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STUDY OF **CR 113810**  
HIGHLY FLOURINATED HETEROCYCLIC POLYMERS  
FOR CRYOGENIC BLADDER APPLICATIONS

FINAL REPORT  
on  
Contract No. NASW-1822

March 1970

by  
Beatrix Y. Sanders  
Walter P. Fitzgerald Jr.

**CASE FILE  
COPY**

Submitted to  
Jet Propulsion Laboratory  
National Aeronautics and Space Administration  
Oak Grove Drive  
Pasadena, California

by  
WHITTAKER CORPORATION  
Research & Development Division  
3540 Aero Court  
San Diego, California 92123

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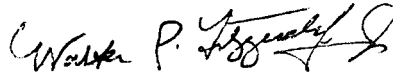
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## FOREWORD

This final report describes research performed during the period 15 October 1968 to 15 March 1970 at Whittaker Corporation, Research & Development Division, San Diego, California, under Contract No. NASW-1822, under our MJO No. 3560. The principal investigator was Dr. Walter P. Fitzgerald Jr., Senior Research Specialist, assisted by J. L. Rogers, Technician. Research was also performed by Beatrix Y. Sanders, Senior Chemist, assisted by J. R. Charter, Senior Technician.

Prepared by:



\_\_\_\_\_  
Walter P. Fitzgerald Jr.

## ABSTRACT

In a quest for a polymer system displaying cryogenic flexibility for bladder applications, a large family of new highly fluorinated heterocyclic elastomers has been prepared. These elastomers have been prepared by a variety of chain-extension and extension-crosslinking reactions on functionally-terminated prepolymers based on poly(perfluoropropylene oxide). Although none of our elastomers was flexible in liquid nitrogen, it was possible to correlate degree of chain-extension and crosslink density with polymer glass transition temperature. In this manner it was possible to prepare highly-extended elastomer systems with  $T_g$  values approaching  $-100^\circ\text{C}$ .

For the extension reactions, both the isocyanate-terminated poly-(perfluoropropylene oxide)bis-urethane (and its derived prepolymers) and the acyl-terminated poly(perfluoropropylene oxide) were used to provide the elastomeric "soft" segment, as well as to impart LOX-compatibility and oxygen nonflammability to the systems. Heterocyclic extensions of several types were investigated. Among the most satisfactory elastomer systems were those prepared with the triazine heterocycle, extended through amino groups (of melamine, or melamine-terminated prepolymer) to cyanurate-urea extensions, as well as through hydrazine linkages (of cyanuric trihydrazine) to cyanurate-semicarbazide extensions. Because of the trifunctionality of these triazines, self-curing elastomers with low crosslink density and low ring multiplicity at the crosslinking site were prepared, as well as more highly crosslinked systems, through linear extensions followed by external cure of the pendant linkages with a fluorinated diisocyanate. A highly-extended poly(acylsemicarbazide), with  $T_g \sim -100^\circ\text{C}$ , was prepared by extension of the isocyanate-terminated prepolymer with an acyl hydrazide-terminated prepolymer. All of these elastomers were nonflammable, or rapidly self-extinguishing in  $\sim 100\%$  oxygen atmosphere.

Heterocyclic extensions through 1,3,4-oxadiazole and 1,3,4-thiadiazole heterocycles, as well as through their amino-derivatives, and also N-aminotriazole groups were also effected, but fully-cured products were difficult to prepare. Similar cure difficulties were encountered with extensions through imide heterocycles.

It was found that, for flammability purposes, aromatic ring hydrogens cannot be tolerated, as was found with a flammable trimesoyl hydrazine-extended elastomer system.



TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
I INTRODUCTION . . . . .	1
II PROGRAM OBJECTIVE . . . . .	2
III SUMMARY OF RESULTS . . . . .	3
A. Poly(perfluoropropylene oxide) Soft Segment . . . . .	3
1. Isocyanate-Terminated Prepolymer and Its Polyurethane . . . . .	3
2. Unsuitable Soft Segments . . . . .	6
B. Heterocyclic-Extended Elastomer Systems . . . . .	6
1. Heterocyclic Extensions . . . . .	6
2. Cyanurate "Fluoromel" Systems (s-Triazine- based Heterocyclics) . . . . .	8
a. General Summary of Cyanurate-Urea Extended Elastomers . . . . .	8
b. Melamine-Extension Reactions . . . . .	8
c. Melamine-Recapped Polyether and Transparent Elastomers . . . . .	12
d. Cyanurate-Urea--Urethane-Co-extended Polyether Elastomer Systems . . . . .	13
e. Tensile Lap-Shear Strengths of Cyanurate-Extended Polyether System . . . . .	16
f. Cyanuric Trihydrazine-Semicarbazide- Extended Polyether System . . . . .	17
g. Non-heterocyclic, Trimesoyl Hydrazide Analogue of Y-Cyanurate Semicarbazide Self-Curing Elastomer . . . . .	21
3. Five-Membered Heterocyclic Extensions and Their Open-Chain Analogues . . . . .	22
a. Semicarbazide-Polyether Systems and Their Heterocyclic Derivatives . . . . .	22
b. N-Aminotriazole Extensions and Cure Studies . . . . .	29

TABLE OF CONTENTS (Continued)

<u>Section</u>	<u>Page</u>
III (Continued)	
4. Bis-Heterocyclic-Extended Polyether Systems . . .	32
a. Aminobenzimidazole-Extended Poly(per- fluoropropylene oxide) Synthesis . . . . .	32
b. Bis-Imide Extended Polyether Systems . . . . .	33
C. Thermomechanical Analysis of Heterocyclic- Extended Polyether Films . . . . .	35
IV    RECOMMENDATIONS FOR FUTURE RESEARCH . . . . .	37
V    EXPERIMENTAL SECTION . . . . .	38
VI    BIBLIOGRAPHY . . . . .	45
APPENDIX I - HETEROCYCLIC-EXTENDED POLY FILMS FORWARDED TO JET PROPULSION LABORATORY . . . . .	47
APPENDIX II- DISTRIBUTION LIST . . . . .	49

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1	Poly(perfluoropropylene oxide) Synthesis . . . . .	3
2	Heterocyclic Systems for Polyether Chain Extension . . . . .	7
3	Cyanurate-Urea Crosslink Profiles . . . . .	11
4	Polyacylsemicarbazide Sulfurization and Thermal Cyclizations . . . . .	27
5	N-Aminotriazole Crosslink Formation . . . . .	31

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LIST OF TABLES

<u>Table</u>		<u>Page</u>
I	Tensile Lap-Shear Strengths of Cyanurate- Extended Polyether System . . . . .	17
II	Thermomechanical Analysis of Heterocyclic- Extended Polyether Films . . . . .	36



## SECTION I

### INTRODUCTION

In designing a polymer system for end-use in cryogenic bladder applications, several atypical structural parameters must be borne in mind. First the elastomer structure must be highly extended with a low degree of interchain bonding to impart low-temperature flexibility. The polymer must remain amorphous throughout processing. At the same time the elastomer system must have a sufficient amount of "stiff" segment to provide enough crosslink density and interchain hydrogen bonding to provide structural integrity at and above ambient temperatures. Superimposed on these physical and mechanical qualifications are the prerequisites of compatibility with cryogenic oxidizers and nonflammability to enriched oxygen environments. This latter set of parameters almost necessarily limits consideration to essentially perfluorinated structures. Collectively, these requirements for a polymer system represent a formidable synthetic challenge.

The Research & Development Division of Whittaker Corporation has for several years been developing fluorinated elastomer systems, principally polyurethane systems, under NASA-sponsorship for LOX-compatible adhesives, and for related end-use applications. The more promising elastomers on this continuing program have been based on poly(perfluoropropylene oxide) as the flexible segment. A variety of derived prepolymers, with acyl-, hydroxyl-, amine-, and isocyanate-termination, based on this highly flexible and LOX-compatible polyether, have been prepared and extensively evaluated in our laboratory.

It was to our distinct advantage to utilize this extensive experience, and utilize functional prepolymers of this type to construct heterocyclic modifications for cryogenic bladder evaluation.

## SECTION II

### PROGRAM OBJECTIVE

The program objective is the synthesis and characterization of highly fluorinated heterocyclic polymer systems suitable for cryogenic bladder applications. For purposes of nonflammability and LOX-compatibility, the heterocycles of choice will be hydrogen-free, and amenable to synthesis by extension-polymerization with a functionally-terminated polyether soft segment. Correlation will be made between degree of polymer extension and resultant polymer flexibility. The fabrication of choice is thin film samples.

SECTION III

SUMMARY OF RESULTS

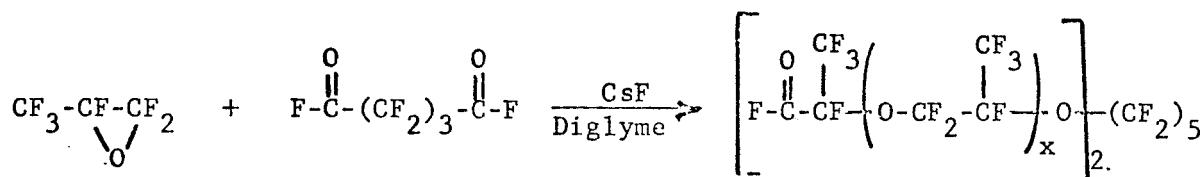
A. Poly(perfluoropropylene oxide) Soft Segment

1. Isocyanate-Terminated Prepolymer and its Polyurethane

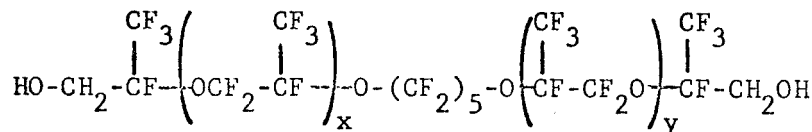
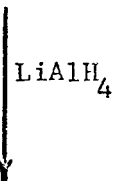
WRD has accumulated over six years experience in the preparation and utilization of the polyethers of hexafluoropropylene oxide,<sup>1</sup> according to the scheme shown in Figure 1.

Figure 1

Poly(perfluoropropylene oxide) Synthesis



I. Polyperfluoropropylene oxide di-acid fluoride



II. Poly(perfluoropropylene oxide) glycol PFPO(OH)<sub>2</sub>

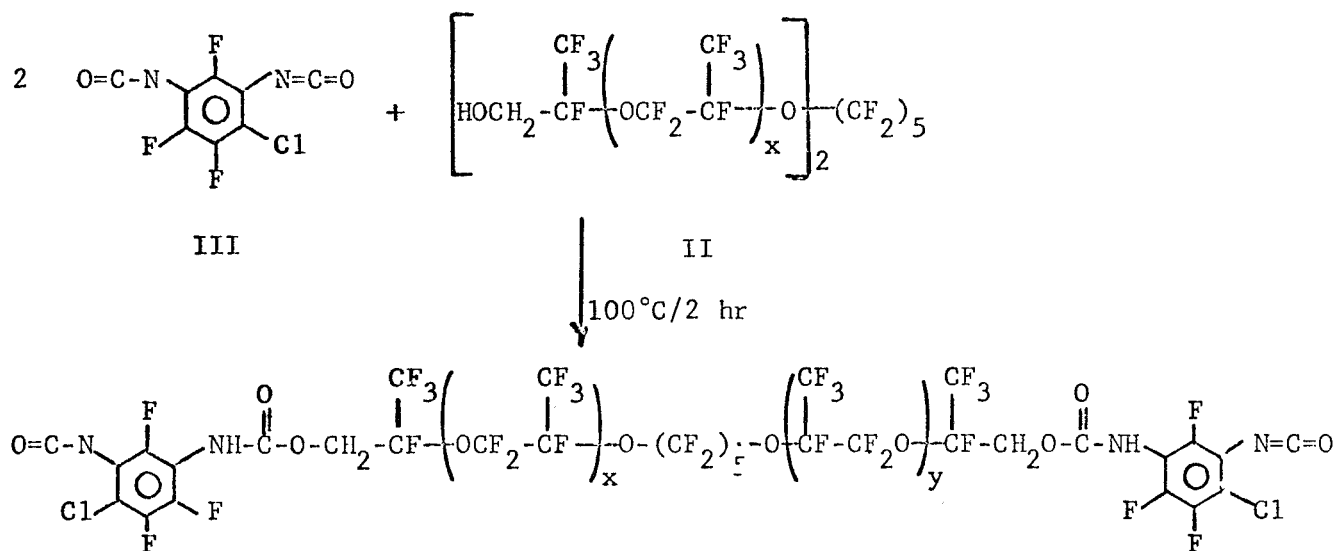
Polyethers ranging in molecular weight from 1000 to over 2500 have been prepared in batches as large as five-pounds. Recent refinements in our laboratory procedures, with respect to cesium fluoride catalyst preparation, have enabled us to achieve a high degree of reproducibility in this polymerization.

Peninsular ChemResearch no longer supplies the required hexafluoropropylene oxide. Following recent negotiations, E. I. duPont de Nemours & Co., Inc., the patent holder,<sup>2,3</sup> has agreed to sell this vital monomer to Whittaker Corporation, for exclusive use on NASA-contracts.

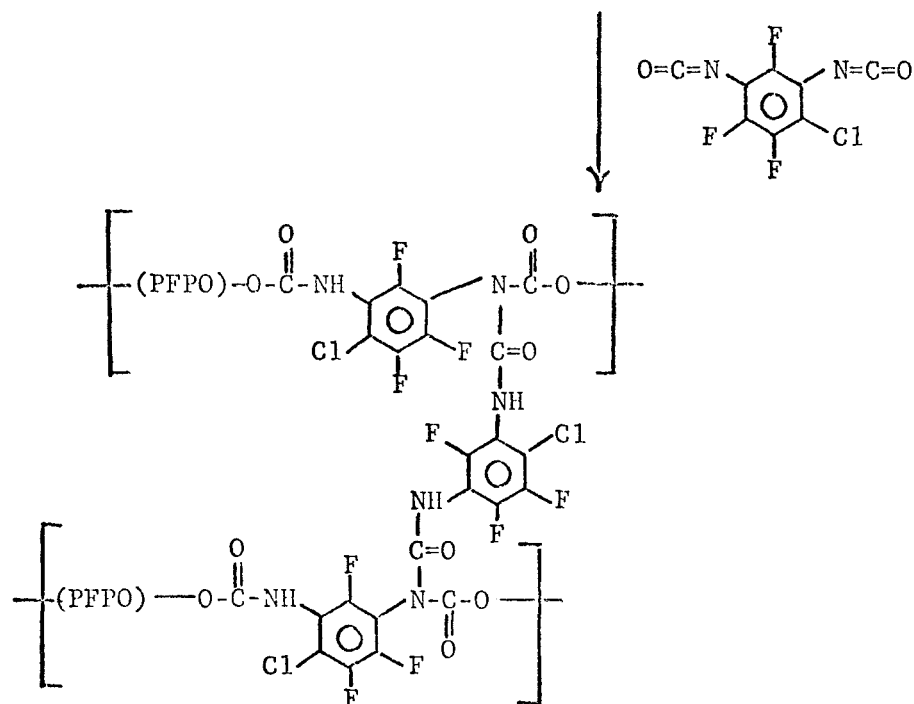
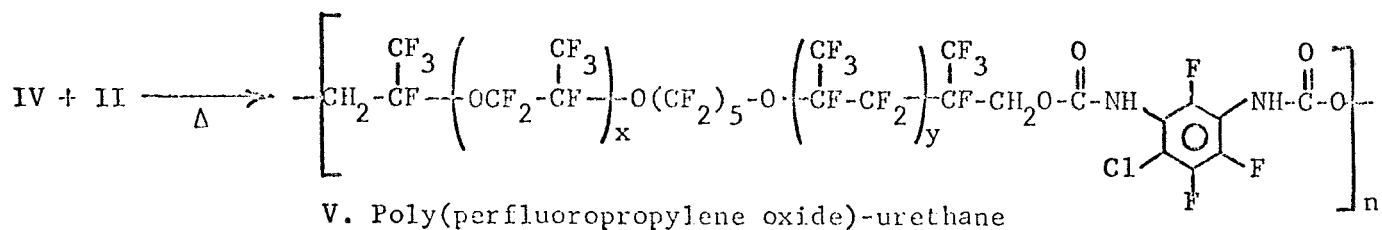
The poly(perfluoropropylene oxide)-di-acid fluoride can be used as such, or, as will be shown below, as one of its other acyl-derived structures. Reduction with complex metal hydride produces the corresponding

glycol-terminated poly(perfluoropropylene oxide) II. This glycol has been used extensively as such, as a copolymer, in polyurethane synthesis. Its molecular weight normally ranges from 1800-2000, and, like its acid fluoride precursor, it is a viscous, stable liquid. Analysis of purity has been obtained by the use of our Hewlett-Packard programmed high-temperature vapor-phase chromatograph.

Glycol-terminated polyether can be efficiently "capped" by reaction with chlorotrifluoro-m-phenylene diisocyanate III. Because of the divergence in reactivities of the two isocyanate groups in III, the termination reaction is clean at 100°C, and the isocyanate-terminated poly(perfluoropropylene oxide)-bis-urethane IV is an extremely viscous liquid, indefinitely stable at room temperature. It is miscible with selected solvents, and with its precursors. Its formation is shown below.



For purposes of comparison with our heterocyclic objective elastomers, the standard polyurethane based on IV was prepared by warming this isocyanate-terminated prepolymer with excess glycol-terminated prepolymer. Cure was effected thermally by allophanate formation by reaction with chlorotrifluoro-m-phenylene diisocyanate in a press, as shown below.



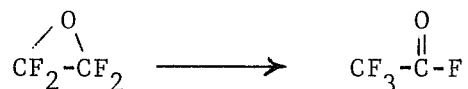
Films of VI, although LOX-compatible, and rapidly self-extinguishing in ca. 100% oxygen, were completely inflexible and quite brittle in liquid nitrogen. It can be noted from a consideration of the structure of the cured polyurethane, that the degree of hydrogen-bonding and ring-multiplicity in the region of the crosslink site are too high for low-temperature flexibility.

Isocyanate-capped poly(ether) IV has been extensively studied in extension reactions, as well as in self-curing studies, on this program. Its uses is described in a subsequent section.

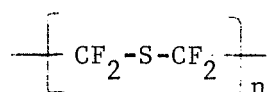
## 2. Unsuitable Soft Segments

In consideration of alternate soft segments for use on this program, the following candidates have been rejected for the reasons specified.

While considerable effort has been expended on the preparation of poly(tetrafluoroethylene oxide), this polymer was not believed to be the material of choice. It remains difficult to prepare, and the starting monomer is extremely reactive<sup>4</sup> and unstable due to rearrangement, as follows:<sup>5</sup>

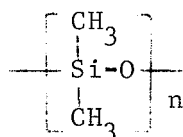


Polyfluorothioethers represented by the following structure



were not considered as the flexible segment due to their known instability at the required curing temperatures. The polythioether polymers unzip thermally to form thiocarbonylfluoride.<sup>6</sup>

Furthermore, siloxanes of the structure



were not investigated inasmuch as these materials are not expected to have sufficient chemical resistance. They also offer very little in the way of synthetic variation to modify properties for our purposes.

## B. Heterocyclic-Extended Elastomer Systems

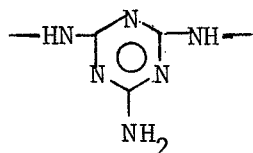
### 1. Heterocyclic Extensions

A variety of extension reactions, as well as extension-curing combinations, have been carried out, using the above-cited functionally-derived poly(perfluoropropylene oxide) prepolymers. Three general classes of heterocyclic systems have been incorporated into perfluoropolyether systems, as discussed below. These three classes are shown in Figure 2, along with the method of their incorporation or formation.

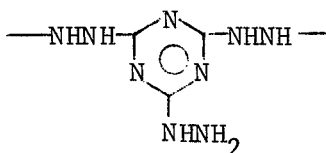
Figure 2.

Heterocyclic Systems for Polyether Chain Extension

Type I. Triazine-Based:

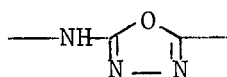


Cyanurate-  
urea extension

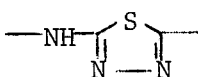


Cyanurate  
Semicarbazide extension

Type II. Five-Membered Ring Systems:

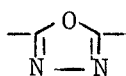


Amino-1,3,4-  
oxadiazole

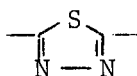


Amino-1,3,4-  
thiadiazole

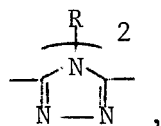
from cyclization of semicarbazides  
(thiosemicarbazides)



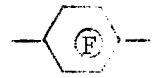
1,3,4-  
oxadiazole



1,3,4-  
thiadiazole

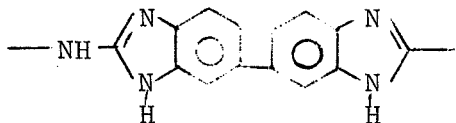


N-  
aminotriazole

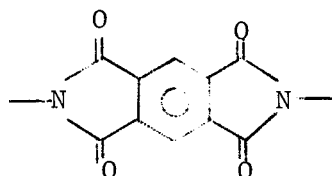
where R =  or nothing

from cyclization of hydrazides  
(oxathiahydrazides)

Type III. Aromatic Bis-Heterocycles



Bis-aminobenzimidazole from  
diaminobenzidine and isocya-  
nate-terminus



Bis-imide from pyromellitic  
dianhydride and isocyanate-  
terminus

The various methods of incorporation of these heterocyclic extensions, as well as the methods of effecting crosslinking during cure, are discussed under the individual system sections below.

## 2. Cyanurate "Fluoromel" Systems (s-Triazine-based heterocyclics)

### a. General Summary of Cyanurate-Urea Extended Elastomers

An excellent series of essentially-perfluorinated heterocyclic elastomeric structures were prepared and processed into films using elastomer technology. Of these systems, most encouraging results have been obtained from structures containing the trifunctional melamine heterocycle. By reaction of isocyanate-capped poly(perfluoropropylene oxide) with melamine, as a chain-extender, a family of polymers were prepared with varying degrees of elasticity, after isocyanate-crosslinking and thermal curing. We feel that these polymer systems represent a significant breakthrough with respect to facility of processing as well as to film integrity and toughness. Moreover, these films were nonflammable (rapidly self-extinguishing) in pure oxygen, and retained their integrity in liquid nitrogen. None were, however, flexible in liquid nitrogen. It is, however, felt that these structures pointed the way to the preparation of more flexible structures through a higher degree of chain extension with correspondingly lower crosslink density.

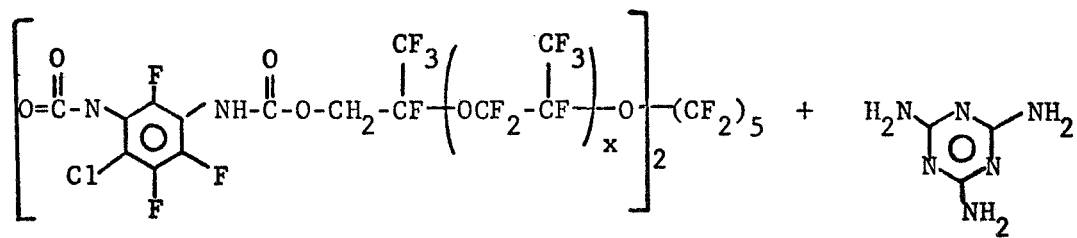
### b. Melamine-Extension Reactions

The choice of melamine as an extending reagent for isocyanate-capped polyether IV was based on: a) the absence of C-H bonds; 2) the amide-like (and thus, attenuated and inherently more stable) character of the -NH<sub>2</sub> groups; and 3) the predictable nonflammability of a melamine-derived polymer. The results to date with this system have been most gratifying.

It has been found, for example, that the isocyanate-capped perfluoropolypropylene oxide prepolymer reacts readily with a molar equivalency of melamine at ca. 70°C in a chain extension reaction to produce an essentially linear system VII, with pendant amino groups. The product VII was extremely viscous, and was fabricated into elastomeric films. The crosslinking, presumably to a structure represented by VIII, was readily accomplished using chlorotrifluoro-m-phenylene diisocyanate in a press at 170°F or at 250°F. From a consideration of the structure of the crosslinked urea extension site, there is an obvious concentration of hydrogen-bonding sites with a multiplicity of seven aromatic rings in a tight cluster in the neighborhood of the crosslink. It is not surprising, therefore, that this elastomeric product VIII was tough and high-melting, despite the large percentage of polyether in the structure (the polyether glycol segment represents a molecular weight of 1800 per repeat unit).

An encouraging facet of this chain extension reaction is the fact that the reactivity of the pendant amino group is significantly attenuated, so as to largely obviate premature crosslinking. The linear polymer VII could still be processed after several days. Further, films of VII were very rapidly self-extinguishing upon ignition in a ~100% oxygen atmosphere with a gas/oxygen flame. The film retained its integrity in liquid nitrogen, but was not flexible. The synthesis of this system is as follows:

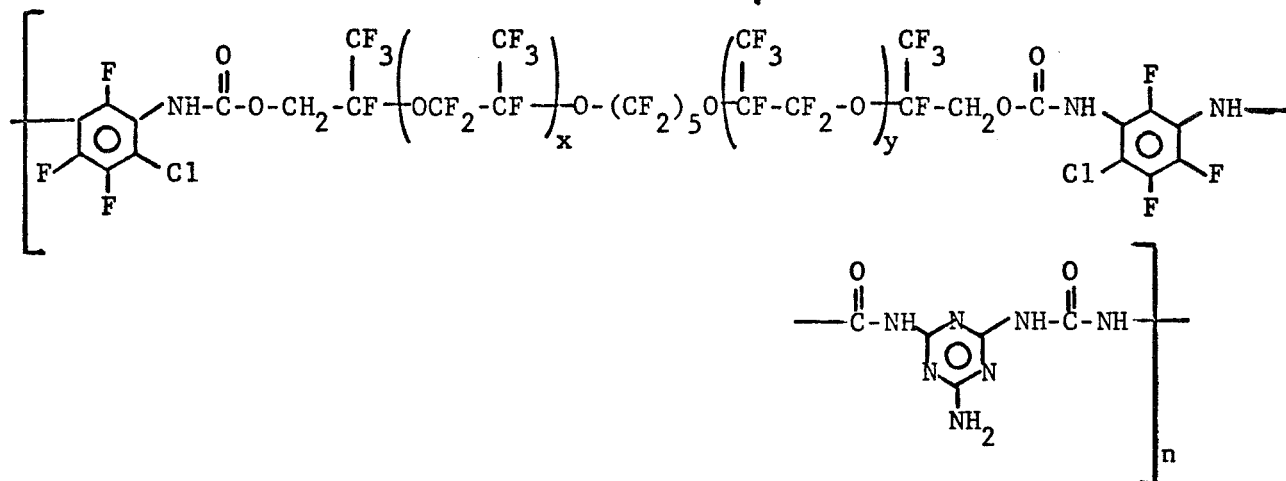




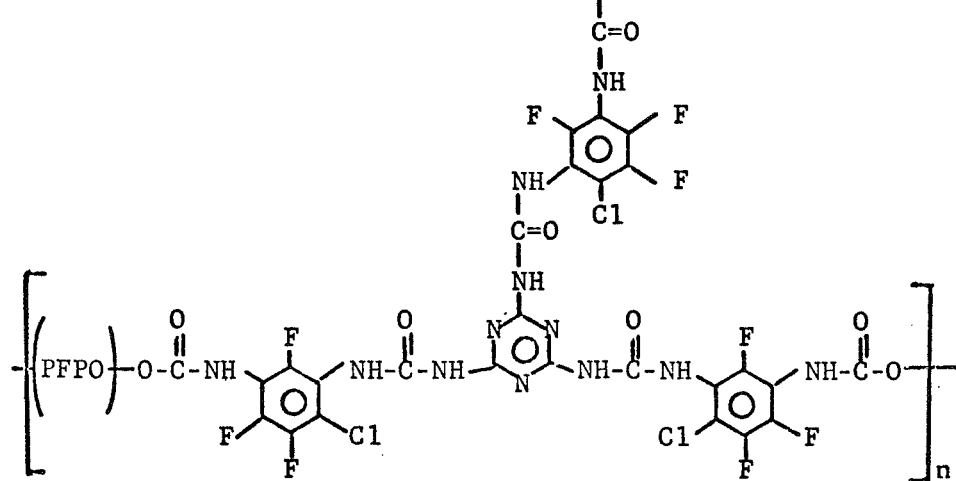
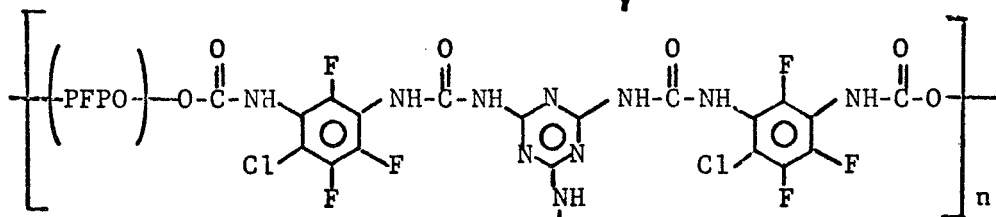
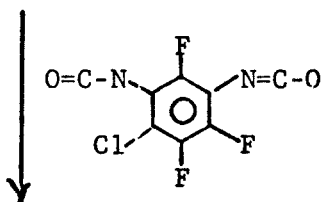
Isocyanate-capped urethane prepolymer

Melamine

↓ 70°C

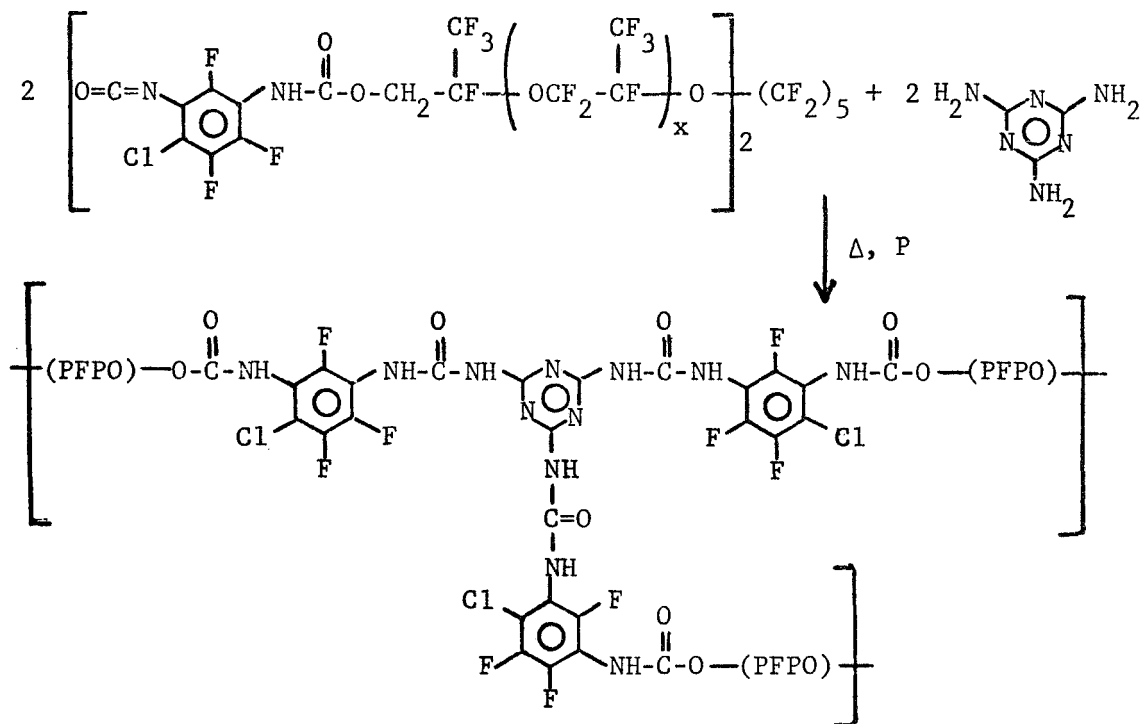


Melamine-extended perfluoropolypropylene oxide-urethane-urea copolymer VII.



Isocyanate-cured urea-crosslinked perfluoropolypropyleneoxide-urethane VIII.

In order to achieve a structure with more flexibility, it was decided, as a first alternative, to eliminate the utilization of an external crosslinking agent. Reacting three equivalents of isocyanate-capped prepolymer with two equivalents of melamine, with rubber mill homogenization, followed by press curing at 250°F produced a strong elastomeric film, presumably entirely crosslinked by urea bridges; as represented by structure IX.

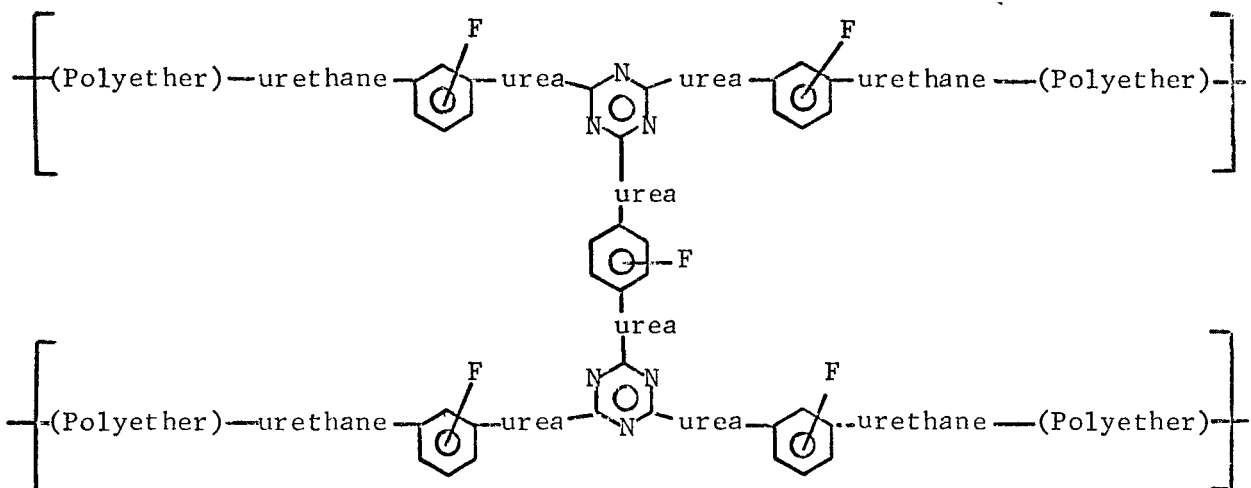


IX. Melamine extended-melamine crosslinked perfluoropolypropylene oxide-urethane

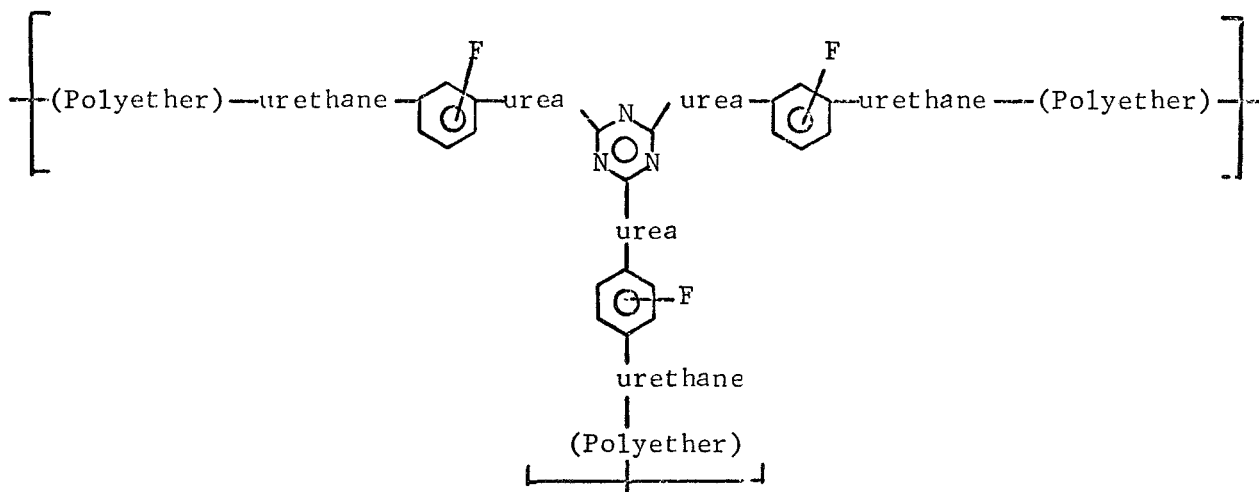
This structure represents the opposite end of the crosslink density scale, and the 2:3 stoichiometry produces a "Y"-type of crosslink with a minimum ring multiplicity for the reagents chosen. The film was opaque, except in thin sections, and was found to be rapidly self-extinguishing in 100% oxygen at low pressure.

The film represented by the self-crosslinked Structure IX, in addition to being more flexible, was also more easily processed. Therefore, it is reasonable to proceed, as one possible route to increased low-temperature flexibility, to advance in the direction of "Y"-crosslinked structures. Figure 3 graphically illustrates the difference between the externally-induced "H"-crosslink and the self-induced "Y"-crosslink, with respect to ring multiplicity and hydrogen-bonding in the neighborhood of the crosslinking site.

Figure 3.  
Cyanurate-Urea Crosslink Profiles



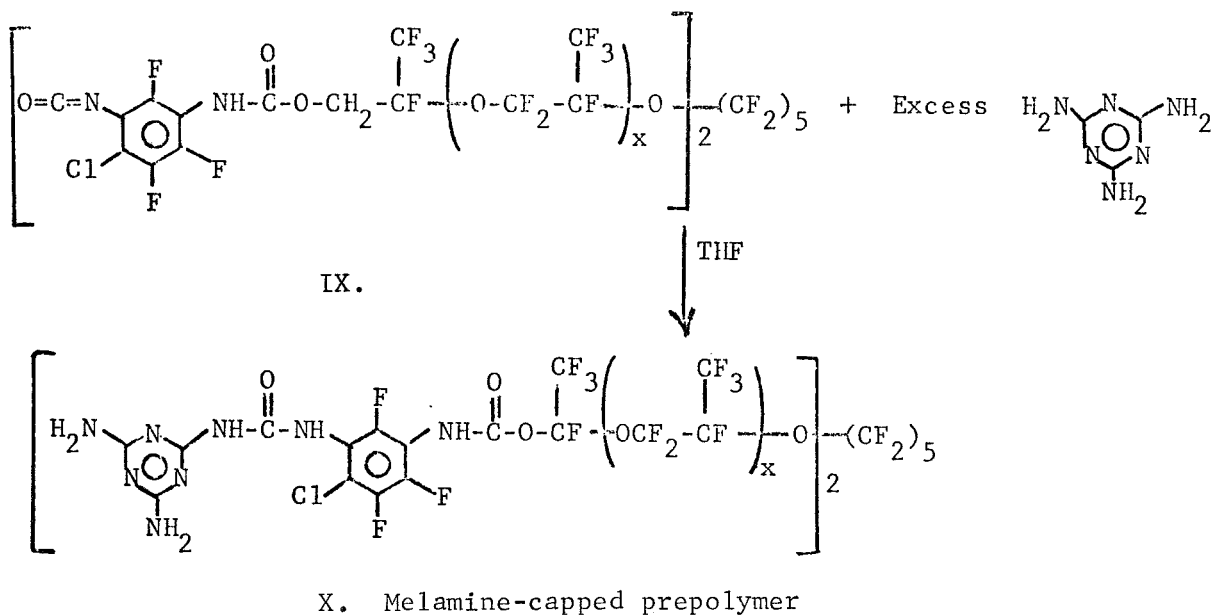
V. Melamine-extended--isocyanate-crosslinked perfluoropolyether urethane



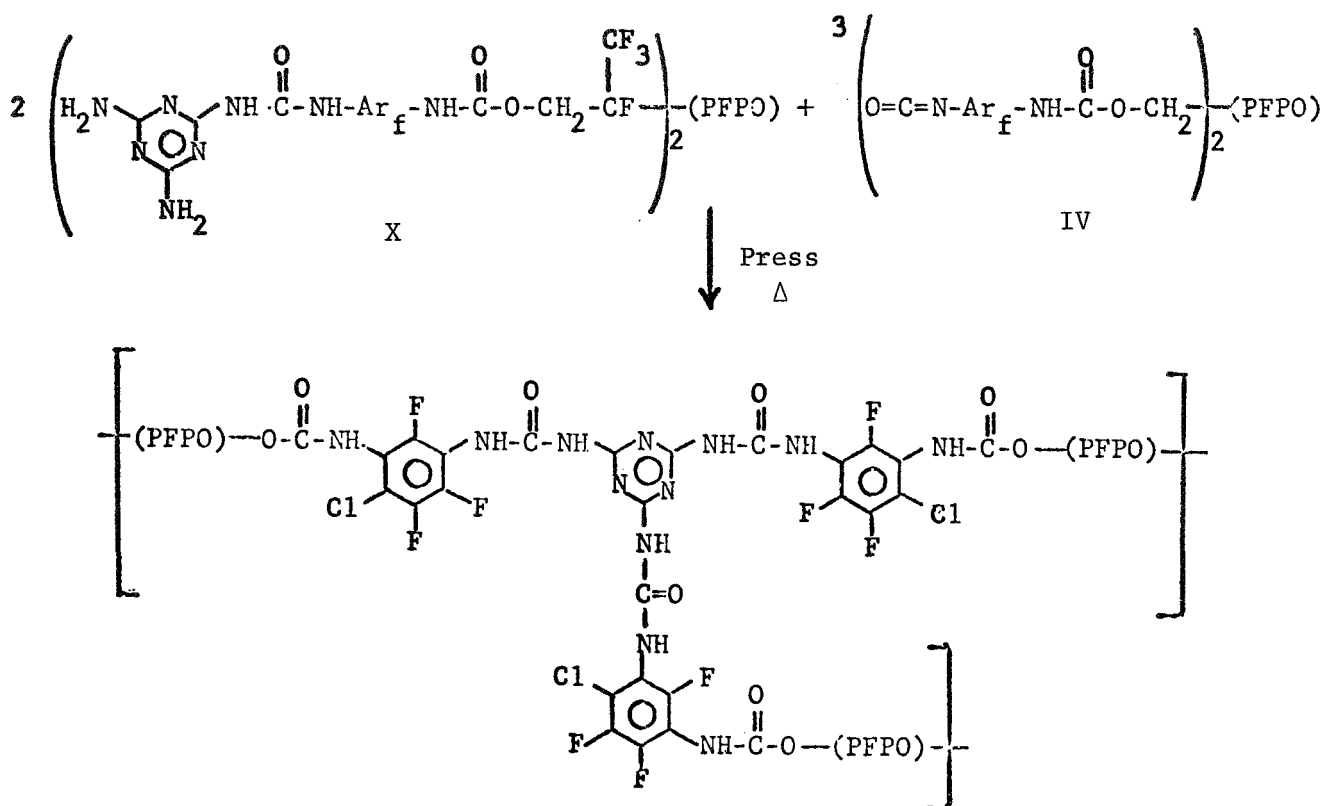
VI. Melamine-extended--melamine-crosslinked perfluoropolyether urethane

### c. Melamine-recapped Polyether and Transparent Elastomers

All of the previously-prepared heterocyclic-extended elastomeric films have been opaque to translucent, owing to heterogeneity of extending reagent. In order to prepare transparent bladder film candidates, a derived prepolymer X was prepared by "recapping" isocyanate-capped prepolymer with excess melamine in refluxing THF. This glass-like solid X showed high solubility in THF. Its purification was facilitated by the lack of solubility of the excess melamine in the reaction medium.



It was then possible to react this unique melamine-capped prepolymer X with its parent isocyanate-capped prepolymer IV in the proper stoichiometry to prepare the crosslinked structure IX, by an alternative method, as a transparent elastomeric film with similar properties to the product obtained directly from IV and melamine. Both films were integral but essentially nonflexible when immersed in liquid nitrogen. Both were rapidly self-extinguishing in ca. 100% oxygen.



IX. Melamine extended-melamine crosslinked  
perfluoropolypropylene oxide-urethane

In the following section, it will be shown how this melamine-recapped prepolymer has also been used to prepare transparent copolymer-extended systems.

d. Cyanurate-Urea-Urethane-Co-extended Polyether Elastomer Systems

As an alternative approach to obtaining a more flexible, highly fluorinated heterocyclic polymer structure, a compromise was made between the above-described pure melamine-urea structures and the non-heterocyclic urethane system V derived from chain-extending the isocyanate-capped prepolymer with its parent polyether -glycol. This polyurethane, discussed above, crosslinked by the agency of the chlorotrifluoro-m-phenylene diisocyanate through allophanate linkages can be incorporated into the cyanurate system due to equivalent reactivities between the glycol-terminated prepolymer and melamine (or the melamine-recapped prepolymer) for the isocyanate functionality.

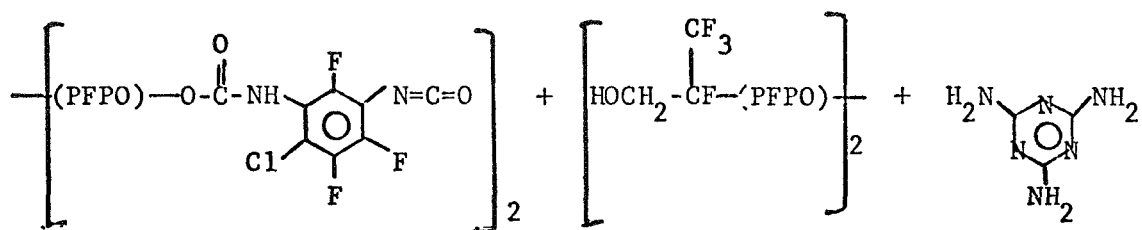
The allophanate crosslink, because it is formed from the low-reactivity urea-NH linkage, should not, however, be formed to any extent as long as the stoichiometry of crosslink is controlled to utilize only the more

reactive, pendant aromatic amine groups in the melamine center. For our purposes, therefore, the urethane blocks are merely linear extension groups of sizeable (2000) molecular weight. When used for a co-extending system, cured through melamine-urea crosslinks, the urethane block should impart more flexibility (through a dilution of hydrogen bonding, primarily) to the overall system without significant loss of dimensional stability and toughness.

From studies performed on this type of co-polymer synthesis, it appears that the co-extension reaction can be controlled to give a range of flexible properties with satisfactory crosslink densities. Here again it was found advantageous to preform the melamine-capped prepolymer for transparency in the final product.

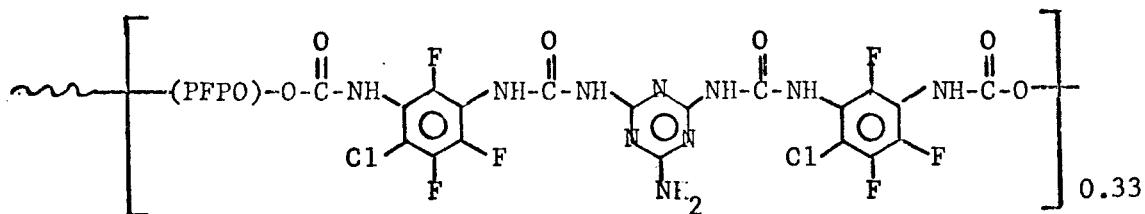
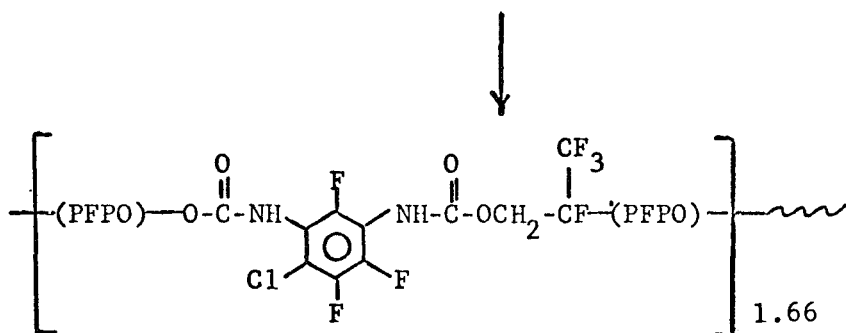
In one example of this approach, reaction of isocyanate-capped prepolymer with a co-extension mixture containing 33 mole-percent melamine and 67 mole-percent glycol-terminated polyether, with isocyanate-curing to form urea crosslinks, produced a flexible elastomeric structure with significantly improved strength over the unmodified polyurethane and more room temperature flexibility than the straight cyanurate-urea extended system. This urea-urethane structure XI was formed by adding finely-divided melamine to a warmed pre-mix of isocyanate-capped prepolymer and glycol. By use of this procedure, a more fluid reaction mixture was obtained. A further increase in processability was obtained when the diisocyanate crosslinking agent is added (cf. equation below). This stoichiometry should yield a 6:1 urethane:urea co-extended system.

The films of XI obtained by this direct approach were opaque, and resembled the cyanurate-extended system rather than the urethane, with respect to physical appearance and tear strength. As expected, the films were rapidly self-extinguishing in ca. 100% oxygen. The film tested in liquid nitrogen was inflexible, but retained its integrity. It was significantly less brittle than the homopolymer polyurethane at the cryogenic temperature. This fact attests to the flexibilizing effect of the extension of uncrosslinked blocks.



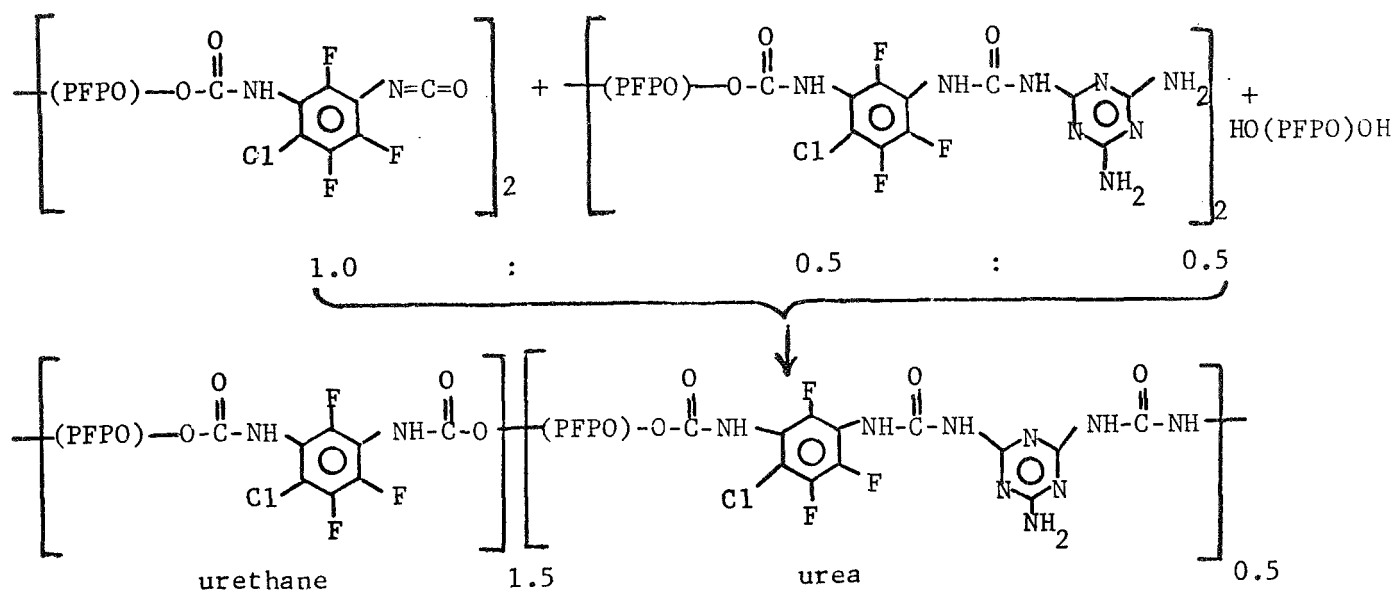
Isocyanate-capped prepolymer

1 : 0.66 : 0.33



### XI. Cyanurate-Urea--Urethane (1:6) Co-extended Polyether

Use was made of the isocyanate-recapped prepolymer to prepare a transparent co-extended system. Thus when one molar equivalent of isocyanate-terminated prepolymer was reacted with an equivalent mixture composed of equimolar quantities of melamine-recapped prepolymer and glycol-terminated prepolymer, and the linear product XII cured with only sufficient chlorotrifluoro-m-phenylene diisocyanate to crosslink the pendant amino-groups, a transparent elastomeric film was obtained with press cure. The structure is believed to be the 3:1 urethane:urea co-extended polyether shown in the following equation.



XII. Cyanurate-urea-urethane (1:3)  
co-extended polyether

In a simplified modification of the above reaction for control purposes, reaction of isocyanate-capped prepolymer with a co-extension mixture containing 50-mole-percent melamine and 50 mole-percent glycol-terminated polyether, with the same molar extent of external diisocyanate curing (to form urea crosslink), produced a flexible, opaque elastomeric structure of equivalent strength and flexibility to its transparent modification. The linear product from this reaction is represented by the same structure, XII.

Both cured films of XII retained their integrity in liquid nitrogen, but neither was flexible. From a nonflammability standpoint, the transparent sample was slightly more rapidly self-extinguishing in ca. 100% oxygen at low pressure.

e. Tensile Lap-Shear Strengths of Cyanurate-Extended Polyether System

For evaluation of cryogenic performance, adhesive tensile lap-shear panels were prepared using 17-7 stainless steel (standard PO4 etch) with our standard bonding fixture. Tensile strengths for self-cured, and isocyanate-cured melamine-extended poly(perfluoropropylene oxide)-bis-urethane were tested. The results are summarized, at room temperature, and in liquid N<sub>2</sub>, in Table I. The results, although not spectacular, are clearly superior at the cryogenic temperature.



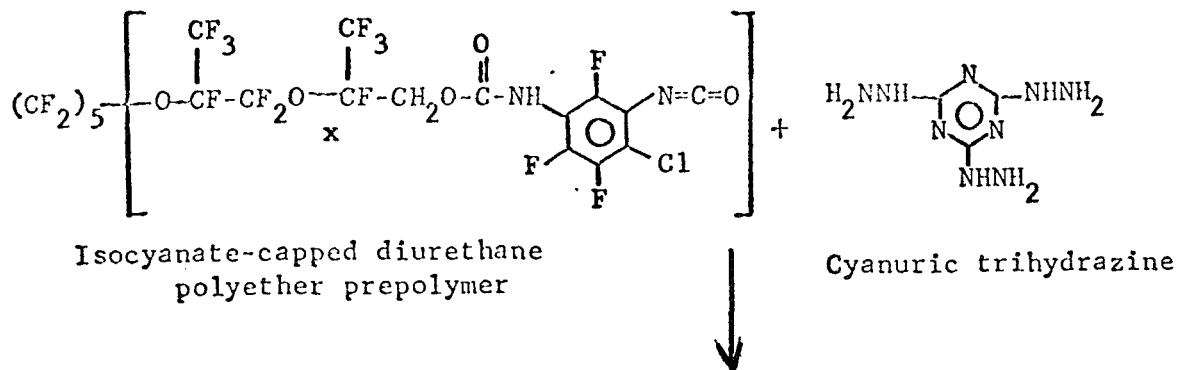
TABLE I

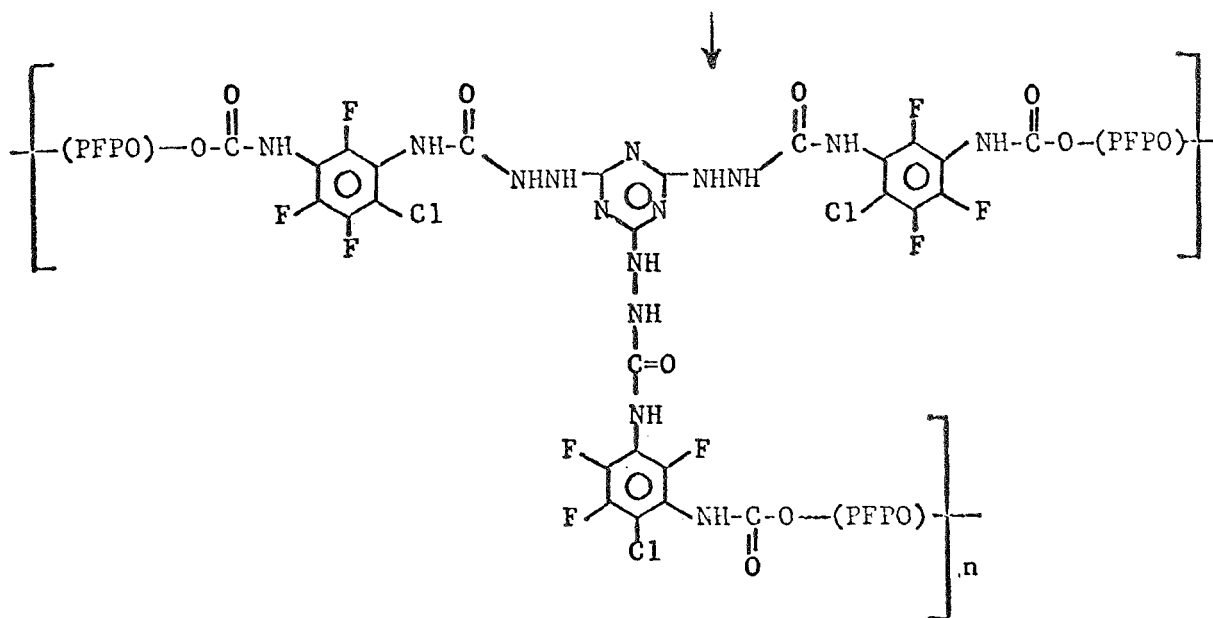
TENSILE LAP-SHEAR STRENGTHS OF  
CYANURATE-EXTENDED POLYETHER SYSTEMS

Sample	Cure	Tensile Strength (psi)	
		Room Temperature	-320°F
WPF-182-67 Linear, isocyanate cured	15 hr @ 250°F	863	928
		850	745
		747	833
		<u>714</u>	<u>788</u>
		Avg. <u>794</u>	<u>824</u>
WPF-182-64 Linear, Self-cured	64 hr @ 250°F	343	1200
		298	812
		327	1250
		<u>333</u>	<u>1280</u>
		Avg. <u>325</u>	<u>1135</u>

f. Cyanuric Trihydrazine-Semicarbazide-Extended  
Polyether Systems

In an extension of the above work, alternative types of "Y" structures have been prepared. The most promising of these has been obtained by substituting cyanuric trihydrazine in the polyether chain extension reaction with self-crosslinking to form a bis(cyanuric semicarbazide) XIII. The cure was effected at 250°F in a press.

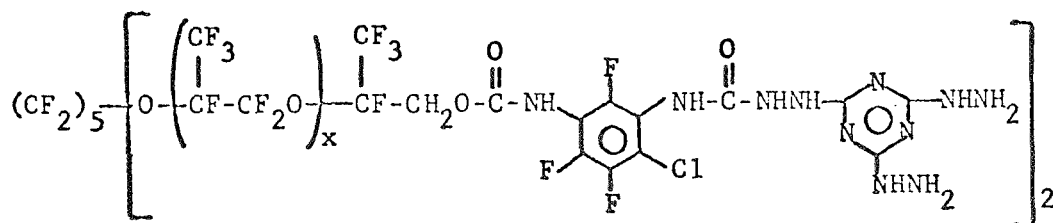




XVIII. Cyanurate-semicarbazide extended, cyanurate-semicarbazide crosslinked poly(perfluoropolypropylene) bisurethane

The elastomer XVIII was opaque, resilient, and somewhat less flexible than its melamine-analogue. It was completely nonflammable in 100% O<sub>2</sub> at low pressure. It also showed cryogenic integrity (liquid N<sub>2</sub>), but virtual inflexibility. In a more extended form, with less dense hydrogen bonding, this type of system should be more flexible.

To prepare a transparent product of this type, a "re-capping" reaction was run with the isocyanate-capped polyether prepolymer and excess cyanuric trihydrazine in THF, to prepare XIV, of uncertain purity.



XIV. Cyanuric-trihydrazine capped polyether bisurethane

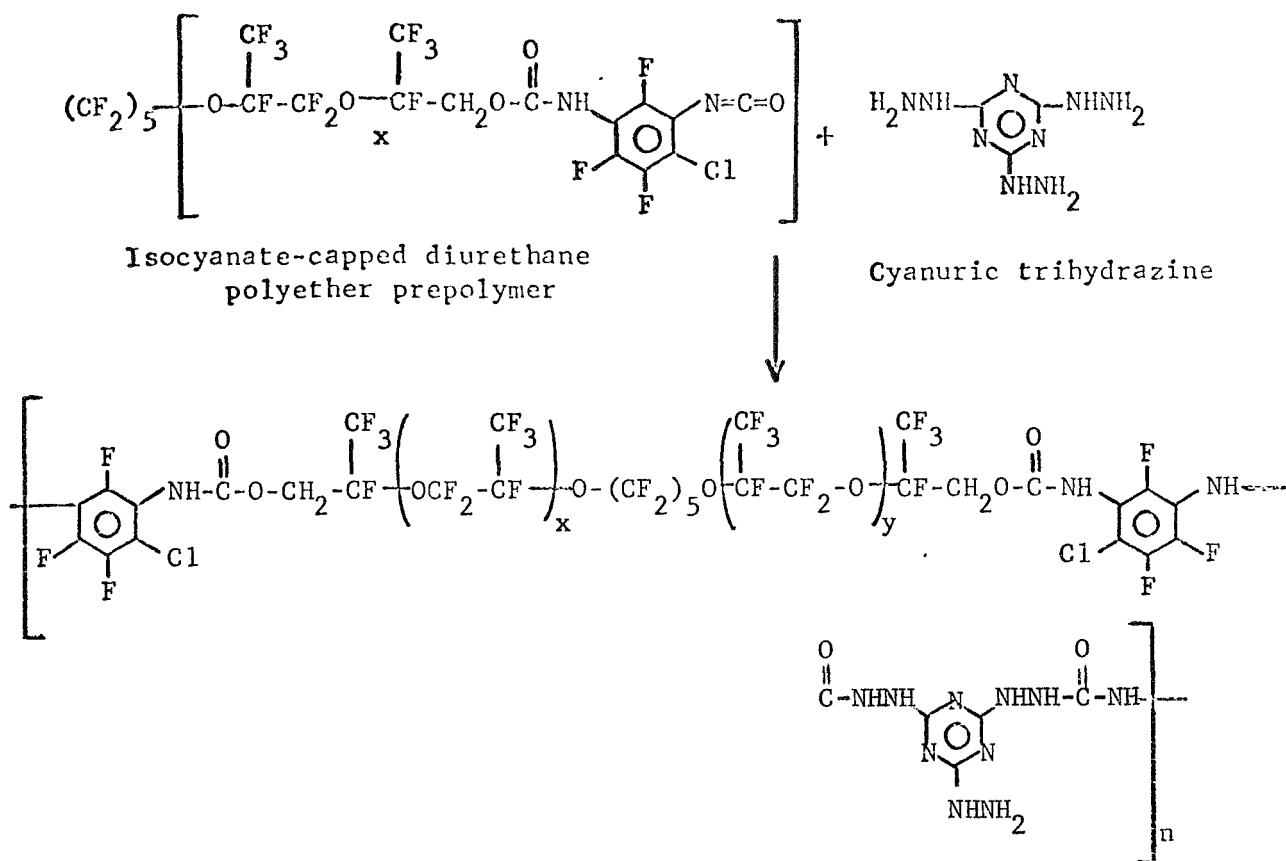
Subsequent reaction with parent isocyanate-capped polyether did not produce a curable elastomer. The product was a viscous, highly tacky mass. The re-capping reaction was not further investigated since a solvent for the cyanuric trihydrazine could not be found.

A superior "H"-type of cyanuric-semicarbazide-extended elastomer XVI was prepared by reacting the isocyanate-terminated pre-

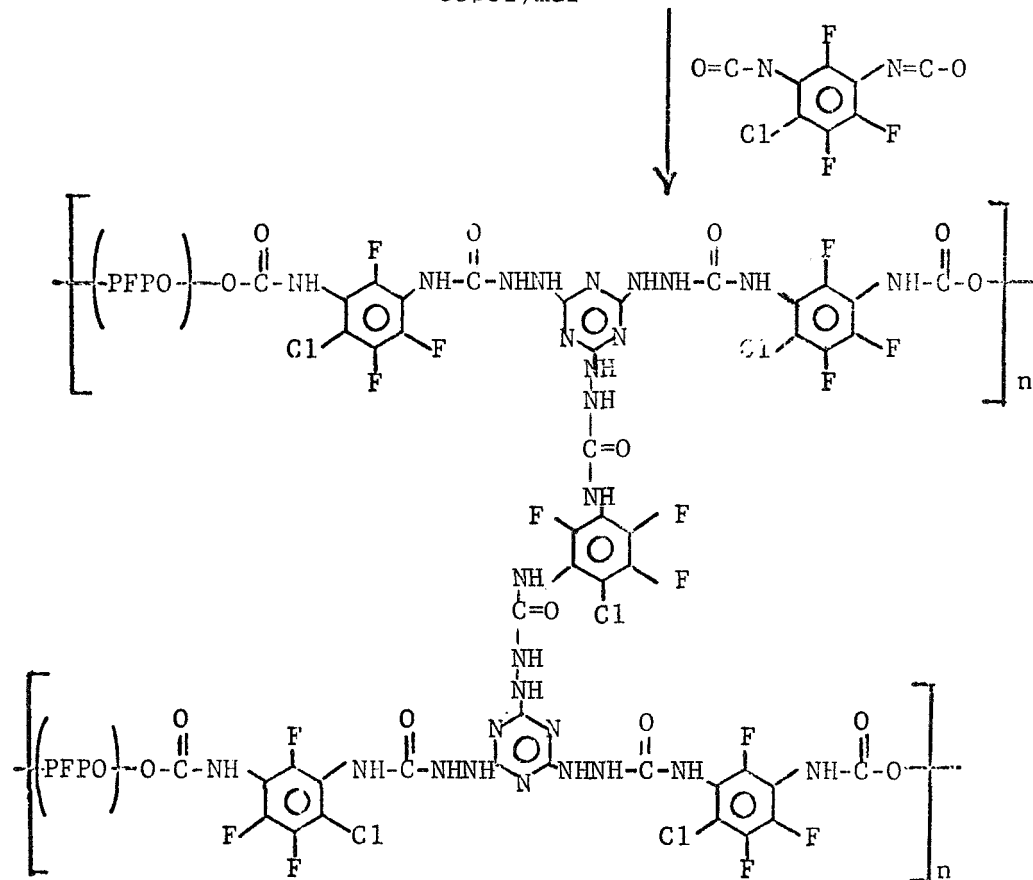
polymer with a molar equivalent of cyanuric trihydrazine with cure of the linear, extended polymer XV through chlorotrifluoro-m-phenylene diisocyanate. The cure cycle at 250°F in a press was estimated to be of the order of five minutes. The product, represented by XVI was tough, but quite flexible at room temperature. It was completely nonflammable in ca. 100% oxygen, but was inflexible at cryogenic temperature.

In our studied opinion, XVI represents the most significant structural elastomer prepared in this triazine series. Further co-extension, as effected with the melamine-extended structures above, should enhance the possibility of promoting low-temperature flexibility.

The very intriguing modification of the melamine extension-cyanurate urea crosslink, obtained by replacing melamine with cyanuric trihydrazine in the extension reaction, has been further investigated. The reaction of cyanuric trihydrazine with the isocyanate-capped diurethane prepolymer in a 2:3 stoichiometry (self-crosslinking) was repeated, with rubber mill-homogenization to prepare the polyether-cyanurate-semicarbazide extended/crosslinked system on a larger scale. The elastomer film has been prepared in two ways: 1) unsupported, and, 2) with a Teflon-coated glass fabric reinforcement. The incorporation of the Teflon-coated porous 112 glass fabric was aimed at improving tear strength while providing unusual flexibility due to the composite-type sandwich structure. Very rapid curing was obtained. This rapid cure produced an elastomeric structure, but did not permit efficient flowing of the prepolymer through the glass fabric. The result was two distinct elastomeric films without adhesion to the glass filler.



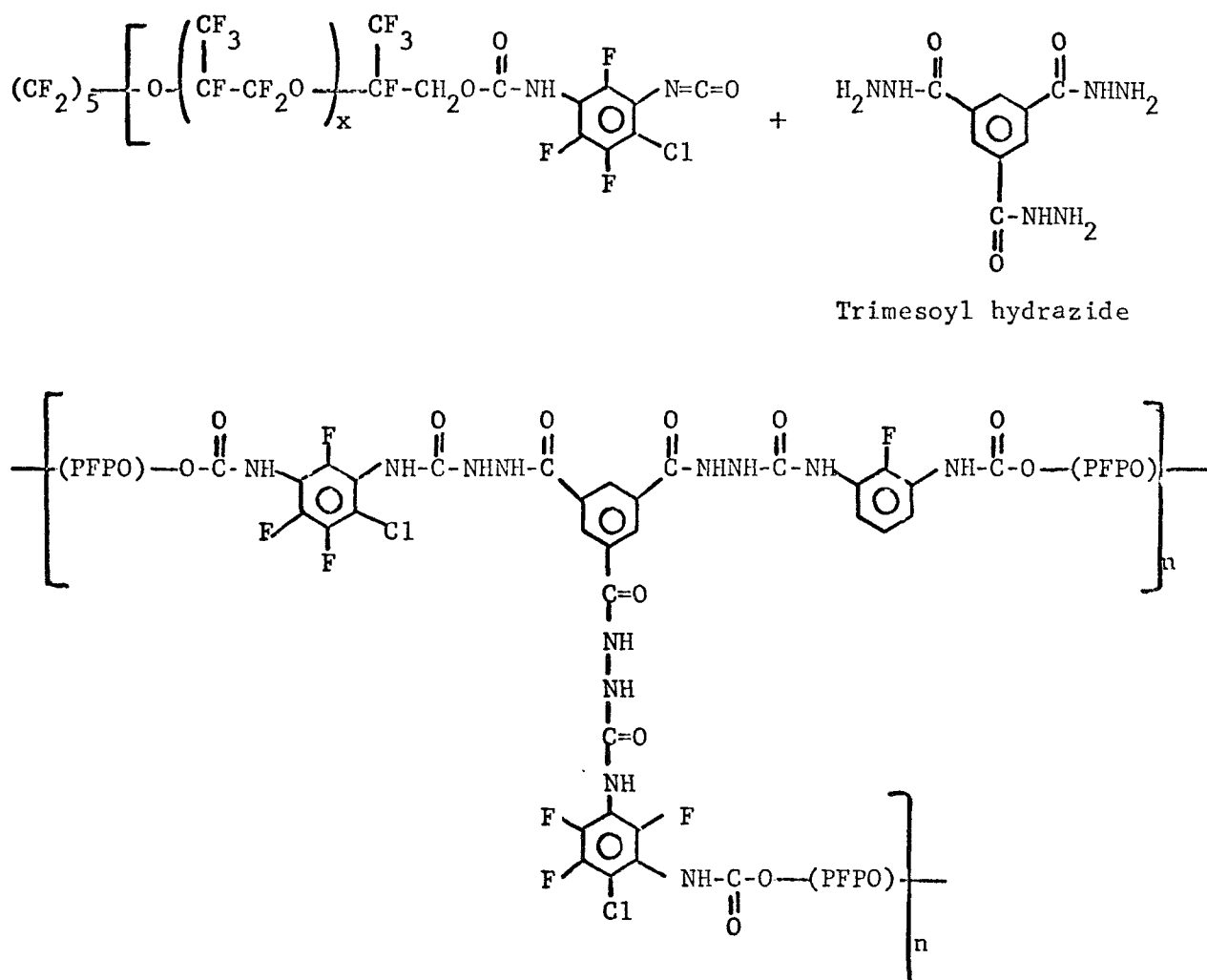
XV. Cyanurate-extended perfluoropolypropylene oxide-urethane-semicarbazide copolymer



XVI. Isocyanate-cured semicarbazide-cured urea-crosslinked perfluoropolypropyleneoxide-urethane

g. Nonheterocyclic, Trimesoyl Hydrazide Analogue of  $\gamma$ -Cyanurate Semicarbazide Self-Curing Elastomer.

An analogous aromatic triacylsemicarbazide was prepared from trimesoyl hydrazide and isocyanate-capped polyether. The product of the self-crosslinking reaction XVII was reasonably tough and elastomeric and cryogenically stable after press curing. However, it did readily burn in 100% oxygen at low pressure. The flammability of this system, XVII, in the face of the complete lack of flammability of the analogous (aromatic C-H free) cyanuric semicarbazide structure XIV, indicates that aromatic C-H bonds probably cannot be tolerated in polymer systems for use with cryogenic oxidizers.



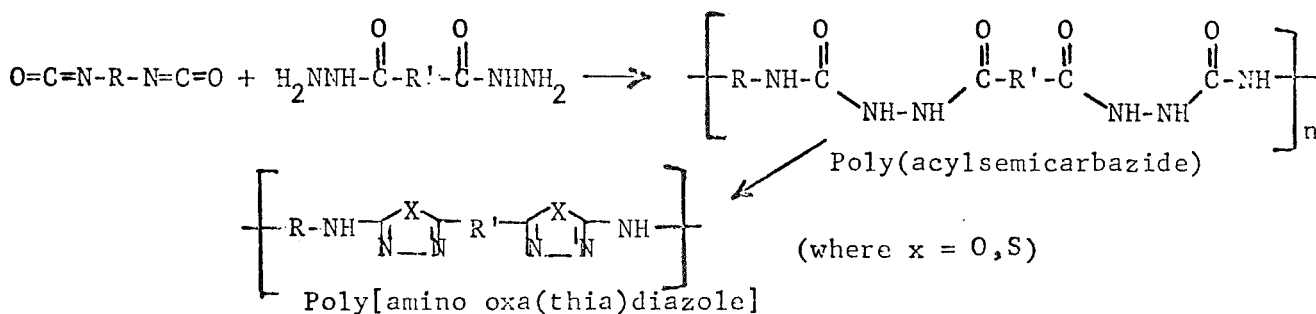
XVII. Trimesoyl semicarbazide-extended, trimesoyl semicarbazide crosslinked poly(perfluoropropylene oxide) bisurethane

### 3. Five-Membered Heterocyclic Extensions and Their Open-Chain Analogues

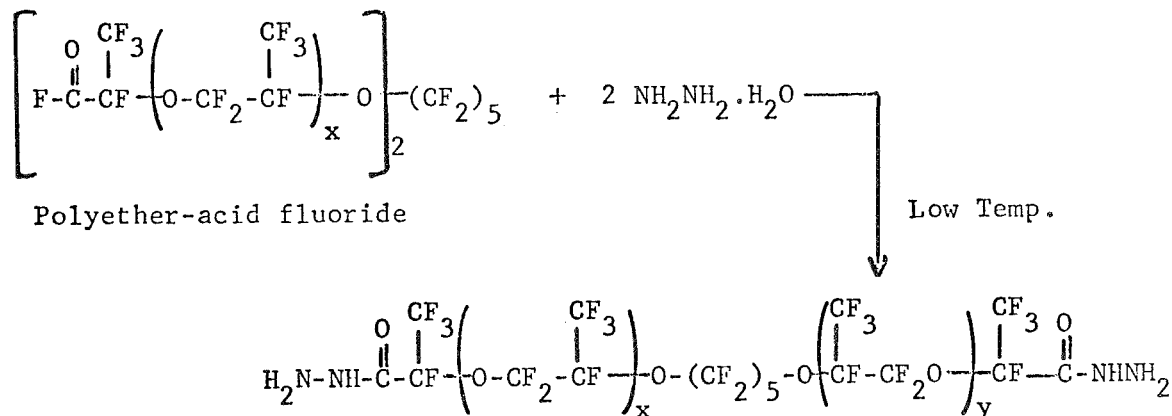
As shown in Figure 2, Type II, several different types of five-membered heterocyclic ring extensions were introduced into the perfluoropolyether prepolymers, by means of thermal (or catalytic) cyclization of open-chain semicarbazides (and thiosemicarbazides) and hydrazides (and oxathiahydrazides). These various extensions are discussed in the following sections.

#### a. Semicarbazide-Polyether Systems and Their Heterocyclic Derivatives

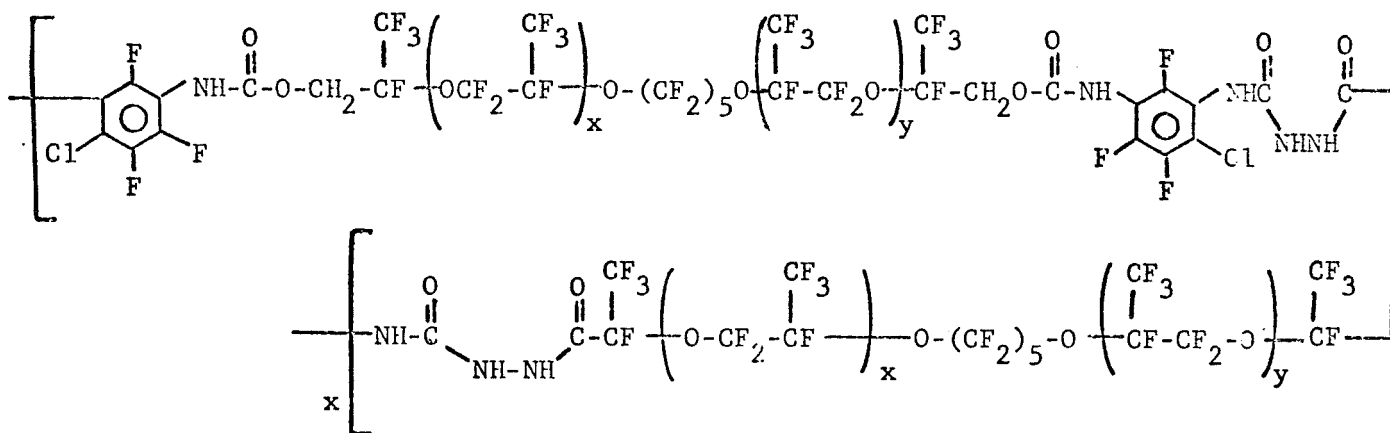
A different approach to a cryogenic-flexible fluorinated heterocyclic system, namely heterocyclic derivatives of acylsemicarbazide systems, has recently shown great promise, although in an unexpected manner. Based on the known reaction of diisocyanates with dihydrazides to produce poly(acylsemicarbazides), we have been synthesizing the corresponding amino-oxadiazoles and amino-thiadiazoles from the semicarbazides by thermal cyclization.



Toward this end, a new, hydrazide-terminated polyether XVIII was prepared from the reaction of the polyether acid fluoride, from perfluoropropylene oxide and perfluoroglutaryl fluoride, with hydrazine hydrate,



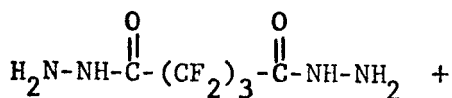
Structure XVIII has, in turn, been reacted with isocyanate-terminated prepolymer III, to produce the most-extended poly(acylsemicarbazide) to date, namely XIX.



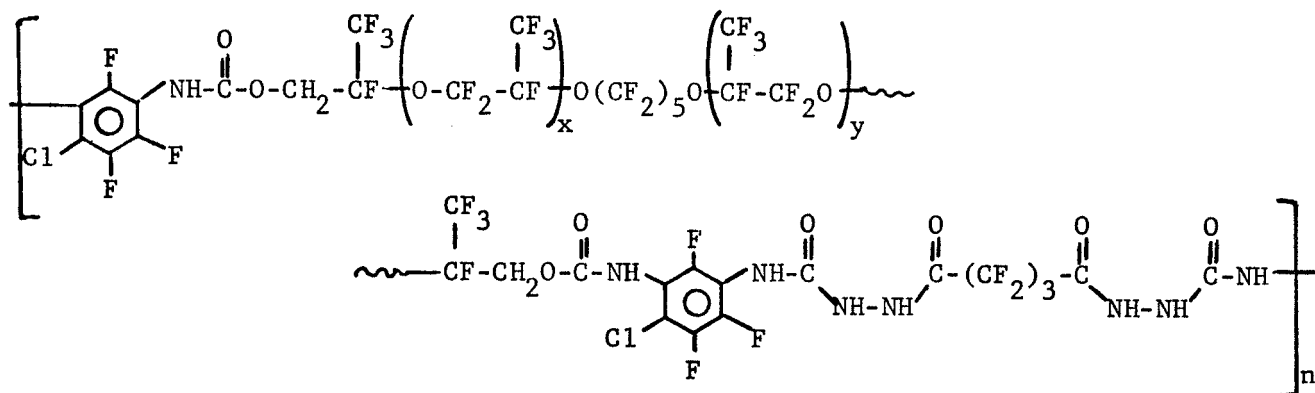
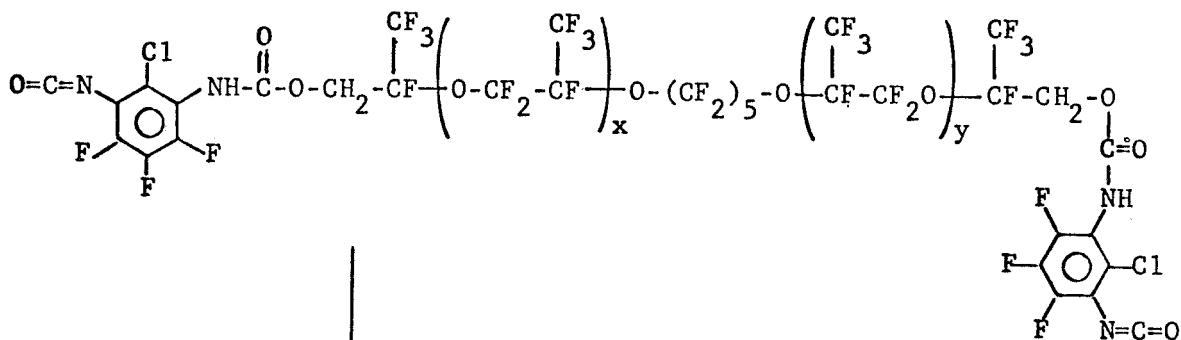
XIX. Perfluoropolyether-urethane-Polyether acylsemicarbazide

This material was thermally-cured, with chlorotrifluoro-m-phenylene diisocyanate crosslinking to a biuret system, and pressed into a film, which was transparent and highly-elastomeric. Although XIX was cryogenically-inflexible, it appears to have the lowest  $T_g$  of any system prepared thus far (thermomechanical measurements are discussed below).

In a related, but less extended system, the perfluoropolyether-perfluoroglutaryl semicarbazide prepolymer XX has been prepared as a low-melting elastomeric solid (PMT  $\sim 80^\circ\text{C}$ ). One preparation had  $\eta_{inh} = 0.07$  (DMAC). This extended system was prepared by reaction of the newly-synthesized perfluoroglutaryl hydrazide XXI and the isocyanate-capped polyether IV.



XXI. Perfluoroglutaryl hydrazide

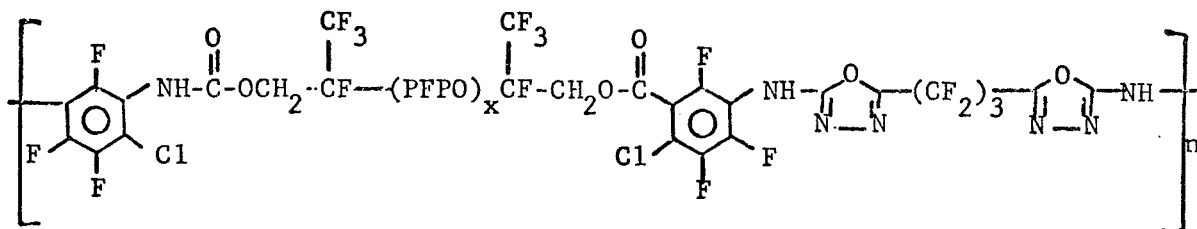


XX. Polyether urethane-perfluoroglutaryl semicarbazide

An attempt to cure this open-chain structure with chloro-trifluoro-m-phenylene diisocyanate produced a sticky amorphous material. Postcuring failed to improve the physical properties.

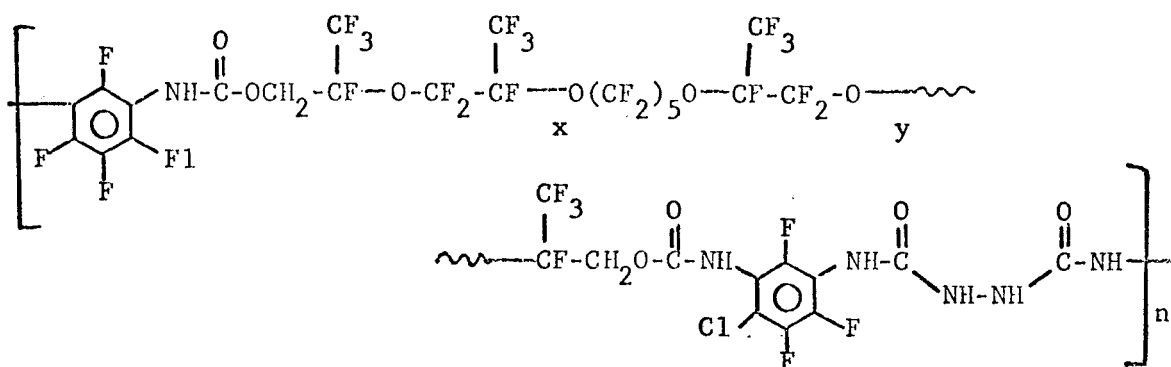
Thermal cyclization of XX to the amino-oxadiazole structure XXII, followed by diisocyanate (biuret) crosslinking produced a brittle film with very low strength.



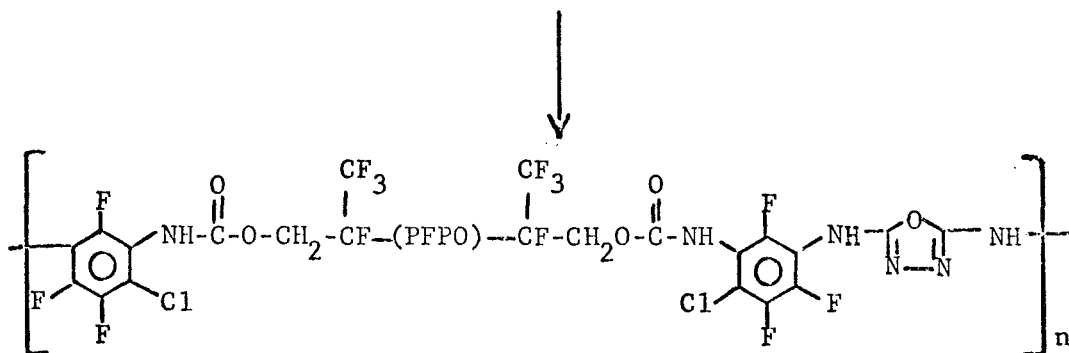


XXII. Polyether-urethane-perfluoropropylene-diamino-(bis-1,3,4-oxadiazole)

A similarly brittle, weak film resulted when the perfluoropolyether-biurea XXIII, prepared from the diisocyanate prepolymer and anhydrous hydrazine was thermally cyclized to the diamino-oxadiazole XXIV and cured as above.



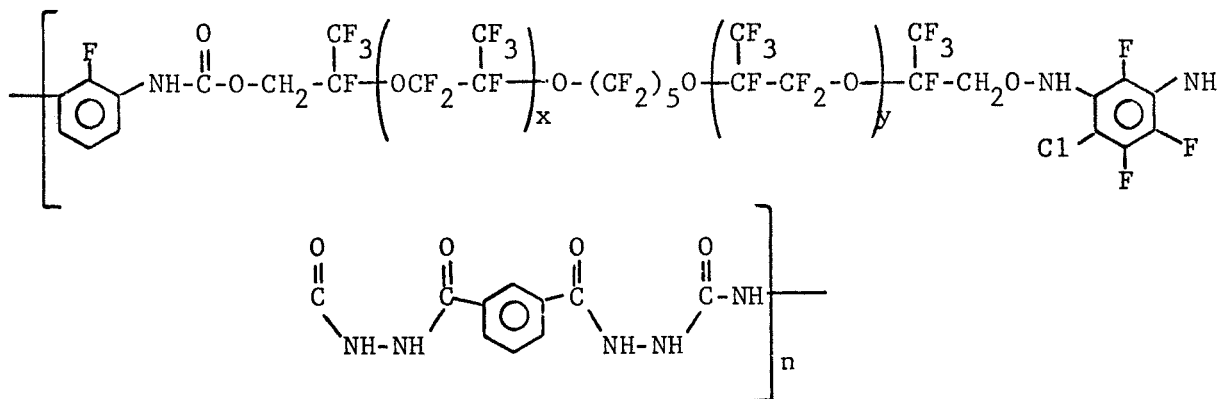
XXIII. Perfluoropolyether-urethane-biurea



XXIV. Perfluoropolyether-urethane-diamino-1,3,4-oxadiazole

It must be noted in both cases, that some degradation and/or incomplete cyclization may have competed with the desired curing reaction. Owing to the physical nature of the products, a "clean" curing reaction is not indicated.

Similarly, reaction of the isocyanate-terminated prepolymer with isophthaloyl hydrazide produced a non-elastomeric extended polymer XXV, with a PMT of 250°C.

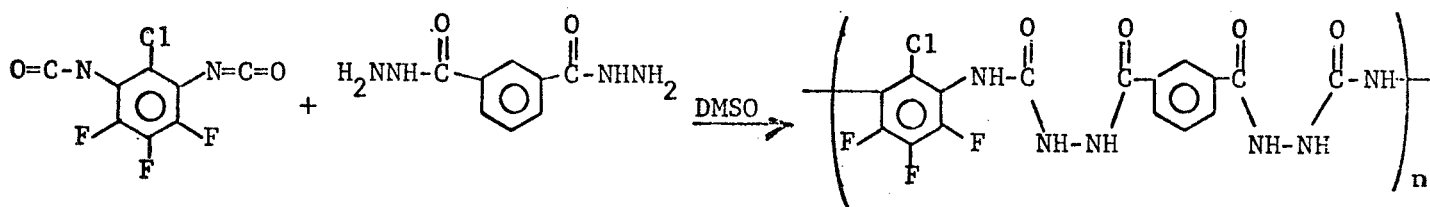


XXV. Isophthaloyl hydrazide-extend perfluoropolyether, PMT - 250°C

The determination of inherent viscosity on these polymers has been hampered in most cases by a lack of solubility in suitable polar aprotic solvents.

The polymerizations have been most satisfactorily carried out by utilizing low temperatures (-20° to -50°) for initial reaction, followed by gradual warming and ultimate heating to 85°-90°C. Prior to complete drying, the products are extremely tacky, suggesting adhesive possibilities. Films can be cast initially from the reaction medium, DMAC, and air dried. Once isolated and dried, these polymers generally cannot be re-dissolved, although they are apparently plasticized by DMAC and by DMSO.

Simple, partially-fluorinated model polymer systems were prepared, based on a wealth of background<sup>7-20</sup> for applicability to these systems. The simple polysemicarbazide was prepared by reaction of chlorotrifluoro-*m*-phenylene diisocyanate with isophthaloyl hydrazide in DMSO.

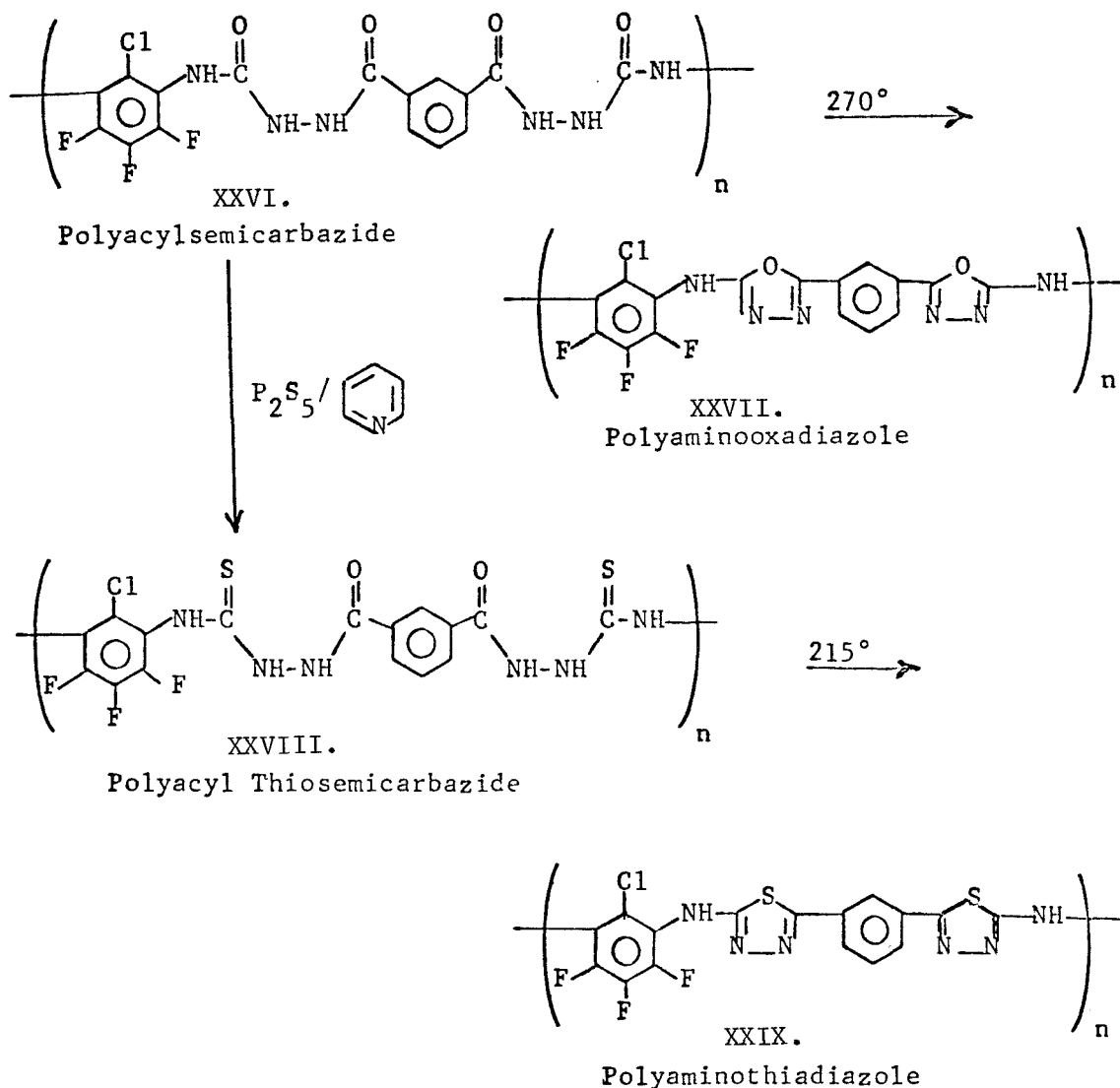


XXVI. Poly-semicarbazide

The soluble polymer,  $\eta_{\text{inh}} = 0.25$  (DMSO) produced clear, flexible, self-supporting films from this solvent. The subsequent sulfurization and thermal cyclization to amino-1,3,4-oxadiazole- and to amino-1,3,4-thiadiazole-systems is shown in Figure 4.

Figure 4

Polyacylsemicarbazide Sulfurization and Thermal Cyclizations

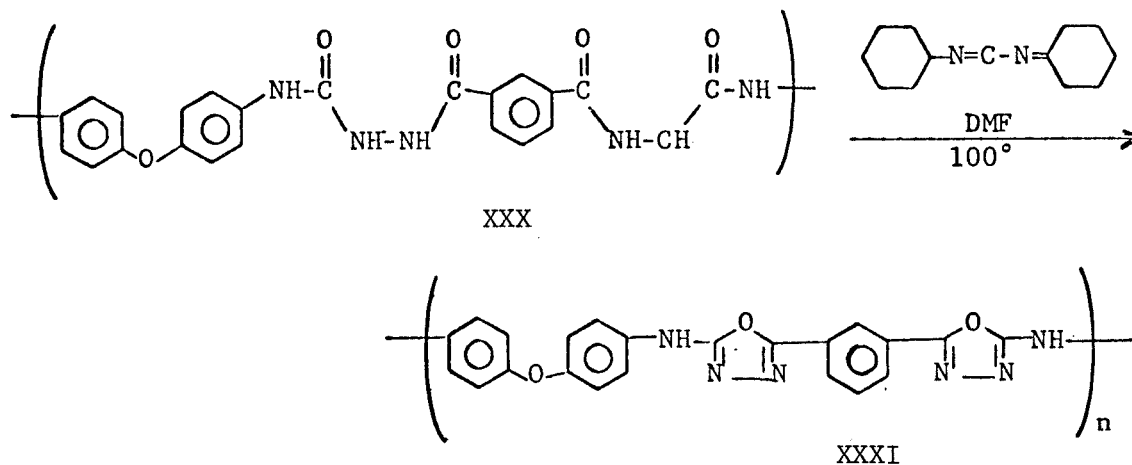


Prolonged heating of XXVI at 270°C under vacuum produced a beige powder with properties and spectra consistent with the desired poly(amino-1,3,4-oxadiazole) structure XXVII. Although the product is infusible, it still retains some solubility in DMAC. However, films cast from this solvent were not self-supporting.

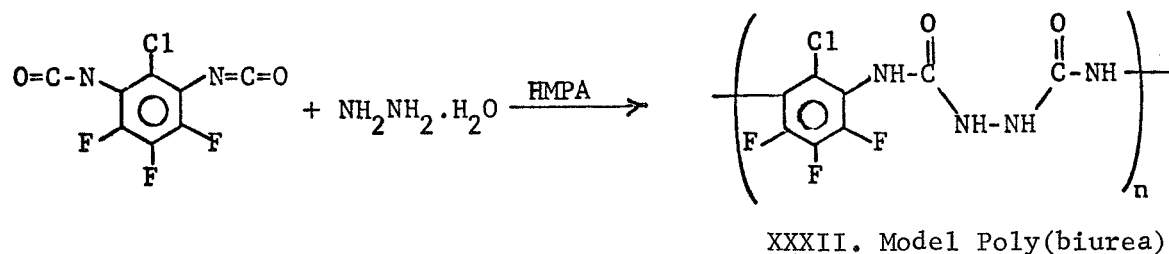
The poly(acylsemicarbazide) XXVI undergoes facile sulfurization to an acyl thiosemicarbazide XXVIII structure upon reaction with  $P_2S_5$ /pyridine. The reaction product is soluble in pyridine, DMSO and DMAC. Inherent viscosities indicate that the sulfurization has been effected without significant degradation. As anticipated, the thermal

cyclization of XXVIII occurs readily at 215°C, which is below the polymer melt temperature. The product appears to be the poly(amino-1,3,4-thiadiazole) XXIX. Unlike the oxygen analogue, XXVII, the aminothiadiazole is fusible, and somewhat soluble in DMSO. Film casting of XXIX from the melt (PMT 280°C was carried out but the molecular weight was insufficient for self-support. Films of precursor XXVIII were transparent, but extremely fragile, at  $\eta_{inh} = 0.2$  (DMSO).

Chemical dehydration has been at least partially successful in a pilot experiment on a nonfluorinated poly(semicarbazide) XXX of higher molecular weight,  $\eta_{inh}=0.5$  (DMSO). Treatment of XXX with di-cyclohexyl carbodi-imide in DMF at 100°C gave a product of much diminished carbonyl content in the infrared, which appears to be largely the expected amino-oxadiazole. Whereas films of precursor XXX are strong and transparent, films of XXXI are not self-supporting. This method of conversion was not generally applied to the fluorinated system, because of separation difficulties with the products.

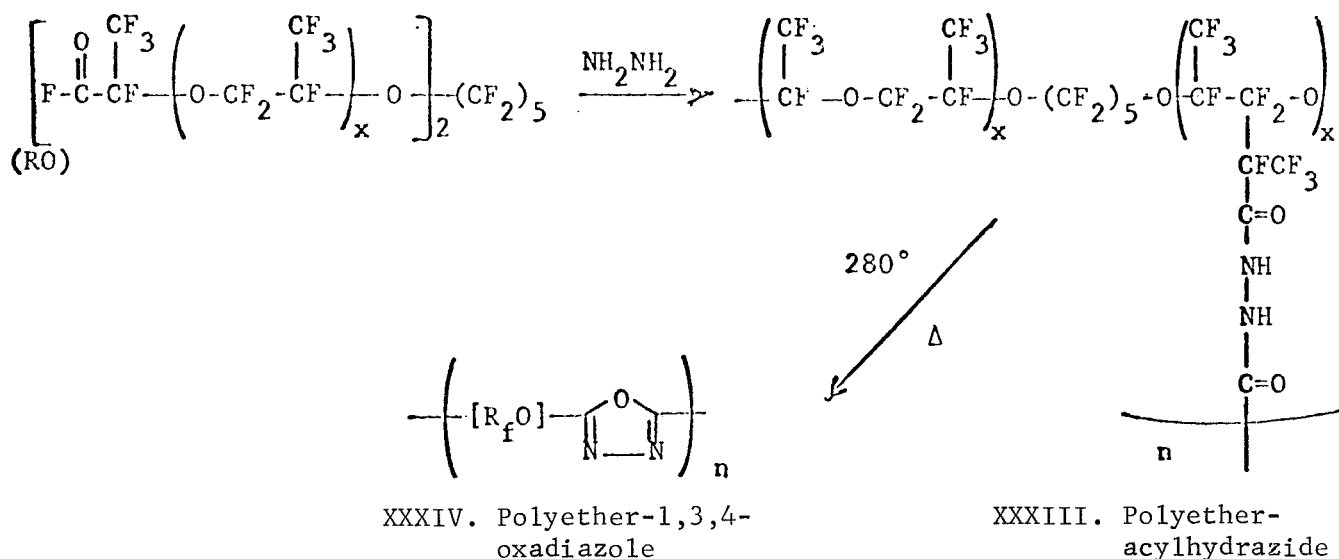


The parent poly(biurea) model XXXII was prepared by low-temperature solution polymerization in hexamethylphosphoramide. As expected, it also showed no elastomeric properties, but was obtained as a granular solid, PMT-248°C,  $\eta_{inh}=1.1$  (DMSO).

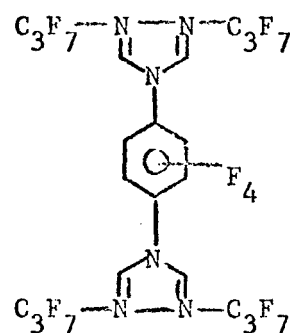
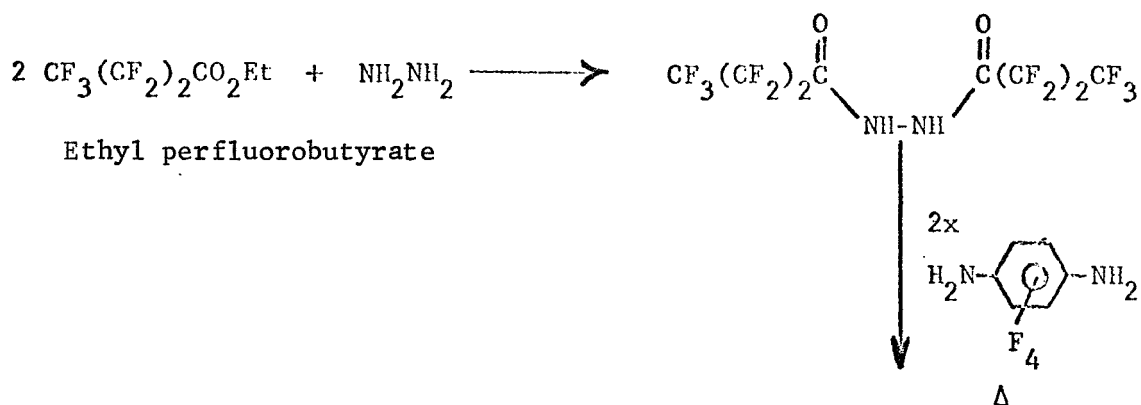


b. N-Aminotriazole Extensions and Cure Studies

An alternate heterocyclic system of great interest, for the attainment of an elastomer with cryogenic flexibility, because of structural inertness and of feasibility of synthesis from open chain polyhydrazide precursors, is the N-aminotriazole cycle. It is known that the thermal reaction of a preformed polyhydrazide with an aromatic amine (or hydrazine, under pressure) produces the stable N-aminotriazole system.<sup>16,17</sup> It was our intent to prepare a partially-cyclized polyoxadiazole or polythiadiazole. This partially cyclized structure could then be reacted with a diamine, through its precursor hydrazide residues to provide an inert crosslink, hydrogen-free (or essentially so), during a thermal cure. The scheme for the chain extension has already been developed above, as well as the thermal cyclization to oxadiazole and thiadiazole. In order to ascertain the mode of cyclization with a weakly basic perfluorinated diamine, a single model compound reaction was run along with the reaction on perfluorinated polyether with polyhydrazide extension.

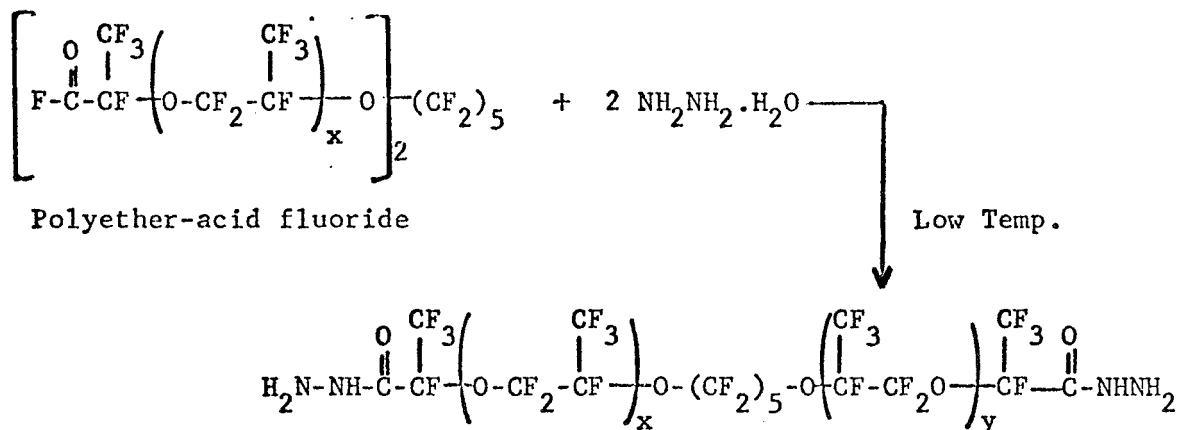


Difficulty was encountered in achieving reaction between the model bis-hydrazide and the sublimable tetrafluoro-p-phenylenediamine. A reaction product was, however, eventually obtained, with consumption of diamine. This product was identified as a partially-cyclized polyhydrazide. The desired model crosslink XXXV is shown below.



XXXV. Model Perfluorinated N-aminotriazole Crosslinked System

The hydrazide precursor polymer XXXVI was prepared by condensation of both acid-fluoride terminated poly(perfluoropropylene oxide), and its derived diester, with the corresponding derived acyl hydrazide terminated polyether:

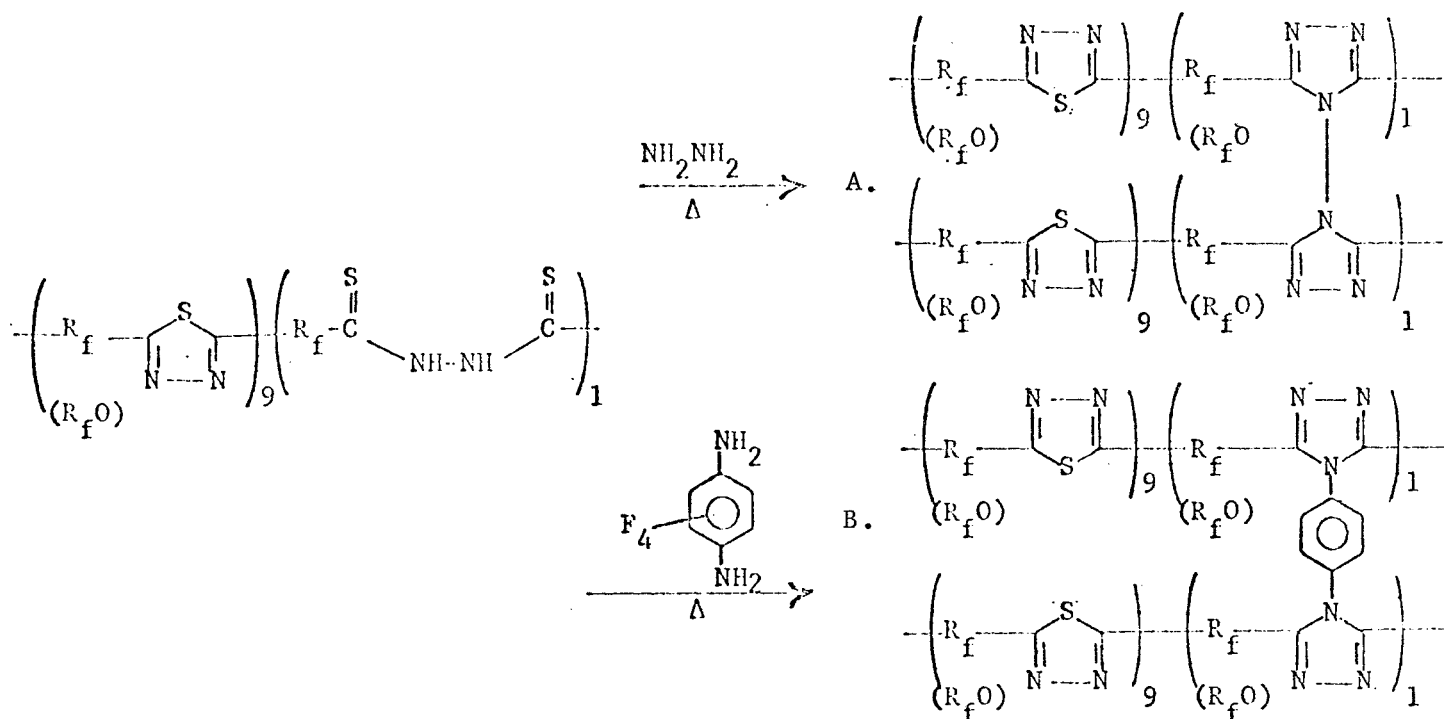
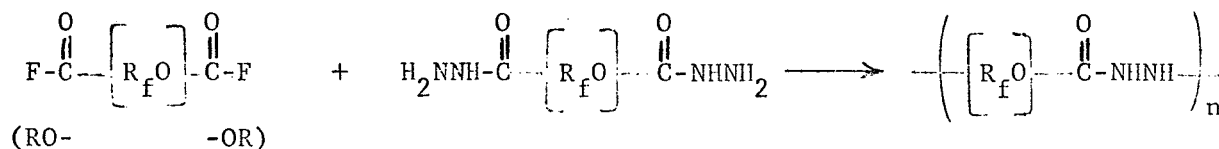


XVIII. Hydrazide-terminated perfluoropolyether

The overall scheme for formation of an N-aminotriazole crosslink formation is shown in Figure 5.

Figure 5.

N-Aminotriazole Crosslink Formation



XXXVI. N-aminotriazole Crosslink

As the first of a series of cyclization-crosslink reactions of the polyhydrazide and its derived structures (shown in the accompanying general equations), the amorphous polyhydrazide was reacted with tetrafluoro-p-phenylenediamine, using prepolymer techniques, in crosslinking stoichiometry. The resultant prepolymer was press-cured under several different thermal conditions. In no case was a "clean" cure effected, although there was definite evidence of reaction having taken place to form XXXVI.

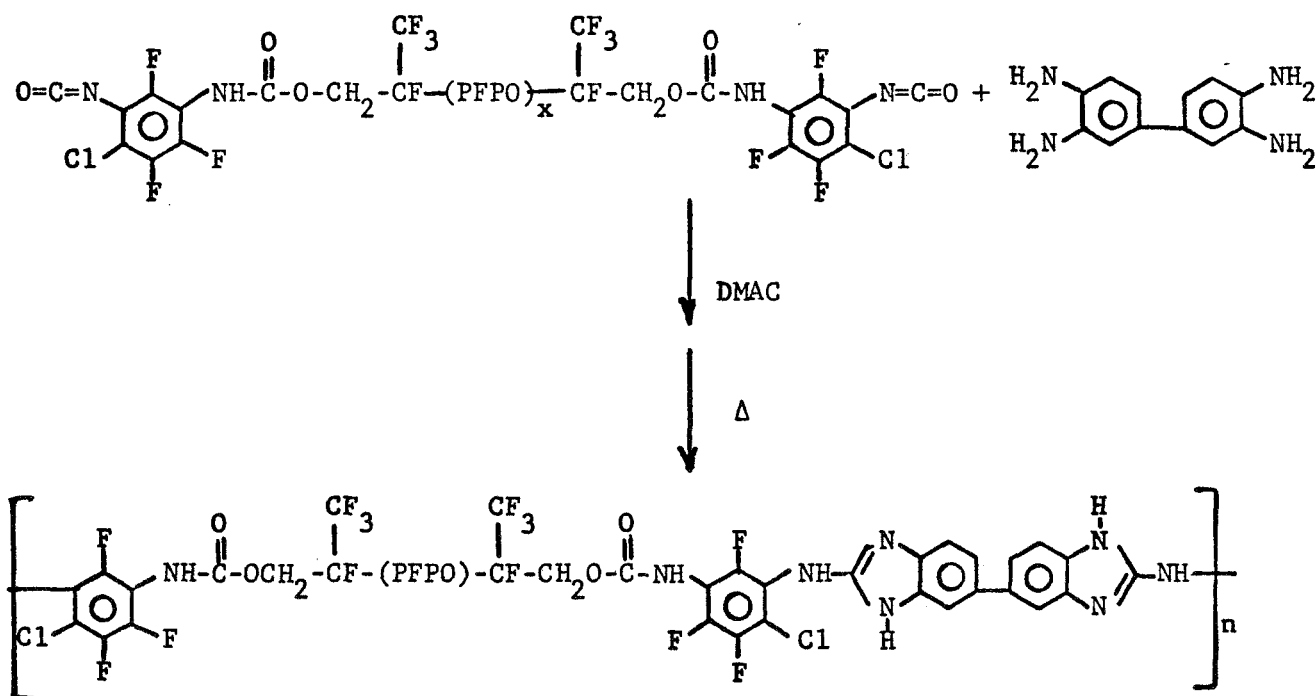
As a control, cure was effected on the polyhydrazide-diamine prepolymer mix (believed to be p-amino-N-acyltriazone, uncrosslinked) using chlorotrifluoro-m-phenylene diisocyanate. The cured film was weak and brittle, unlike the excellent elastomeric acylsemicarbazide films obtained from this system.

Because of the low order of nucleophilicity of the tetrafluoro aromatic amines, the cure was repeated with anhydrous hydrazine to generate the analogous N,N'-bis-triazole crosslinked (hydrogen-free) heterocyclic system through the highly reactive diamines. This reaction is also shown above. The product obtained was not, however, homogeneous. When drastic cure conditions were imposed, degradation also occurred, and the product did not appear to be at all cured. It is known<sup>17</sup> that N-aminotriazole (the precursor to the cured system) heterocycles are formed under pressure conditions analogous to our press cures. Both types of triazole systems should be inert and nonflammable, once their cyclization could be effected.

#### 4. Bis-Heterocyclic Extended Polyether Systems

##### a. Aminobenzimidazole-Extended Poly(perfluoropropylene oxide) Synthesis

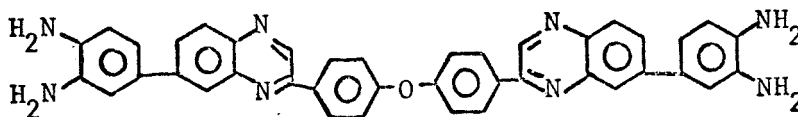
It has been found that the perfluoro-polyether diisocyanate reacts with diaminobenzidine to produce, after facile thermal cyclization, the bis(aminobenzimidazole) extended system XVI. This high-melting heterocyclic



XXXVII. Perfluoropolyether-urethane-di(aminobenzimidazole)



system was subjected to diisocyanate crosslinking (biuret) and pressed into a film. This film after 250° cure was quite brittle. A similar, more brittle product was obtained, when diaminobenzidine was replaced by XXXVIII in the above reaction.

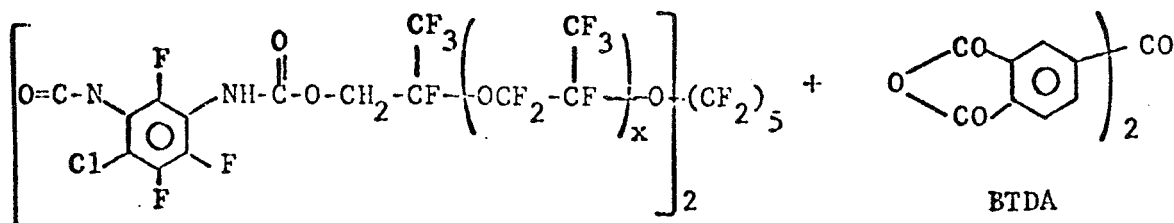


XXXVIII.

This system was not pursued further, because of the difficulty of obtaining fusability, and also because of the uncertainty of non-flammability to oxygen-enriched environments because of the aryl ring hydrogens.

#### b. Bis-Imide Extended Polyether Systems

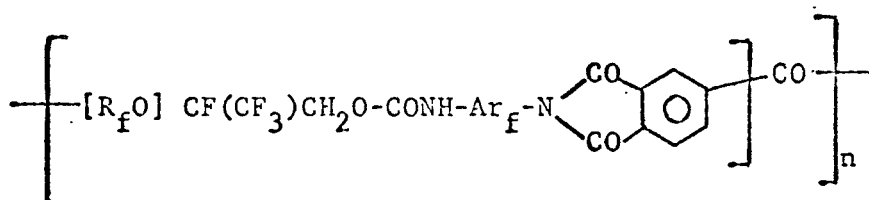
Toward the synthesis of an unusual heterocyclic-extended polyether system for cryogenic flexibility the polyimide synthesis of Meyers,<sup>22</sup> based on the reaction of a diisocyanate with a tetracarboxylic dianhydride, through the isolable intermediacy of a cyclic adduct, was applied to our isocyanate-capped poly(perfluoropropylene oxide)-bis-urethane prepolymer IV. Thus, reaction of IV with benzophenone-tetracarboxylic acid dianhydride, BTDA, was carried out, initially in THF. Gradual mutual dissolution occurred, accompanied by formation of a pale-green solution. The product isolated appeared to be a partially-cyclized precursor to the desired heterocyclic structure XXXVIII, isolated as a pliable, transparent film. This film was not rendered elastomeric by self-curing in a 250°F press (overnight heating). Repeat of the thermal press treatment in the presence of chlorotrifluoro-m-phenylene diisocyanate (to form allophanate crosslinks), did not produce a completely homogeneous product.



IV. Isocyanate-capped  
poly(perfluoropropylene oxide)  
bis-urethane

BTDA

THF  
-CO<sub>2</sub>  
Δ



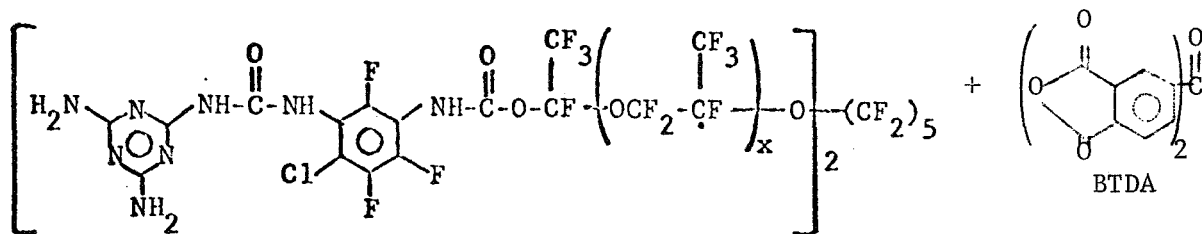
XXXVIII. Imide-extended perfluoropolypropylene-bis-urethane

The preparation of the imide-extended polymer XXXVIII was repeated in DMF, producing more rapid mutual dissolution. The reaction was allowed to proceed initially under autogeneous temperature development, followed by a warming treatment in solution at 80°C. Solvent removal under vacuum deposited an amber colored sticky film, whose infrared spectrum was inconclusive with respect to extent of imidization (broad carbonyl multiplet absorption from 5.5-6.2 μ). This product, apparently partially-cyclized to XXXVIII, was heated in a 250°F press as above. It was not found to be self-curing under this treatment.

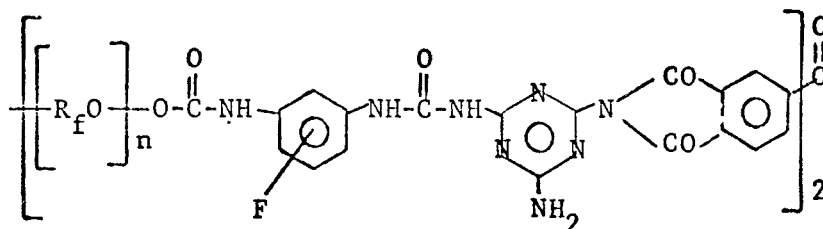
The allophanate-cure sequence using chlorotrifluoro-m-phenylene diisocyanate in a 250°F press overnight produced some evidence of elastomeric properties. The product, however, was still highly tacky and imperfect. This indicates complication due to evolved water of cyclization.

This reaction should be repeated with additional heating time applied prior to introduction of the diisocyanate curing agent. This repeat was not, however, possible on this program.

In a modification of the above chemistry, a hybrid cyanurate-imide system can be considered. Thus it is contemplated that reaction of the melamine-recapped polyether prepolymer with a dianhydride such as BTDA should produce a novel heterocyclic-extended structure, namely the melamine-imide, XXXIX, after thermal cyclization:



X. Melamine-capped prepolymer



XXXIX. Melamine-Imide Extended Polyether

Structure XXXIX should offer the potential of stable cyanurate urea crosslink formation through the pendant amino group. This "clean" cure mechanism, since: 1) it does not involve water of cyclization, and 2) it has been successful in previous heterocycle synthesis on this program, may produce a useful flexible elastomer. This study will be reserved for future work in this area.

### C. Thermomechanical Analysis of Heterocyclic-Extended Polyether Films

In order to ascertain the effect of degree of polymer extension at low crosslink density with depression of glass-transition temperature (or other plastic transition), thermomechanical analysis of the heterocyclic-extended polyether film samples, supplied to the Jet Propulsion Laboratory, was carried out, using the DuPont Model 941 thermomechanical analyzer equipped with a penetration probe. The results correlate very well with the degree of extension. The more extended structures, with a low ring multiplicity in the region of the crosslink, especially at low crosslink density, produced the most marked depression in  $T_g$ . As stated above, the highly-extended acylsemicarbazide structure has given the lowest value to date. These results are summarized in Table II.

TABLE II

## THERMOMECHANICAL ANALYSIS OF HETEROCYCLIC-EXTENDED POLYETHER FILMS

<u>Notebook Code</u>	<u>Report Structure Reference</u>	<u>Film Code</u>	<u>Description and Cure</u>	<u>Penetration Transition Temp (T<sub>g</sub>) (°C)</u>
1) WPF-182-75F	XI	Fluoromel-312	Urethane-Cyanurate Co-Extended	-60°
2) WPF-182-72F	IX	Fluoromel-230	Y-Cure	-75°
3) WPF-182-86F	XVII	PFPO-TMS	Trimesoyl Hydrazide Modification	-25°
4) WPF-182-84F	XIII	PFPO-CTS	Cyanuric Trihydrazine Modification	-30°, -80°
5) WPF-182-71F	XII	Fluoromel-211	Urethane-Cyanurate Co-Extended	-70°
6) WPF-182-67F	VIII	Fluoromel-110	Melamine Extended-H-Cure	-27°
7) WPF-182-70F	XII	Fluoromel M-211	Co-Extended System	-10°, -65°
8) WPF-182-80F	XIX	PFPO-PFPOS	Acylsemicarbazide Copolymer	-18°, -98°
9) WPF-182-REF	VI	PFPO-U	Allophanate-Cured Polyurethane	-25°
10) WPF-182-94F	XIII	PFPO-CTS	Y-Cured Cyanuric Trihydrazine Extended	-35°, -75°
11) WPF182-95F	XV	PFPO-CTS-H	H-Cured Cyanuric Trihydrazine Extended	-30°

## SECTION IV

### RECOMMENDATIONS FOR FUTURE RESEARCH

Highly promising results have already been obtained toward novel imide extensions on perfluorinated ether systems. This type of co-extension can be via the diisocyanate-dianhydride route (similar to P13-N) or via the melamine-amine functionality. These systems offer superior cure mechanisms, and offer great potential as nonflammable (O<sub>2</sub>) elastomer systems for a variety of aerospace applications. We would propose to explore these systems, as well as derived and related systems, to further exploit the area of superior low-temperature elastomers.

We also propose to exploit the ultra-low temperature capability of the more highly extended systems, constructed by extension reaction of two dissimilarly-terminated polymer systems (e.g., perfluoropolyethers). This work would be an extension of the highly-promising acyl semicarbazide extended polyether system which provided the low T<sub>g</sub>. It is anticipated that such a system could easily provide superior elastomer performance at low- and high-temperatures, to CNR and other available systems.

As an extension of this research, curing of the above, and other promising systems (e.g., the cyanurate-urea-- and cyanurate semicarbazide-extended systems) with isocyanate-terminated polyethers, instead of the customary monomeric diisocyanate, will be studied. This crosslinking method should produce elongated "H"-type crosslinkages for higher degree of extension with improved tear strength in the transverse direction.

The extension of the polyether system through preformed heterocyclic linkages, by reaction with such monomers as diamino-1,3,4-oxadiazole and diamino-1,3,4-thiadiazole, will also be studied. This route to heterocyclic extension should produce "clean" cure, without the complications encountered with the previous methods used. Such systems should also display greater flexibility, especially when cure is effected as described in the preceding paragraph.

Further attempts at increasing flexibility and also tear strength, by inclusion of glass-fabric reinforcement into the elastomer film, will also be studied. This approach holds great promise of improving low-temperature performance, if a slow-curing system can be utilized.

## SECTION V

### EXPERIMENTAL

#### General Remarks

All melting points and PMT-values are uncorrected. Infrared spectra were recorded on a Beckman IR10 Infrared Spectrophotometer, a grating instrument. Thermogravimetric differential scanning calorimetric and thermomechanical measurements were made on a DuPont No. 900 Modular Thermal Analyzer. Structural references by roman numeral in the following sections refer to the corresponding structure in the foregoing text. Molecular weights cited are VPO-averages; the actual range has been narrowed as much as is feasible, with programmed VPC monitoring of distribution, (Hewlett-Packard Programmed Gas Chromatograph).

#### Preparation of Hydroxyl-Terminated Poly(perfluoropropylene oxide) II (Ref. FT-2119-24)

Glycol-terminated prepolymer II was prepared according to the published procedure,<sup>1</sup> from hexafluoropropylene oxide, (molecular weight range: 1800-1850 by VPO).

#### Chlorotrifluoro-m-phenylene Diisocyanate III

Diisocyanate III was purchased from Whittaker Corporation, Research & Development Division, Chemical Sales Department and used without further purification (Lot 17).

#### Preparation of Isocyanate-Capped Poly(perfluoropropylene oxide)bis-urethane IV, (Ref WPF-182-43, 51)

In a typical preparation, a mixture of 39 g (0.0215 mole) of II and 11.5 g (0.044 mole) of III were heated with stirring under nitrogen at 100°C for 4 hours, producing a viscous clear liquid. The reaction completeness was indicated by disappearance of -OH absorption at 2.85  $\mu$ , and appearance of a 4.4  $\mu$  (vis.) isocyanate band in the infrared spectrum. The product was cooled, sealed and stored in a dry box until needed. IV was conveniently handled at room temperature by cutting into small pieces with a rubber knife and weighing, all in the dry box.

#### Preparation and Curing of Melamine-Extended Poly(perfluoropropylene oxide) Urethane-Urea Copolymer VII and VIII (Ref. WPF-182-67)

An intimate mixture of 79 g (0.034 mole) of IV and 4.3 g (0.034 mole) of melamine was warmed to 70°-75°C with stirring to 30 minutes, then homogenized to an opaque tacky white mass on a rubber mill, then 8.5 g (0.034 mole) of III was milled into the prepolymer mass, and the resultant mix used to prepare tensile lap-shear specimens in a standard bonding fixture. Cure was effected at 250°F for 15 hours in an oven. The remainder of the prepolymer VII was pressed between two Teflon sheets

(20-mil shims) and press-cured at 250°F for 40 hours, producing a buff-colored, resilient film of VIII; PMT ~ 300°C (DSC) which was analyzed for oxygen-flammability and T<sub>g</sub> as discussed above (Code: Fluoromel-110).

Preparation of Melamine-Self-Extended, Self-Cured Poly(perfluoropropylene oxide)-Urea-Urethane; Y-Cure, IX (Ref. WPF-182-72)

A mixture of 35 g (0.0015 mole) of IV and 0.28 g (0.00225 mole) of melamine was homogenized, first under an infrared lamp, and finally in a rubber mill producing a pliable beige-colored mass. The product was then pressed between two Teflon sheets with 20-mil shims and press-cured at 260°-270°F for 20 hours. The opaque, tar elastomer IX, produced was quite flexible but had diminished tear strength. It was tested for non-flammability and glass transition temperature (Code: Fluoromel-230).

Preparation of Melamine-Capped Poly(perfluoropropylene oxide)bis-urethane X (Ref. WPF 182-69, -76)

To 10 g (0.005 mole) of IV dissolved in 500 ml absolute tetrahydrofuran with stirring under nitrogen was added 25 g (0.2 mole) of finely-divided melamine. The milky suspension was then heated, and stirred at reflux for 17 hours then filtered hot through sintered glass. Removal of the solvent from the filtrate under high vacuum and further drying of the glassy residue at 100°C under vacuum deposited a stable, transparent solid X, PMT-273°C (DSC), which was soluble in THF. An infrared spectrum of a neat film of X showed broad, strong -NH absorption at 2.8-3.2, and heterocyclic C=N bonding absorption at 6.2 μ, as well as very strong C-F bands from 7.0-9.0 μ. This re-capped prepolymer was also found to be soluble in Freon-113, but not in hexafluorobenzene. It was used as such in the following reactions.

Preparation of Melamine-Self-Extension, Self-Curing Poly(perfluoropropylene oxide)-Urea-Urethane IX as a Transparent Film (Ref. WPF-182-77)

A mixture of 4.0 g (0.0016 mole) of X and 7.5 g (0.0032 mole) of IV was warmed to ca. 80°C, then homogenized in a rubber mill to a pliable mass, which was pressed between two Teflon sheets with 10-mil shims and press-cured at 250°F for 24 hours. The transparent pale yellow film produced (coded: Fluoromel-M-230) was characterized as above. It had poor tear strength like its opaque counterpart, and was inflexible in liquid nitrogen.

Preparation of Cyanurate-Urea--Urethane (1:6) Co-extended Polyether XI  
Isocyanate Cure (Ref. WPF-182-7F)

A mixture of 7.5 g (0.003 mole) of IV and 3.6 g (0.002 mole) of II were warmed together with mixing to 100°C, before introduction of 0.13 g (0.001 mole) of melamine to the fluid mixture. The cohesive mass produced was stirred for 3 hours at 100°C, then homogenized in a rubber mill, before addition of 1.0 g (0.004 mole) of chlorotrifluoro-m-phenylene diisocyanate, and press-curing of the prepolymer at 250°F and 10,000 psi pressure, with 10-mil shims (Teflon sheets) for 16 hours. The product, XI, was obtained as an off-white, resilient elastomer with slightly improved tear strength as compared to the parent polyurethane. It was tested as above for flammability and cryogenic flexibility.

Preparation of Cyanurate-Urea--Urethane (1:3) Co-extended Polymer XII,  
Isocyanate-Cure (Ref. WPF-182-71)

A mixture of 39.5 g (0.017 mole) of IV, 1.17 g (0.0085 mole) of melamine and 15.3 g (0.0085 mole) of II were processed as in the preceding preparation, with 4.25 g (0.0017 mole) of III added to the prepolymer mass after rubber-mill homogenization. Press cure was effected, between Teflon sheets and 20-mil shims, at 250°F for 19 hours. The off-white opaque, resilient film of XII showed goo strength and flexibility. It was cryogenically-inflexible, and rapidly self-extinguishing in ca. 100% oxygen (Code: Fluoromel-211).

Preparation of Cyanuric Trihydrazine-Semicarbazide-Extended Poly(per-  
fluoropropylene Oxide); Y-Cure; XIII (Ref. WPF-182-84)

To 13 g (0.0057 mole) of IV was added 0.58 g of cyanuric trihydrazine (0.0038 mole) with manual stirring at 80°-85°C. The mixture was then homogenized in a rubber-mill and press-cured at 250°F between Teflon sheets with 20-mil shims and 800 psi pressure for 24 hours. A flexible film IV was obtained (flesh-colored) which was cryogenically inflexible in liquid nitrogen and completely nonflammable in ca. 100% oxygen (Code: Fluoromel-CTS).

Glass-Reinforced Fluoromel-CTS (XIII) Film Composite Preparation  
(Attempted) (Ref. WPF-182-95)

The preceding reaction was repeated, using 20 g (0.0088 mole) of IV and 1.02 g (0.0059 mole) of cyanuric trihydrazine. The homogenized extended polymer was pressed into a large thin film at 250°F (momentary contact in a press between Teflon sheets, then folded, then a sheet of Type 112 Teflon-coated glass fabric was "sandwiched" between the two leaves of the film. The composite sandwich was replaced in the 250°F press for 15 minutes at 10,000 psi. The cured film of XIII was found to have not substantially penetrated into the glass fabric, due to premature cure. Two discreet films were isolated.



Preparation of Cyanuric-Trihydrazine-Capped Poly(perfluoropropylene oxide)-bis-urethane XIV (Ref. WPF-182-88)

To a solution of 10 g (0.0043 mole) IV in 1200 ml of tetrahydrofuran with stirring was added 25 g (0.15 mole) of cyanuric trihydrazine. The heterogeneous reaction mixture was heated, and stirred at the reflux temperature for 22 hours under nitrogen. The reaction mixture was then filtered hot through sintered glass, and the filtrate combined with hot-THF washings of the filter cake. The solvent was removed under high vacuum to deposit a pasty, white semi-solid. This material resisted efforts at solidification by various trituration treatments, and it did not react to produce a curable system under analogous reaction conditions successful with the melamine-capped analogue. The purification was complicated by an almost total lack of solubility with cyanuric trihydrazine.

Preparation of Cyanuric Trihydrazine-Semicarbazide-Extended Poly(perfluoropropylene oxide); H-Cure, XVI (Ref. WPF-182-96)

A mixture of 23 g (0.01 mole) of IV and 1.7 g (0.01 mole) of cyanuric trihydrazine was mixed briefly at 100°C, then homogenized in a rubber mill. Then 2.5 g (0.01 mole) of III was added and the homogenized mass was press-cured at 250°F for 1 hour with 800 psi applied (20-mil shims between Teflon sheets). The cured, tan-colored elastomer XVI was strong and resilient, but inflexible in liquid nitrogen. It was completely nonflammable in ca. 100% oxygen (Code: Fluoromel-CTS-H).

Preparation of Self-Cured, Trimesoyl Hydrazide-Extended Poly(perfluoropropylene oxide), Y-Cure, XVII (Ref. WPF-182-86)

A mixture of 13 g (0.0056 mole) of IV and 0.93 g (0.0037 mole) of trimesoyl hydrazide was mixed at 80°C, then homogenized in a rubber mill before 22-hour press cure at 250°F, between Teflon sheets. The dark-tan elastomer obtained, XVII, was tough, but flexible. It was found to be inflexible in liquid nitrogen, and to be flammable in ca. 100% oxygen in laboratory testing.

Preparation of Acyl Hydrazide-Terminated Poly(perfluoropropylene oxide) XVIII (Ref. WPF-182-38, -39)

To 300 ml of stirred absolute methanol was added 95 g (ca. 0.1 mole) of I over 5 minutes, with a spontaneous exotherm to 45°C. Stirring was continued for 22 hours, and then the supernatant excess methanol was removed by decantation in a separatory funnel. The diethyl ester was shown to be free of unreacted acid fluoride by infrared spectral comparison. A 73-g (ca. 0.07 mole) sample of this intermediate was added dropwise over 10 minutes to a mixture of 25 g (0.5 mole) of hydrazine hydrate and 100 ml of ethanol. The cloudy reaction mixture was stirred without external heat for 20 hours. The viscous product XVIII, insoluble in the supernatant solution was isolated as above, washed several times with water, and vacuum-dried for a prolonged period. The infrared spectrum of the dried product was confirmatory.

Preparation of Highly Extended Perfluoropolyether-Urethane--Polyether Acylsemicarbazide Elastomer, XIX, Isocyanate-Cured (Ref. WPF-182-80)

To 3.0 g of XVIII (ca. 0.0027 mole) was added 6.2 g (0.0027 mole) of IV with stirring at 80°C. Then 0.5 g (0.002 mole) of III was added, and the mixture homogenized on a rubber mill, then press-cured, with 10-mil shims, between Teflon sheets at 250°F for 20 hours. An extremely flexible cured, transparent film of XIX was obtained, which was nonflammable in ca. 100% oxygen, but which was essentially nonflexible in liquid nitrogen (Code: PFPO-PFPOS).

Preparation of Polyether Urethane-Perfluoroglutaryl Semicarbazide-Extended System, XX, Isocyanate-Cure Attempt (Ref. WPF-182-34)

A mixture of 26 g (0.01 mole) of IV and 250 ml of anhydrous dimethylacetamide at -40°C (frozen) was treated dropwise over 1 hour with 4.4 g (0.016 mole) of perfluoroglutaryl hydrazide in 50 ml of DMAC. The reaction mixture was warmed, and stirred at room temperature for 64 hours, then at 50°C for 3 hours. The polymer XX was precipitated as an amorphous mass in excess water. The precipitated mass was isolated, washed with water, ethanol, then THF, and vacuum dried, to produce a glassy solid, PMT 80°C, insoluble in DMSO, DMF, pyridine, DMSO, diglyme, formic acid and sulfuric acid. It displayed slight solubility in DMAC, and had an  $\eta_{inh}$  of 0.07 in this solvent.

(Ref. WPF-182-83). A 12-g sample of XX and 1.0 g (0.004 mole) of III were mixed with warming and homogenized in a rubber mill, then press-cured for 24 hours at 250°F. The heterogeneous product showed some cured areas, but was largely a tacky, light brown colored mass. It is suspected that water from cyclization had largely precluded biuret-cure (Code: PFPO-PFGS).

Preparation and Cure of Biurea-Extended Poly(perfluoropropylene oxide)bis-Urethane, XXIII (Ref. WPF-182-30)

To 10 g (0.009 mole) of IV in 100 ml of anhydrous DMAC at -50°C was added 0.45 g (0.009 mole) of hydrazine hydrate in 50 ml of DMAC. The reaction mixture was warmed, and stirred at room temperature for 17 hours, then at 50°C for 3 hours. The polymer XXIII was isolated in a similar manner to that used in the preceding preparation, and dried, as a viscous liquid, whose infrared spectrum was confirmatory. It displayed general insolubility.

(Ref. WPF-182-82). A mixture of 12.0 g of XXIII and 1.0 g (0.004 mole) of III was homogenized in a rubber mill, then press-cured at 250°F for 24 hours. The resultant brown product showed brittle regions intermixed with tacky amorphous sections. Here again cure was complicated by water of thermal cyclization (Code: PFPO-BU).

Preparation of Isophthaloyl Hydrazide-Extended Poly(perfluoropropylene oxide) Semicarbazide System XXV (Ref. WPF-182-33)

To a frozen solution of 1.0 g (0.005 mole) of isophthaloyl hydrazide in 100 ml of hexamethylphosphoramide at -50°C was added all at once 11.0 g (0.005 mole) of IV and 25 ml of additional HMPA. The reaction mixture was warmed, and stirred at room temperature for 16 hours, then at 50°C for 4 hours. The polymeric product was isolated by precipitation as above and dried. The glassy solid product XXV, PMT-250°C (DSC), showed a general lack of solubility in dipolar aprotic solvents. No cure study was attempted (Code: PFPO-OIO-S).

Preparation of 4,4'-Isophthaloyl-1,1'-Chlorotrifluoro-m-phenylene Semicarbazide Model Polymer System XXVI

A charge of 10.0 g (0.04 mole) of III was added dropwise over 10 minutes to a solution of 7.8 g (0.04 mole) of isophthaloyl hydrazide in 120 ml of anhydrous dimethylsulfoxide cooled to 15°C with stirring, accompanied by spontaneous exothermicity to 50° (in ice bath). The reaction mixture was stirred at room temperature for 68 hours, then filtered to remove trace insolubles. Excellent, transparent, self-supporting films of XXVI could be cast directly from this viscous solution. The film spectrum was confirmatory, and the polymer had an  $\eta_{inh}$ -0.25 (DMSO) (Code ClTrFM-OIO-S).

Preparation of Poly(chlorotrifluoro-m-phenylene-biurea) XXXII (Ref. WPF-182-15)

To 2.0 g (0.04 mole) of hydrazine hydrate in 50 g of HMPA, cooled to -10°C with stirring was added dropwise over 30 minutes, 10.0 g (0.04 mole) of III, with slight exothermicity (30°C). The reaction mixture was stirred at room temperature for 18 hours, then at 75°-80°C for 2 hours. The polymer XXXII was precipitated, worked up and dried as above, and isolated as a glass-like solid, PMT-248°,  $\eta_{inh}$ -1.1 (DMSO). Its infrared spectrum was confirmatory (Code: ClTrFM-BU).

Preparation of N-Perfluoroarylene-Triazole Crosslinked Poly(perfluoropropylene oxide) Elastomer System XXXVI-B (Attempted) (Ref. WPF-182-99)

To 20 g of XVIII was added 1.05 g (0.0045 mole) of tetrafluoro-m-phenylenediamine with stirring, and the fluid product step-cured in a press between Teflon sheets through the following incremental stages: 20 hours at 200°F; 24 hours at 250°F; 48 hours at 350°F; and 22 hours at 400°F, with inspection between stages. The final product was a tacky brown film, indicating that thermal degradation has competed with cyclization to XXXVI-B.

Preparation of N,N'-Bis-aminotriazole-crosslinked Poly(perfluoropropylene oxide) Elastomer System XXXVI-A (Attempted) (Ref. WPF-182-99)

A mixture of 10.0 g of XVIII and 0.07 g (0.0025 mole) of anhydrous hydrazine was hand mixed to a viscous mass, which was then press-cured at 300°F under 800 psi between Teflon sheets for 30 hours. A dark amber amorphous product, with no elastomeric properties, was obtained, indicating that only partial cyclization to XXXVI-A had occurred in the face of competing degradation.

Preparation of Bis-aminobenzimidazole-Extended Poly(perfluoropropylene oxide) XXXVII, Biuret-Crosslinking (Ref. WPF-182-44, -59, -79)

A solution of 4.6 g (0.02 mole) of diaminobenzidine in 150 ml of anhydrous DMF was added to 46 g (0.02 mole) of IV, and the heterogeneous reaction mixture was stirred at room temperature for 64 hours, then at 90°C for 24 hours. The reaction mixture was then poured into water and the precipitated beige-colored polymer XXXVII was isolated and dried as above. This product, PST-260°C, PMT >320°C, and had  $\eta_{inh}$ -0.063 (part. insol. in H<sub>2</sub>SO<sub>4</sub>).

A 15-g sample of XXXVII was homogenized with 5.0 g (0.02 mole) of III in a rubber mill, then cold-pressed to 10,000 psi between Teflon sheets, then heated to 200°F and maintained at this temperature in the press for 62 hours. The cured light-brown film was quite brittle, and exhibited no elastomeric properties (Code: PFPO-ABI).

Preparation of Benzophenone Tetracarboxylic-bis-Imide--Extended Poly-(perfluoropropylene oxide)-bis-Urethane System XXXVIII, Attempted allophanate Cure (Ref. WPF-182-102, -103)

A mixture of 10 g (0.004 mole) of IV and 1.3 g (0.04 mole) of benzophenone-tetracarboxylic acid dianhydride were slowly dissolved in 150 ml of anhydrous THF with stirring for 48 hours. The solution was then stirred at reflux for 24 hours, accompanied by formation of a pale-green color. Removal of the solvent under vacuum deposited a pliable, transparent film of XXXVIII, with confirmatory spectral evidence for partial cyclization. Cure was effected by press-treatment of a mixture of 5.5 g of XXXVIII with 1.0 g (0.004 mole) of III at 250°F/800 psi between Teflon sheets for 20 hours. The product did show some cure regions, but the majority of the film was tacky. This indicates that crosslinking (allophanate) was largely obviated by the released water of cyclization (Code: PFPO-BI).

## SECTION VI

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APPENDIX I

HETEROCYCLIC-EXTENDED POLY(PERFLUOROPROPYLENE OXIDE)  
FILMS FORWARDED TO JET PROPULSION LABORATORY

a) Samples on NASW-1822 sent on Packing Slip 1869C, 8-28-69

<u>Notebook Code</u>	<u>Film Code</u>	<u>Description</u>
1) WPF-182-75F	Fluoromel-312	Urethane - Cyanurate Co-Extended
2) WPF-182-72F	Fluoromel-230	Y-Cure
3) WPF-182-86F	PFPO-TMS	Trimesoyl Hydrazide Modif.
4) WPF-182-84F	PFPO-CTS	Cyanuric Trihydrazine Modif.
5) WPF-182-71F	Fluoromel-211	Urethane-Cyanurate Co-Extended
6) WPF-182-67F	Fluoromel-110	Melamine Extended-H-Cure
7) WPF-182-70F	Fluoromel M -211	Co-Extended System
8) WPF-182-80F	PFPO-PFPOS	Acylsemicarbazide Copolymer

b) Samples on NASW-1822 sent on Packing Slip 2088C, 3-2-70

9) WPF-182-94F	PFPO-CTS	Y-Cured Cyanuric Trihydrazine-Extended
10) WPF-182-95F	PFPO-CTS-H	H-Cured Cyanuric Trihydrazine-Extended





APPENDIX II

DISTRIBUTION LIST FOR FINAL TECHNICAL REPORT

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