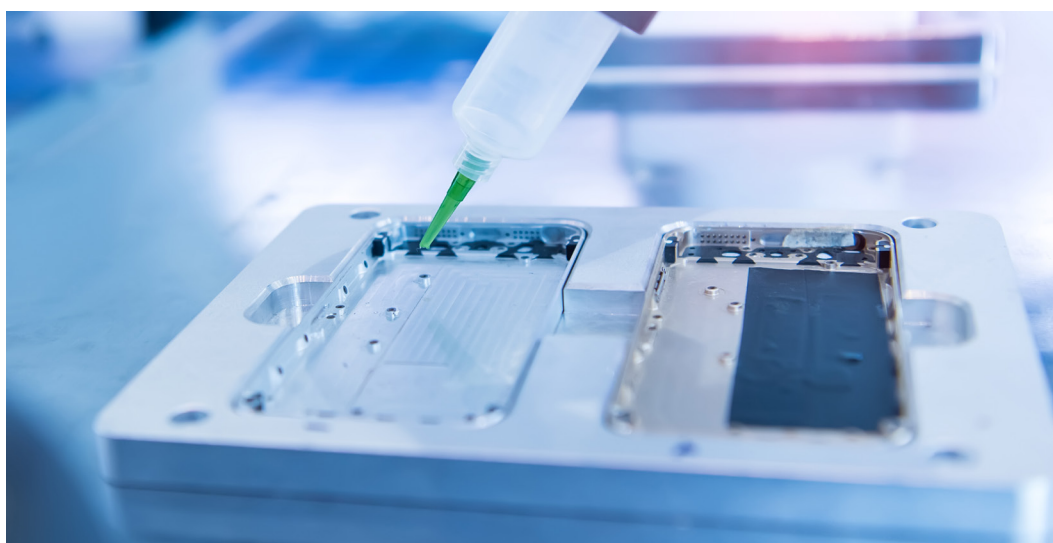


## Silicon NMR on Spinsolve benchtop spectrometers



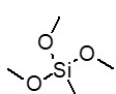
Silicon is an element that can be found in a wide range of materials, like mortars and cements, porcelain, high-strength ceramics, speciality glasses, alloys, silicones, semi-conductors and many more. Polysiloxanes (silicones) in particular are used for example in lubricants (greases and oils), caulk, cooking ware, coatings and more. The first polysiloxanes were produced as homopolymers where their properties were determined by the functional groups of the monomer and the length of the polymers. By combining different monomers together and by using monomers able to crosslink, copolymers and block-copolymers are created and the variety of polysiloxanes drastically increased. The analysis of the composition of copolysiloxanes and the linkage of block copolysiloxanes are essential for developing polysiloxanes with desired properties.

Silicon NMR is a powerful analytical method used to characterize this type of materials. The NMR-active isotope is  $^{29}\text{Si}$ . Although it has a low natural abundance of 4.70 % and a small gyromagnetic ratio that defines a relatively low receptivity of  $3.69\text{E-}4$  (compared to  $^1\text{H}$  NMR), silicon signals of different chemical groups spread over a wide chemical shift range. This high sensitivity of silicon to the surrounding atoms makes NMR suitable to identify polymer compositions. A comprehensive article that reviews the practical aspects of  $^{29}\text{Si}$  NMR was written by Heinrich C. Marsmann.<sup>[1]</sup>

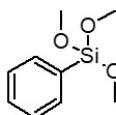
In this case study we show a few examples of small molecules containing silicon and where silicon NMR can be used to confirm the internal compositions of polysiloxanes.

Figure 1 shows the three  $^{29}\text{Si}$  DEPT spectra of trimethoxymethylsilane (top), trimethoxyphenylsilane (middle) and dimethoxydimethylsilane (bottom) measured on a Spinsolve 80 MHz Silicon spectrometer. Each of these molecules has a unique chemical shift and can be easily differentiated from the other molecules.

Number of scans = 64, Acquisition time = 1.638 s, Repetition time = 10 s, Measurement time = 10.68 min



Number of scans = 64, Acquisition time = 1.638 s, Repetition time = 10 s, Measurement time = 10.68 min



Number of scans = 64, Acquisition time = 0.819 s, Repetition time = 10 s, Measurement time = 10.69 min

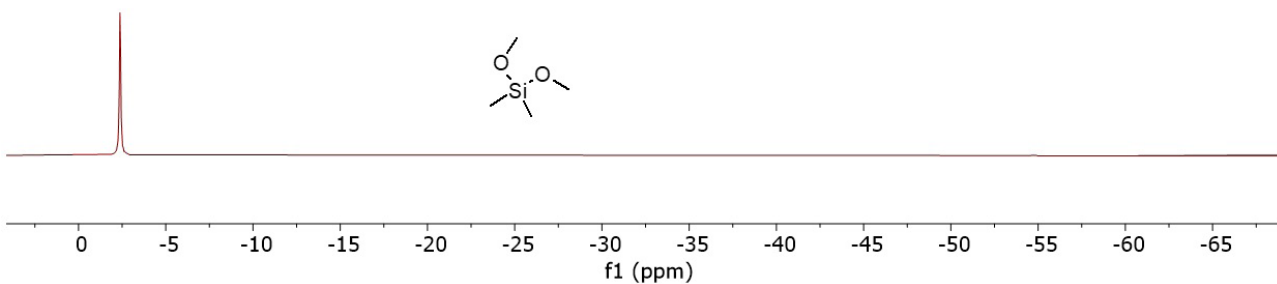


Figure 1:  $^{29}\text{Si}$ -DEPT spectra of trimethoxymethylsilane (top), trimethoxyphenylsilane (middle) and dimethoxydimethylsilane (bottom).

To distinguish between different kinds of polysiloxanes the nomenclature used by Marsmann is very helpful (Figure 2).

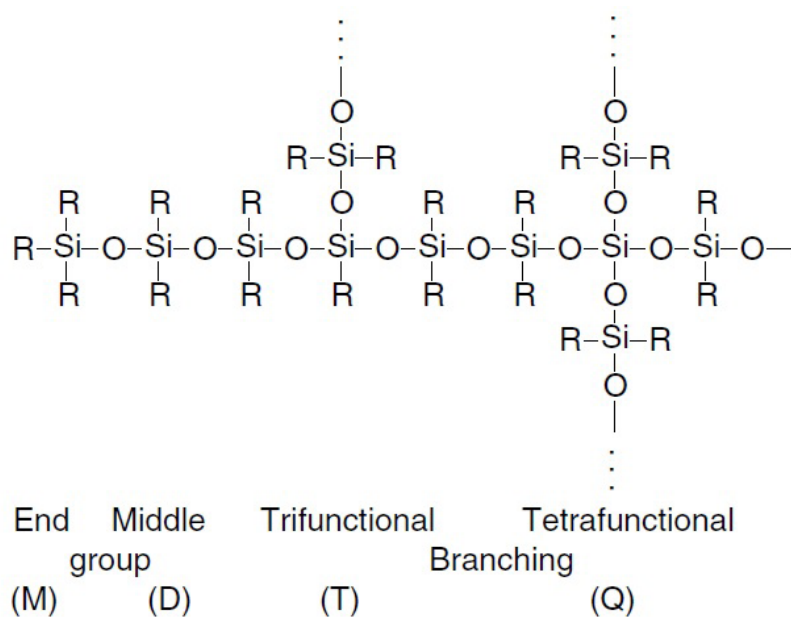


Figure 2: Nomenclature of different building blocks of polysiloxanes.

Depending on the branching and the functional groups the silicon atoms in polysiloxanes have different chemical shifts. These are shown in Figure 3. The superscripts state how many of the possible methyl groups are substituted by the functional group. For example, an end group (M) has three methyl groups and substituting one methyl group by a phenyl group is labelled M<sup>Ph</sup>.

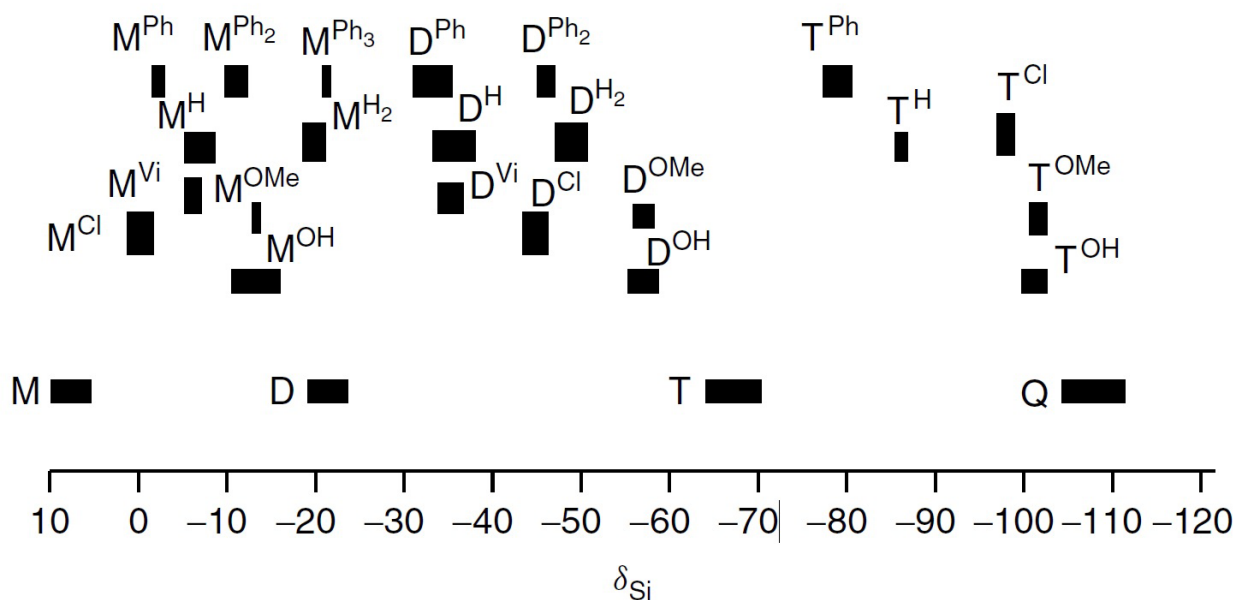


Figure 3: Chemical shifts of silicon atoms in different polysiloxane building blocks.

Figure 4 shows the <sup>29</sup>Si DEPT spectrum of poly(dimethylsiloxane-co-methylhydrosiloxane), trimethylsilyl terminated, measured on a Spinsolve 80 MHz Silicon spectrometer and the excellent agreement of the single building blocks to the predicted chemical shifts.

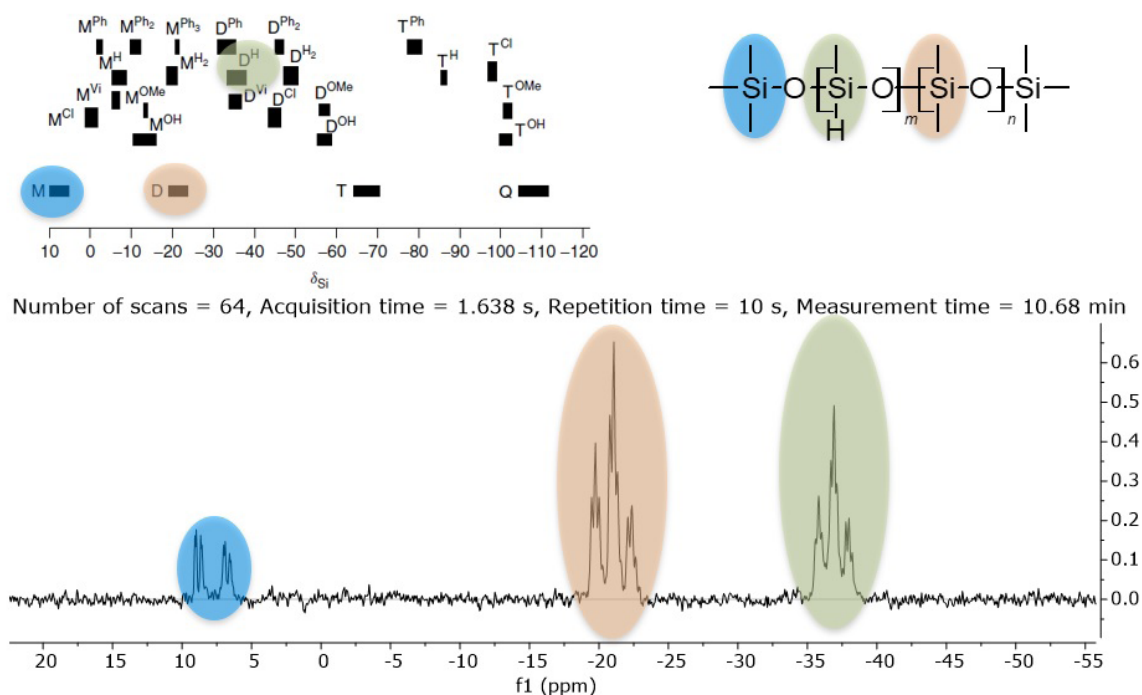


Figure 4: <sup>29</sup>Si-DEPT spectrum of poly(dimethylsiloxane-co-methylhydrosiloxane) (CAS 68037-59-2, 950 g/mol) and the assignment of the NMR signals.

Figure 5 shows the  $^{29}\text{Si}$  DEPT spectrum of poly(dimethylsiloxane-*co*-diphenylsiloxane), divinyl terminated. The relative signal of the vinyl end groups is smaller due to the higher molar mass of the polymer. The intensity difference between the signals of the dimethyl and the diphenyl building blocks indicates that the dimethyl building block is the dominant one in this copolymer.

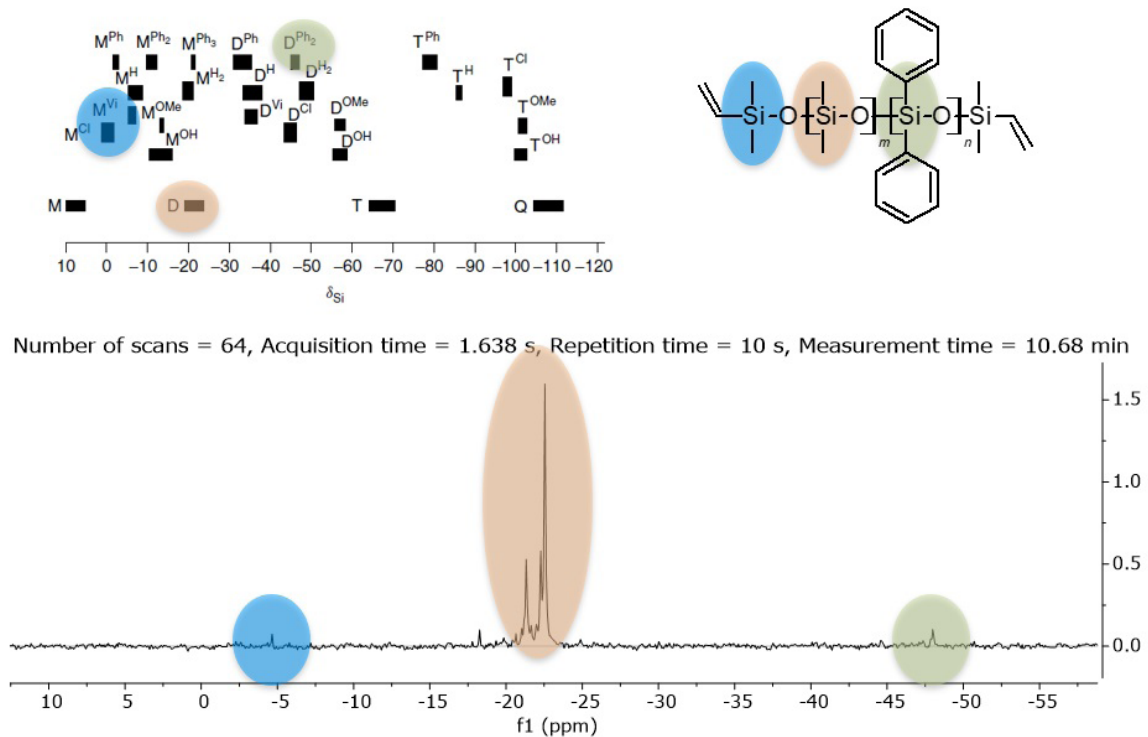


Figure 5:  $^{29}\text{Si}$ -DEPT spectrum of poly(dimethylsiloxane-*co*-diphenylsiloxane) (CAS 68951-96-2, 9300 g/mol) and the assignment of the NMR signals.

Figure 6 shows the  $^{29}\text{Si}$  DEPT spectrum of poly(dimethylsiloxane-*co*-methylphenylsiloxane), trimethylsilyl terminated. In this copolymer the dimethyl building block is also the dominant one.

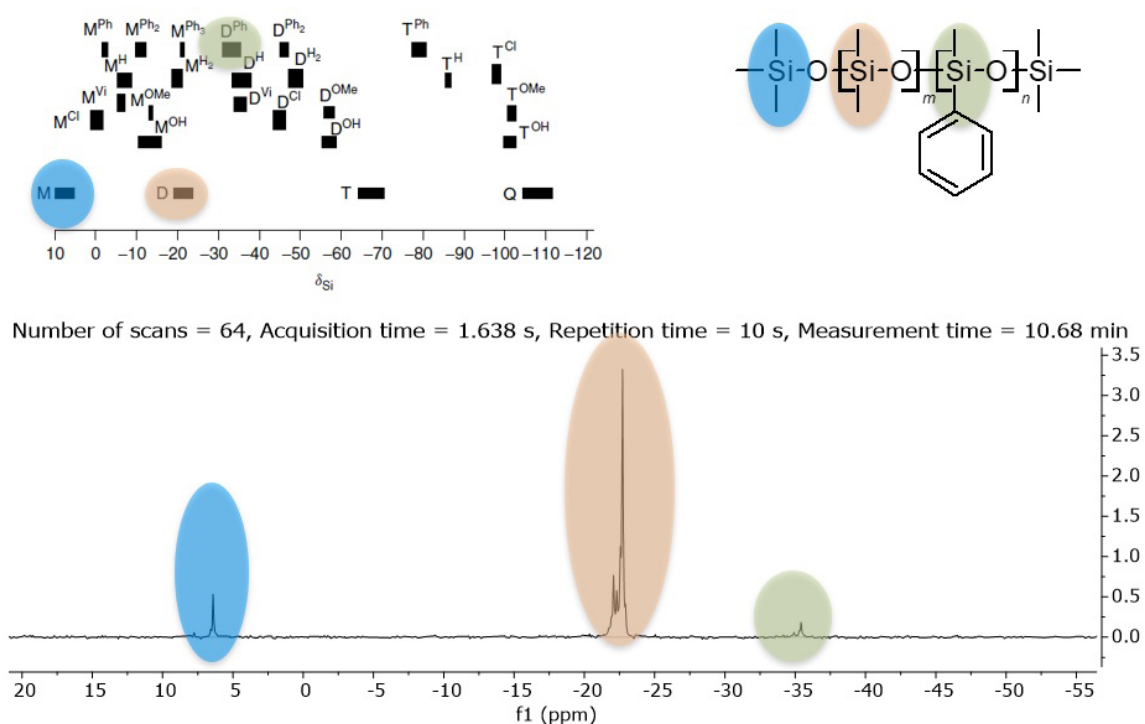


Figure 6:  $^{29}\text{Si}$ -DEPT spectrum of poly(dimethylsiloxane-*co*-methylphenylsiloxane) (CAS 63148-52-7) and the assignment of the NMR signals.

The dimethyl building block as the dominant one is also indicated by the proton NMR spectrum (Figure 7). The signals of the methylphenyl building block are separated from the end groups and the dimethyl building block.

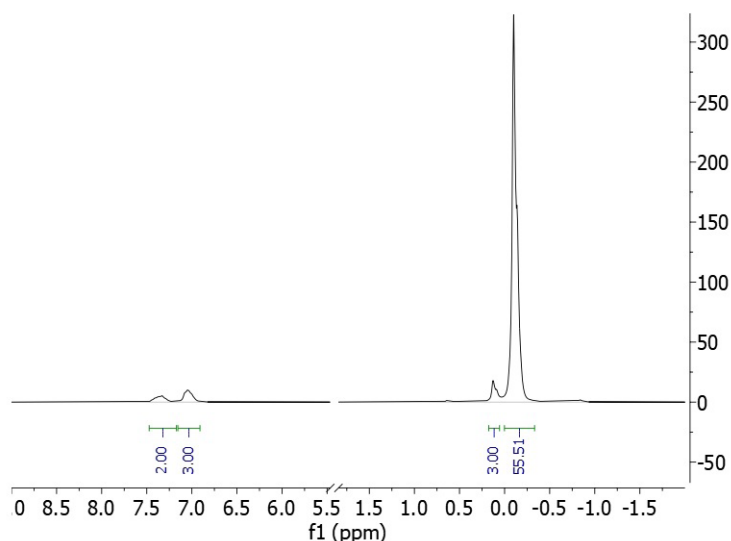


Figure 7:  $^1\text{H}$  spectrum of poly(dimethylsiloxane-co-methylphenylsiloxane) (CAS 63148-52-7).

To verify the assignment of the proton signals of poly(dimethylsiloxane-co-methylphenylsiloxane) a  $^{29}\text{Si}$ -HSQC spectrum can be used. In Figure 8 this spectrum clearly shows which proton signals couple to which silicon signals and confirms the assignment.

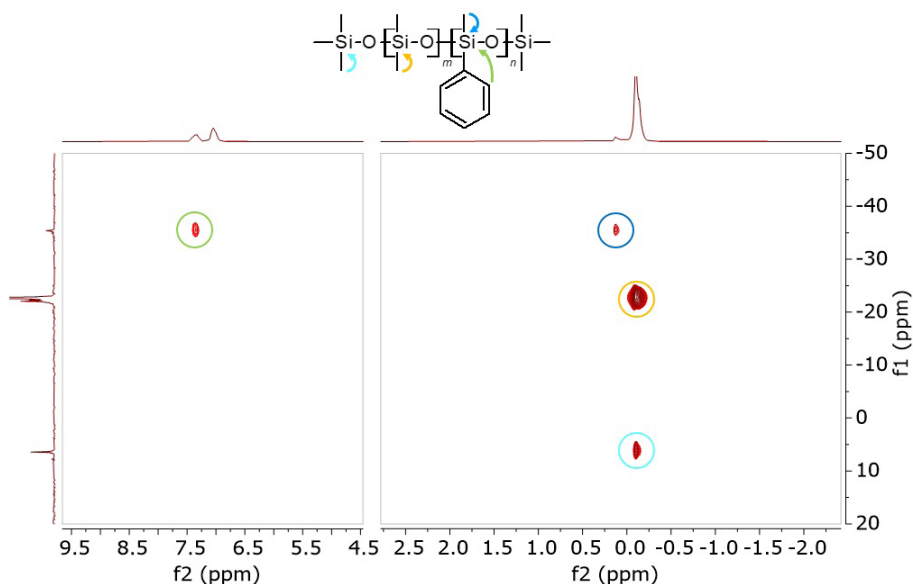


Figure 8:  $^{29}\text{Si}$ -HSQC spectrum of poly(dimethylsiloxane-co-methylphenylsiloxane) (CAS 63148-52-7) and assignment.

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