Macromolecules 1986, *19*, 2194–2196

Topology of Poly(dimethylsiloxane) Elastomeric Networks Studied by Variable-Temperature Solid-State Nuclear Magnetic Resonance

Kebede Beshah,[†] James E. Mark, and Jerome L. Ackerman*[‡]

Department of Chemistry and Polymer Research Center, University of Cincinnati, Cincinnati, Ohio 45221. *Received January 10, 1986*

ABSTRACT: The silicon-29 cross polarization/magic-angle spinning NMR spectra of model end-linked tetrafunctional poly(dimethylsiloxane) (PDMS) networks at $T = 300$ K and at $T = 150$ K (in the vicinity of the PDMS glass transition temperature) are examined. The three Q silicon resonances of a vinyl end-linked network, previously assigned tentatively to (1) the true junction, (2) a single-loop difunctional junction, and (3) a double-loop nonbonded molecule, are found in the present study to have relative chemical shifts that change upon cooling. The differences in these shifts occur in increasing amounts, corresponding to the number of loops being zero, one, or two, as the temperature is lowered. The connection between this observation and the chemical shift assignment is discussed. Networks above the glass transition have line widths less than those of crystalline but chemically similar compounds, while glassy networks have line widths greater than those of crystalline compounds. This results from the presence in the networks of substantial isotropic molecular motion above the glass transition and the presence of static disorder (as reflected in a distribution of isotropic shifts) in the glassy state.

Introduction

Low-temperature high-resolution solid-state NMR measurements have been used to study dynamic processes,[1] motional parameters,[2] and conformations[3] of macromolecules. In our continuing interest in characterizing poly(dimethylsiloxane) (PDMS) networks, we have examined several model end-linked networks at temperatures well above and in the vicinity of the PDMS glass transition temperature. We have previously found silicon-29 solid-state NMR employing cross polarization and magic-angle spinning (CP/MAS) to be extremely useful in characterizing the various structural features of these networks at room temperature.[4] In particular, many of the chemical moieties associated with the junctions of model end-linked networks[5] may be identified on the basis of their chemical shifts. The N, M, D, T, and Q notation[6] represents siloxane subunits corresponding respectively to non-, mono-, di-, tri-, and quad-oxygen-substituted methylsiloxanes

$$SiO_{n/2}(CH_3)_{4-n}; \qquad n = 0, 1, 2, 3, 4$$

It also conveniently predicts the chemical shift range for that silicon. The corresponding chemical shift ranges for N, M, D, T, and Q are approximately 3, 7–9, −19 to −23, −55 to −66, and −99 to −110 ppm downfield from tetramethylsilane (Me_4Si). Within these five basic classes of chemical, or spectroscopic, functionality, substitution of other groups for methyl produces secondary chemical shifts characteristic of the substituted groups. Substitution of methyl is denoted with an appropriate superscript in the notation. The typical spectral resolution in these materials, about 0.4 ppm FWHH (full width at half-height), is normally adequate to distinguish these shifts in PDMS networks at room temperature. The smaller shifts associated with the distance of a particular group from a junction are marginally resolvable: it is possible to resolve XD^*D_n from XDD^*_n in low molecular weight vinyl end-linked networks, where X is the tetrafunctional junction structure $Q(M^{CH_2}M^{CH_2}–)_4$.

We must distinguish this chemical functionality from the network, or topological, functionality. For example, the D subunit

$$–O_{1/2}Si(CH_3)_2O_{1/2}–$$

and the M^{CH_2} subunit

$$–O_{1/2}Si(CH_3)_2CH_2–$$

are both difunctional in terms of network functionality. Yet they appear in distinct regions of the chemical shift spectrum because the number of oxygens bonded to silicon is the major determinant of the chemical shift.

The objective of the present study is to confirm the assignments of multiple Q resonances previously observed[4] in densely cross-linked tetrafunctional vinyl end-linked PDMS networks. Nominally, only a single Q resonance should be observed if the network were perfect, i.e., if every junction is connected via chains to four other junctions. All networks we have examined so far, including vinyl and hydroxyl end linked, exhibit either two or three Q resonances. We have tentatively assigned these resonances in the vinyl end-linked systems to (a) the perfect junction, (b) a topologically difunctional junction bearing a third chain forming a loop, and (c) a double-loop molecule bearing two chains not bonded to the network.[4] The low-temperature measurements described below reveal that the chemical shift differences between the Q resonances are temperature dependent and may reflect relative differences in restrictions imposed by the surrounding medium on thermal motions. The cross-link density in these networks is such that there is sufficient residual proton–silicon dipolar coupling at room temperature to make cross polarization effective. Direct excitation of a silicon FID is not satisfactory because of the exceedingly long T_1 of Q groups. We have observed that the Q groups tend to cross polarize at somewhat comparable rates, so that Q signal intensities may be very roughly compared. However, these rates may differ substantially from those of other types of silicon such as D.

Experimental Details

We synthesize vinyl end-linked PDMS networks by reacting a vinyl-terminated PDMS polymer with a cross-linking agent $Si[OSi(CH_3)_2H]_4$ by means of a chloroplatinic acid catalyst.[7,8] NMR spectra were obtained on a home-built instrument at 6.0-T magnetic field strength. The proton and silicon Larmor frequencies were 255.49 and 50.75 MHz, respectively. Cross polarization times were around 20 ms for room temperature networks and 3–5 ms for networks at 150 K.

Low-temperature spectra were obtained with a temperature control system built especially for this application.[9] Nitrogen gas

---

[†] Current address: Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139.

[‡] Current address: Department of Radiology, NMR Facility, Baker 2, Massachusetts General Hospital, Boston, MA 02114.

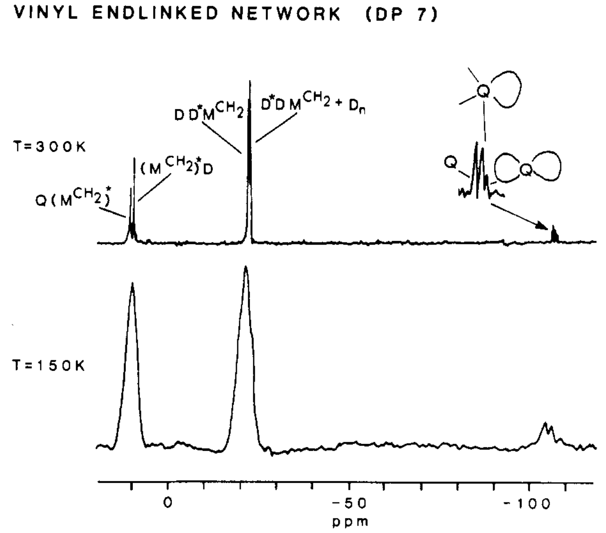
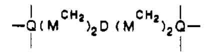


Figure 1. ^{29}Si CP/MAS spectra of an unextracted tetrafunctional vinyl end-linked PDMS network, synthesized from chains of M_n = 520, DP = 7. This corresponds most nearly to a network structure 1, with M_c = 795. Total spectral width is 20 kHz (not all shown), buffer zero filled to 4K complex points. Chemical shifts are in ppm downfield from external neat liquid (T = 300 K) Me_4Si. Top: temperature, 300 K; 20-ms mix time; 3-s recycle; 2.6-kHz spin rate; 1857 acquisitions of 1K complex points. Bottom: temperature, 150 K; 5-ms mix time; 3-s recycle; 2.8-kHz spin rate; 500 acquisitions of 512 complex points.


$-\overset{|}{\underset{|}{Q}}(M^{CH_2})_2D(M^{CH_2})_2\overset{|}{\underset{|}{Q}}-$

1

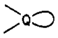
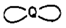
from a storage Dewar was cooled with liquid nitrogen in a heat exchanger, reheated in a controlled heater, and fed to the spinner drive and bearing inlets. Careful control of the liquid nitrogen level in the heat exchanger and proportional/integral/derivative control of the power to the reheater provided a stable spinning speed and sample temperatures accurate to ±3 K.

Results and Discussion

PDMS networks have glass transition temperatures T_g in the neighborhood of 150 K. Silicon-29 CP/MAS spectra of a vinyl end-linked network taken at 300 and 150 K are compared in Figure 1. This network was synthesized from vinyl-terminated chains of M_n = 520 (degree of polymerization DP = 7). The spectrum taken at 300 K has excellent resolution (about 0.3 ppm FWHH) due to substantial rapid isotropic molecular reorientation which allows fast exchange between locations of slightly differing isotropic shifts. As the temperature is lowered toward the glass transition, a loss of resolution is observed due to the freezing out of molecular motion and the concomitant expression of the full distribution of isotropic shifts.[10] The M and D doublets merge because of the increased line widths to give single broad peaks for each type of resonance.

The magic-angle rotation removes the anisotropy of the chemical shift but cannot have any effect on the value of the isotropic shift. In any disordered system, such as a polymer glass, there will be a plurality of chemical environments available to a particular chemical group. These environments may differ because of local differences in packing, bond angle, rotational conformation, and the like. All of these can have small but easily observable effects—of the order of a few ppm—on the chemical shift tensor elements. We therefore expect to see in these systems a distribution of isotropic shifts, reflecting, in this case, glassy disorder. The M and D line widths, defined as FWHH, increase from 0.3–0.4 ppm at 300 K to about 4.3 ppm at 150 K. The M and D resonances of a vinyl end-linked network of much lower cross-link density, DP = 70, and the D resonances of a DP = 3 hydroxyl end-linked network behave similarly.

Table I
Temperature Dependence of Silicon-29 Chemical Shifts in a DP = 7 Vinyl End-Linked Network

	chem shift δ, ppm[a]		
siloxane subunit	T = 300 K	T = 150 K	δ(300 K) − δ(150 K)[b]
$-D_n(M^{CH_2})(M^{CH_2})^*Q$	9.2		
(average)	(8.6_5)	8.5	-0.0_5
$-D_n(M^{CH_2})^*(M^{CH_2})Q$	8.1		
$-D_nD^*(M^{CH_2})Q$	−22.1		
(average)	(−22.4)	−22.3	−0.3
$-D_n{}^*D(M^{CH_2})_2Q$	−22.7		
Q	−104.1	−104.3	0
	−104.7	−105.8	+0.9
	−105.2	−108.4	+3.0

[a] In ppm downfield from external neat liquid (T = 300 K) Me_4Si. Digital resolution is 0.096 ppm. [b] Calculated with the normal Q resonance of each spectrum as an internal chemical shift standard.

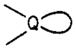
In contrast, the spectrum of hexamethylcyclotrisiloxane, HMCTS, a crystalline compound with a well-defined crystal field environment for each silicon, remains sharp as the temperature is lowered from 300 to 150 K. The FWHH at each of these temperatures is about 1 ppm. As expected, this width is intermediate between the 300 K PDMS width (where molecular motion averages away the effects of molecular packing) and the 150 K PDMS width (where rigid glassy disorder determines the isotropic shift range). There are no magnetic susceptibility discontinuities or magnetic susceptibility anisotropy in the networks because of the continuous, isotropic, and noncrystalline nature of our PDMS samples. The HMCTS spectra may contain broadening contributions from magnetic susceptibility discontinuities and anisotropy, from crystal defects, and from possible crystallographic inequivalence among chemically equivalent silicons in the unit cell. Our HMCTS spectra provide a check that adequacy of proton-decoupling power, magic-angle misadjustment, and magnetic field inhomogeneity are not factors causing the broadening of the PDMS spectra at low temperature.

As an added note, we observe that the HMCTS resonance, a singlet at 300 K, splits into a 1:1:1 triplet at 150 K, implying the possible existence of a rotor phase of this compound at the higher temperature. The molecule is compact and roughly oblate spheroidal in shape, thus allowing for the possibility of a threefold reorientation. This spectral evidence has also been noticed by other workers.[3] The triplet is well enough resolved for us to ascertain the low-temperature line width.

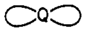
The chemical shift values for the DP = 7 network are reported in Table I and are referenced to an external sample of neat liquid tetramethylsilane at 300 K. The M and D chemical shifts exhibit no significant change with temperature, although we cannot draw hard conclusions from absolute chemical shift measurements in the absence of an adequate internal reference.

The chemical shift values for the cross-link sites, however, display a clear dependence on temperature. To circumvent the absence of a chemical shift reference, we examine the differences between the Q shifts, using the downfield Q resonance as a reference value as indicated in Table I.

There are three cross-link site Q resonances. For the 300 K silicon-29 CPMAS measurement, the resonances were assigned[4] as follows. The most downfield of the three resonances is the genuine cross-link Q site at −104.1 ppm, with all four chains linked to other Q sites. Hence, this site has a topological functionality of four. The central Q resonance at −104.7 ppm was assigned to an inner loop structure[11]



It has a topological functionality of 2. The most upfield resonance at −105.2 ppm was assigned to the so-called "butterfly"[11] structure



This is a molecule, not chemically bonded to the network structure, and can be extracted by swelling the network with appropriate solvents. Its topological functionality is 0. Although it is in principle possible for this molecule to be permanently entangled in the network by catenation of one of its loops with network chains, the probability of forming such a structure is not high; experimentally it is found that its resonance indeed disappears when the network is extracted. The differences in silicon-29 chemical shift between the three structures was attributed to variations in mean Si–O–Si bond angles in these three Q site structures. Q resonances with strained Si–O–Si bond angles show an upfield chemical shift as illustrated by the loop-forming Q sites. The greater strain produces the more upfield shift (compare shifts for inner loop and butterfly resonances). This conjecture is reasonable since the sensitive dependence of silicon-29 chemical shifts on Si–O–Si bond angles has been demonstrated in detail with inorganic crystalline silicates in which bond angles are known from X-ray analysis.[10,12–15] Engelhardt and Radeglia have developed an empirical formula that correlates observed chemical shifts and bond angles in inorganic silicates.[16,17]

The genuine Q-site resonance appears to have essentially the same shift at both temperatures. On the other hand, the Q site hypothesized to carry an inner loop showed a further 0.9 ppm upfield shift at the glass transition temperature. The butterfly Q-site resonance was even further shifted upfield by 3.0 ppm at T_g. These experimental results are consistent with the explanation given above for the differences in Q-site resonances.

Chemical shift differences due to purely chemical differences are not expected to display significant variation with temperature in the absence of electronic effects, phase transitions, or the shifting of an equlibrium constant in a reactive system. However, we expect that shift differences arising from conformational or steric effects will show variation with temperature because molecular motions, which are thermally activated, can modulate conformational and steric factors. Examples of this are seen in the freezing out of isotropic chemical shift distributions upon cooling as discussed above and in the classic case of the syn and anti conformers of crystalline dimethoxybenzene.[18] For our tetrafunctional junctions, the chemical shifts move upfield as conformational or steric constraints vary with the number of loops equal to 0, 1, and 2. Because the "magnitude" of constraint is different among the zero-, one-, and two-loop sites, it is reasonable for thermal motions to modulate these constraints to somewhat differing extents. We therefore expect the changes in chemical shifts to differ for these three situations as temperature is varied.

Conclusions

We have examined the ^{29}Si CP/MAS NMR spectra of model end-linked PDMS networks at 300 K, where substantial molecular motion is present, and at 150 K, where the material is in the glassy state. In a vinyl end-linked DP = 7 network, we can easily observe three junction Q resonances, which we have previously assigned to the true junction, an inner loop structure, and a nonbonded two-loop molecule. The present observation that the nominally similar chemical shifts of these structures change by differing amounts (which increase in value in correspondence to the number of loops) suggests that the structures giving rise to the resonances differ only in the extent to which their motions are constrained by the network (i.e., differ in network functionality).

Acknowledgment. We are pleased to acknowledge financial support from the National Science Foundation, Division of Materials Research, Grant No. DMR 8118816.

References and Notes

(1) Lyerla, J. R.; Fyfe, C. A.; Yannoni, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 1351.
(2) Lyerla, J. R.; Yannoni, C. S.; Bruck, D.; Fyfe, C. A. *J. Am. Chem. Soc.* **1979**, *101*, 4770.
(3) Cantow, H.-J.; Emeis, D.; Gronski, W.; Hasenhindl, A.; Lausberg, D.; Möller, M.; Shahab, Y. *Macromol. Chem. Phys., Suppl.* **1984**, *7*, 63.
(4) Beshah, K.; Mark, J. E.; Himstedt, A.; Ackerman, J. L. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 1207.
(5) Mark, J. E.; Llorente, M. A. *J. Am. Chem. Soc.* **1980**, *102*, 632.
(6) Hurd, C. B. *J. Am. Chem. Soc.* **1946**, *68*, 364.
(7) Llorente, M. A.; Mark, J. E. *Macromolecules* **1979**, *12*, 521.
(8) Valles, E. M.; Macosko, C. W. In *Chemistry and Properties of Crosslinked Polymers*; Labana, S. S., Ed.; Academic: New York, 1977; *Rubber. Chem. Technol.* **1976**, *49*, 1232.
(9) Beshah, K.; Ackerman, J. L., to be published.
(10) Mägi, M.; Lippmaa, E.; Samoson, A.; Engelhardt, G.; Grimmer, A. R. *J. Phys. Chem.* **1984**, *88*, 1518.
(11) Leung, Y. K.; Eichinger, B. E. *J. Chem. Phys.* **1984**, *80*, 3885.
(12) Smith, J. V.; Blackwell, C. S. *Nature (London)* **1983**, *303*, 223.
(13) Dupree, E.; Pettifer, R. G.; *Nature (London)* **1984**, *308*, 523.
(14) Smith, J. V.; Blackwell, C. S.; Hovis, G. L. *Nature (London)* **1984**, *309*, 140.
(15) Selvaray, U.; Rao, K. J.; Rao, C. N. R.; Klinowski, J.; Thomas, J. M. *Chem. Phys. Lett.* **1985**, *114*, 24.
(16) Engelhardt, G.; Radeglia, R. *Chem. Phys. Lett.* **1984**, *108*, 271.
(17) Radeglia, R.; Engelhardt, G. *Chem. Phys. Lett.* **1985**, *114*, 28.
(18) Maricq, M.; Waugh, J. S. *Chem. Phys. Lett.* **1977**, *47*, 327.