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Deuterium NMR Study of the Dynamics of Solid State Polymethylphenylsilane

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**13. ABSTRACT (Maximum 200 words)**

Polymethylphenylsilane-d$_3$ (PMPS-d$_3$) has been synthesized and labelled in the methyl position. Its dynamics were then probed with $^2$H 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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by

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Deuterium NMR Study of the Dynamics of Solid State Polymethylphenylsilane
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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 microolithography 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 been investigated.1,2 In this work, we report investigations of the dynamics of solid state polymethylphenylsilane-d3 (PMPS-d3) 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 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

$$\omega_\perp = \omega_0 + 2Q_{cc} \cos(2\theta) - 1$$

where \(\omega_0\) is the Larmor frequency, \(Q_{cc}\) is the quadrupole coupling constant, and \(\theta\) is the 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 \(\theta\). This convolution results in the powder patterns shown in Figure 1.

For a completely rigid aliphatic deuterium the splitting between the singularities (or humps) 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 made up of 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.5

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 \(3\cos^2(2\beta) - 1/2\) where \(\beta\) is the angle of the rotation axis to the 2H bond. This reduces the splitting from 125 kHz to about 42 kHz. Other motions, besides simple rotations, may alter the line shape as well.

Experimental
Synthesis: PMPS-d3 was prepared by first synthesizing PhSiH3Cl, converting it to PhSiH2CD3 through a Grignard reaction, then chlorination to PhSiCl2CD3, and finally polymerization with Na to PMPS-d3.

Phenyltrideuteriomethylsilane: In an oven dried, argon filled 3-neck flask, 8 mmol of PhSiH2Cl, prepared as described by H. Schibdau,6 was dissolved in 100 ml of dry THF. After cooling to 0 °C, 100 ml of a 1 M solution of CD3Mgl in diethyl ether (Et2O) 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 Et2O and the combined organic phase was washed with brine, dried over MgSO4, filtered, and concentrated. The remaining THF was distilled off under argon at ambient pressure, then PhSiH2CD3 was distilled at 135-140 °C into a Kontes storage flask equipped with a teflon valve.

Dichlorophenyldideuteriomethylsilane: In an oven dried, argon filled flask, 8.7 g of PhSiCl2CD3, 75 ml of CCl4, and a few milligrams of Pt(II)Cl2 were refluxed at 80 °C for 27 hours. The mixture was concentrated to a brown oil, CaH2 was added, and PhSiCl2CD3 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.

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 PhSiCl2CD3 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

Figure 1. Solid echo spectra at different temperatures for PMPS-d3.
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3

minutes and filtered with an additional 40 ml of

t wbnm added to wash the salt nsidu. The organics were

washed with water and dried with MgSO₄. After adding 100

ml of methanol, a cloudy suspension resulted and 12 hours

later the precipitate was collected and vacuum dried to yield 40

mg of PMPS-d₃, Mₙ = 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 repetition 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-d₃ from 24 to 100
°C. At low temperatures, the spectrum 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-d₃. 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 remnants 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
T₂ 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-d₃ 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
T₂g of PMPS-d₃ occurs over a broad range of temperatures.
Preliminary investigations on the backbone motion in PMPS-
d₃ 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.

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8) Spectra similar to Figure 1 for poly(vinyl acetate)-d₃ have
been taken in our labs.

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