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Polymethylphenylsilane-d_3 (PMPS-d_3) has been synthesized and labelled in the methyl position. Its dynamics were then probed with ^2H NMR. Quadrupole echo spectra were acquired from 24 to 100 °C with varying echo delays. At low temperature, the spectra are consistent with methyl rotation only. As the temperature increased, the spectra appeared to be a superposition of a rigid and mobile component with the mobile component gradually developing over a 50° temperature range. There is only a small variation of line shape with echo delay suggesting that there are few motions in the intermediate motion range. Thus, PMPS-d_3 may have a bimodal distribution of correlation times. In addition, the NMR probe of the T_g is consistent with the material glassing over a broad range of temperatures.

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Introduction

Polysilanes are relatively new materials. Their properties differ from similar carbon based polymers because of the Si-Si bond. The bond is more sensitive to UV radiation and longer than a C-C bond. The bond's UV sensitivity makes polysilanes candidates for microlithography and related applications.[1,2] Its increased length allows for more diverse side chain substitution. These enhanced properties might be exploited though an understanding of the polymers' structure and dynamics. The structure of several polysilanes have recently being investigated.[1,2] In this work, we report investigations of the dynamics of solid state polymethylphenylsilane-d_3 (PMPS-d_3) with ^2H NMR.

We have deuterated the methyl group on PMPS in an effort to study its backbone motion. Using the quadrupole echo pulse sequence, we have acquired ^2H spectra from 24 to 100 °C with varying echo delay. The expected spectra should be indicative of normal methyl rotation with backbone motion superimposed. If the backbone motion is slow, there should be no change in the spectra. If it is fast, the spectra should be further narrowed, perhaps converging to a liquid-like line. If the backbone motion is on the order of the echo delay, the line shape will be a function of the delay. Finally, a distribution of motion will result in a superposition of the above cases.

^2H NMR

In addition to the Zeeman interaction, ^2H NMR of solids is dominated by the coupling of the nuclear electric quadrupole with the electric field gradient (EFG) at the ^2H nucleus. For ^2H bonded to carbon, to a good approximation the EFG is axial symmetric along the bond and the frequencies of ^2H's two NMR transitions are:[3,4]

$$\omega_{\pm} = \omega_0 \pm \frac{3}{4}Q_{cc}(3\cos^2\theta - 1) \qquad (1)$$

where ω_0 is the Larmor frequency, Q_{cc} is the quadrupole coupling constant, and θ is th polar angles describing the orientation of the magnetic field with respect to the principal axis of the EFG tensor. For a non-crystalline solid, the frequencies must be weighted by the fraction of bonds with angle θ. This convolution results in the powder patterns shown in Figure 1.

For a completely rigid aliphatic deuteron the splitting between the singularities (or horns) is about 125 kHz with the entire spectrum covering 250 kHz. The quadrupole echo sequence (QES) overcomes the receiver dead time problem associated with broad lines.[5] The QES is two 90° pulses 90° out of phase with each other and separated by a delay, **d**. With this sequence, a signal echo appears at 2**d** from the initial pulse. To avoid intensity loss from relaxation, **d** is usually from 10^{-5} to 10^{-6} s. The QES reproduces the original FID as long as the motion is much faster or much slower than **d**. Motion with correlation times on the order of **d** result in an intensity loss which depends on **d**, frequency, and type of motion.[6]

Though the QES reproduces the original signal for rapid motion, rapid motion (correlation times $<< \delta^{-1}$) will result in an average EFG tensor and consequently an average coupling constant. For a freely rotating, but otherwise rigid methyl group, the spectrum retains its shape but the splitting is reduced to $(3\cos^2\beta - 1)/2$ where β is the angle of the rotation axis to the ^2H bond. This reduces the spitting from 125 kHz to about 42 kHz. Other motions, besides simple rotations, may alter the line shape as well.

Experimental

Synthesis: PMPS-d_3 was prepared by first synthesizing $PhSiH_2Cl$, converting it to $PhSiH_2CD_3$ though a Grignard reaction, then chlorination to $PhSiCl_2CD_3$, and finally polymerization with Na to PMPS-d_3.

Phenyltrideuteriomethylsilane: In an oven dried, argon filled 3-neck flask, 9 mmol of $PhSiH_2Cl$, prepared as described by H. Schidbaur[7], was dissolved in 100 ml of dry THF. After cooling to 0 °C, 100 ml of a 1 M solution of CD_3MgI in diethylether (Et_2O) was added over a period of 30 minutes. The white mixture was stirred for an additional 30 minutes and then washed with water. The aqueous phase was extracted with Et_2O and the combined organic phase was washed with brine, dried over $MgSO_4$, filtered, and concentrated. The remaining THF was distilled off under argon at ambient pressure, then $PhSiH_2CD_3$ was distilled at 135-140 °C into a Kontes storage flask equipped with a teflon valve.

Dichlorophenyltrideuteriomethylsilane: In an argon filled flask, 8.7 g of $PhSiH_2CD_3$, 75 ml of CCl_4, and a few milligrams of $Pt(II)Cl_2$ were refluxed at 80 °C for 27 hours. The mixture was concentrated to a brown oil, CaH_2 was added, and $PhSiCl_2CD_3$ was distilled at 60-70 °C/10 mm Hg to yield 7.0 g. GC indicated a purity of 96.8% with several close boiling impurities.

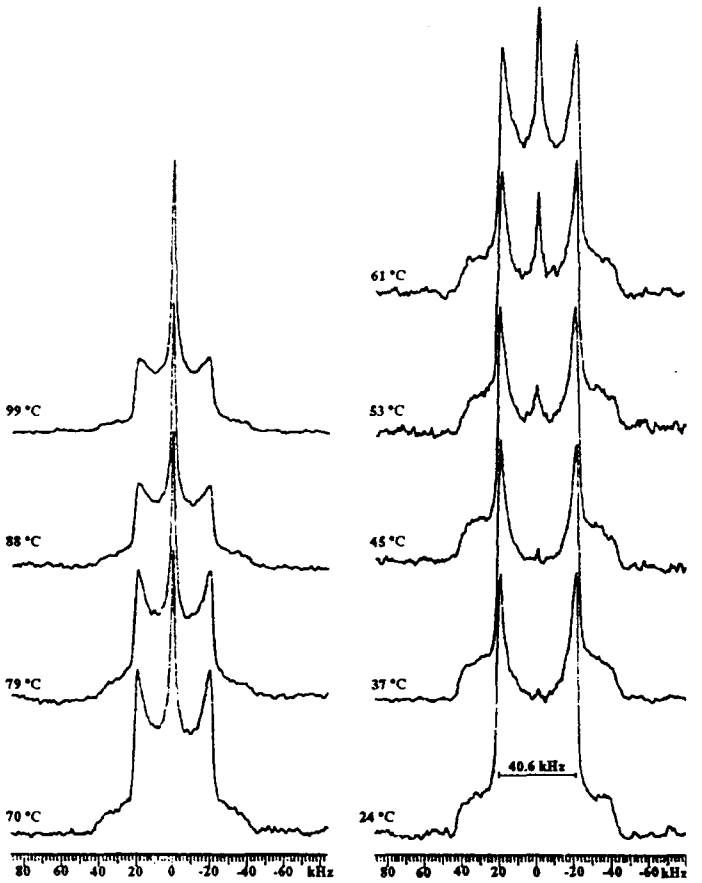

Figure 1. Solid echo spectra at different temperatures for PMPS-d_3

Polymerization: 79 mmol of Na spheres were dispersed in 40 ml of dry toluene. The mixture was heated to 65 °C and, while stirring, 36 mmol of $PhSiCl_2CD_3$ dissolved in 10 ml of dry toluene was added dropwise. The mixture became purple about half way though the addition. The mixture was stirred for an additional hour at 65 °C. The heat bath was removed and 20 ml of dried toluene, 5 ml iso-propyl alcohol, and then 60 ml of toluene were added in succession. The mixture was

stirred for 5 minutes and filtered with an additional 40 ml of toluene added to wash the salt residue. The organics were washed with water and dried with $MgSO_4$. After adding 100 ml of methanol, a cloudy suspension resulted and 12 hours later the precipate was collected and vacuum dried to yield 40 mg of PMPS-d_3, M_n = 426 kg/mol and PD = 2.3 as compared to polystyrene (GPC).

NMR measurments: The ^2H NMR experiments were performed at 30.7 MHz with a Varian VXR spectrometer. The temperature was maintained to ±2 °C by an Oxford VTC4 VT unit. Using the QES, the spectra were acquired with 4k points, 8k scans, a digitization rate of 2 MHz, a 2.4 μs 90° pulse width, an echo delay of 35 μs, and a scan repetition rate of 0.5 s. With this repetion rate, the spectra are fully relaxed. The sample was allowed to equilibrate for at least 30 minutes at each temperature. The FID's were shifted to the echo maximum, zero filled to 8k, and Fourier transformed with 1000 Hz line broadening.

Results

Figure 1 shows the spectra of PMPS-d_3 from 24 to 100 °C. At low temperatures, the spectum is a reduced powder pattern with a splitting of 40.6 kHz - the expected pattern for a rotating methyl group with no other motion. As the temperature increases, a mobile component, the narrower central peak, gradually emerges from the rigid component. As it builds, the rigid component retains its 40 kHz splitting. This gradual appearance of a mobile component over a 50° range was not expected for a homogeneous polymer like PMPS-d_3. For instance, with poly(vinyl acetate) the entire spectrum collapses into one broad line within about 10 degrees.[9]

Figure 2 shows the results of varying the echo delay at 88 °C. The spectra retain their basic shape after about 50 μs. The initial change from 35-50 μs may be due to remants of the mobile FID after the last 90° pulse. There is a moderate intensity drop at ±10 kHz as the delay is increased. Similar spectra run at 25 °C (not shown) do not have this intensity loss, suggesting that the loss is not from frequency dependent T_2 relaxation.

Discussion

At high temperatures, the spectra appear to be superpositions of a rigid and mobile component. Thus, the backbone motion could be modelled by a bimodal distribution of correlation times. Such a conclusion is supported by the x-ray and tacticity studies on PMPS-d_3 polymerized with Na.[1,2] The x-ray diffraction pattern has three peaks suggesting three different domain sizes in the polymer and the tacticity studies indicate long runs of mm and rr triads. These domains and sequences may be related to the rigid and mobile fractions.

A broad distribution of correlation times might also account for the apparent two component behavior if it had significant intensity in both the fast and slow regimes. Without being bimodal, though, such a distribution would also have significant, if not more, intensity in the intermediate regime where the echo delay affects the spectrum. The spectra of Figure 2 do not *appear* to be greatly affected by the delay, but the intensity change as a function of frequency and delay for backbone motion superimposed on methyl rotation has not been calculated. Without this calculation or further experimental evidence, the possibility of a broad distribution covering both fast and slow regimes can not be eliminated.

Conclusions

From the ^2H NMR point of view (a kHz time scale), the T_g of PMPS-d_3 occurs over a broad range of temperatures. Preliminary investigations on the backbone motion in PMPS-d_3 may be in favor of a bimodal system. Undoubtedly, there is some sort of distribution of correlation times governing the system. However, the nature of the distribution has not been conclusively characterized by these two experiments. Further work on the types and rates of motion is underway.

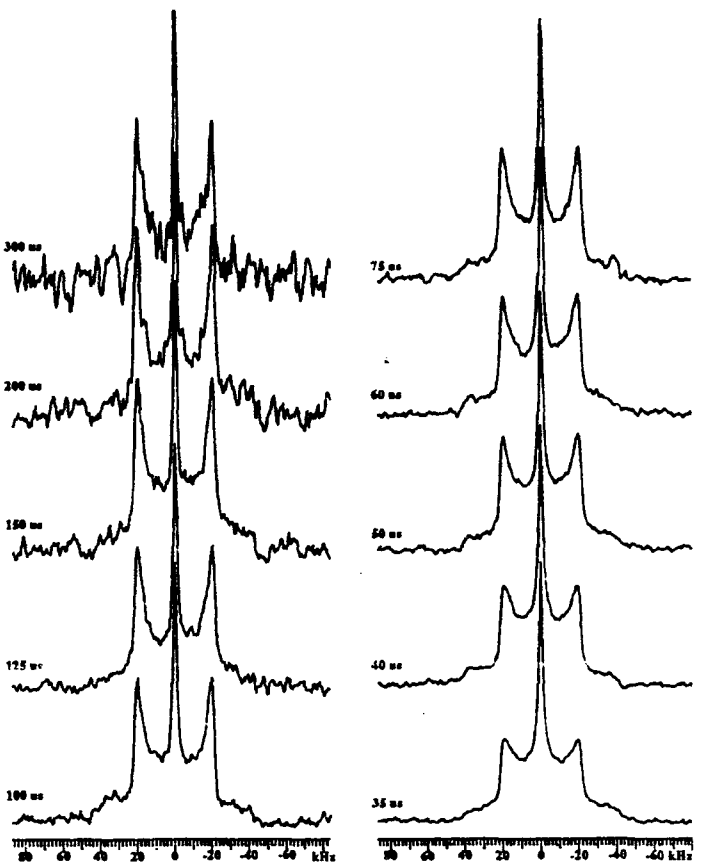

Figure 2. Solid echo spectra of PMPS-d_3 at 88 °C with varying echo delays

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