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Solid-State NMR Observations of the Crystalline Conformation of Poly(dimethylsiloxane)

Nearly 30 years have lapsed since Damaschun[1] first proposed a ribbonlike, 2-fold helical conformation for crystalline poly(dimethylsiloxane) (PDMS). His X-ray diffraction observations were performed on a PDMS rubber filled with 35 wt % silica (Aerosil) and stretched to an extension ratio of 4 at -90 °C. From the fiber X-ray diffraction pattern a fiber repeat distance of 8.3 Å was determined and all reflections were indexed using a monoclinic unit cell.

From the volume of the proposed unit cell and the observed crystalline density, Damaschun concluded that six PDMS repeat units (12 Si-O bonds) occupy each unit cell. Two conformational models for crystalline PDMS chains were suggested based on the observed 8.3-Å fiber repeat and the derived number of PDMS repeat units (six) contained in the proposed unit cell. These are (i) two extended chains each of three repeat units contained in the unit cell and (ii) one folded chain with six repeat units passing through each unit cell.

Damaschun selected the single-folded chain conformer (ii) for crystalline PDMS based on a comparison of observed and calculated X-ray intensities, though no details of this comparison were presented. The structural model for crystalline PDMS suggested by Damaschun is presented in Figure 1. The ribbonlike, 2-fold helix consists of the regular repeat of the $tts^+s^-g^+g^+$ conformation, with bond rotation angles of ca. 0°, 0°, 60°, -60°, 120°, 120°, respectively. Newman projections of the t, $s^\pm$, and g^+ bond conformers are presented in Figure 2.

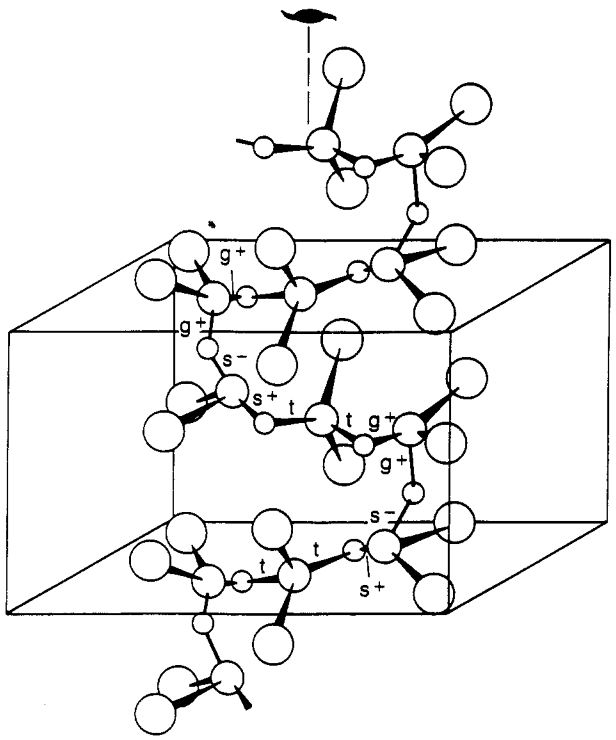

Figure 1. Ribbonlike, 2-fold helix proposed by Damaschun[1] for crystalline PDMS. The monoclinic unit cell chain fragment (six repeat units) adopts the ($tts^+s^-g^+g^+$) conformation. Spheres of increasing size represent the O, Si, and CH_3 atoms and groups, respectively.

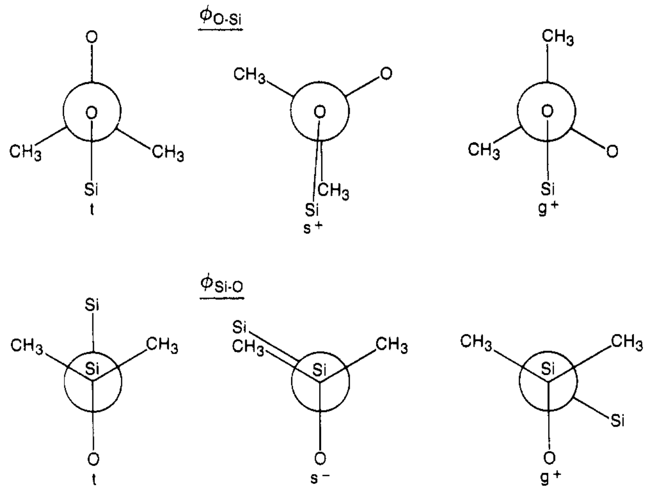

Figure 2. Newman projections along the O-Si and Si-O bonds for the crystalline conformation of PDMS suggested by Damaschun.[1]

Of the six Si atoms in the proposed unit cell of PDMS (Figures 1 and 2), two are gauche to three γ-methyls and one γ-oxygen, two are gauche to two γ-methyls and cis to one γ-methyl, and two are gauche to one γ-methyl and one γ-oxygen and cis to one γ-methyl substituents. At the same time, of the 12 methyl groups in the unit cell four are gauche to one γ-silicon, four are gauche to two γ-silicons, two are cis to two γ-silicon, and two are neither gauche nor cis to their γ-silicon substituents. On the basis of the demonstrated[2] sensitivity of ^{13}C and ^{29}Si chemical shifts to the local conformation of polymers (γ-gauche effect[2,3]), as observed both in their solution- and solid-state NMR spectra, we would expect three ^{29}Si and four ^{13}C resonances for the nuclei residing in the crystalline domains to be observed in the CPMAS/DD ^{29}Si and ^{13}C NMR spectra of semicrystalline PDMS.

We would particularly expect the ^{13}C NMR spectrum of crystalline PDMS to manifest the conformational heterogeneity of the Damaschun crystalline conformation. For example, those methyl carbons that are cis to both of their γ-silicon atoms should be strongly shielded compared to the pair of methyl carbons that are neither gauche nor cis to their γ-silicon substituents. The dispersion of ^{29}Si chemical shifts for crystalline PDMS would not be expected to be large because the Si atoms are either gauche to four of their γ-methyl and γ-oxygen substituents or gauche to two and cis to one of the γ-methyl and γ-oxygen substituents.

We have measured the solid-state ^{13}C and ^{29}Si NMR spectra of PDMS under conditions of magic angle spinning (MAS) with high-power proton dipolar decoupling (DD) on a Varian Unity 400 spectrometer. The low-temperature spectra of crystalline PDMS recorded with and without cross polarization (CP) are presented in Figures 3 and 4. The data do not evidence multiple resonances and appear inconsistent with the 2-fold helical, ribbonlike conformation proposed for crystalline PDMS by Damaschun.[1] (Similar spectra were reported previously by Cantow et al.[4]) Instead, we observe single resonances for both the crystalline ^{13}C and ^{29}Si nuclei which appear slightly downfield (0.8 ppm) and slightly upfield (0.5 ppm), respectively, from the corresponding peaks of the amorphous nuclei. The resonances of the amorphous nuclei are observed in isolation in the spectra recorded without CP (Figures 3a and 4a), because the temperatures of observation are substantially above the glass transition of PDMS. An extended helical structure, on the other hand, with 35-40° rotations away from the trans conformation about each of the backbone bonds,[5] is consistent with the observed 8.3-Å fiber repeat distance and would be expected to lead to single resonances for both crystalline ^{13}C and

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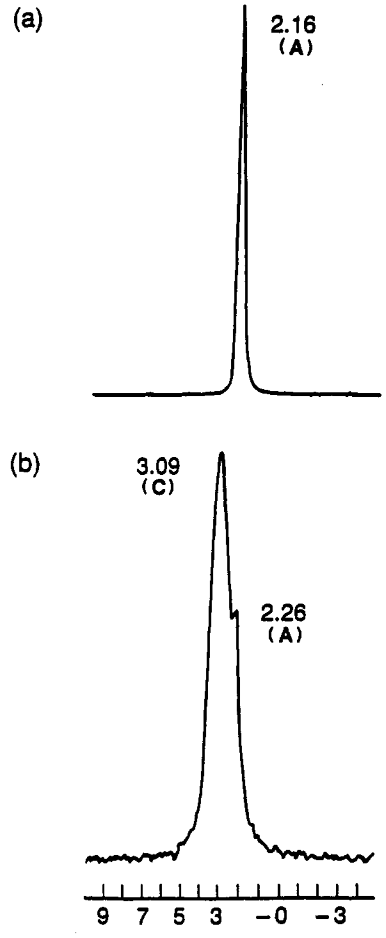

Figure 3. 100.6-MHz ^{13}C NMR spectra of PDMS recorded with MAS/DD at −60 °C without CP (a) and at −80 °C with CP (b). A = amorphous (2.26 ppm), and C = crystalline (3.09 ppm).

^{29}Si nuclei, because of the homogeneous conformational environment provided by this structure.

Our PDMS sample was obtained from Aldrich (no. 18,184-6) and had M_w = 103 400 and M_n = 43 900. A Perkin-Elmer DSC-7 differential scanning calorimeter was employed to determine the melting temperature and crystallinity of our PDMS sample. After quenching to −80 °C and annealing there for 10 min, the sample was heated to 30 °C at a rate of 10 °C/min. Two endothermic peaks at −42 and −36 °C were observed, and the lower temperature peak had an area 3–4 times that of the higher temperature endotherm. The total area for both peaks corresponded to a ΔH = 34.3 J/g. Comparison to the heat of fusion of completely crystalline PDMS,[6] ΔH_m = 63.4 J/g, indicates that our cooled PDMS sample was 54% crystalline.

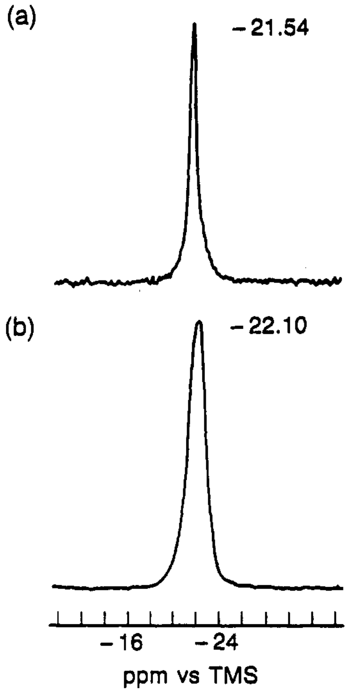

Figure 4. 79.5-MHz ^{29}Si NMR spectra of PDMS recorded with MAS/DD at −95 °C without CP (a) and with CP (b) and corresponding to the resonances of the amorphous and crystalline nuclei, respectively.

We are currently conducting a careful variable-temperature study[7] of our PDMS sample by both DSC and solid-state ^{13}C and ^{29}Si NMR to learn more about the origin of the endotherms observed in our initial DSC scan.

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References and Notes

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