a), 5.5(a) and 5.6(a) show plots of $(Area)^{(1-Order)}$ vs time for the best estimate of internal order in each case. Table 5.4 below shows the estimated order with respect to temperature as well as the tacticity of polymer produced in each case.

Table 5.4:

Temperature	Internal Order	Tacticity i : h : s
250K	1.7(±.1)	60 14 26
240K	1.5(±.1)	66 22 12
230K	1.1(±.1)	63 16 21

Estimates of internal order were made on the basis of correlation coefficient, with conversions in each case being taken to greater than 75%. The variation in micro-

Fig. 5.4 Plot of Vinyl Peak Area vs. Time (min)

PhMgBr/MMA/d_8Tol/Toluene

Reaction parameters: .17/.03/∿.01

$Br/_{PhMg}$ = $.6_o$

Temperature : 250K

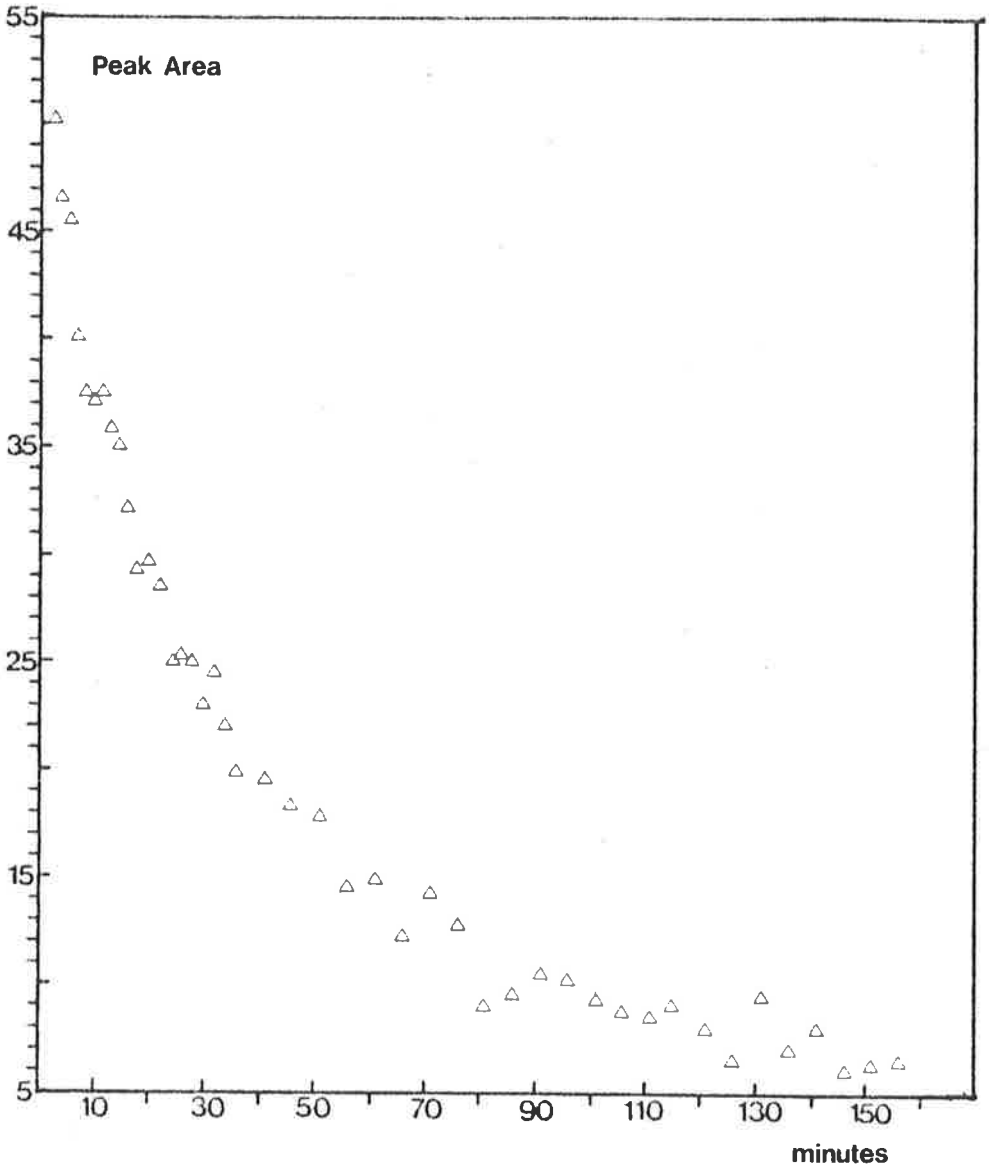


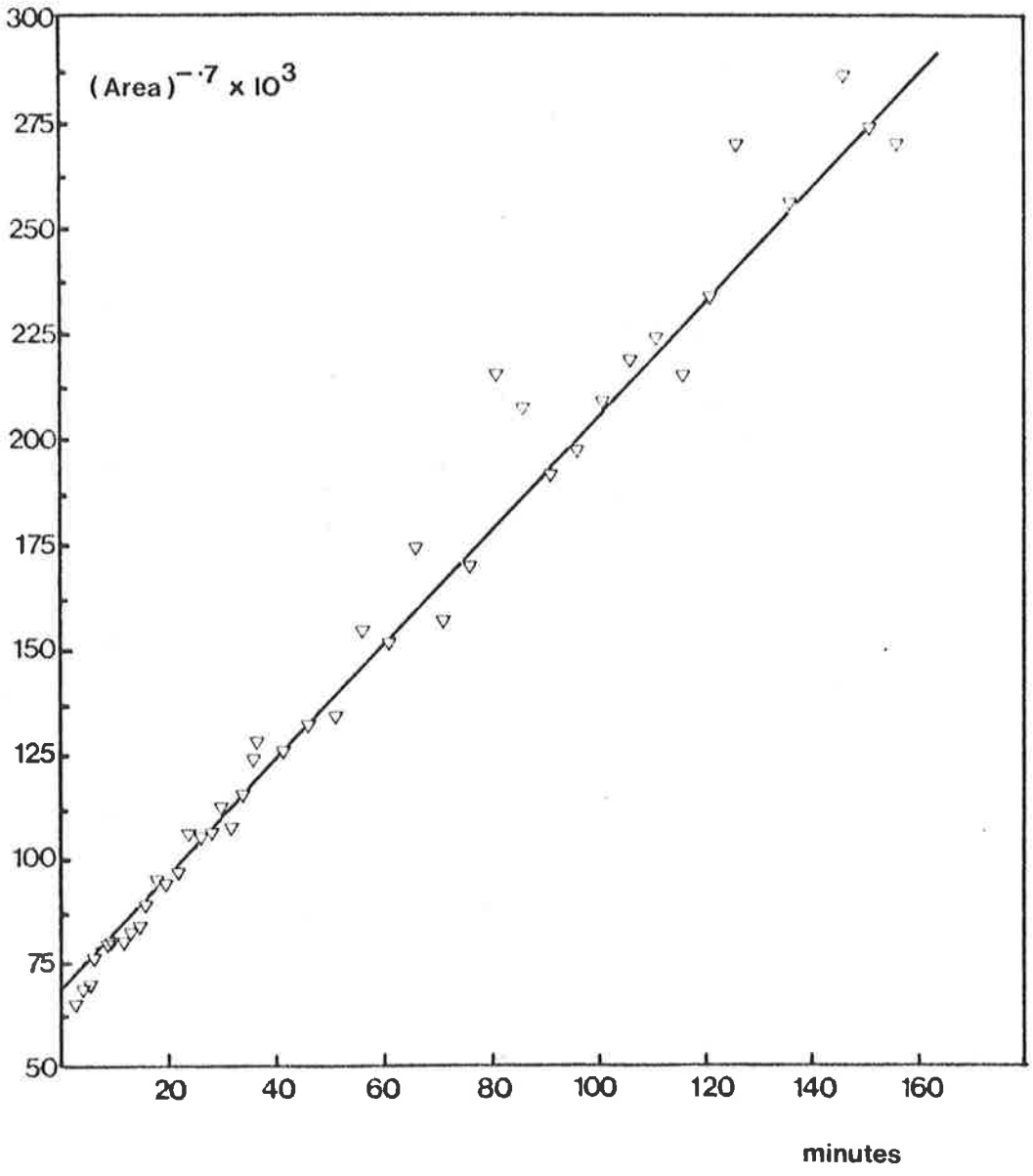
Fig. 5.4(a) Plot of $(Area)^{-.7}$ vs. Time

PhMgBr/MMA/Toluene/d_8Toluene

Reaction Parameters: .17/.03/∿.01

Br/PhMg = $.6_o$

Temperature : 250K



Linear Least Squares Regression:

Slope	: $1.363 \times 10^{-3}(Area)^{-.7}\ min^{-1}$
Intercept	: $6.837 \times 10^{-2}(Area)^{-.7}$
Sample Std. Deviation	: 1.223×10^{-2}
S.E. in Slope	: $.038 \times 10^{-3}$
S.E. in Intercept	: $.030 \times 20^{-2}$

Fig. 5.5 Plot of Peak Area vs. Time

PhMgBr/MMA/Toluene/d$_8$Toluene

Reaction parameters: .21/.03/∿.01

Br/PhMg = .6$_o$

Temperature : 240K

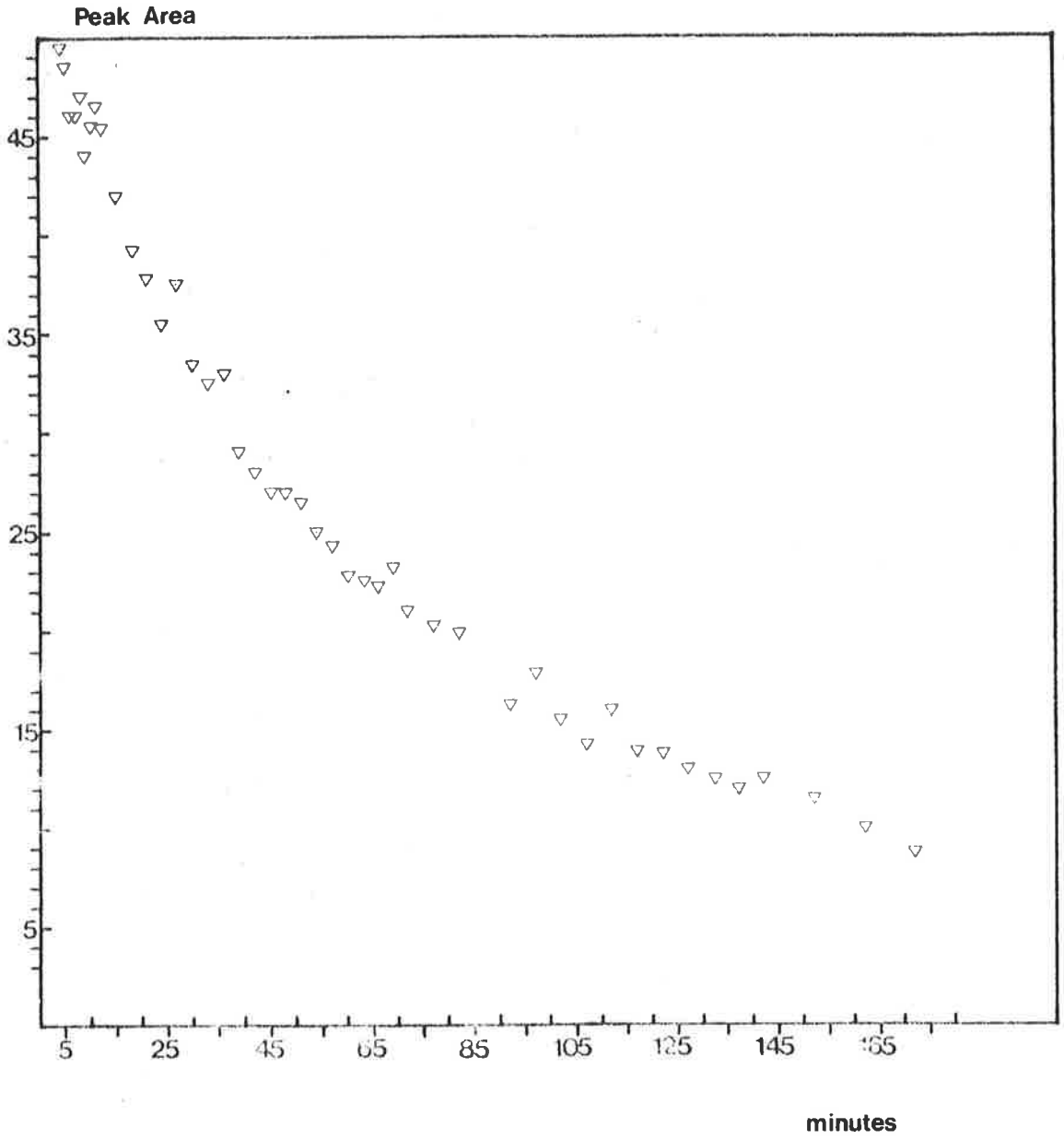
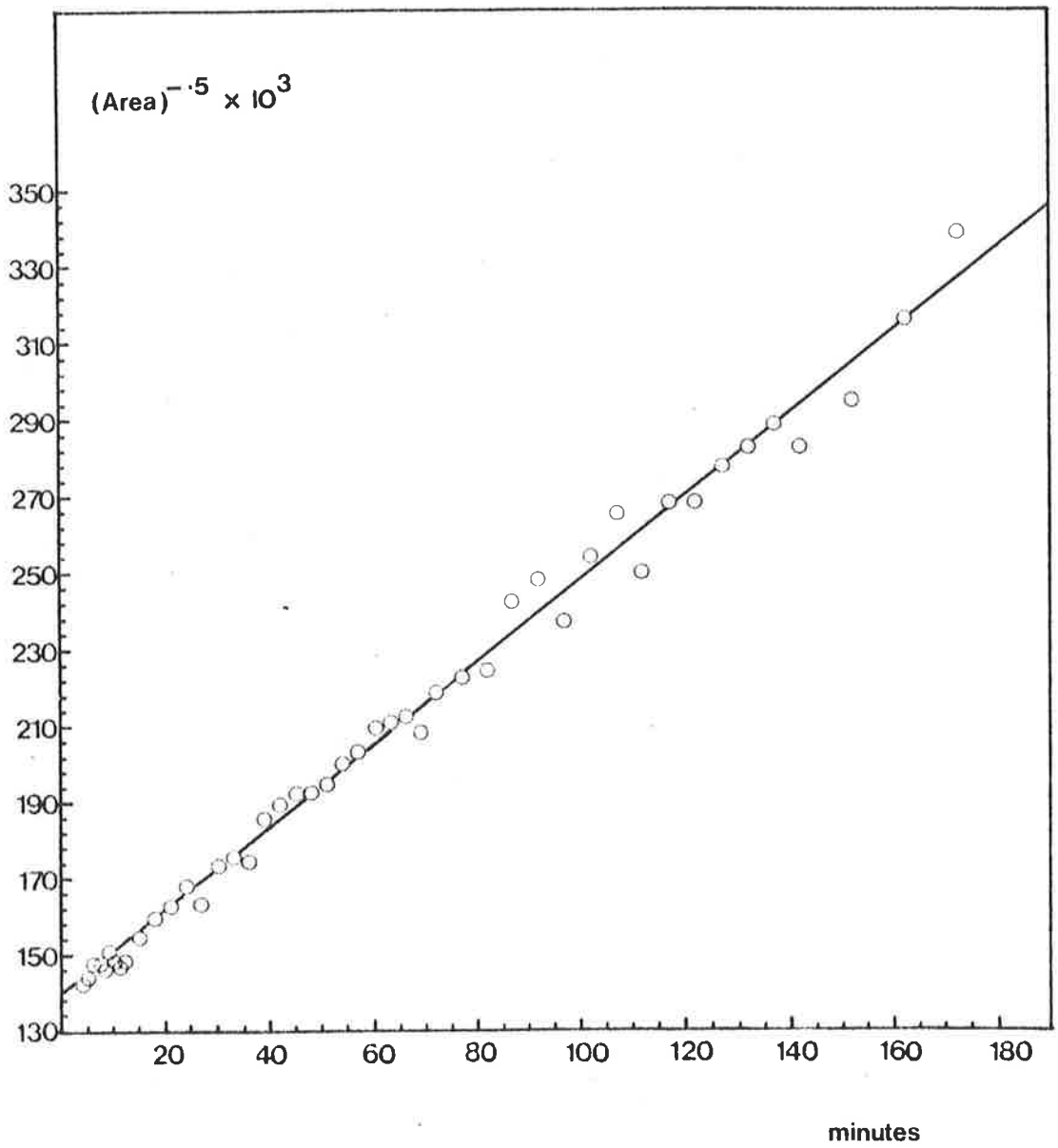


Fig. 5.5(a) Plot of $(Area)^{-.5}$ vs. Time
PhMgBr/MMA/Toluene/d_8Toluene
Reaction parameters: .21/.03/∿.01
Br/PhMg = $.6_o$
Temperature: 240K



Linear Least Squares Regression:

Slope	: $1.090 \times 10^{-3}(Area)^{-.5}min^{-1}$
Intercept	: $1.391 \times 10^{-1}(Area)^{-.5}$
Sample Std. Deviation	: 5.024×10^{-3}
S.E. in Slope	: $.015 \times 10^{-3}$
S.E. in Intercept	: $.012 \times 10^{-1}$

Fig. 5.6 Plot of Peak Area vs. Time

PhMgBr/MMA/Toluene/d_8Toluene

Reaction parameters: .21/.03/∿.01

Br/MsMg = $.6_o$

Temperature: 230K

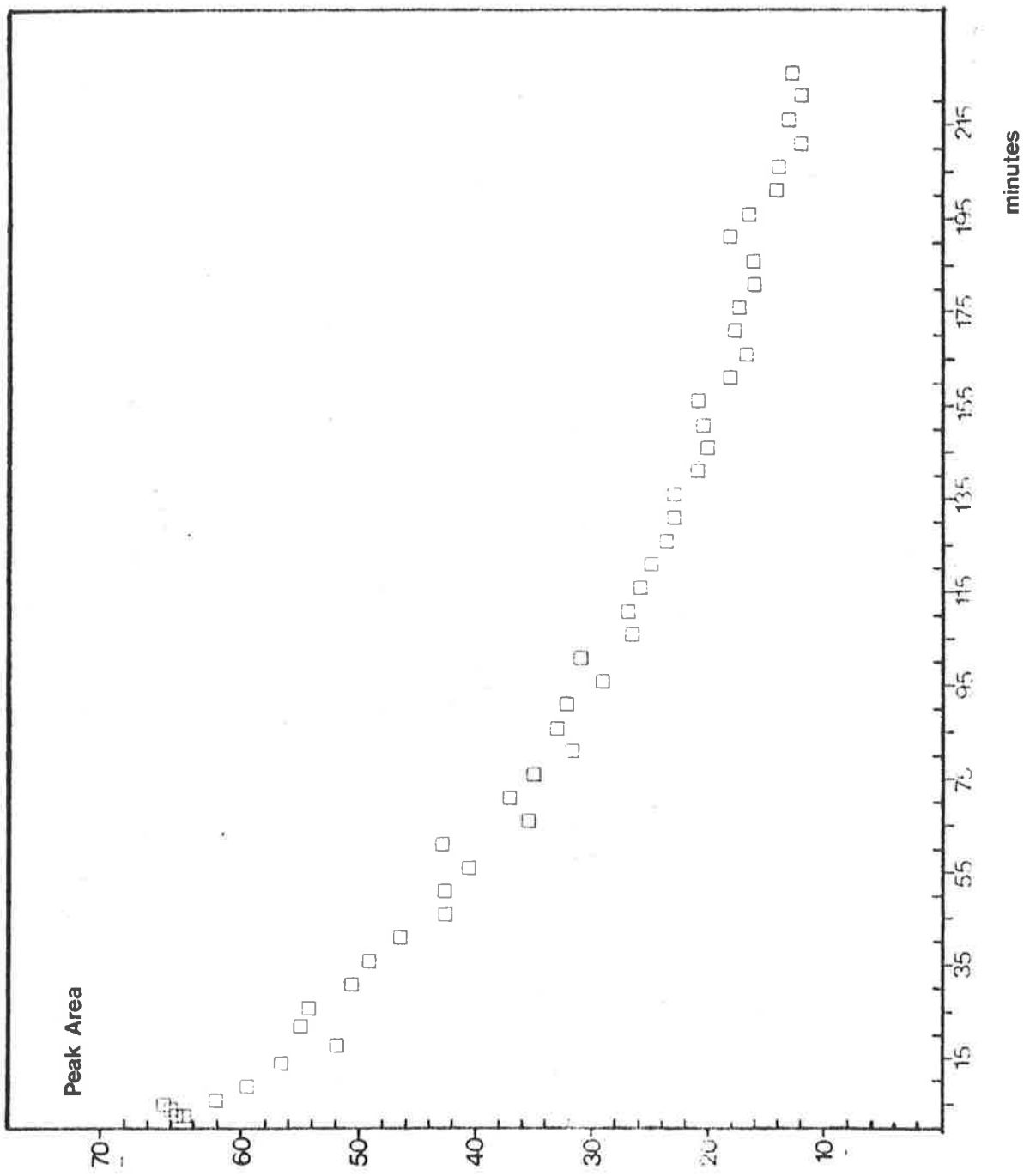


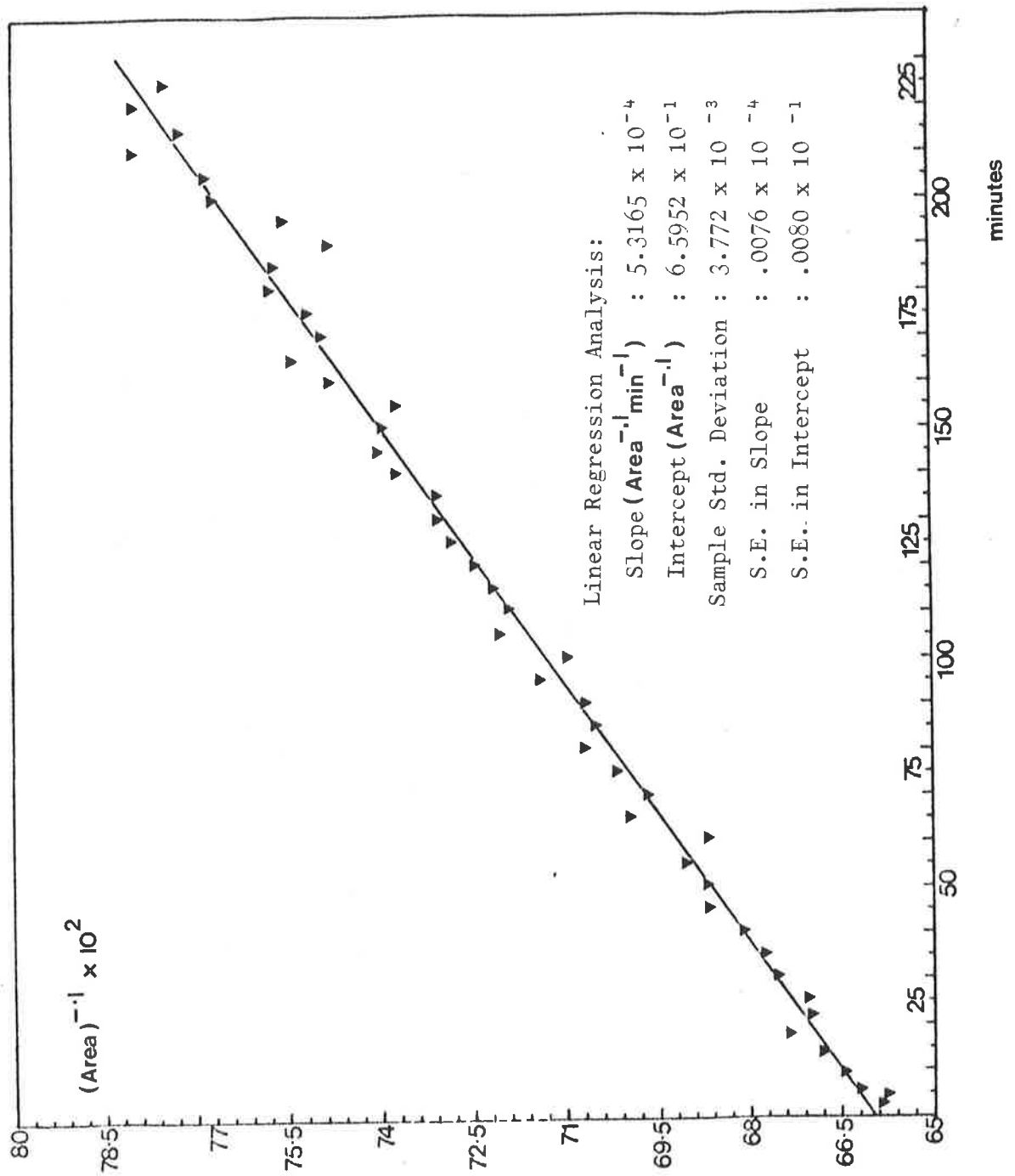
Fig. 5.6(a) Plot of $(Area)^{-.1}$ vs. Time

PhMgBr/MMA/Toluene/d_8Toluene

Reaction parameters: .21/.03/~.01

Br/PhMg = $.6_o$

Temperature: 230K



structure with temperature varied in an erratic manner although the small amounts of polymer obtained from these NMR runs meant the tacticity data was less accurate.

The same increase in internal monomer order with temperature has been observed by Mair[6] for terBuMgBr initiated polymerisations under similar low mole fraction THF solvent conditions over the temperature range 200-275K, although under these circumstances internal order varied between zero and one, with some evidence of a mixture of these orders at intermediate temperatures.

Some anomalies exist between dilatometric data examined in section 5.4.1.1 at 250K and the NMR kinetic experiment at the same temperature. The deviations from linearity in meniscus height-time plots at 2-3% conversion, observed in the determination of external order with respect to monomer at constant active bond concentration were designated as a probable effect of chain termination. In particular, one of the dilatometric runs carried out at 250K with $[MMA]_o = .37_7 M$ and $[PhMg]_o = 8.7_1 \times 10^{-3} M$ deviated from linearity at 3% conversion. However, the NMR kinetic run showed a consistent internal order of reaction for monomer over the duration of examination of vinyl peak integrals, with $[MMA]_o = .3_7 M$ and $[PhMg]_o = .07_6 M$. A simple termination reaction, in the absence of chain transfer processes, should manifest itself in terms of $t_{3/4}/t_{1/2}$ and $t_{1/2}/t_{1/4}$ values indicative of different orders of reaction, with $t_{3/4}/t_{1/2}$ implying a higher order of reaction than $t_{1/2}/t_{1/4}$. Such is not the case in the NMR experiment (Fig. 5.4, Fig.

5.4(a)). Goode and co-workers[12] have shown that chain transfer does not occur in the PhMgBr/MMA/Toluene/trace diethyl ether reaction and so termination by this process can be discarded. Possible reasons for the discrepancies in behaviour between NMR and dilatometric experiments are:

(1) The different mode of initiation, and in particular the inexact specification of the initiation temperature when NMR reaction solutions were melted from the frozen state, may render dilatometry unsuitable for comparison with NMR results.

(2) Matsuzaki and co-workers[13] noted that pMMA produced by PhMgBr (Br/PhMg=1) reactions in toluene had molecular weight distributions which were unaffected by conversion and were described as slow initiation-rapid propagation systems. For this to be satisfied in an eneidic pathway, the different types of active centres must slowly become available in the same relative proportions otherwise relative intensities of GPC peaks would change with respect to each other over time. These workers did not clarify how such a system would operate. If this were the case in the NMR kinetic experiment using PhMgBr(Br/PhMg=.6_0) examined at 250K, where the initial active bond concentration was approximately ten times that of a similar dilatometric run, then the effects of termination observed at about 3% conversion in the dilatometric run may be masked in the NMR kinetic experiment by the slow availability of potential active centres from a larger source of organomagnesium bonds. This

may also explain why NMR kinetic runs with $\chi_{PhMg/MMA}$ = .04 showed little or no conversion in comparison to runs examined at a similar $\chi_{MMA/Solvent}$ and with $\chi_{PhMg/MMA}$=.2-.3. Dilatometric runs for the evaluation of external order with respect to active bonds (section 5.4.1.1(b)) confirm that as the initial concentration of phenyl magnesium bonds increases, then so does the conversion at which termination (manifest in deviations from linearity of height vs time plots) becomes evident. The pool of inert active bonds, from which potential active polymerisation sites becomes available could be envisaged as arising from the same source which endowed inactivity on large scale polymerisations in Chapter 4 using PhMgBr in toluene as initiator at 200K i.e., the previously proposed polymerisation inert aggregates. Although the presence of aryl magnesium bonds could not be confirmed for polymerisations in toluene using ^{1}H NMR, due to solvent overlap, the terBuMgBr/MMA/ toluene kinetic system examined by Mair[6] showed residual active bonds even at high monomer conversion, indicating that these bonds were different to those responsible for polymerisation.

The issue as to whether molar mass distributions remain invariant with conversion, as proposed by Matsuzaki,[13] and hence whether the above explanation for discrepancies between dilatometric and NMR kinetic experiments is valid, remains contentious. Fig. 4.18, where samples from a single reaction mixture were decanted into

sidearms and terminated at 250K, shows chromatographs which vary with time. This result has been confirmed by Hagias[14] under similar conditions to those of Fig. 4.18, although changes occurred over a longer period of time. Fig. 4.22(A) and Fig. 4.23(A), where reactions were carried out in separate reaction vessels, do, however, show invariance of chromatographs with time/conversion. The cause of this variation in behaviour is not known. It is possible that the decantation process used to extract samples of polymer from the same reaction vessel (Fig. 4.18) modifies the type/proportions of discrete active centres operating, in comparison with the separate unperturbed reactions of Figs 4.22(A) and 4.23(A). If this is so, then unperturbed NMR scale reactions could most effectively be represented by a slow initiation/rapid propagation/termination character as proposed by Matsuzaki.[13]

5.4.2.2 NMR Kinetic Experiment Ph_2Mg/MMA/ Toluene/d_8-Toluene/residual THF

Figs 5.7, 5.8 and 5.9 show plots of vinyl peak area decrement vs time at 270K, 250K and 230K, respectively. In each case termination is evident at about 60% monomer conversion. The nature of these conversion curves confirmed the futility of dilatometric studies using this initiator, since the reaction was already retarded after the ten minute re-equilibration time required before significant measurements could be made.

The implication of these NMR results upon PhMgBr(Br/PhMg=.6_0) initiated reaction systems of Figs 5.4, 5.5 and 5.6 is that discrete Ph_2Mg entities cannot be present,

Fig. 5.7 Plot of Peak Area vs. Time
Ph_2Mg/MMA/Toluene/d_8Toluene
Reaction parameters: .30/.02/∿.02
Temperature: 270K

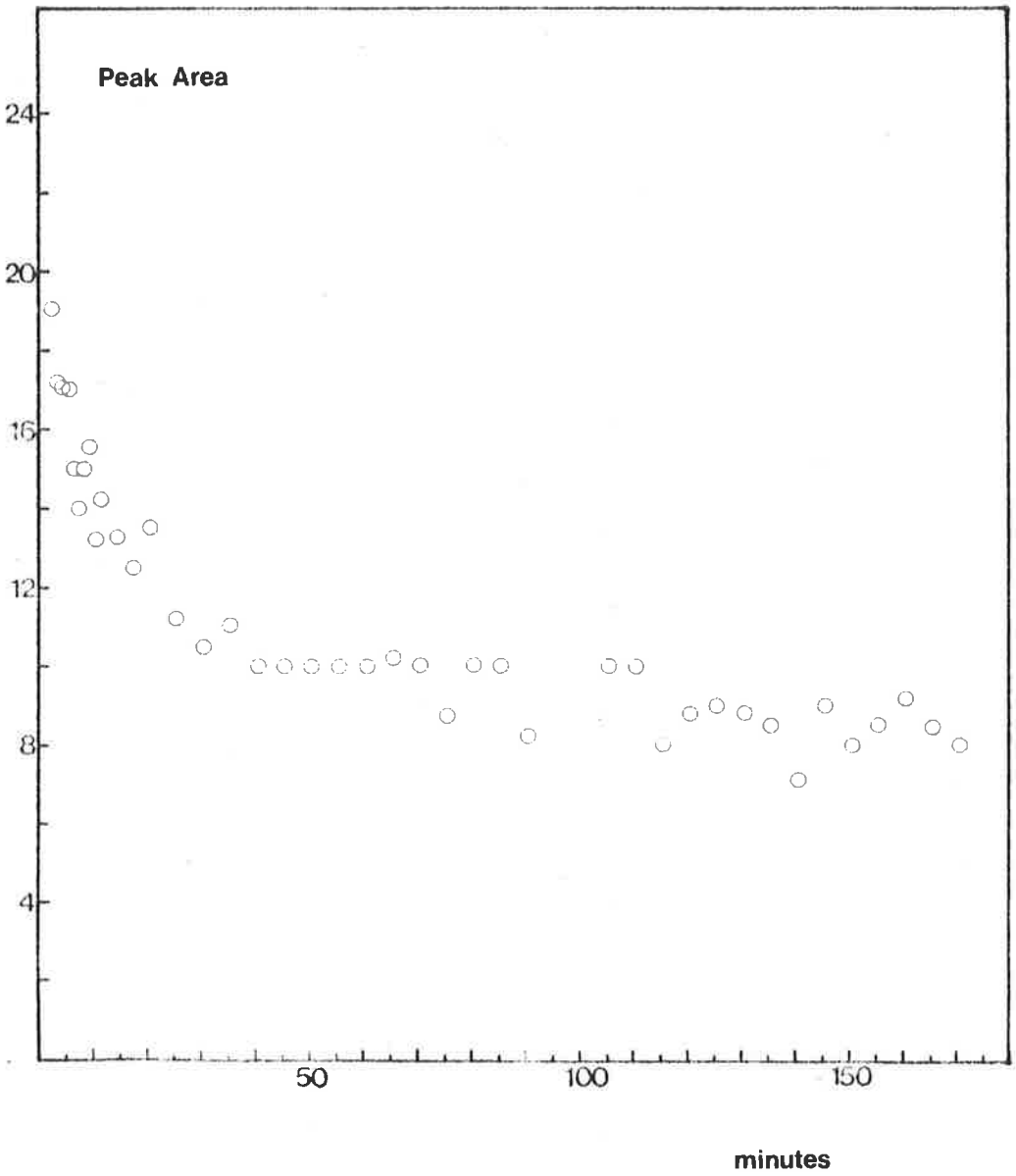


Fig. 5.8 Plot of Peak Area vs. Time
Ph_2Mg/MMA/Toluene/d_8Toluene
Reaction parameters: .30/.02/∿.02
Temperature: 250K

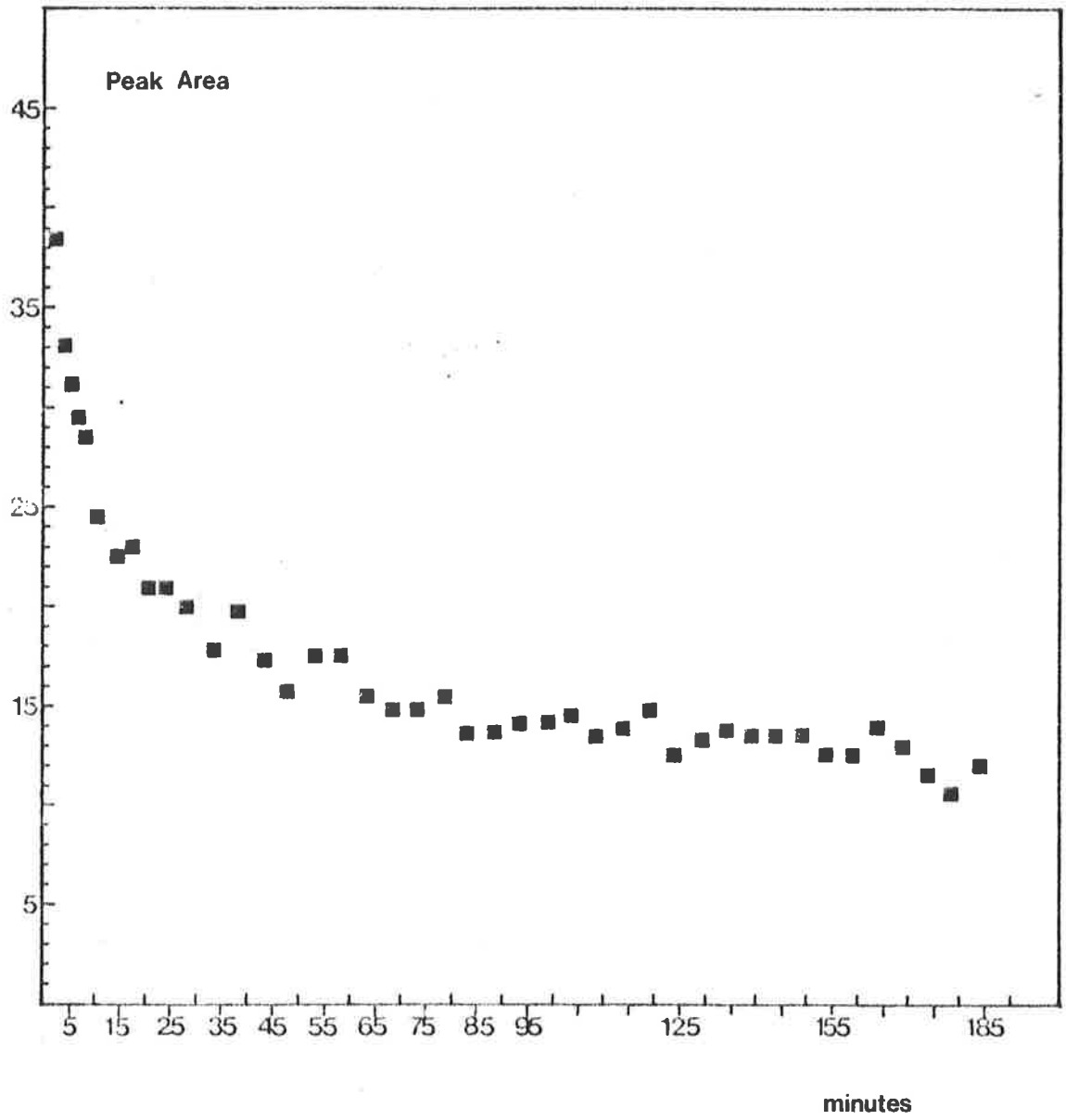
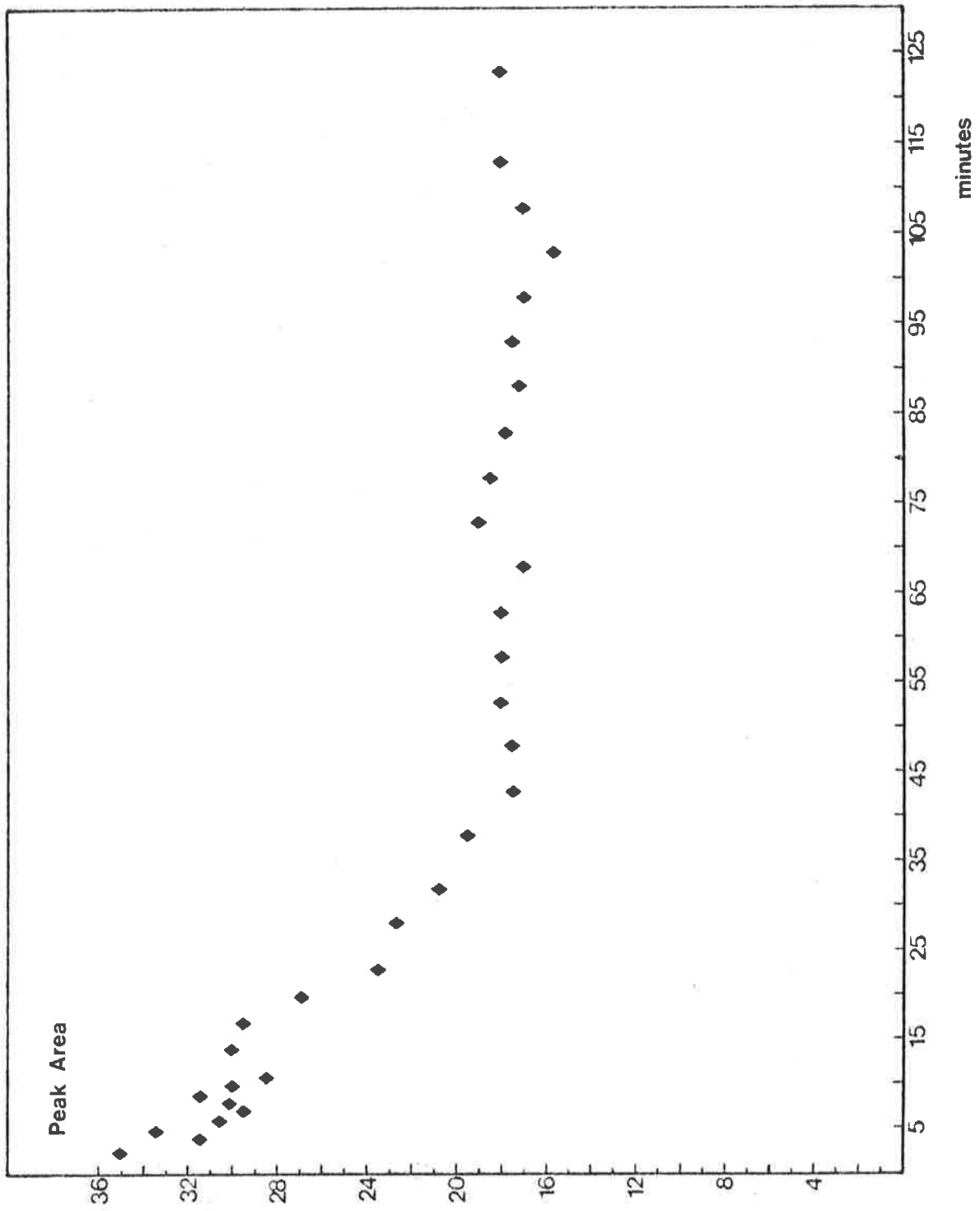


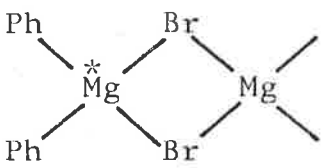
Fig. 5.9 Plot of Peak Area vs. Time
Ph_2Mg/MMA/Toluene/d_8Toluene
Reaction parameters: .30/.02/∿.02
Temperature: 230K



otherwise termination would have been manifest here also, given that the Br/PhMg quotient indicates that "Ph_2 Mg-like" active centres should be theoretically available. This observation is in accordance with the conclusions reached in the dilatometric studies of sections 5.4.1.1 and 5.4.1.2. The kinetic behaviour of Ph_2 Mg under these circumstances must be modified by the presence of bromide.

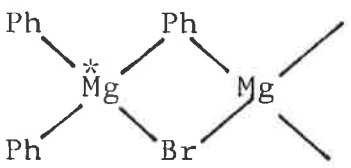
Fractionation of polymers obtained by Matsuzaki[13] using PhMgBr(Br/PhMg=1) in toluene as initiator have been shown to produce low and medium molar mass material which these workers attributed, on the basis of microstructure, to "Ph_2 Mg-like" active centres. Variations in microstructure have also been noted in this thesis (Chapter 4) across the molar mass distribution for the PhMgBr(Br/PhMg = $.4_o$) initiated MMA polymerisation at 250K, indicating that "Ph_2 Mg-like" active centres could be operating. Although the behaviour of such centres may be kinetically altered by the prsence of bromide, the mode in which monomer addition occurs may not change, for Ph_2Mg present in PhMgBr(Br/PhMg=$.6_o$) initiated kinetic runs of Figs 5.4, 5.5 and 5.6.

If one Ph_2 Mg entity were to become associated with one $MgBr_2$ or PhMgBr unit, for example, to provide either:



I

or



II mixed bridge associate

it is conceivable that the magnesium centre (*) at which a co-ordination or covalent bond insertion polymerisation takes place may be kinetically altered in both instances, but if the mode of addition of a monomer unit is affected by groups surrounding a potentially active site, the micro-structure of the polymer would probably also be affected by the presence of bromide adjacent to the active magnesium site. Tacticities would not be indicative of a "Ph_2Mg-like" centre.

One means by which kinetic variation could be achieved while the active centre retained its "Ph_2Mg-like" behaviour in terms of the tacticity of the polymer produced, would be to again invoke the slow initiation/ rapid propagation/termination theory. In this manner kinetics would be governed by the dissociation of a potential "Ph_2Mg-like" centre from more extended forms of I and II above, prior to initiation, with the mode of monomer addition decided subsequently. This approach does not negate the feasibility of eneidic pathways with discrete, different, non-exchanging sites, particularly if only high order associates are associated with active bond inactivity, with dissociation into discrete, low order associated species (monomers, dimers etc.) providing potentially active polymerisation sites of different reactivity and stereospecificity.

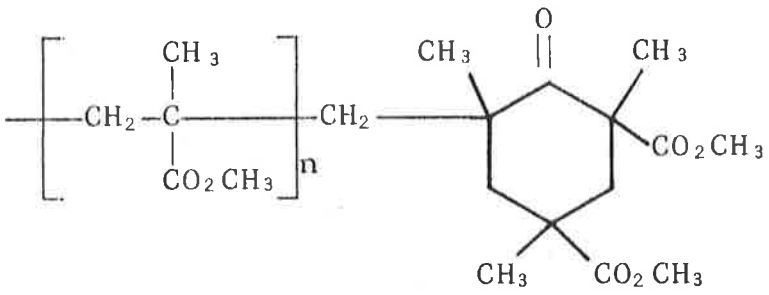
The differences between the kinetic NMR plots obtained with PhMgBr(Br/PhMg=$.6_0$; Figs 5.4, 5.5. and 5.6) and those obtained using Ph_2Mg (Figs 5.7, 5.8 and 5.9)

could be explained by the unfavourable disposition of aryl/alkyl groups toward the formation of three-centre-two-electron bonded associates in the case of the Ph_2Mg initiator, although some aryl bridging groups might be expected to be present. Given the plausibility of aggregation, inferring inactivity of organomagnesium bonds, the number of active bonds capable of reacting at the instant of initiation for Ph_2Mg may constitute the great majority of phenyl magnesium bonds capable of polymerising anyway, in contrast to the situation where more favourable bromo-bridged associates form, from which potential active centres are slowly released. If those centres formed with the Ph_2Mg initiator are rapid propagation/termination entities then the obvious termination revealed in Figs 5.7, 5.8 and 5.9 could be readily explained.

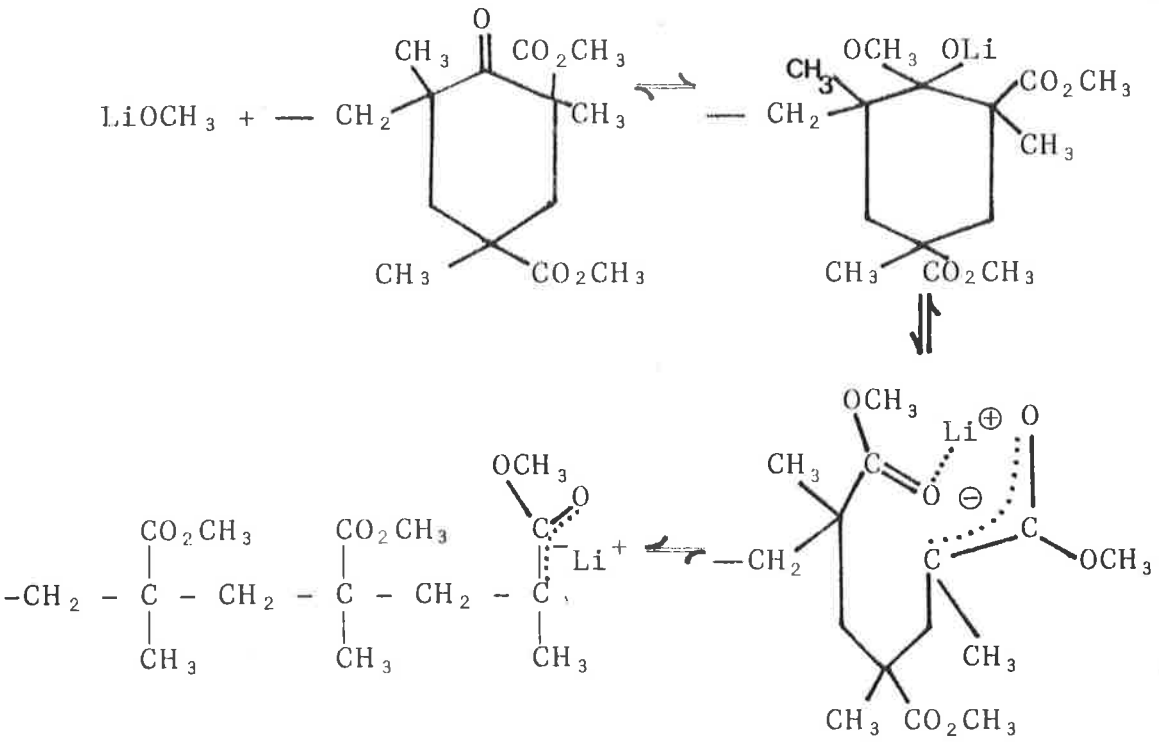
It is not certain whether the kinetic plots for the Ph_2Mg initiator come to a full stop (Figs 5.7, 5.8 and 5.9). Fig. 4.20, where polymer products from large scale runs using the Ph_2Mg initiator in toluene were examined as a function of reaction time, indicate that there is a slow increase in conversion coincident with a relative increase in the proportion of medium molecular weight polymer at longer reaction times, possibly indicating the presence of pseudo-terminated or "sleeping centres".

The possibility of centres that terminate but which reactivate at some later time, arises as a consequence of the possible termination of growing chains by an intra-molecular "back biting" reaction, initially proposed by Glusker,[15] whereby the final three monomer units in the

growing chain cyclise in the following manner:



Goode and co-workers,[12] examining polymerisation products from PhMgBr initiated runs in toluene at 0° C, found significant amounts of the cyclic β-keto ester (resulting from termination of chains after three monomer units) and spectra of low molar mass polymer also contained this moiety. The reactivation of this cyclised end group, described with respect to the lithium counter ion examined by Glusker,[15] was explained by the following equilibria:

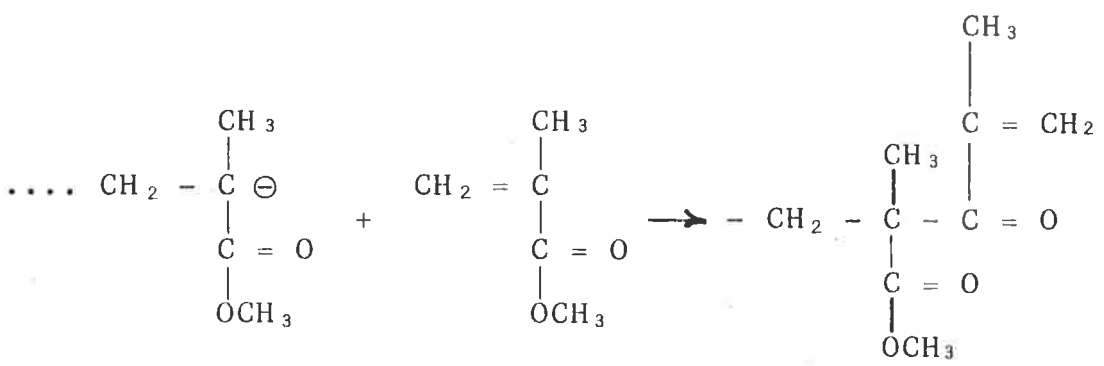


Lochmann and Trekoval [16] have shown, in support of the concept of site reactivation, that β-keto esters are capable of cleavage in the presence of sodium ter-butoxide.

Goode and co-workers noted [12] that, in the case of isotactic chains, cyclisation is unfavourable because the ring so formed would be forced into a conformation in which the bulky polymer chain or the carbomethoxy groups occupy axial positions. In contrast, chains not exhibiting isotactic stereochemistry would show disposition to ring closure, since a more stable conformation of the ring, with all or at least two of the bulky groups in equatorial positions, would be formed. Thus, since Ph_2Mg initiators produce non-stereospecific polymer, even in non-polar solvent, termination by intramolecular cyclisation is feasible, and as a consequence future reactivation of such a terminated site is also possible.

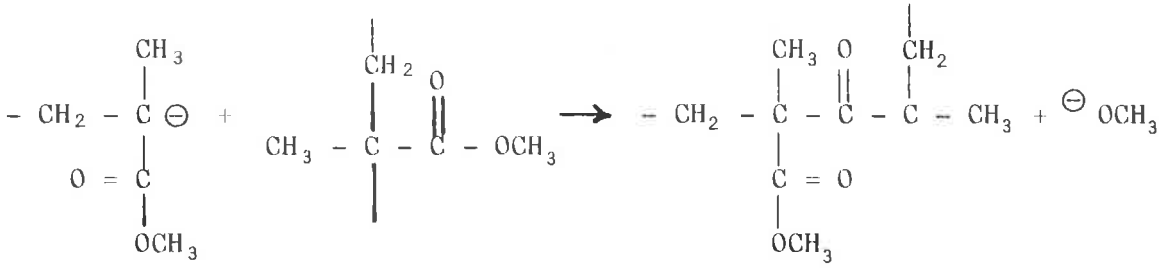
Other modes of living end termination, summarised by Warzelhan, Höcker and Schulz [17] in their examination of the anionic polymerisation of MMA using sodium as counter ion are:

(1) Termination reaction with monomer:



Diagnostic of this manner of termination is the presence of low molecular weight tailing in GPC elution curves.[18,19,20]

(2) Intermolecular termination by reaction of a living end with the ester group of another polymer chain:



This mode of termination has been shown[21,22] to be slow on the basis of grafting experiments for the polystyryl anion on pMMA, and is manifest in GPC elution curves by the presence of high molecular weight tailing. Its appearance in phenyl magnesium initiated polymerisations is doubtful, based upon the work of Goode and co-workers,[12] who utilised radioactivity studies to show that it does not occur to any measurable extent.

5.4.2.3 NMR Experiment MsMgBr/MMA/Toluene d_8-Toluene/THF Systems

Figs 5.10, 5.11 and 5.11(a) show plots of peak area decrement with time at 250K, 230K and the best estimate evaluation of Vinyl Area $^{(1\text{-Internal Order})}$ vs time at 230K, respectively. These reactions were carried out in predominantly toluene solvent. At 250K (Fig. 5.10) termination is apparent at high conversion (ca. 80%) in contrast to the same reaction examined at 230K (Fig. 5.11, 5.11(a)) where an internal order of 2.0 ± .1 was estimated on the

Fig. 5.10 Plot of Peak Area vs. Time

MsMgBr/MMA/Toluene/d_8Toluene

Reaction parameters: .20/.03/∿.01

Br/MsMg = $.8_o$

Temperature: 250K

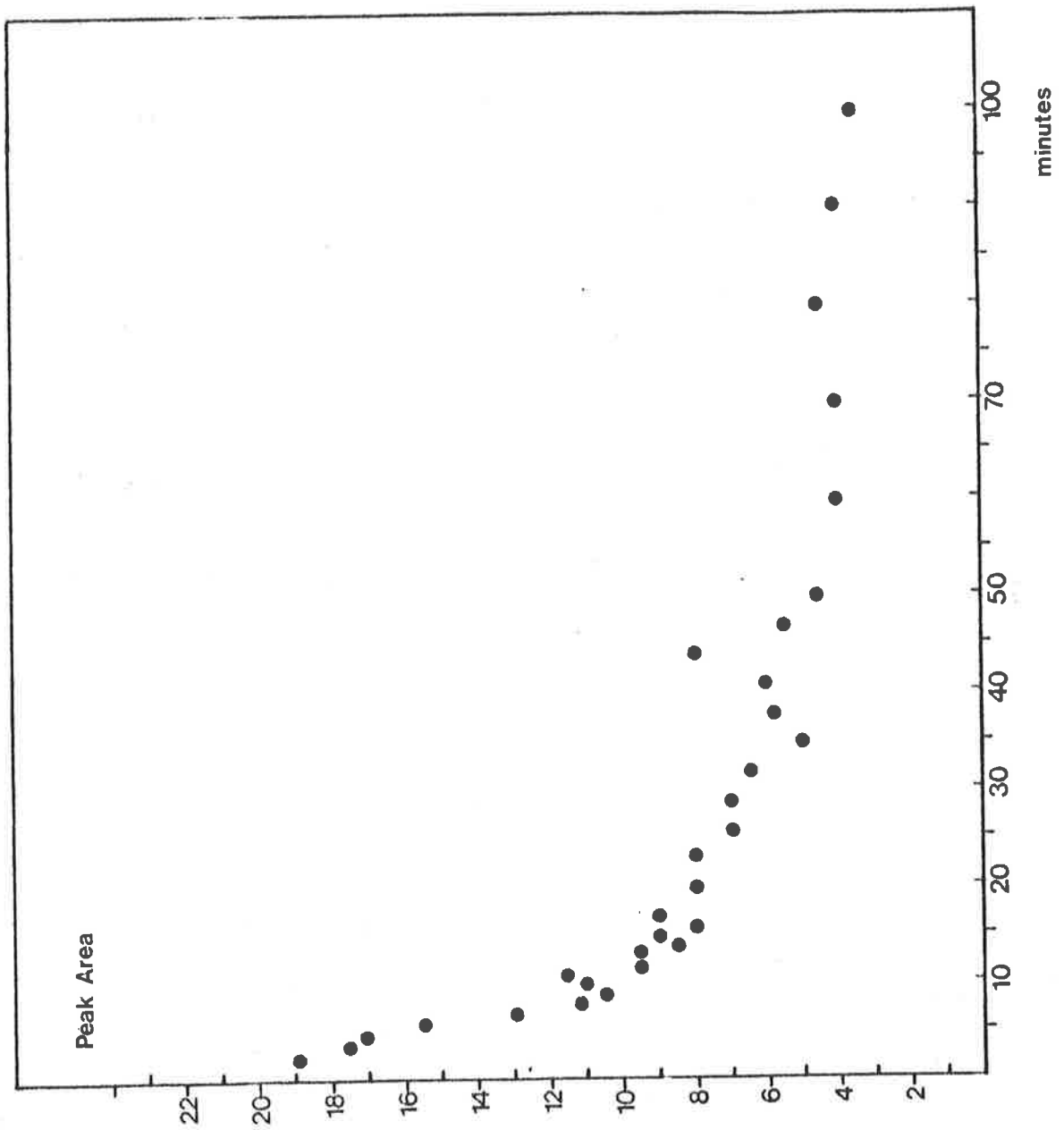


Fig. 5.11: Plot of Vinyl Peak Area vs. Time (min)
MsMgBr/MMA/d_8Tol/Tol
Reaction parameters: .20/.03/∿.01
Br/MsMg = .8$_o$
Temperature: 230K

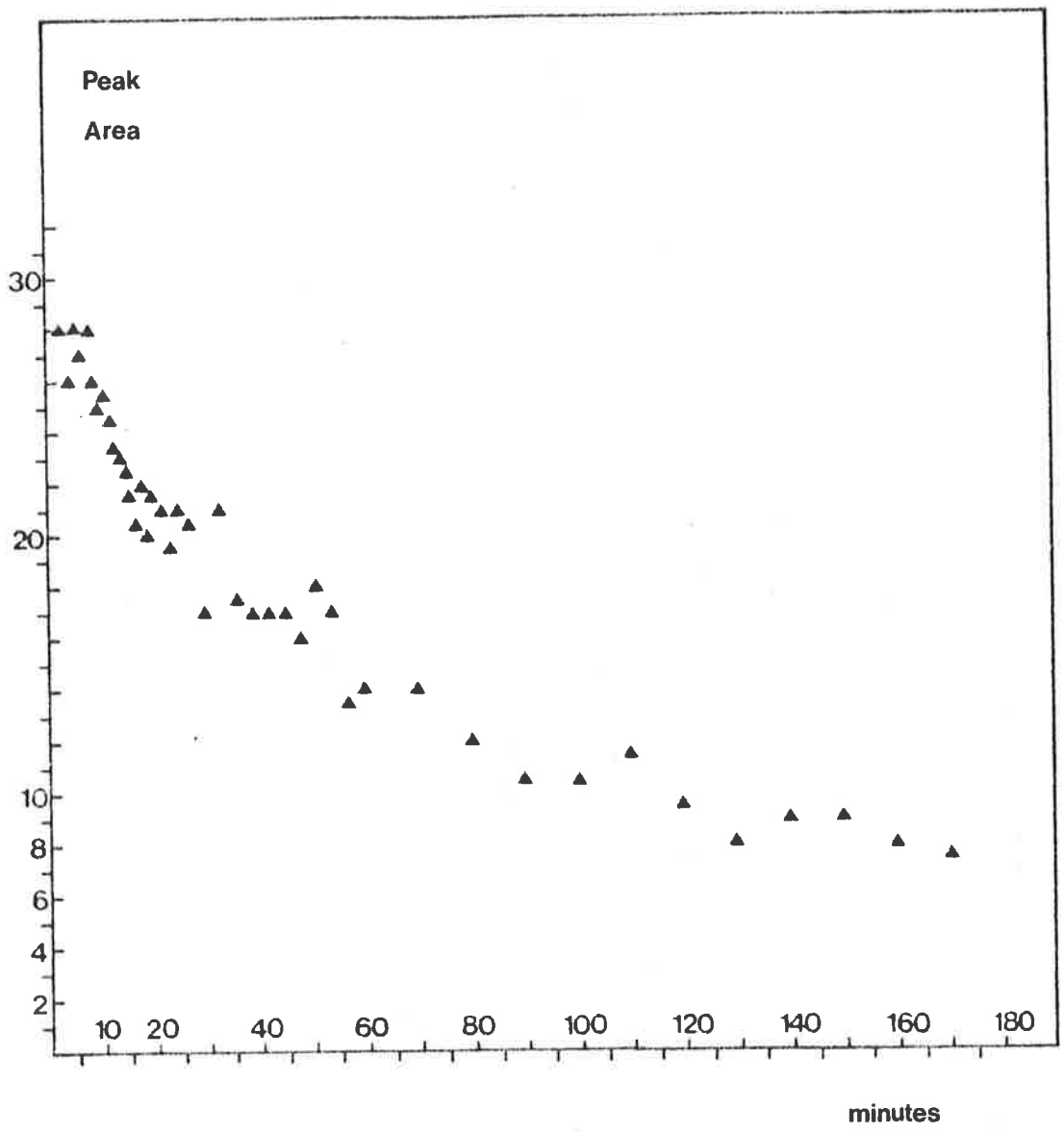
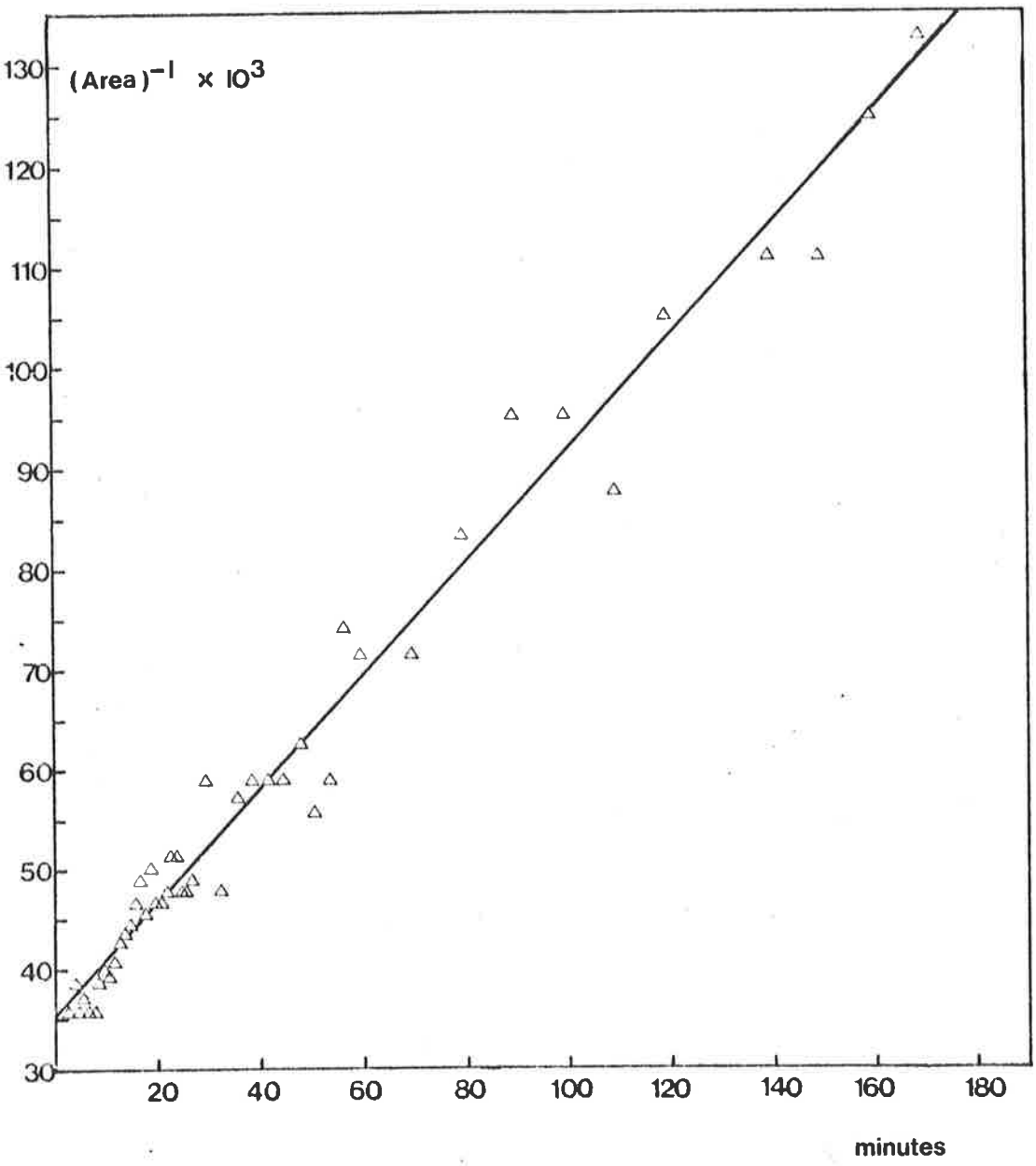


Fig. 5.11(a) Plot of Reciprocal Peak Area vs. Time
MsMgBr/MMA/Toluene/d_8Toluene
Reaction parameters: .20/.03/∿.01
Br/MsMg = $.8_o$
Temperature: 230K



Linear Least Squares Regression

Slope	: 5.719×10^{-4} $(Area)^{-1}min^{-1}$
Intercept	: 3.497×10^{-2} $(Area)^{-1}$
Sample Std. Deviation	: 4.613×10^{-3}
S.E. in Slope	: $.148 \times 10^{-4}$
S.E. in Intercept	: $.096 \times 10^{-2}$

basis of correlation coefficient. If this initiator behaves in a similar manner to PhMgBr and the reaction does constitute a slow initiation/rapid propagation/termination system, with slow initiation imparted by the presence of inert associated species, then the tendency to shorter half life at higher temperatures ($t_{1/2} \sim$ 10-15min at 250K (Fig. 5.10); $t_{1/2} \sim$ 60min at 230K (Fig. 5.11)) may reflect the ability of these associates to be thermally disrupted, giving rise to polymerisation active monomeric species or low order associates. Extended half lives at depressed temperatures are also evident for the PhMgBr initiator (Figs 5.4, 5.5 and 5.6), despite the fact that examination of the Schlenk equilibrium has indicated that potentially more reactive[23] Ph_2Mg entities should exist at lower temperature.[24]

Figs 5.12 and 5.12(a) show pictorial and graphical representations respectively of a polymerisation using MsMgBr carried out in mixed toluene/THF solvent at 250K. Again, termination is apparent at high conversion (ca. 80%). The lower value of $\chi_{MsMg/MMA}$(=.07) is generally reflective of the ability of this initiator to produce higher yields of polymeric material at lower initiator: monomer ratios, in comparison with the PhMgBr initiator (Chapter 4), particularly when THF is the principal solvent component.

If initiator inactivity is explained by inert associates, then explanation as to why, in particular, PhMgBr produces such low yields of polymer in relatively polar

Fig. 5.12 Pictorial Representation of Vinyl Proton Resonances showing Time Dependency of peak areas.

Relevant to the kinetic data of Fig. 5.12(a)

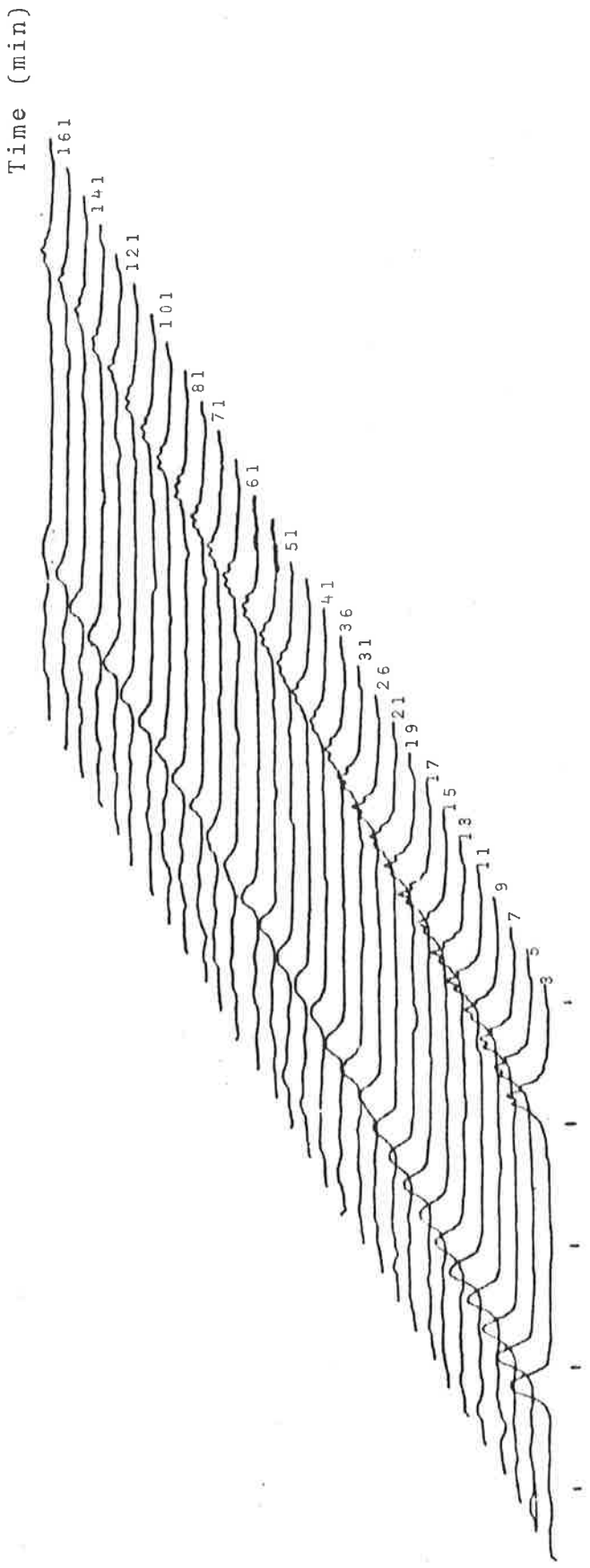
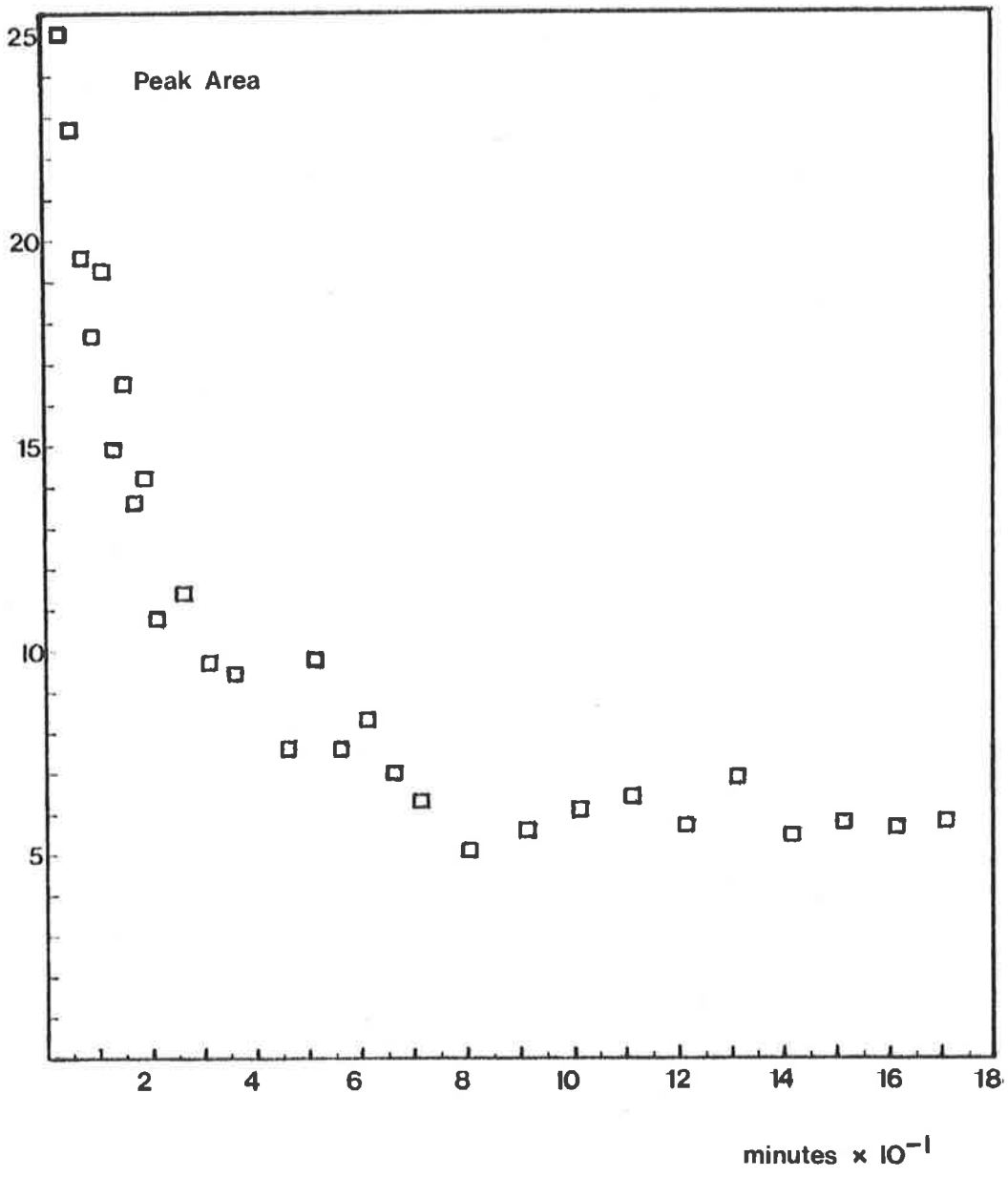


Fig. 5.12(a): Plot of Peak Area vs. Time
MsMgBr/MMA/Tol/d_8THF
Reaction parameters: .07/.04/.6_7
Br/MsMg = .8 - .9
Temperature: 250K



THF is required. Evidence for this behaviour was found in the large scale runs of Chapter 4, and diminished yields at high $\chi_{THF/Tol}$ were also noted for MsMgBr. Under conditions of high solvent polarity the tendency to form aggregates of a high degree of association should be greatly diminished, allowing for high conversions of pMMA. This argument neglects some important points:

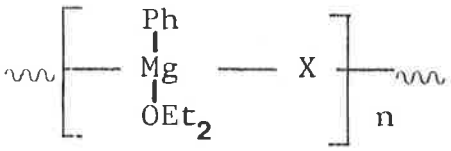
(1) If the mechanism for monomer addition is via co-ordination of monomer at the active site prior to insertion into the C(polymer)-Mg covalent bond, as proposed by Erusalimskii,[3] Allen[25] and Bateup,[2] this site may be effectively blocked by THF leading to slow or negligible reaction.

(2) Those active sites operating in PhMgBr, MsMgBr and chexMgBr systems are fundamentally different from those present in THF if the variation in micro-structure, from isotactic-like behaviour in toluene to less stereoregular configurations in THF, is considered. As such, potentially active sites in THF may be differently disposed to the possibility of side reaction with monomer carbonyl groups, reducing initiator efficiency.

5.4.3 Alternative Mechanisms for Alkyl/Aryl Magnesium Polymerisations

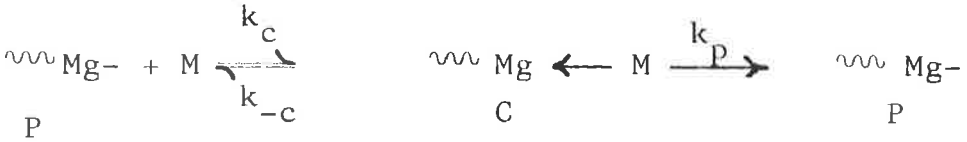
The provided kinetic data for PhMg initiated polymerisations has been used to partially vindicate the slow initiation/rapid propagation mechanism proposed by Matsuzaki.[13]

However, although a generalised theory for alkyl/aryl magnesium initiated polymerisation of MMA is desired, particularly in toluene where high stereoregularity is evident, there is no certainty that such a theory is attainable. If the origins of a slow initiating system do lie with the presence of associated species in solution, from which active sites become available, then the tendency for a given Grignard reagent to form such entities in a given solvent may be vital in a kinetic examination. This may be particularly so in the case of PhMgBr which has been shown by Ashby and co-workers[10,11] in diethyl ether to be associated past the dimer stage, and to be effectively represented by a linear polymeric model of the form:



5.4.3.1 Rapid Initiation Mechanisms

Allen and Bateup[26] have proposed that polymerisations of MMA initiated by n-butyl magnesium bromide or di-n-butyl magnesium proceed via a rapid initiation-insertion mechanism proceeding through a complex between monomer and active centre:



where

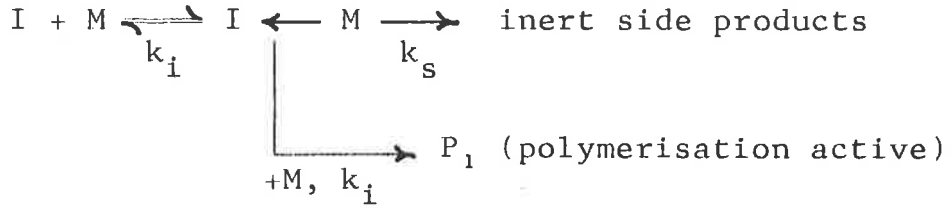
$$v_p = -\frac{d[M]}{dt} = k_c[\sim\!\sim Mg-][M] - k_{-c}[\sim\!\sim Mg\leftarrow M] \qquad \text{Equn 5.6}$$

$$= k_c\,[P][M] - k_{-c}[C]$$

and M = monomer

A similar mechanism has been proposed by Erusalimskii[27] for alkyl magnesium initiated polymerisations of acrylonitrile.

Using n-butyl magnesium initiators the initiation stage was viewed by Bateup and Allen[26] as being a rapid but inefficient process, completed early in the polymerisation. The following kinetic scheme was envisaged for initiation:



where I = initiator ; M = monomer

Assuming rapid initiation:

$$[\sim\!\sim Mg\text{-}] + [\sim\!\sim \underset{|}{Mg} \leftarrow M] = f\,[I]_o$$

P C

$$= (\,k_i[M]_o/(k_i[M]_o+k_s))[I]_o$$

f = initiator efficiency Equn 5.7

If steady states in P and C are assumed then the overall kinetic relationship resulting is:[6]

$$v_p = k_c\,(1 - 1/(1+(k_p/k_{-c})))(1/(1+(k_s/k_i[M]_o))) \cdot ([M]/(1+(k_c[M]/(k_{-c}+k_p))))\,[I]_o \qquad \text{Equn 5.8}$$

where the second bracket represents the initiator efficiency, f, varying between unity and zero. Examination of the limiting conditions of the brackets indicates that

internal order with respect to monomer can vary between 0 and 1 whereas the external order shows a variation between 0 and 2. Zero orders internally with respect to monomer arise when the $k_c[M]/(k_{-c}+k_p)$ term of the third bracket becomes large, indicating that the complexed form of the growth centre becomes predominant and:

$$v_p = k_p f\ [I]_o$$

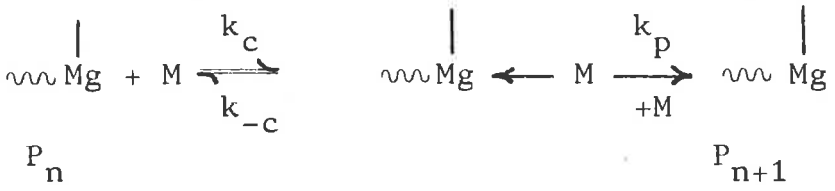
where f is low for the nBuMgBr system examined by Allen and Bateup[26] in THF-toluene solvent. The variation of internal order between 0 and 1, found by Mair[6] for the terBuMgBr/MMA/toluene system over the temperature range 200-275K, conforms with the mechanism presented above, with internally first order reactions with respect to monomer occurring under the critical condition:

$$k_c\ [M]/(k_{-c} + k_p) \longrightarrow 0$$

$$\text{where}\quad v_p = f\ k_c k_p\ [I][M]/(k_{-c} + k_p)$$

This reaction scheme is obviously unsuitable for the NMR kinetics described in this thesis since the PhMgBr system shows variations in internal order between 1 and 2 over the temperature range 230-250K while at 230K the MsMgBr initiator shows an internal order of 2, with termination at high conversion for the 250K reaction.

Some modifications to the scheme described above, however, can be used to satisfy internal orders between 1 and 2, although this mechanism cannot cope with the problems of living end termination observed with MsMgBr at 250K. The propagation reaction could be envisaged as:



which differs from the already cited mechanism in its requirement that another monomer unit should be available for co-ordination at the active centre before insertion of the already co-ordinated MMA unit into the growing chain. Such a condition does not appear too stringent, particularly for reactions examined in non-polar solvent, where there exists a paucity of electron donors capable of replacing the co-ordinated monomer unit.

Applying Bateup initiation conditions to the above modified propagation mechanism, as well as the steady state parameters indicated in the previous mechanism, leads to a rate equation of the following form:

$$v_p = -d[M]/dt = 2(k_p k_c/k_{-c})([I]_o/(1+(k_s/k_i[M]_o)) \cdot([M]/(1+(k_c+k_p)[M]/k_{-c})) \qquad \text{Equn 5.9}$$

Examination of the critical conditions of this rate equation imply:

(1) External Orders between 1 and 3

(2) Internal Orders between 1 and 2

The integrated form of this equation is:

$$C - k't = k'' \ln[M] - 1/[M] \qquad \text{Equn 5.10}$$

where $C = k'' \ln[M]_o - 1/[M]_o$

and $k' = 2(k_p k_c/k_{-c})([I]_o/(1+(k_s/k_i[M]_o)))$

and $k'' = (k_c + k_p)/k_{-c}$

indicating that the reaction is a linear combination of first and second order kinetics with k'' defining extent of contribution of the first order component.

5.4.4 Preliminary Kinetic Experiments using ^{13}C Enriched Monomer.

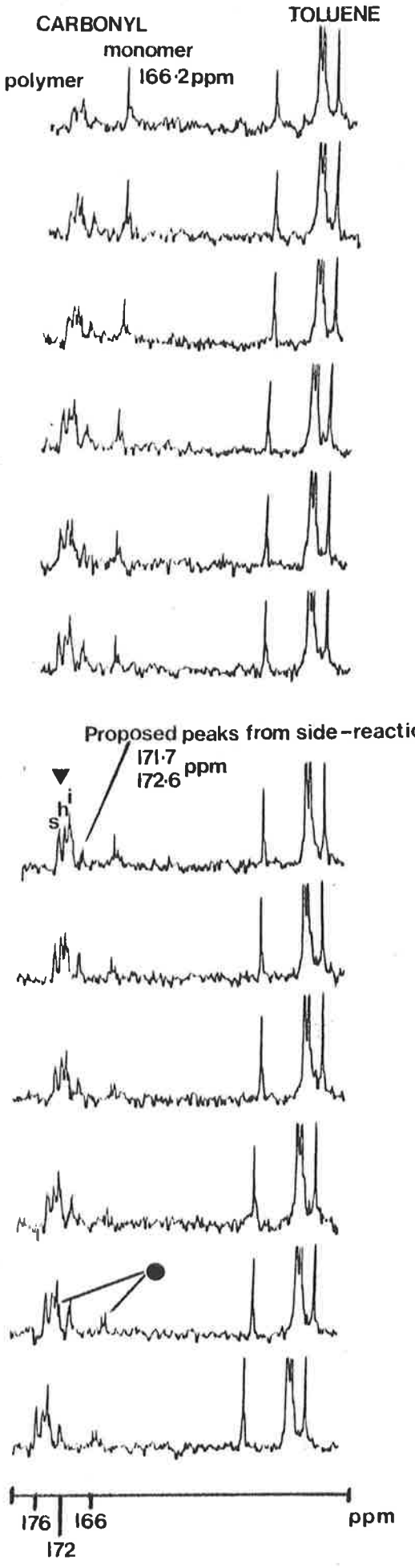
An intensive kinetic examination using carbonyl carbon enriched MMA was thwarted by the presence of impurities in the vicinity of both monomer and polymer carbonyl resonances (Fig. 5.13). These impurities persisted despite fractional distillation procedures and drying of the enriched monomer/toluene solution over sodium benzil.

Despite these difficulties, the results indicated in Fig. 5.13, for the MsMgBr initiated run carried out in toluene at 250K for the cited reaction parameters, indicate the applicability of this technique to the study of MMA polymerisation:

(1) The downfield resonances ($\sim$177ppm) of the polymer carbonyl show sensitivity to stereochemical environment with overlapping isotactic, heterotactic and syndiotactic contributions to the triad structure clearly evident, and the relative peak area of this environment slowly increasing with conversion/time. The polymer formed appears less isotactic than material produced in large scale reactions (Chapter 4), possibly due to the higher THF content in the initiator solution made up for this run.

(2) The upfield resonance ($\sim$166ppm) of the carbonyl diminishes with time/conversion.

Fig 5·13 ^{13}C Enriched Kinetics using MsMgBr in Predominantly Toluene Solvent; 250K



$X_{MsMg/MMA} = ·2_0$

$X_{MMA/Solv} = ·02_5$

$X_{^{13}C\,MMA/Solv} = ·01_4$

▼ i, h & s denote triad components

i 175·4 ppm
h 176·7
s 177·0

● denotes impurity present prior to reaction initiation

165·3
174·4 ppm

Shifts relative to toluene methyl, 20·4 ppm

(3) A multiplet consisting of at least two peaks is apparent at a chemical shift intermediate between monomer and polymer carbonyls, which appears soon after reaction initiation. Its most likely origins are due to the presence of side reactions and/or termination products. Most recent studies[28] carried out on totally pure, enriched monomer using the terBuMgBr initiator under conditions suitable for side reaction (elevated active bond concentrations and higher mole fractions of THF) show a great increase in the intensity of this peak, consistent with its postulated origins.

Studies are presently under way using pure, enriched monomer to obtain more detailed numerical evaluations.

5.5 Summary

Kinetic observations of phenyl magnesium systems and the MsMgBr initiator indicate that the reactions examined are complicated, not simply because an unknown variety of discrete, different active centres may be operating, but also because centres are terminating and possibly pseudo-terminating with reactivation at some later stage. Evidence for termination is manifest in dilatometric examinations carried out here with the PhMgBr initiator at 250K in predominantly toluene solvent with $Br/PhMg=.6_0$, and is also obvious in NMR kinetics using the Ph_2Mg initiator in toluene.

The influence of bromide is kinetically important. In its absence, dilatometric data using Ph_2Mg in toluene as initiator at 250K shows that theoretical yields are much less than the actual yield and the initial rates estimated are much slower than the actual yield predicts. These observations concur with NMR kinetic evidence where fast reaction/termination properties applied.

The presence of bromide altered behaviour markedly. At 250K using PhMgBr ($Br/PhMg=.6_o$) as initiator, dilatometry indicated that theoretical and actual yields for reactions in toluene were in agreement. At constant initial active bond concentration, meniscus height-time plots deviated from linearity at between 2-3% conversion, despite changes in the initial monomer concentration. At constant initial monomer concentration but with varying initial active bond concentration, meniscus height-time plots showed deviation from linearity at conversions of 2-7%, correlating with the increase in active bond content. At 250K, in predominantly toluene solvent with $Br/PhMg=.6_o$, external orders with respect to both monomer and active bonds were found to be unity.

Differences were also apparent between the behaviour of PhMgBr ($Br/PhMg=.6_o$) initiated NMR kinetic runs and dilatometry. NMR experiments indicated that, between 230K and 250K, constant internal orders of reaction were achieved with respect to monomer at conversions greater than 75%, despite the fact that dilatometry indicated the presence of termination. Successful NMR analysis was only

achieved by increasing the active bond concentration to about ten times that used in dilatometry (section 5.4.2.1) to achieve high conversion. Internal orders varied between 1 and 2 between 230-250K.

Both dilatometry and NMR kinetics support the observation that Ph_2Mg, which must be present in PhMgBr solutions with $Br/PhMg=.6_o$, must be kinetically modified by the presence of bromide.

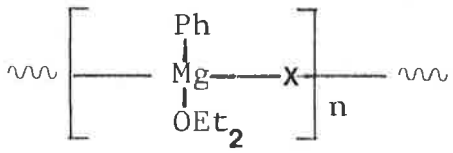
The current model for phenyl magnesium initiated polymerisations is the slow initiation/rapid propagation/termination model proposed by Matsuzaki.[13] This theory was based upon the invariance of molar mass distribution with conversion, but the basis for slow initiation has not been explained by these workers. Results from Chapter 4, combined with those of this chapter tend to indicate that (high order) associates may be linked with inactivity and that polymerisation active bonds become slowly available from these associates, perhaps as monomeric species or as entities of low association (dimers etc.) capable of producing an eneidic mechanism. This postulate is based upon the following evidence:

(1) Large scale runs of Chapter 4 using PhMgBr as initiator indicate inactivity of phenyl magnesium bonds at 200K which could be reactivated at 250K. This could indicate thermal disruption of associates present at 200K.

(2) Although impossible to note here because of solvent toluene overlap with phenyl resonances of the

initiator using ^{1}H NMR, it is assumed that a considerable proportion of potentially active phenyl magnesium bonds remain unreacted even at high monomer conversions, based upon results by Mair[6] using the terBuMgBr initiator. These bonds are fundamentally different from those which are polymerisation active.

(3) Ashby and co-workers[10,11] have proposed that in diethyl ether PhMgBr is highly associated and they proposed a linear polymeric model of the form:



(4) Between 230-250K, for similar reactions using PhMgBr in toluene, the monomer half life increases as the temperature decreases, consistent with aggregation at lower temperature.

(5) Bateup[2] and Mair[6] have noted that as the concentration of bromide increases, the rate of reaction decreases. This could be explained in terms of the enhanced bridging ability of bromide, giving rise to inert, higher orders of association. Such an effect may explain the difference between NMR decay curves for PhMgBr and Ph_2Mg initiators since, if association is not highly favoured in the case of Ph_2Mg due to 3-centre-2-electron bonds, then the number of bonds capable of reaction at initiation constitutes the greater proportion of those reacting anyway. Rapid propagation/termination would then make Ph_2Mg decay curves self evident. PhMgBr initiated runs would have

the effects of termination masked by the slow availability of further active centres emanating from (high order) associates. This model does not explain how the different types of active centre arise in the same relative proportion so as to create the invariance of GPCs with time/conversion, as proposed by Matsuzaki. [13]

Rapid initiation mechanisms, based on information obtained by Bateup and Allen,[26] were examined. The propagation step involved monomer complexation before insertion at the growing end of an active site. Based on this scheme internal order varied between zero and one, which did not fit the data in this chapter. However, inclusion of an extra monomer term was capable of varying orders between one and two, where internal orders seem to lie in this chapter. These theories do not translate well to terminating systems.

In conclusion, the monomer co-ordination-insertion propagation mechanism cited above for fast initiation processes may be common to a slow initiation process as well, the only difference between slow and rapid initiation being the propensity for different Grignard reagents to form associated species.

CHAPTER 6

6. STEREOCHEMICAL ASPECTS AND CONCLUDING COMMENTS

6.1 Stereoregular Monomer Addition

Observations in Chapter 4 reveal that at least some of the active centres present in PhMgBr, MsMgBr and chexMgBr initiated polymerisations add monomer in stereoregular isotactic fashion, but little attempt has been made to present an evaluation of previous or present models offered in an attempt to explain the mechanism of stereoregular addition.

For the systems examined in this thesis, the ideal model should be sufficiently versatile to explain the following phenomena:

(1) The loss of highly stereodirecting centres as the polar component of the solvent is increased.

(2) The tendency to lower isotactic content at low temperature.

(3) The appearance of highly isotactic centres when halide is present, but not when the initiator is halide free, dialkyl/diaryl magnesium.

(4) Monomer co-ordination at the active site before addition, in keeping with kinetic evidence.

Heterogeneous catalysis using Ziegler-Natta catalysts, such as $TiCl_3/Et_3Al$, for the stereoregular formation of polyhydrocarbons[1,2] provide some insight into the possible controlling factors for the homogeneous polymeris-

ation of polar MMA using alkyl/aryl magnesium compounds. Heterogeneous stereospecific polymerisations are believed[3] to arise at the surface of the catalyst which steers the monomer to the active centre in such a way that factors such as direction of delivery, rotation of active end group, aspect of presentation and mode of bond opening (cis/trans) are controlled. These factors are also critical in homogeneous polymerisation. In the various models for stereospecific homogeneous polymerisation to be discussed here, the role of the surface in heterogeneous catalysis is assumed by a cyclic intramolecular complex of the end group formed by chelation of the penultimate or antepenultimate pMMA carbonyl[4,5,6] to the metal of the active centre.

Examinations of Grignard initiated polymerisations of α, β unsaturated carbonyl compounds have been performed by Yoshino and co-workers[7] using PhMgBr and α, β dideutero-isopropyl acrylate. These examinations concerned themselves with the mode of double bond opening in such systems. Double bond opening can be envisaged as occurring by one of three possible pathways.

1) Cis opening, where the Metal-R bond (postulated to be formally a covalent bond for organomagnesium systems, but it could alternatively be defined as an ion pair or solvent separated ion air for typical anionic systems) lies on the same side with respect to the approaching monomer double bond:

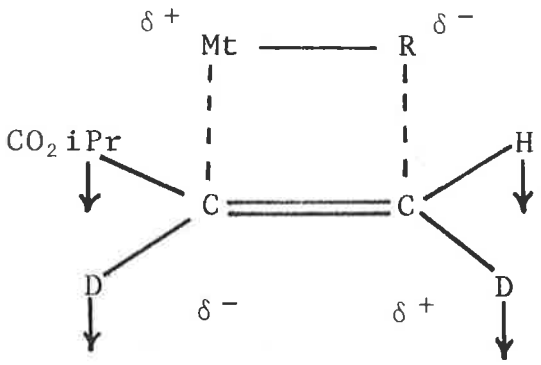
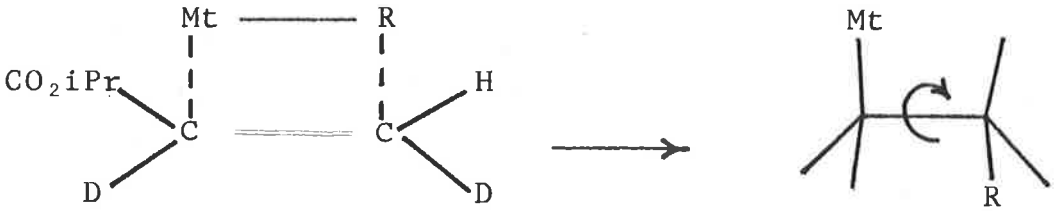


Fig. 6.1

2) Cis/Apparent Trans Opening

The evidence for trans opening of the monomer double bond observed by Yoshino[7] and Bovey[8] creates some problems for those proponents[9] of an active centre which is a covalent magnesium carbon bond with insertion of the monomer unit into that bond. The solution invokes the process of an isomerisation following a cis addition process:



cis addition

Fig. 6.2

3) Trans Addition. This model assumes the existence of a four centred, skew transition state similar to that observed in the insertion reactions of acetylenes with metal hydrides:[10]

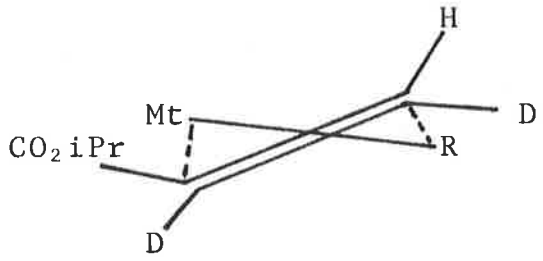


Fig. 6.3

The consequences of cis and trans double bond opening with respect to the deutero-methacrylate monomer are as follows:

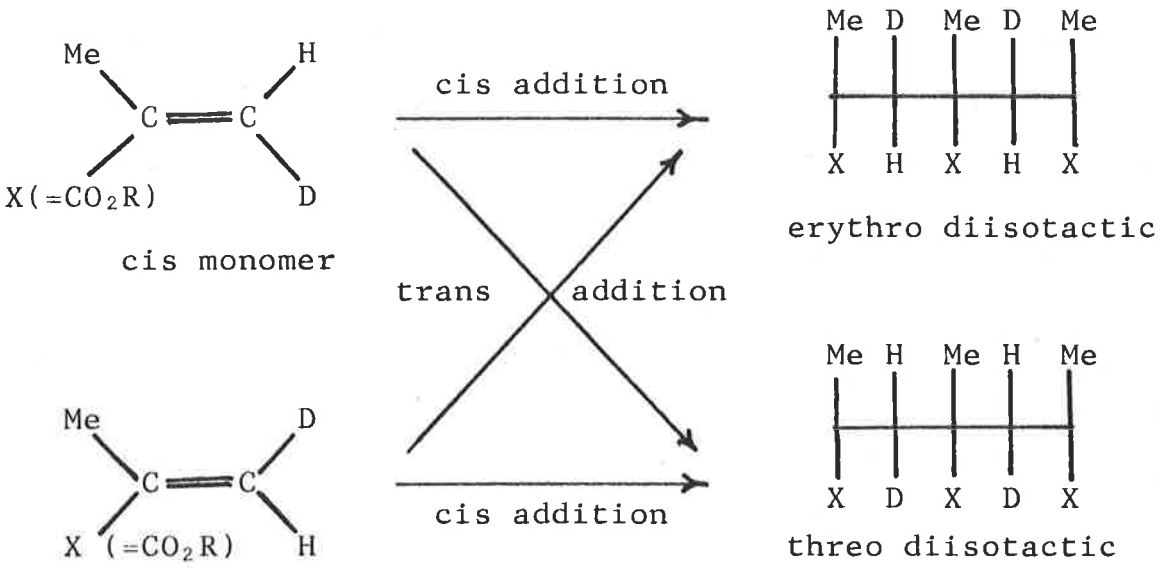


Fig. 6.4

Utilising the Isopropyl α-cis- β-dideuteroacrylate monomer/PhMgBr/Toluene and/or diethyl ether system at 195K, the results of both Bovey[11] and Yoshino[7] show that in predominantly toluene solvent, with trace amounts of diethyl ether, both cis and trans opening modes occur producing nearly equal amounts of erythro and threo diisotactic forms, based upon ^{1}H NMR evidence. In the near total absence of ether trans addition is precluded, but this mode dominates in excess ether.[7]

The mode of double bond opening shows temperature dependence,[7] with high temperatures favouring a trans opening (> 215K) and cis opening becoming increasingly predominant at lower temperatures.

Perhaps the most serious defect in the examination of double bond opening modes by Yoshino and co-workers[7] as a function of solvent composition and temperature lies in the lack of definition of the molar mass distribution as a function of these parameters. As such it is conjectural as to whether the change in double bond opening from cis to trans under conditions of varying temperature or solvent occurs for a unimodal molar mass distribution or, as has been intoned in this thesis, the mode of bond opening has been altered by virtue of the destruction/appearance of different types of non-exchanging active centre postulated to explain the multi-modal distributions evident in Chapter 4.

Using the diphenyl magnesium initiator similar behaviour was observed,[7] although the changeover from a trans to cis opening mechanism occurred at higher temperatures. By variation of the initiation and propagation temperatures, Yoshino[7] was able to show that the mode of bond opening, which persisted throughout the polymerisation, was determined in the first few minutes of the reaction. If reactions of PhMgBr with MMA are correctly described as slow initiating, then the observations of Yoshino may not be correct, particularly if the nature of different active centres released varies, for example, with the decreasing

polarity of the solvent as polar monomer is removed by polymerisation at already activated sites. Yoshino's experiments involve examination of the β methylene proton NMR signal and related stereochemistry, which is less important than that arising at the α carbon in the determination of the physical properties of the polymer formed. Study, by Yoshino,[12] on the various oligomers formed from isopropyl acrylate - α, β -d_2 , confirms that the regular isotactic placement of terminal α methine carbons of a growing chain do not require the prior occurrence of an isotactic placement and is independent of the mode of incorporation of the β carbon of the terminal unit into the growing chain. Monomer units other than the last two of a growing chain appear to be of no importance in directing the mode of approach of another monomer unit into a transition state.

Further evidence by Yoshino and co-workers[12] suggests that isotactic ends formed in the phenyl magnesium bromide initiated polymerisation of isopropyl acrylate show the same stereospecificity in their reactions with water, hydrochloric acid, acetic acid and monomer. Allen and Bateup[13] have interpreted these results as indicating that the symmetry of the polymer chain carbon is determined before the addition of a succeeding monomer unit and that this condition is most readily satisfied if the chain end carbon has a tetrahedral configuration, as would be evident if it were covalently bonded to the magnesium atom of an alkyl magnesium initiated system. These workers discount a tetrahedral carbon end formed in an intimate

ion pair with the magnesium ion on the basis that rapid ion-ion pair and intimate-loose ion pair equilibria would result in rapid inversion of configuration, in violation of the observations of Yoshino.[7]

Glusker, Lysloff and Stiles,[5] examining alkyl lithium initiated polymerisations of MMA, have postulated that centres responsible for isotactic addition to a pMMA anion are the result of lithium counter ion complexation with both the ultimate and penultimate ester groups on the polymer chain. Displacement of the penultimate ester group from the complex by the entering monomer is forced to occur in a specific direction. They found that the introduction of an alternative complexing agent such as diethyl ether led to competition with the ester groups for the lithium ion leading to a decrease in isotacticity of the polymer formed.

Cram and Kopecky[14] have postulated the following cyclic intermediate for stereospecific isotactic polymerisation:

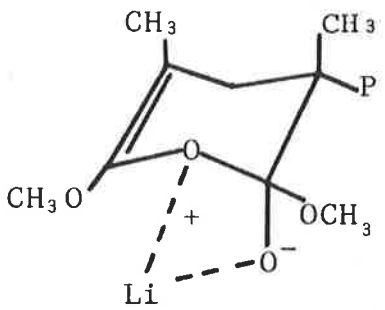


Fig. 6.5

In this model they propose that an incoming monomer unit must enter from below at each step because of hindrance from the axial methyl group.

Goode and co-workers[15] have presented a similar intermediate as a source of isotactic propagation, but it is assumed that preliminary complexation of monomer to the lithium counterion (or other metal centres such as magnesium) is the driving force rather than hindrance by the axial methyl group.

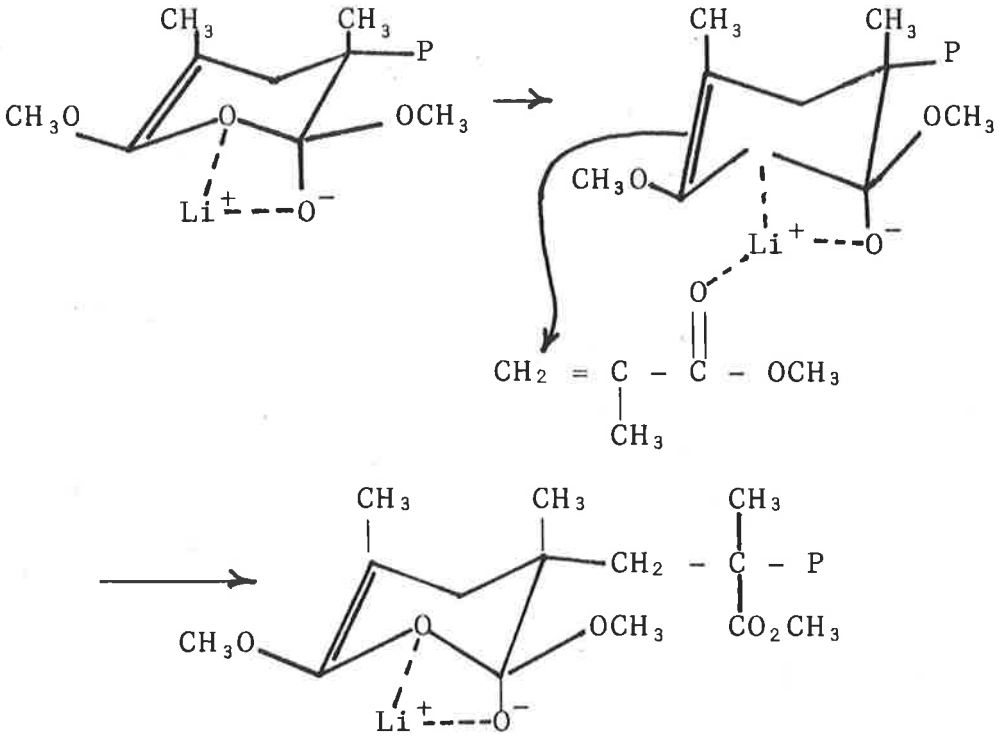
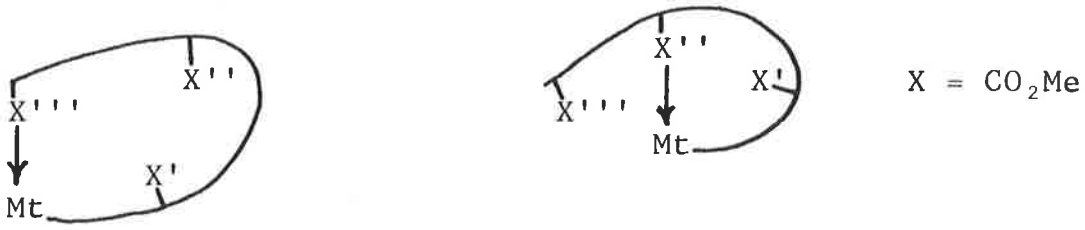


Fig. 6.6

These workers introduced the concept of monomer complexation in order to explain the possibility of isotactic polyacrylates, which could not be explained by the model of Cram and Kopecky[14] in the absence of bulky axial α methyl groups. Prior complexation would constrain the monomer to enter from below the ring since it could not complex with the cation and enter from above. The corollary to the above model is that the addition of monomer is random until at least three monomer units have been added.

The models presented by both Cram and Kopecky[14] and Goode and co-workers[15] involve participation by previously added monomer units at the active site and as such Markovian statistics at these centres should prevail. Little has been said about the capability of active sites becoming involved in equilibria with centres which propagate with different stereospecificity, with the lifetime in each different active site sufficiently long that monomer units add in a manner characteristic of that site i.e., where Coleman-Fox statistics prevail. The PhMgBr initiated polymerisation of MMA in toluene at 195K has been found[16] to follow such behaviour. However, equilibria between sites does not always confer Coleman-Fox statistics, with such statistics very dependent upon the lifetime of each state. For example, Schulz and co-workers[17-20] have examined the cumyl caesium initiated polymerisation of MMA in THF under conditions of supressed ion pair formation and have described the following equilibrium as being responsible for Markov statistics:

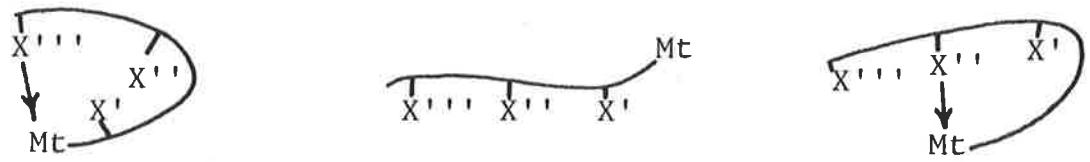


(a) (b)

Fig. 6.7

with infrequent transformations of (a) into (b), and (b) being of lower stereospecificity than (a). Penultimate and antepenultimate ester carbonyl co-ordination under these circumstances must persist, despite the fact that the

reaction has been examined in THF, an efficient complexing reagent. Analogous sodium systems[21] indicated that Bernoullian statistics were followed, with the assumed rate of transformation of these active centres being higher than the propagation rate. Erusalimskii and co-workers[22] have used an alternative equilibrium to explain the differences apparent between the caesium and sodium counterion:



(a) (c) (b)

Fig. 6.8

with the reactivity of the extended active centre greater than that of the cyclic forms.[23] Stability of these cyclic forms is dependent on the nature of the metal atom and is lowest for the Cs counterion, thus implying that cyclisation only influences to a small degree the reactivity of the (polymer)-Mt bond. Polymerisation under these conditions proceeds through all of (a), (b) and (c) above. Contrary to this, the pseudocyclic forms for the the Na counterion are stable and show lower reactivity than the extended form, so polymerisation proceeds primarily through (c) with resultant Bernoullian statistics.

Bovey and co-workers[4] provide an alternative model for stereospecific propagation. Using organolithium compounds as initiators these workers proposed that differences in the configuration of polymers under varying experimental conditions reflected the different propor-

tions of three propagating species: unsolvated contact ion pairs, peripherally solvated contact ion pairs and solvent separated ion pairs. These species predominate in hydrocarbon, hydrocarbon/trace ether and ether-rich systems, respectively. Presence of free ions was discounted on the basis of conductivity measurements, even in THF.

The intermediates postulated by these workers for unsolvated and peripherally solvated contact ion pairs are shown in Figs 6.9, 6.10, respectively. The unsolvated contact ion pair has both terminal and penultimate carbonyl groups co-ordinated to lithium, giving rise to an eight membered ring (Fig. 6.9). Monomer is deemed to co-ordinate with the lithium ion before incorporation in the chain and adopts an isotactic-like disposition before insertion in the growing chain. Using deuterium labelled monomer, threo meso sequences are seen to result. The presence of trace amounts of ether effectively blocks prior co-ordination to lithium, but does not displace the chelated polymer chain. Monomer approaches in a sterically preferred syndiotactic sense (Fig. 6.10). Addition to the growing chain followed by rotation about the α, β bond produces erythro meso placements via syndiotactic like approach. The driving force behind such α, β bond rotation is, in the opinion of Bovey and co-workers,[4] the preference for chelation of the terminal carbonyl function with the lithium ion. Some racemic placements should also occur, however, before reorganisation and formation of the new terminal/penultimate carbonyl complex. The third source of changing chain configuration, solvent separated

Figs 6.9 and 6.10

Bovey models for Isotactic and Syndiotactic-Like Addition

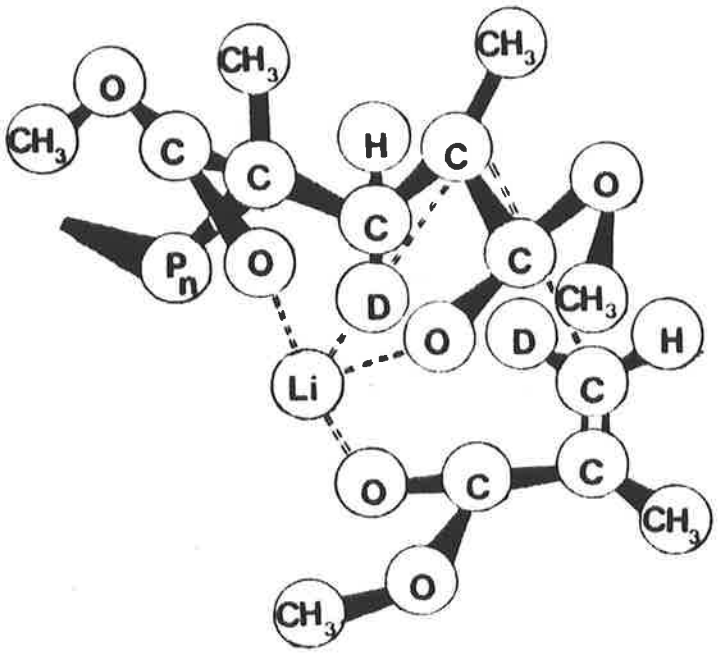


Fig. 6.9: Isotactic-Like

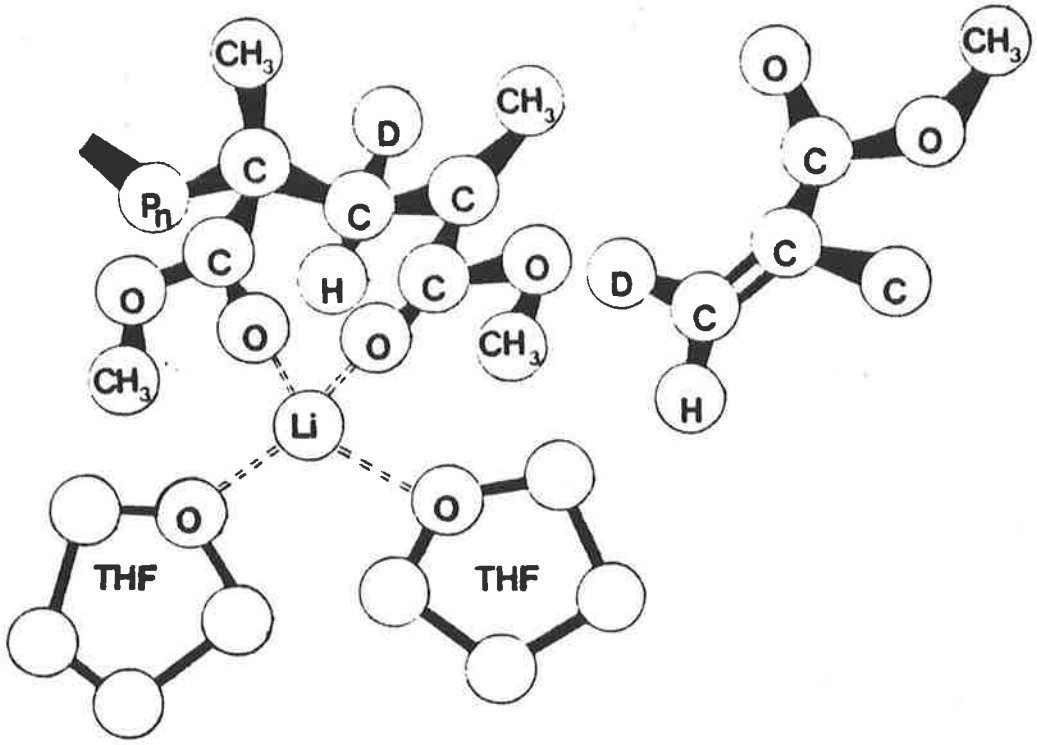


Fig. 6.10: Syndiotactic-Like

ion pairs, are viewed as possessing no co-ordination of previously added monomer units, with monomer approaching in a syndiotactic sense (similar to Fig. 6.10) and with terminal units adopting a syndiotactic configuration. The mechanistic model proposed by Bovey and co-workers[4] has advantages over those of Cram[14] and Goode[15] in that it is able to explain the changes in stereospecificity evident at the β carbon; observable when monomer is labelled at this site with deuterium.

Allen and Mair[24] have proposed a slightly different model for propagating sites in Grignard reagent initiated polymerisations of MMA. This model has as its basis the following observations and assumptions:[13]

(1) The ultimate unit added in the growing chain has its asymmetric carbon configuration conferred before addition of the next monomer unit.

(2) The end carbon of the growing chain is assumed to have a tetrahedral configuration with the α carbon of the final unit covalently bound to magnesium. A tetrahedral configuration present in an intimate ion pair is discarded since the lability of ion-ion pair and intimate-loose ion pair equilibria would lead to rapid inversion of configuration.

(3) Addition of the next monomer unit into the growing chain involves prior co-ordination of this monomer unit to the active site followed by insertion into the covalent C-Mg bond. Evidence for this was mainly kinetic,[24,25] with analogies to organoaluminium polymer-

isations suggesting[26] co-ordination via the monomer carbonyl.

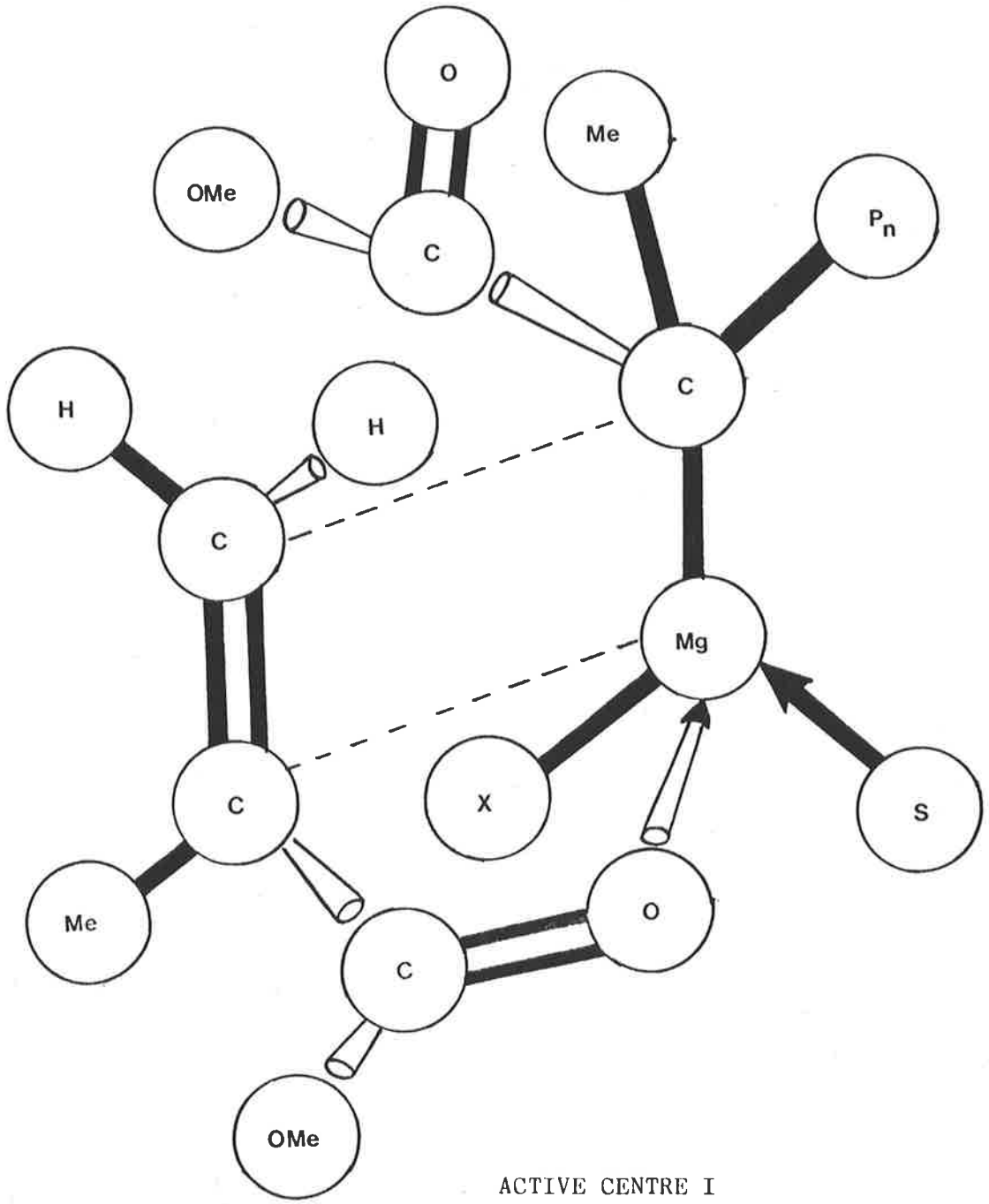
According to Allen and Mair[24] two forms of an active centre can be postulated for such a covalent C-Mg bond insertion reaction at a tetrahedral site. Models for these forms are reproduced in Figs 6.11-I and 6.12-II, the principal difference between them being the absence or presence of chelation of monomer residues in the polymer chain to the magnesium atom. Both models are shown introducing the co-ordinated monomer unit so as to complete a meso dyad. The difference between them lies in the propensity for each model to persist in adding monomer in such a fashion, which is in turn dependent upon the constancy in aspect of presentation of the monomer unit, and the invariance of asymmetry at the chiral magnesium centre. In Fig. 6.11, which could be imagined as operating in the presence of strongly solvating THF which has destroyed penultimate carbonyl chelation, dyad formation could be altered from meso to racemic by either:

(1) Rotating the co-ordinated monomer unit 180° about the Mg ——O bond followed by a 180° rotation about the monomer (carbonyl)C-(α)C bond such that the opposite side of the monomer double bond is presented.

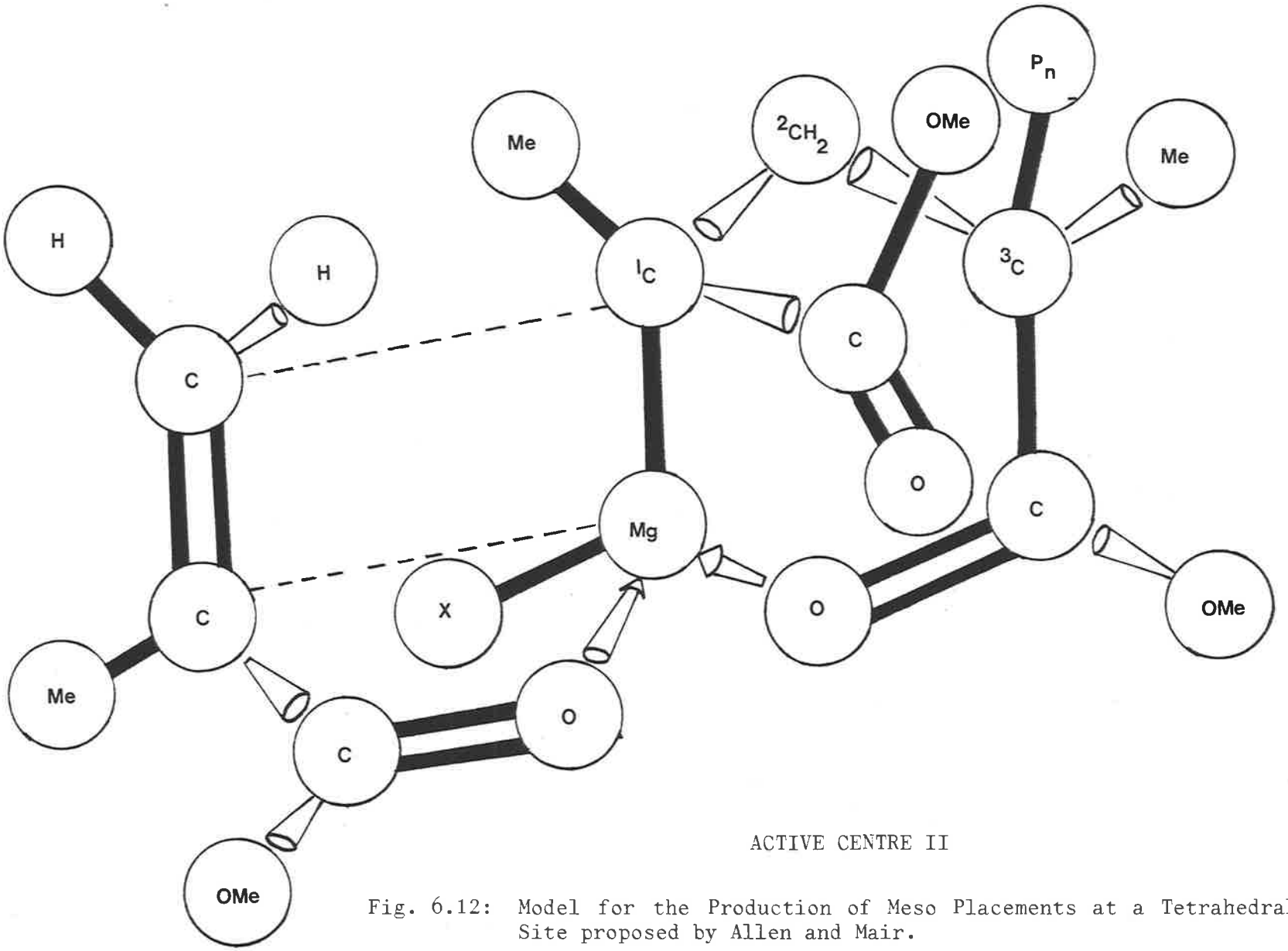
(2) The inversion of chirality of the magnesium centre.

The rapid occurrence of either of these processes would induce a Bernoullian distribution.

Fig. 6.11: Model for the production of Stereoblock or Bernoullian Polymer (dependent on the rate of inversion of the chiral magnesium site or the frequency of internal rotations of the co-ordinated monomer) Proposed by Allen and Mair.



ACTIVE CENTRE I



ACTIVE CENTRE II

Fig. 6.12: Model for the Production of Meso Placements at a Tetrahedral Covalent ^{1}C-Mg Site proposed by Allen and Mair.

When polymer chain chelation is evident (Fig. 6.12-II), which might be envisaged as occurring in a paucity of solvating solvent, approach of the monomer vinyl from the opposite side is negated by forward aspects of the carbomethoxy group attached to ^{1}C and the ^{1}C methyl group. The presence of the ring prevents attack of monomer or THF leading to inversion of symmetry at the Mg centre. Following insertion of the monomer an eight membered ring results, with the originally co-ordinated polymer carbonyl remaining intact until the chain relaxes to the more stable six membered ring, thereby protecting the Mg centre from inversion. This aspect of the model is similar to that suggested by Bovey.[4]

In toluene, where at least one of the centres formed persists in the production of isotactic polymer, centre II (Fig. 6.12) and its enantiomer (II') are deemed responsible by Allen and Mair.[26] In an eneidic mechanism, where other centres may be present producing less stereoregular polymer, propagation at such sites is thought to occur in an isotactic manner via II (or II') for some period, followed by transformation in the presence of THF (disrupting penultimate co-ordination of II(II')) to the less stereodirecting active centre I or its enantiomorph I' (Fig. 6.11):

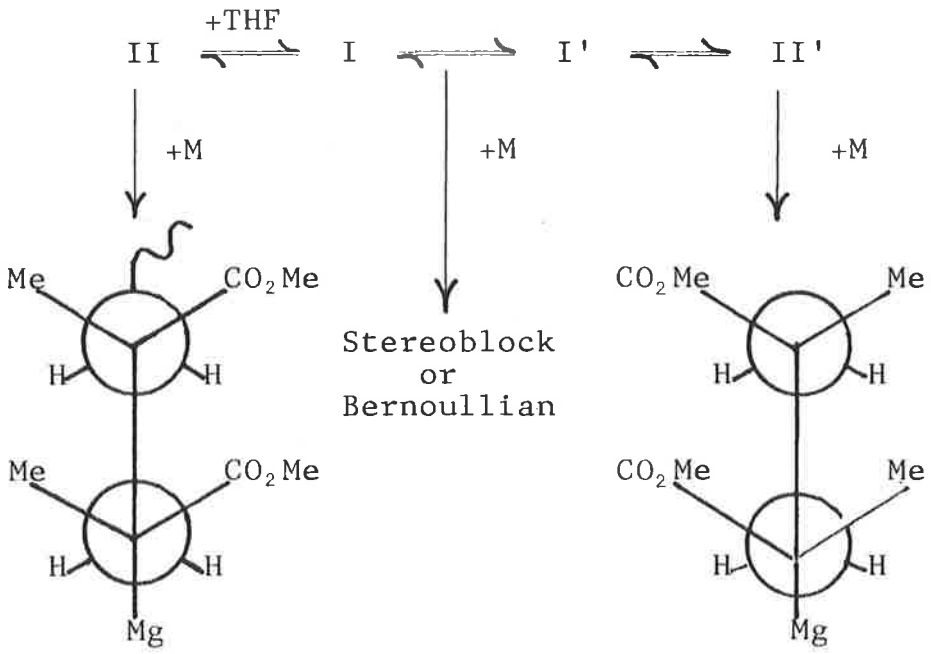


Fig. 6.13

This mechanism is similar to a Coleman-Fox system. The following observations are relevant to this model:

(1) At rapidly inverting centres or in situations where free chain growth occurs, the influence of temperature is explained by the thermodynamic tendency for syndiotactic placements at low temperature, as was experimentally noted in Chapter 4.

(2) With all four permutations in Fig. 6.13 at a given centre, isotactic blocks arise, separated by Bernoullian or near Bernoullian blocks.

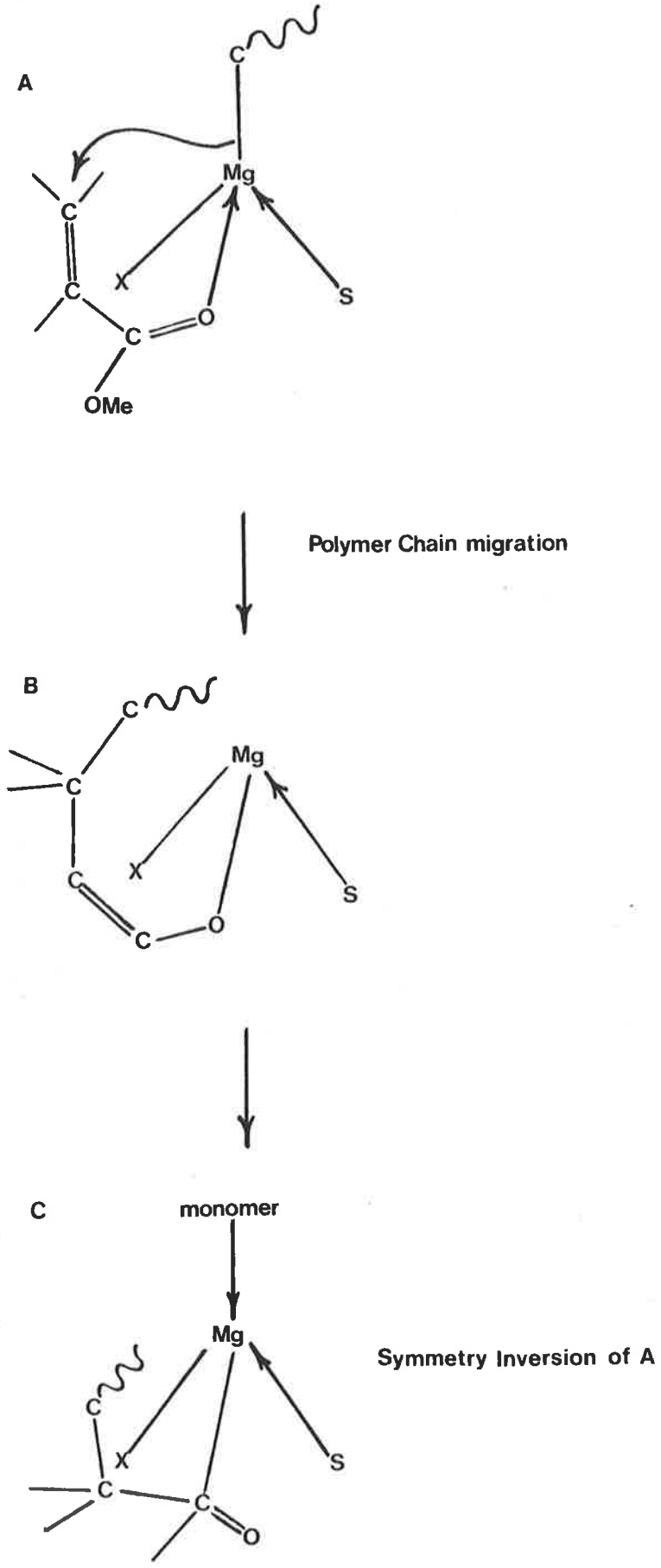
(3) Both models employed by Allen and Mair in Figs 6.11 and 6.12 involve a 2+2 cycloaddition with opening in a cis fashion at the monomer double bond. The observation by Yoshino[7] that trans opening is also evident in Grignard reagent initiated polymerisations under certain conditions, can only be rationalised by the cis/apparent trans opening behaviour observed in Fig.

6.2, where rotations occur after the double bond has developed single bond character.

(4) Totally syndiotactic polymer was never observed in these systems. If the models of Allen and Mair[24] are correct, the active centre I (Fig. 6.11) would either have to alternate the chirality of the magnesium centre between each addition or present alternate aspects of the monomer double bond by 180° rotations about Mg ——O and (carbonyl)C-(α)C bonds, which is unlikely. Another model, presented by Allen and Mair[24] for syndiotactic placements (Fig. 6.14), involves a ligand migration mechanism, which seems just as infeasible.

In the models I and II depicted in Figs 6.11 and 6.12 the entity X is assumed to be halide. Some inconsistencies between these models and experimental results are evident if X is an unreacted aryl or alkyl group formed at an "R_2 Mg-like" centre. Under these circumstances the chelated isotactic producing centre of II (Fig. 6.12) appears just as likely to add with high meso placement, independent of whether X is a halide or an unreacted alkyl/aryl group. Highly isotactic polymers have not been observed with R_2Mg initiators, although Matsuzaki[27] suggests with the PhMgBr system that one of the "isotactic-like" sites produced is attributable to Ph_2Mg. This problem with the model of Allen and Mair[24] could be solved by invoking the principle that both alkyl/aryl magnesium bonds induce polymerisation, with the magnesium atom losing its chirality. Alternatively, the effect of bromide may be secondary,

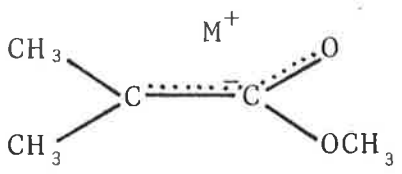
Fig. 6.14: Ligand Migration Mechanism for Production of Syndiotactic Polymer.



allowing the formation of more favourable bromo bridged associates (in comparison to electron deficient alkyl/aryl bridges), through which isotactic polymerisation proceeds. Mair[28] has indicated a model whereby bromo bridged dimers may assist in the production of such polymer, by prior co-ordination of the incoming monomer at the magnesium site next to the active centre.

Pham and co-workers[29-33] interpret the effect of halide in a different manner. Studies of MMA/THF/$MgCl_2$ model systems using ^1H NMR suggest complexes of the form $MgCl_2$.n THF and $MgCl_2$.m MMA. Equating these results with terBu_2 Mg/$MgCl_2$ ratios for actual polymerisations, these workers claim that the polymer structure formed is dependent on whether MMA in the reaction mixture exists in the free form or complexed with $MgCl_2$ or the active centre.

A further source of information on the nature of active centres is provided by model compounds, normally α-metallated oligomers with a degree of polymerisation of one or two. Bywater[34] has examined the ^{13}C NMR spectrum of α-metallated methyl isobutyreate in THF:



M = Li, Na, K

Fig. 6.15

which gave evidence of a planar sp^2 hybridised structure. The α-methyl groups were found to be non-equivalent at least up to room temperature, confirming a degree of double bond character.

Equivalent studies were attempted in this thesis with the Grignard reagent formed from ethyl α-bromoisobutyreate, in order to investigate the hypothesis of covalent C-Mg bond formation, with consequent sp^3 hybridisation at the α-carbon and free rotation of the α-methyl groups. However, this Grignard reagent showed a tendency to react with itself, evidenced by the increased complexity of the NMR spectra as a function of storage time. Any further studies on such Grignard models will also have to be conducted via the R_2Mg species to avoid the complications of the Schlenk equilibrium on the observation of equivalence/non-equivalence of the α methyl resonances.

Bywater and Vancea[35] have also examined living dimers of MMA in THF using Li, Na and K as counter ions. In such dimers two possible forms of the centre exist in principle, with the counter ion on one side or the other of the plane of the anion. The preference for one form or the other may be based on steric effects or on the enhanced interaction of the cation with polar groups on the penultimate unit. Although ^{13}C NMR by these workers did show evidence of two species whose proportions were dependent on counterion, these species appear to arise from cis and trans forms of the active centre rather than diastereoisomers. No observations could be made in toluene due to solubility problems.

Lochmann and Trekoval[36] have claimed success in the infra-red examination of α-metallated oligomers of MMA in both benzene and THF solutions. Esters of these α-metallated (Li, Na or K) diacids and oligo (carboxylic

acids) have an intensive band in benzene between 1630 and 1645cm^{-1} corresponding to absorptions of the (C .....C ..... O)$^{-}$Mt^{+} group. In the presence of THF this band is found between 1626 and 1660cm^{-1}. In hydrocarbon solution an absorption near 1712cm^{-1} corresponding to a more remote alkoxy carbonyl group co-ordinated with the counterion is evident and shows decreased intensity in the presence of THF. At 1738cm a further alkoxy carbonyl absorption is evident, probably due to free carbonyl groups.

Provided the absorption at 1712cm^{-1} can unequivocally be related to intramolecular co-ordination of remote alkoxy carbonyl groups to the counterion and not to intermolecular effects that could be evident in aggregated forms of metallated dicarboxylic acids which have to be shown to exist,[37] then these results are in agreement with the previously cited models presented by Goode,[15] Cram,[14] Glusker,[5] Bovey,[4] Allen[24] and their co-workers who have all postulated that at least one isotactic producing state, present in apolar solvents, must involve co-ordination of carbonyl groups from previously added monomer residues in the growing chain.

6.2 Concluding Comments

The problems associated with Grignard reagent initiated polymerisations of MMA seem to correlate with the uncertain composition of the initiator. Factors which seem interrelated with the Schlenk equilibrium:

$$R_2Mg + MgX_2 \rightleftharpoons 2RMgX \qquad \text{Equn 1.1}$$

and which affect the molar mass, molar mass distribution and stereochemistry of pMMA formed are: nature of solvent, temperature, halide to active bond ratios and the extent of association.

A consensus among different workers, using the same initiator to produce pMMA, has been difficult to attain, with pMMA properties for similar reaction conditions varying greatly. For example, Goode and co-workers,[38] by addition of PhMgBr/diethyl ether to monomer in toluene under nitrogen at 273K, reported high yields (69%) of highly isotactic polymer after 4 hours. Nishioka,[39] using a toluene solution of PhMgBr added to monomer in toluene produced highly isotactic polymer (38% yield) under nitrogen atmosphere at reaction times of 46 minutes at 273K. Matsuzaki and co-workers[27] carried out in vacuo polymerisations by pouring neat monomer on to PhMgBr/toluene/trace THF solutions at 273K, but only succeeded in producing a polymer of 57% isotacticity in low yield (3%) after 24 hours. This result seems in agreement with in vacuo experiments carried out in this thesis where PhMgBr/toluene/trace THF solutions were added to monomer/toluene mixtures producing, at 273K, only trace amounts of polymeric material after 3 hours reaction time.

Allen[13] has noted, in agreement with the observations of Yoshino,[7] that conditions applying at the moment of initiation may be critical in the determination of the type of polymer formed, which may help to explain discrepancies. A number of "hidden" parameters exist which could

affect the initiation conditions and hence the polymer formed for different workers:

(1) The adventitious presence of trace amounts of water adsorbed to the reaction vessel walls. Under these circumstances isotactic producing centres have been shown[40] to be favoured.

(2) Whether the initiator is added to the monomer or the reverse. Mair[28] has shown this to be relevant in NMR kinetic experiments, although the observed retardation of reaction observed here may be due solely to the inefficiency of introduction of the initiator into the NMR tube with correspondent decrease in the number of potential active centres.

(3) For polymerisations initiated at low temperature the nature of the initiator solvent may be important. Evidence from MsMgBr polymerisations at low temperature (200K; Fig. 4.6) suggests that initiator added in THF provides a significant increase in the proportion of intermediate molar mass material, in comparison to initiator added in toluene, for reactions where the final mole fraction of THF was high. The observations prompted speculation that magnesium sites existed in initiator/THF solution with co-ordination number higher than the solid state predicted value of 4, which are responsible for production of intermediate molar mass polymer.

(4) Nishioka and co-workers[39] claim that the tacticity of pMMA produced with PhMgBr is dependent upon the

maximum temperature of the reaction mixture and not the equilibrated bath temperature of the reaction components. For reaction volumes of about $30cm^3$, maximum reaction temperatures 20°-30°C above equilibration temperatures were noted. These temperature rises were far above those noted (Chapter 4) in this thesis using similar reaction volumes.

(5) The initial mole fraction of monomer may be important since its consumption during polymerisation means that polarity of the medium is constantly changing. Its importance is two-fold:

a) In a slow initiation system, which seems plausible based upon kinetic evidence presented in this thesis and those results presented by Matsuzaki,[27] decreasing polarity of the medium may affect the types of centres produced, in a reaction following eneidic pathways, by altering the position of the Schlenk equilibrium, its lability and the degree of association of centres becoming slowly available. This factor may be less important for rapid initiation systems proposed by Bateup and Allen[13] and by Mair,[28] were active centres are assumed to be created soon after reagent mixing.

b) Assuming the active centre models of Allen and Mair[24] (Figs 6.11, 6.12) are correct, then the persistence of isotactic growth centres is governed by the frequency of inversion at the chiral magnesium site. In a similar manner to THF, excess monomer is likely

to decrease the isotactic content by increasing the frequency of inversions, even when little or no THF is present. In this thesis the initial mole fraction of monomer has been kept deliberately low to minimise the effects of (a) and (b).

(6) For reactions carried out in non-polar solvent, the presence of residual ether (THF) in the initiator/toluene solutions has become a vital parameter because it affects the uptake of $MgBr_2$. De-etheration of PhMgBr solutions in this work has characteristically yielded Br/PhMg ratios of about .6 under mild evaporation conditions, while drastic de-etheration has produced Br/PhMg values of about .4. The presence of bromide has a pronounced effect on both molar mass distribution and microstructure.

The object of Chapter 3 has been an attempt to characterise initiator solutions on the basis of variables: active bond content, the bromide to active bond ratio and temperature by the use of ^{13}C NMR. Grignard reagent/diaryl magnesium concentrations have been elevated far above those used for polymerisations to make ^{13}C NMR a viable tool for these studies, so a direct correlation with the initiation conditions applying in polymer forming reactions should be made with caution. Variable temperature studies of PhMg, MsMg and chexMg systems in the presence of bromide seem to confirm the presence of an exchange reaction, with aryl/alkyl groups existing in two chemically distinct environments corresponding to $\underline{R}MgX$ and $\underline{R}_2Mg$ of the Schlenk equilibrium. NMR evidence for the

presence of associates is less well defined, especially in the case of bromo bridged RMgBr species where chemical shift difference between R groups of associated and monomeric forms may not be significantly different at 22.62MHz resolving power. Additionally, the exchange between monomeric and associated forms may be too fast for the NMR time scale so that only a time average signal may be evident. NMR evidence for associates is more likely for R_2 Mg solutions since the R group is present in a 3-centre-2-electron bond, with consequent deshielding and downfield chemical shift with respect to terminal and monomeric R groups. Even so, evidence for association is only confirmed in this thesis for Ph_2Mg/toluene solutions (Fig. 3.9) as a precursor to precipitation. Additional evidence for association may be present in the MsMgBr/THF system (Fig. 3.11), where at low temperature the high field position of the ^{1}C-Mg resonances (farthest downfield) corresponding to the R_2Mg site shows distinct broadening indicating the possibility of the onset of slow exchange between monomeric and associated forms.

Broad molecular weight distributions in RMgX/R_2 Mg initiated polymerisations have been attributed to discrete, independent centres propagating with different rates and stereospecificity.[13,27,28,32,33] Under conditions employed by Bateup and Allen[41] in nBuMgBr or nBu_2 Mg initiated systems, where the presence or absence of bromide has little effect on reaction products, it is assumed that the more reactive species of the Schlenk equilibrium, R_2Mg, carries out initiation. The relaxation

rate of this equilibrium in the direction of R_2Mg is thought to be so rapid compared with the rate of reaction of RMgX with monomer that RMgX initiated polymerisations may be neglected. Under circumstances where RMgX is highly reactive it may contribute significantly to the polymerisation, even if such sites are at low concentration. In summary, equilibrium position, the lability of the Schlenk equilibrium and species reactivity are critical factors in the nature of the polymerisation - factors governed by those obvious parameters of temperature, solvent and halide content as well as those less obtrusive elements such as initiator solvent and exothermicity of reaction, examined more fully at the beginning of this section.

The same critical conditions - equilibrium position, lability and species reactivity - must also apply to the extent of contribution of the various associated species in a polymerisation following eneidic pathways:

monomer $\rightleftharpoons$ dimers, trimers etc.

Association studies for organoaluminium compounds indicate[42] that these equilibria have short relaxation times at ambient temperature so that only the position of the equilibrium and relative reactivities are important. For alkyl lithium compounds this is not the case and slow relaxation of association equilibria have a pronounced effect on the polymerisation process.[42] Kinetic studies have assumed that monomeric forms of alkyl lithium initiators are the most reactive in hydrocarbon media,[43,44] even though absolute evidence for those monomeric forms still

does not exist. The same observation may be true for alkyl magnesium initiators as well. Although variable temperature NMR studies of terBuMgBr[28] and isoBuMgBr[45] in THF have revealed the presence of associated species, its importance as a means of determining the nature of potential active centres is severely limited by its inability to distinguish the extent of association, although Mair[28] does tentatively assign 2 of the 4 methyl resonances of terBuMgBr in THF to a dimeric form of this initiator. Future studies of initiator solutions by NMR will have to be coupled with variable temperature ebulliometry for a fuller understanding of initiator constitution.

Chapter 4 presents a study of polymer products formed from PhMg, MsMg and chexMg compounds as a function of THF concentration, temperature, bromide to active bond ratio and initiator solvent. The nature of GPC traces for polymerisation reactions in toluene with the presence of bromide provides complex, broad molar mass distributions for all initiators studied. The high molar mass component ($MW \sim 2 \times 10^6$) seems very dependent upon the presence of bromide and in all cases is destroyed by the presence of THF. The relative proportion of this high molar mass material increases with temperature, which is consistent with increased equilibrium concentrations of RMgX under these conditions. The sensitivity to THF content implies that associated forms of RMgX may be responsible for high molar mass forming, isotactic centres. Simultaneous with the greater proportion of high molecular weight pMMA at elevated temperatures in apolar solvent, is the increased

isotacticity of the polymer formed. There appear to be at least three different independent centres operating to produce the broad molar mass distributions for PhMgBr, MsMgBr and chexMgBr in non-polar solvent, which concurs with observations made by Matsuzaki et al.,[27] who ascribed the high molar mass, highly isotactic component to "PhMgBr-like" active centres, and the low molar mass, isotactic-like and intermediate molar mass syndiotactic-like polymer to centres based upon Ph_2Mg. Mair[28] has noted that terBuMgCl and terBuMgBr operate via similar eneidic pathways with 3 or possibly 4 different active centres, while secBuMgBr operates with 2 or 3 centres present.

The addition of THF has a three-fold effect on polymer formed. This is best illustrated in the case of the MsMgBr system (Figs 4.3-4.6). Beside the effects of reduced isotacticity and loss of high molar mass peaks, the yield of methanol insoluble polymer is lowered which, in terms of monomer-active centre co-ordination mechanisms proposed by Bateup and Allen[41] and Erusalimskii,[46] is satisfactorily explained by blocking of co-ordinating sites by strongly solvating THF. In the case of MsMgBr, addition of THF produces unimodal/near unimodal low molar mass polymer ($1\text{-}2\times10^4$). At 250K the heterodispersity index of this peak increases with increasing THF content (Fig. 4.4), but varies erratically at 230K. At 200K (Fig. 4.6) the molecular weight distributions in the presence of THF are complex and dependent on the initiator solvent (Chapter 4). PhMgBr and chexMgBr systems behave in a similar fashion to MsMgBr at 250K with the low molar mass peak

($1\text{-}2\times10^4$) dominating (Figs 4.15 and 4.26) in the presence of THF.

Diaryl magnesium initiators examined here produce less isotactic polymer under all solvent conditions than their bromo equivalents. Lower molar mass material ($1\text{-}2\times10^4$) predominates (Figs 4.10-4.13) under all circumstances for Ms_2Mg, although at 273K reactions in high final mole fractions of toluene show small amounts of higher molecular weight material (Fig. 4.10D-H). In accordance with MsMgBr systems, polymer yield is higher for reactions carried out in toluene but diminishes when THF is added. At 200K (Fig. 4.13) the presence and proportion of intermediate molar mass polymer is directly dependent on the nature of the initiator solvent at high final mole fractions of THF, in a similar manner to MsMgBr. At 250K the unimodal low molar mass polymer produced by both MsMgBr and Ms_2Mg (Figs 4.4, 4.11) in the presence of THF show similar increases in the polydispersity index with increasing amounts of THF, suggesting that this peak in chromatographs produced with the initiator MsMgBr may be due to active centres formed at "Ms_2Mg-like" sites. A similar comparison between Ph_2Mg and PhMgBr initiated polymer product is less conclusive (Figs 4.15, 4.19), with pMMA formed with the Ph_2Mg initiator producing large proportions of intermediate molar mass material in the mid-range of THF/toluene solvent polarities.

Results from Chapter 4 which are important considerations in an interpretation of kinetic data in Chapter 5 are:

(1) The inactivity of the PhMgBr initiator in toluene at 200K, with its reactivation at 250K to produce polymer identical to that found when the system is thermostatted and initiated at 250K.

(2) The presence, under certain conditions, of invariant GPC eluograms with increased conversion. The reaction conditions for such observations appear more exacting than those specified by Matsuzaki:[27]

a) The Br/PhMg quotient may be quite critical in the observation of chromatograph invariance. Figs 4.22 and 4.23 show that, particularly when a Br/PhMg value of $.3_1$ is used, obvious differences are apparent in the nature of eluograms at 30 minutes and 3 hours reaction time.

b) The temperature at which reaction occurs may be critical. Fig. 4.17, where a series of unstirred reaction vessels were left to react at 230K (Br/PhMg $\sim$1), produced GPC traces which varied with both time and conversion.

c) The manner in which polymerisations are carried out in terms of the method of collection of product may be another important parameter. At 250K, with Br/PhMg=$.6_2$, the chromatographs of pMMA product for reactions in toluene are similar (Figs 4.22A, 4.23A) at varying reaction time. These products were produced from separate unperturbed reaction vessels. However, when samples were withdrawn from the same reaction vessel (Fig. 2.9) by removing the vessel from the thermostatted bath, followed by decantation

into sidearms (at 250K and with Br/PhMg=.6_1), the molecular weight distribution varied drastically with time (Fig. 4.18). If the reaction follows a slow initiation mechanism, then the origin of this phenomenon, suggested in this thesis as initiator aggregation, may be altered by removal of the mixture from equilibrated bath conditions, creating different active centres to those which might be released under unperturbed conditions at 250K. The Schlenk and association equilibria may be altered during the 40-60 seconds required for removal from the bath and decantation into sidearms. If this is so, then the MsMgBr initiated reaction carried out at 250K with Br/MsMg =.7_4 (Fig. 4.14) under similar conditions shows diminished sensitivity to such a variable. After 5 minutes reaction time GPC traces remain quite similar. Although access to yields is not possible for samples from the same reaction vessel, the increasing viscosity of the reaction mixture indicates GPC similarities occur with increasing conversion.

A slow initiation-rapid propagation mechanism does seem to be reinforced by kinetic ^{1}H NMR measurements made in Chapter 5. The conditions used here closely resemble the large scale unperturbed runs of Figs 4.22A and 4.23A where GPC traces were similar with time/conversion. The differences in the nature of the monomer conversion curves for PhMgBr (Br/PhMg=.6_0) and Ph_2Mg initiated runs (e.g., at 250K, Figs 5.4 and 5.8, respectively) have been interpreted as arising from different propensities of each

initiator to form inert, highly associated species in toluene - that tendency being enhanced in the presence of bromo-bridging groups. In the presence of bromide slow release of discrete, different potentially active sites obscures the observation of termination effects, which must be evident if GPC traces remain invariant with conversion. If Ph_2Mg is used as the initiator, then the unfavourable disposition toward formation of aryl bridged associates may imply that a much larger proportion of polymerisation active monomeric or lower order associated forms are present at the time of mixing, so that if termination of growing chains occurs, it will be obvious in the upward deflection of the monomer decay curve.

Some inconsistencies are apparent with this model:

(1) Figs 4.22 and 4.23 reveal that for a given reaction time, the yields of methanol insoluble polymer are approximately the same across the range of Br/PhMg ratios, which seems inconsistent with an anticipated slower release of active sites when bromide is present. Other factors may be operating which negate a valid correlation between large scale and NMR kinetic runs - in particular the mode of initiation in NMR kinetic experiments, described in Chapter 5, and its relation to the number and type of potential active centres available at initiation. Other forms of the initiator beside linear, highly associated species may be responsible for inactivity. Allen and Hagias[47] have noted for di-isobutyl magnesium that either cyclic or cluster compounds may be evident,

or, if linear, they have an average degree of polymerisation of 10.

(2) Slow initiation-rapid propagation does not seem compatible with the idea of a maximum reaction temperature being attained in the first few minutes of reaction, as proposed by Nishioka et al.[39] Monomer-initiator adduct formation and propagation are likely to be exothermic but these appear to be pre-empted by availability of initiator in the rate determining step. Side reactions at the monomer carbonyl should also be exothermic but most recent theories[41] suggest that both initiation of polymerisation and side product formation proceed through the same monomer-initiator adduct, which is again pre-empted by availability of potential active sites. For similar reaction volumes, temperature rises noted in this thesis are much lower than those of Nishioka et al.[39]

Those factors which support the concept of initiator inactivity via association are:

(1) The observations of Ashby,[48,49] who suggested that PhMgBr may exist in polymeric form.

(2) The previously described inactivity of PhMgBr toward polymerisation at 200K, with reactivation on transfer to a higher temperature bath.

(3) The longer half life for reactions involving PhMgBr at lower temperature, despite the fact that more reactive Ph_2Mg is thought to become predominant under these conditions. This supports the concept of

thermal disruption of inactive associates to produce potential active sites.

(4) The MsMgBr initiator, which for reactions in toluene also presents the prospect of slow initiation, shows, at 230K (Fig. 5.11), $t_{3/4}/t_{1/2}$ and $t_{1/2}/t_{1/4}$ values indicative of the same internal order of reaction, but at 250K (Fig. 5.10) termination is present with $t_{3/4}/t_{1/2}$ implying a higher order than $t_{1/2}/t_{1/4}$. This supports argument (3) above.

(5) Grignard reactions with MMA, particularly in toluene, produce intense colorations on mixing, which have been assigned to the formation of a monomer-initiator adduct.[25,28] These colour changes have not been evident using PhMgBr and MsMgBr initiators. In Chapter 4 it was proposed that the change transfer band produced by the monomer-initiator adduct may be hindered by overlap of p orbitals of the π aromatic system with the orbital of magnesium responsible for accepting electrons from the carbonyl group of the MMA donor. Given the evidence suggesting slow initiation, absence of coloration may be alternatively explained by the fact that such a monomer-initiator adduct never reaches a concentration high enough to produce colorations visible to the eye. A corollary to this argument is that the intense orange colour apparent in the toluene reactions of chexMgBr with MMA may indicate that the rate determining step of this reaction is not dependent upon aggregation of the initiator.

(6) Although no experiments were performed in this thesis, the presence of excess bromide has been shown to retard the rate of polymerisation for nBuMgBr[25] and terBuMgBr.[28] This is consistent with the model proposed here, where bromide should favour the presence of inert aggregates.

(7) Unreacted organomagnesium bonds noted by Yoshino[50] and Mair[28] in polymerising systems must be different to those initiating polymerisation.

Studies of Grignard initiated polymerisations have been instigated in an attempt to examine and control factors which affect stereochemistry, molecular weight and molecular weight distribution, with the ultimate aim of producing tactic pMMA with well defined physical and mechanical properties. These polymers are also ideal for testing the properties of blends and work has been undertaken by Truong,[51] using some of the pMMA produced here, in such endeavours.

In Grignard reagent initiated polymerisations following eneidic pathways, the production of pMMA of narrow molar mass distribution equates with an understanding of the different active centres present. The choice of aromatic Grignard reagents, in particular PhMgBr, has followed the precedent of other workers[15,39] who have routinely used this initiator to produce highly isotactic polymer. However, results presented in this thesis tend to indicate that PhMgBr is unsatisfactory in this regard. Isotactic content, for reactions performed in toluene, is

low and accompanied by broad molar mass distributions. The Grignard reagent of choice for the production of isotactic polymer appears to be terBuMgBr, which provides high yields of isotactic polymer at short reaction times, and, under certain circumstances,[52] narrow molar mass distributions.

In conclusion, a greater control of polymer properties must lie with a fuller understanding of the nature of active centres present. This will entail:

(1) Intensive studies on the nature of aggregation in initiator solutions.

(2) Utilisation of ^{13}C enriched monomer studies which provide kinetic data, time dependent microstructure evaluations and details of side reactions.

(3) Examination of higher order microstructure data such as pentad assignment, using rapidly advancing NMR technology, to examine the mode of monomer addition.

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