time $\tau_2 = 20$ ms. This proves[7] that the time-averaged FGT of the mobile deuterons remains constant over this period. The decay of the amplitude is solely determined by the spin–lattice relaxation due to the fast anisotropic motions, leading to time constants T_{1Q} of 20–100 ms, essentially equal to T_1 measured independently by standard techniques.[10] At 213 K, the line shape changes as a function of τ_2. We believe, however, that this change should be explained by a distribution of correlation times: deuterons with higher mobility show a motionally narrowed spectrum and have a shorter T_1 than others with lower mobility showing the rigid solid spectrum and longer T_1. An alternative explanation implying a change of the FGT during τ_2 can be excluded by comparison with experiments at lower temperatures indicating that only at temperatures as low as about 140 K the decay of the spin alignment echo is no longer determined by spin–lattice relaxation but by the correlation time of the slowed down three-bond motion.[10]

Our experimental findings can be summarized in terms of the free volume picture.[17] It has been shown from studies of thermal expansion in the amorphous regions[18,19] that the free volume increase above ~140 K is similar to that of a glass above T_g. The increasing free volume allows for an increasing number of conformations accessible to molecular motion. This number is increased further above room temperature in connection with the α process in the crystalline regions.[20] Thus, only three-bond motions[12] occur at low temperatures, augmented by five-bond motions[13] at room temperature, and motions with more than 10 bonds occur below the melting point.[5] The number of accessible conformations cannot change appreciably on a time scale of at least 50 ms, whereas the correlation time for a single conformational change is below 10^{-7} s at temperatures above 235 K. This has to be contrasted with our findings in amorphous chain deuterated polystyrene[21] where the constraints considered above are *absent*. Here the spin alignment time is drastically reduced above the glass transition, and neither spin alignment nor solid echoes are found above 400 K. The ^{2}H line shape changes within ~50 K from the "rigid solid" limit at 390 K to the motionally narrowed Lorentzian at 440 K.

Similarly, spin alignment cannot be detected in LPE above the melting point. Thus by exploiting the various pulse techniques in ^{2}H NMR, we can clearly detect substantial differences of the segmental motion of polymer chains in truly amorphous systems, e.g., PS, and in the amorphous regions of semicrystalline materials such as LPE.

References and Notes

(1) Gaur, U.; Wunderlich, B. *Macromolecules* **1980**, *13*, 445.
(2) Beatty, C. L.; Karasz, F. E. *J. Macromol. Sci., Rev. Macromol. Chem.* **1979**, *17*, 37.
(3) Abragam, A. "The Principles of Nuclear Magnetism"; Oxford University Press: Oxford, 1961.
(4) Hentschel, D.; Sillescu, H.; Spiess, H. W. *Makromol. Chem.* **1979**, *180*, 241.
(5) Rosenke, K.; Sillescu, H.; Spiess, H. W. *Polymer* **1980**, *21*, 757.
(6) Spiess, H. W. In *NMR: Basic Princ. Prog.* **1978**, *15*.
(7) Spiess, H. W. *J. Chem. Phys.* **1980**, *72*, 6755.
(8) Hentschel, R.; Spiess, H. W. *J. Magn. Reson.* **1979**, *35*, 157.
(9) Hentschel, R.; Sillescu, H.; Spiess, H. W. *Polymer*, in press.
(10) Hentschel, D. Ph.D. Thesis, 1981, Mainz, unpublished.
(11) Spiess, H. W.; Sillescu, H. *J. Magn. Reson.* **1981**, *42*, 381.
(12) Wunderlich, B. *J. Chem. Phys.* **1962**, *37*, 2429.
(13) Schatzki, T. F. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1965**, *6*, 646.
(14) Collignon, J.; Sillescu, H.; Spiess, H. W. *Colloid Polym. Sci.* **1981**, *259*, 220.
(15) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572. *Macromolecules* **1976**, *9*, 587, 597.
(16) Jeener, J.; Broekaert, P. *Phys. Rev.* **1967**, *157*, 232.
(17) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.
(18) Stehling, F. C.; Mandelkern, L. *Macromolecules* **1970**, *3*, 242.
(19) Fischer, E. W.; Kloos, F. *J. Polym. Sci., Polym. Lett. Ed.* **1970**, *8*, 685, and unpublished results.
(20) Olf, H. G.; Peterlin, A. *J. Polym. Sci., Part A-2* **1970**, *8*, 771.
(21) Pschorn, U.; Sillescu, H.; Spiess, H. W.; Wehrle, M., to be submitted for publication.

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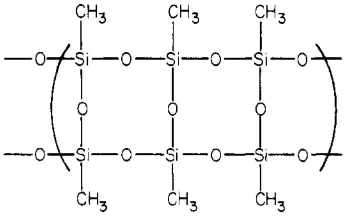
Carbon-13 and Silicon-29 Nuclear Magnetic Resonance Spectra of Solid Poly(methylsiloxane) Polymers

Polymeric siloxanes have been of considerable interest because of promising bulk properties, including thermal stability.[1] Low molecular weight siloxane polymers, as well as model oligomers, have been studied previously in solution by ^{1}H, ^{13}C, and ^{29}Si NMR.[2] As part of an effort to find suitable reference compounds for solid-state NMR studies, we have prepared poly(methylsiloxane) polymers and have obtained their *solid-state* ^{13}C and ^{29}Si NMR spectra.

Solid samples of poly(methylsiloxane) polymers were prepared by the following two methods: (A) Methyltrichlorosilane was added to a large excess of water; a white precipitate immediately formed from the resulting warm mixture; the polymer was separated by filtration and air-dried at 55 °C. (B) To a solution of methyltriethoxysilane (30% by weight) in ethanol was added about 10% concentrated HCl (in water), and the resulting mixture was left undisturbed overnight; the resulting solid polymer was collected by filtration, washed with ethanol, and dried under vacuum. Both types of samples were found to be essentially insoluble in common solvents. Repeated elemental analyses on these two samples at two commercial laboratories gave results that are qualitatively consistent with the empirical formula $CH_3SiO_{1.5}$, which corresponds to the suggested polymeric siloxane structure I; however, the elemental composition data are not sufficiently reproducible or accurate to warrant conclusions on structural details.



I

^{13}C and ^{29}Si spectra were obtained in spectrometers operating with 1.4-T magnetic fields (JEOL FX-60QS for ^{29}Si and a home-built system[3] for ^{13}C). High-power ^{1}H decoupling with cross polarization (CP) was employed to overcome broadening by ^{1}H dipolar effects and the time bottleneck of excessively long spin–lattice relaxation times, respectively,[4] and magic-angle spinning (MAS) was employed to minimize the broadening influences of chemical shift anisotropy.[5]

^{13}C CP/MAS spectra of poly(methylsiloxane) polymers prepared by the procedures described above are shown in

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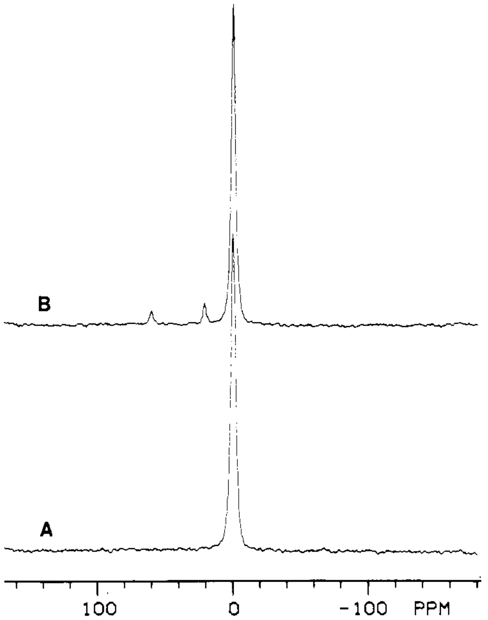

Figure 1. ^{13}C CP/MAS NMR spectra of solid poly(methylsiloxane) polymers. Chemical shifts are in parts per million from liquid Me_4Si; larger values correspond to lower shielding. Contact time, 5.0 ms; 2.0-s repetition time. (A) Sample prepared from CH_3SiCl_3; 4300 repetitions. (B) Sample prepared from $CH_3Si(OCH_2CH_3)_3$; 5000 repetitions.

Figure 1. The single sharp resonance line shown in Figure 1A corresponds to the methyl carbon in a polymer of the general type I. Structural moieties with a $CH_3Si(OH)(OSi<)_2$ arrangement would not likely be distinguished from a $CH_3Si(OSi<)_3$ moiety with the ^{13}C NMR resolution obtained by CP/MAS experiments on amorphous polymers such as these.[6] Figure 1B, showing the ^{13}C spectrum of material prepared from $CH_3Si(OCH_2CH_3)_3$, consists of the strong sharp methyl peak occurring in Figure 1A and small peaks that can be identified with $CH_3CH_2OSi<$ carbon resonances. The ethoxy resonances imply that the average molecular weight of this polymer is small enough that ethoxy end groups constitute an appreciable fraction of the carbon content.

The ^{29}Si CP/MAS spectra corresponding to spectra 1A and 1B are given in spectra 2A and 2B of Figure 2, respectively. The strong peaks at −65 ppm in spectra 2A and 2B correspond well, on the basis of analogous solution spectra on $CH_3Si^*(OSi<)_3$ systems,[2b,7] to the general siloxane framework of structure I. The additional peak at −55 ppm in spectrum 2A is assigned on the basis of previous solution work[8] to a moiety of the type $CH_3Si^*(OH)(OSi<)_2$, not distinguishable from $CH_3Si^*(OSi<)_3$ in the ^{13}C CP/MAS spectrum. This additional peak shows a substantial quantity of $HOSi<$ end groups in the polymer. The small shoulder on the low-shielding side of the peak at −65 ppm in spectrum 2B is probably a manifestation of the $CH_3Si^*(OC_2H_5)(OSi<)_2$ end-group moieties exhibited by the ethoxy carbon resonances in the ^{13}C spectrum (spectrum 1B). These patterns in the CP/MAS spectra are consistent with differences in the "average" elemental composition data (larger C and H values for B, and larger Si value for A).

In summary, one can see that CP/MAS NMR provides spectra on solid samples of organosiloxane polymers with a degree of resolution that is highly useful for structural characterization. Furthermore, the combination of ^{13}C and ^{29}Si NMR provides considerably more information than would be available from either nuclide in the absence of the other or from elemental analyses. The spectra are sufficiently sharp and intense to permit relaxation studies for exploring submicroscopic motion in these materials and for quantifying the results. Experiments of this nature are under way.

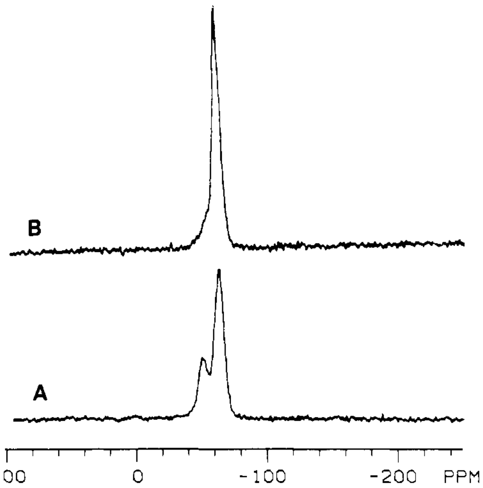

Figure 2. ^{29}Si CP/MAS NMR spectra of solid poly(methylsiloxane) polymers. Chemical shifts are in parts per million from Me_4Si; larger values correspond to lower shielding. Contact time, 10 ms; 4.0-s repetition time. (A) Sample prepared from CH_3SiCl_3; 15964 repetitions. (B) Sample prepared from $CH_3Si(OCH_2CH_3)_3$; 21464 repetitions.

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References and Notes

(1) Rochow, E. D.; Gilliam, W. F. *J. Am. Chem. Soc.* **1941**, *63*, 798.
(2) (a) Liu, Kang-Jen; Ullman, R. *Macromolecules* **1969**, *2*, 525. (b) Engelhardt, G.; Janke, H.; Magi, M.; Pehk, T.; Lippmaa, E. *J. Organomet. Chem.* **1971**, *28*, 293. (c) Harris, R. K.; Robins, M. L. *Polymer* **1978**, *19*, 1123.
(3) Bartuska, V. J.; Maciel, G. E. *J. Magn. Reson.* **1981**, *42*, 312.
(4) Pines, A.; Gibby, M. G.; Waugh, J. S. *J. Chem. Phys.* **1973**, *59*, 569.
(5) (a) Schaefer, J.; Stejskal, E. O. *J. Am. Chem. Soc.* **1976**, *98*, 1031. (b) Andrew, E. R. *Prog. Nucl. Magn. Reson. Spectrosc.* **1971**, *6*, 1.
(6) (a) Schaefer, J.; Stejskal, E. O. *Top. Carbon-13 NMR Spectrosc.* **1978**, *3*, 283. (b) Earl, W. L.; VanderHart, D. L. *Macromolecules* **1979**, *12*, 762.
(7) Marsmann, H. C. *Z. Naturforsch., B* **1974**, *26b*, 495.
(8) Horn, H.-G.; Marsmann, H. C. *Makromol. Chem.* **1972**, *162*, 255.

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Change in Polymerization Mode of 7,7,8,8-Tetracyanoquinodimethane and 2-Chloroethyl Vinyl Ether upon Replacement of Solvent

In a previous paper,[1] tetracyanoquinodimethane (TCNQ) was reported to copolymerize alternatingly with vinyl acetate, phenyl vinyl ether, and 2-chloroethyl vinyl ether (CEVE) in acetonitrile but to initiate the cationic polymerization of *n*-butyl vinyl ether (nBVE) and isobutyl vinyl ether (iBVE). It was proposed that the difference in electron character between TCNQ and vinyloxy com-

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