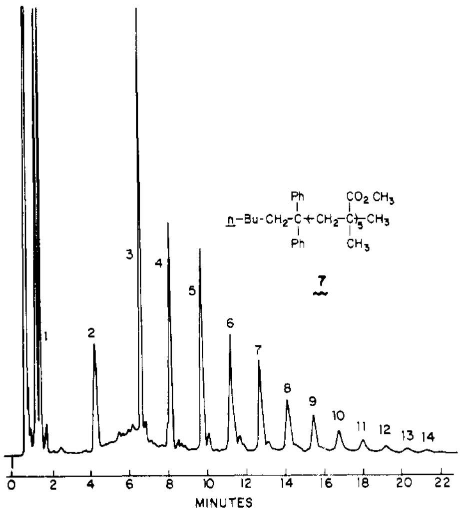
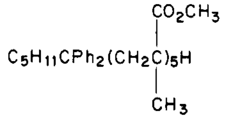


Figure 4. HPLC separation of methyl-capped PMMA oligomers under the same conditions as Figure 3.

has been separated from homopolystyrene by TLC.[5] An elegant separation of poly(styrene)carboxylic acid from polystyrene by TLC and column chromatography has been reported.[6] Our studies show that the separations are general and can be used with polar polymers.

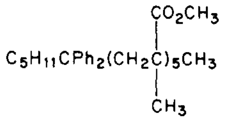
That such narrow peaks are observed for these polymers is remarkable because a polymer of DP = 10, prepared by anionic polymerization, has significant amounts of oligomers from DP = 3 to DP = 18.[7] Also, a polymer such as PMMA has 2^{n-1} possible diastereomers for each oligomer of DP = n (512 for DP = 10). A solvent of sufficient polarity to overcome the adsorption of the ester groups onto the silica gel must be used to obtain narrow peaks. When a solvent less polar than ethyl acetate is used, the peaks become broader because of the adsorption of the ester groups. If a sufficiently nonpolar solvent is used, individual oligomers of the PMMA can be separated. Figure 3 shows a separation of PMMA 6, prepared by initiation of MMA polymerization with (diphenylhexyl)lithium.[1]

Analysis of individual components of 6, purified by



$C_5H_{11}CPh_2(CH_2\overset{CO_2CH_3}{\underset{CH_3}{C}})_5H$

6



$C_5H_{11}CPh_2(CH_2\overset{CO_2CH_3}{\underset{CH_3}{C}})_5CH_3$

7

preparative HPLC, verified the molecular compositions of the oligomers with DP = 1-3. The presence of two major peaks per chain length suggested that separation by the relative stereochemistry of the last two methacrylate units occurs. This was confirmed by the observation that for PMMA 7, which lacks the terminal asymmetric center present in 6, only one major peak is observed for each chain length (Figure 4). There are many reports of HPLC separations of oligomers in the literature, but none of oligomers with the stereochemical complexity of PMMA.[8]

HPLC has great potential utility for the analysis of polymers. The examples here demonstrate this for some highly structured polymers made by anionic polymerization. In the future we will report on the use of HPLC to analyze both simple and complex polymers such as polyethers and polyesters.

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Chain Motion in the Amorphous Regions of Polyethylene As Revealed by Deuteron Magnetic Resonance

The renewed discussion about the nature of molecular motion and glass transition in polyethylene[1,2] prompts us to give a preliminary report of a detailed study employing ^2H NMR. Deuterons offer unique possibilities for studying molecular motions:

i. The NMR parameters of ^2H with spin $I = 1$ are almost exclusively governed by the quadrupole interaction[3] which originates from the electrons in the C-H bond. Thus ^2H NMR yields direct information about rotational motions involving the C-H bond direction.[4,5]

ii. The ^2H NMR line shapes can quantitatively be analyzed to discriminate between different types of motion.[5,6] Since the rigid solid spectrum spans a frequency range of approximately 250 kHz, the line shape will only be affected by motions with spectral densities extending above 10^6 Hz.

iii. The standard spin relaxation times[3] T_1 and T_2 yield information about the spectral densities of the motion at the NMR frequency ($\sim 10^8$ Hz) and at low frequencies ($\sim 10^4$ Hz), respectively. The latter value is determined by the natural line width of ^2H NMR lines due to the dipolar coupling between the deuterons. This limitation has recently been overcome by the creation of deuteron spin alignment, offering the possibility of extending the accessible range down to frequencies as low as 10-100 Hz as in case of mobile deuterons in polyethylene.[7]

iv. Over the temperature range studied (125-390 K) the ^2H spin-lattice relaxation time, T_1, in the mobile amorphous regions is shorter by at least a factor of 50 than T_1 in the crystalline regions. This can be exploited to separate the respective contributions to the NMR signal. Thus, all the spectra presented here correspond essentially to the mobile deuterons, the rigid ones being largely saturated.

In this communication, we present some preliminary results of applying these ^2H NMR techniques to polyethylene. We have investigated a sample of perdeuterated linear polyethylene (LPE) ($M_w \approx 100\,000$, $M_w/M_n \approx 10$, Merck, Darmstadt) that was isothermally crystallized from the melt at 396 K. The ^2H spectra shown in Figures 1 and 2 originate essentially from deuterons in the amorphous regions: In the temperature region ($\sim$230-380 K) where the line shape of the mobile deuterons is motionally narrowed, their contribution to the *total* intensity of ^2H NMR signals amounts to about 29%, to be compared with an amorphous fraction of 26% as determined by X-rays.[4]

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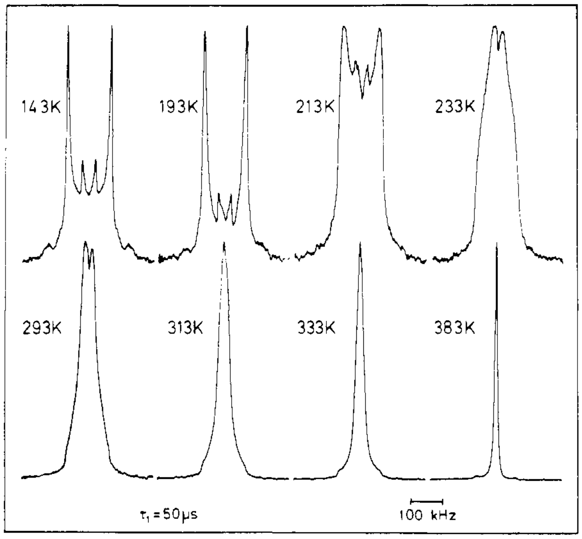

Figure 1. ^{2}H spectra of LPE at 55 MHz obtained from a complex Fourier transform of the solid echo with pulse separation τ_1 = 50 μs for various temperatures; the number of scans ranged from 64 to 255. The total magnetization was saturated first by a series of 90° pulses and then the solid echo was created after a waiting period $\tau_0 \approx T_1$ (amorphous), ranging from 25 to 200 ms. This ensures that the signal is due to the deuterons in the amorphous regions only, since for those in the rigid crystalline regions T_1 (crystalline) > 50 τ_0 at all temperatures.

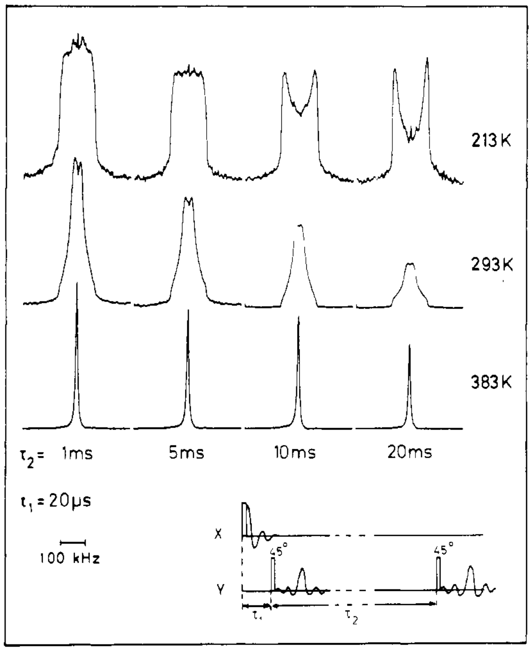

Figure 2. ^{2}H Fourier transform spectra of the spin alignment echo[7] for different waiting periods τ_2. The pulse separation τ_1 between first and second pulse of the Jeener–Broekaert sequence[16] was kept constant at τ_1 = 20 μs. For other experimental conditions see Figure 1.

Let us first discuss the line shapes shown in Figure 1 that were obtained by the solid echo technique described elsewhere.[8-10] At 143 K, the ^{2}H line shape corresponds to that of a rigid solid[8,9] except for two small central peaks due to <0.5% of rotating methyl groups present in the sample. (The apparent CH_3 line shape fraction shown in Figure 1 is increased by a factor of at least 10 since the methyl deuterons appear in full intensity whereas the signal of the chain deuterons is attenuated by incomplete recovery from saturation. A precise CH_3 group determination is not possible from our present ^{2}H NMR data.) At 193 K, considerable intensity is lost in the *central* region of the otherwise solid-like line shape. This indicates the presence of a reorientational process with a correlation time τ_c of the order of the solid echo pulse distance τ_1 = 50 μs. Corresponding spectra have been calculated for jumps of the C–H bond between only two possible orientations.[11] The line shape at 213 and 233 K can also be understood as originating from this process but for τ_c values of $\sim 10^{-6}$ and $\lesssim 10^{-7}$ s, respectively.

The spectra at 233 and 293 K can be explained by a superposition of two line shapes. The one predominant at 233 K corresponds to a time-averaged field gradient tensor (FGT) with an asymmetry parameter η = 1, the other to η = 0 but reduced in width by a factor of 3 compared with the rigid solid spectrum; for details see ref 5 and 11. The η = 1 spectrum is consistent with a three-bond motion[12] where each C–H bond involves jumps between two orientations; see above. The η = 0 spectrum, which has a higher weight at 293 K, can be explained by assuming a five-bond crankshaft motion.[5,13] A full analysis of our data giving the fractions of chains involved in three-bond and five-bond motions, respectively, at various temperatures will be published at a later date.

The narrowing of the ^{2}H spectrum at temperatures between 300 and 390 K (cf. Figure 1 and also ref 4) proves that at higher temperatures the number of conformations accessible for a given segment steadily increases. However, the motion is still constrained even at 383 K since on melting, the line width of the ^{2}H spectrum is reduced further by an order of magnitude.[14] In our model calculation,[5] we have assumed that the total chain in the amorphous region can be divided in flexible subchains of variable lengths. Comparison of Figure 7 in ref 5 and the experimental spectra between 313 and 383 K given here shows that such a model fully accounts for the line shapes observed and it can be inferred that the average length of flexible chains increases from 3–5 bonds at room temperature to 10–15 bonds at 380 K. In ref 5 we used the term entangled chains to specify our model but pointed out that similar results would be obtained from other models describing the *restricted* motional mobility of macromolecular chains.[15] We have also found it helpful to compare the constrained motion with that in a liquid crystal in contrast to the unconstrained motion in a liquid. In order to avoid misunderstanding, we stress that independent of the specific model employed the ^{2}H line shape provides a spectroscopic measure of the extent to which the number of conformations accessible for a given segment increases as the free volume increases with temperature.

Our ^{2}H data in fact *prove* that at all temperatures studied the constraints on the motion mentioned above must persist for long times. As long as these constraints do not change, each deuteron on a given subchain will experience a partially averaged FGT determined by the limited number of conformations accessible and, therefore, the FGT will be independent of time.[5] As mentioned in ref 5 and 11 the existence of such a time-independent FGT is a necessary condition for the formation of a solid echo. The very fact that the spectra of Figure 1 could be obtained via the solid echo proves immediately that this condition must be fulfilled at temperatures above ~230 K on the time scale of τ = 50 μs. By making use of deuteron spin alignment[7] (cf. also iii above), we can prove that the constraints cannot change appreciably even on a much longer time scale. In Figure 2, ^{2}H spectra obtained by Fourier transform of the alignment echo[7] are given for three temperatures and different waiting times[7,16] τ_2. At 293 and 383 K, the line *shape* does not change during the 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 $\sim$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 $\sim$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.

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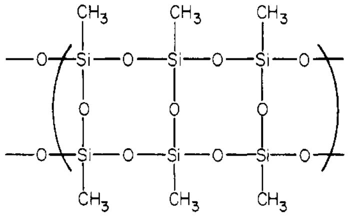
Carbon-13 and Silicon-29 Nuclear Magnetic Resonance Spectra of Solid Poly(methylsiloxane) Polymers

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.



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^{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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