^{2}H NMR Study of Benzene-d_6 in a Liquid-Crystalline Polysiloxane

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ABSTRACT: ^{2}H NMR line-shape and spin–lattice relaxation measurements for benzene-d_6 in poly[methyl-[8-(7-pentylfluoren-2-yloxy)octyl]siloxane] (PMFS) from 16 to 434 K are presented. The two-component system has both a smectic A and a smectic E phase and forms a partially ordered glass at lower temperatures. The spectra in the smectic E and smectic A phases indicate the presence of two distinct average environments; the one partially ordered and the other isotropic. In contrast to this, the relaxation curves are characterized by a single spin–lattice relaxation time, T_1. This discrepancy is explained as resulting from the fact that the spectra reflect the reorientation of the symmetry axis whereas T_1 is determined largely by rotations about the 6-fold axis. The glass transition upon cooling is characterized by a marked change in the temperature dependence of T_1 and the onset of nonexponential relaxation. In the glass phase the spectra and relaxation curves are dominated by a nonaveraged distribution of the local environments. The distribution of activation energies for the rotation of benzene about its 6-fold axis, $g(E)$, is derived from the spectra and compared to results obtained in other polymer/probe systems. No discernible effects due to the ordering of the matrix are observed. The effect of this ordering on the glass-phase spectra is calculated by using mean-field theory and the order parameter for benzene at T_g. It is shown that the anisotropy of the orientational distribution function is small and has little influence on the slow motion spectra in agreement with the experimental results.

Introduction

In recent years a great deal of attention has been given to liquid-crystal polymers.[1-5] These materials, which are formed by incorporating a mesogenic unit into a polymer structure either as part of the main backbone or as a side chain, show the properties of both liquid crystals and polymers. This has led to a number of proposed industrial applications ranging from high strength plastics and fibers to optical storage devices and nonlinear optical devices for fast data transmission. The characterization of these materials is fundamental to an understanding of the relationship between their chemical structure and physical properties. One technique that can be particularly useful in this regard is the study of small solute molecules using NMR. The ordering and dynamics of the solute are determined by its interaction with the surrounding polymer matrix and are reflected in the NMR spectrum. The solute molecule thus acts as a probe of its environment and can yield information about the microscopic and macroscopic state of the sample. Despite the fact that many publications involving the study of liquid-crystalline polymers using NMR have appeared (ref 4 and references therein), the use of small probe molecules has not been fully exploited. This is particularly true for studies in the glass phase. Here, the use of probe molecules with intrinsic motion is necessary because long relaxation times make direct measurement of the polymer matrix impracticable.

In this work we demonstrate the use of ^{2}H NMR for characterizing liquid-crystalline polymers using fully deuterated benzene as a probe. Because the rotation of benzene about its 6-fold axis provides an efficient relaxation mechanism, its NMR signal can be measured down to very low temperatures. Further, because the ^{2}H signal is dominated by the quadrupolar interaction, spin diffusion does not play a significant role. These two features make perdeuterated benzene an ideal probe of microscopic inhomogeneity in the glass phase. Line-shape and spin–lattice relaxation measurements for benzene-d_6 in poly[methyl[8-(7-pentylfluoren-2-yloxy)octyl]siloxane] (PMFS) have been carried out over a temperature range from 16 to 434 K and thus include results for all phases of the system.

Experimental Section

The structural formula of the liquid-crystalline side-chain polysiloxane (PMFS) is shown in Figure 1, and a detailed description of its synthesis and purification is given in ref 6. Prior to use, the polymer was degassed and dried under vacuum at 200 °C for 1 h. Commercial-grade benzene-d_6 with a degree of deuteration higher than 99% was used without further purification. A sample containing 10 wt % benzene-d_6 in PMFS was prepared as follows: appropriate amounts of the two compounds were added to a 5-mm-o.d. NMR tube, which was then cooled to liquid-nitrogen temperature and sealed under vacuum. The sample was not further degassed after the addition of benzene. For ^{2}H NMR the influence of oxygen is negligible for relaxation times below 100 s.[7] In order to fully orient the smectic phase of the sample, it was heated above the S_A–I phase transition and cooled at a rate of approximately 0.1 °C/min in the 7-T magnetic field of the spectrometer.

The NMR experiments were performed on a Bruker CXP 300 spectrometer operating at a frequency of 46.07 MHz for deuterons. The measurements above room temperature were carried out in a home-built probe equipped with a temperature controller consisting of a copper block around the NMR coil, which was heated by a flow of hot air. Below room temperature, a second home-built probe inserted into an Oxford helium-flow cryostat was used. In both probes the temperature could be controlled to better than ±0.1 K. The length of a $\pi/2$ pulse was in the range 2.5–3.0 μs and was adjusted for each temperature. All spectral and relaxation measurements were performed by applying a solid-echo sequence consisting of two $\pi/2$ pulses with a 90° phase shift with respect to each other. The first pulse was phase-cycled to minimize artifacts from the second pulse, and a pulse delay of 25 μs was used for all spectra. The amplitude of the NMR signal resulting from this solid-echo sequence is a function of the

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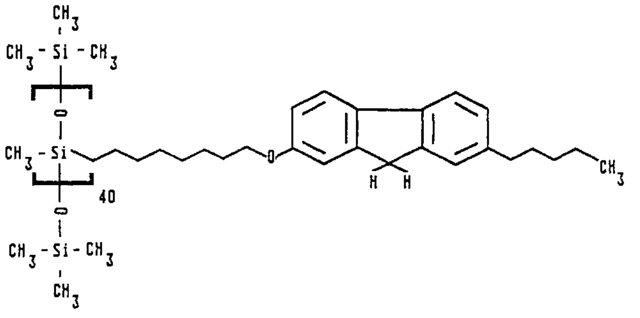

Figure 1. Structural formula of poly[methyl[8-(7-pentylfluoren-2-yloxy)octyl]siloxane] (PMFS).

effective transverse relaxation time, T_2*. Thus, in the case of a two-component spectrum where the components have different T_2* relaxation times, the two NMR signals are weighted differently. However, a pulse delay of 25 μs is short compared to the values of T_2* observed in the temperature range studied, and, hence, only minor distortions are expected. For the freezing of the benzene rotation below 100 K no influence of the pulse delay is observed because a very broad distribution of correlation times is involved.[8]

The spectra were obtained by Fourier transformation of the solid-echo decays. The spin-lattice relaxation time was measured by applying a pulse comb of five $\pi/2$ pulses to saturate the magnetization followed, after a variable delay, by a solid-echo sequence to probe the magnetization for a given time. The amplitude of the echo as a function of the delay time yields the relaxation curve. Differential scanning calorimetry (DSC) measurements were made by using a Heraeus TA 500 instrument with Al_2O_3 as a reference and a scanning speed of 10 °C/min for heating and cooling runs. For neat PMFS the second heating cycle was used for the determination of the phase-transition temperatures. For the 10 wt % benzene-d_6 sample the initial heating cycle was used (vide infra). Phase textures were determined by using a Leitz Laborlux K polarizing microscope equipped with an electrical heater.

Results and Discussion

DSC and polarizing microscopy measurements on neat PMFS yield the following phase-transition temperature ranges. (a) Cooling curve: I–S_A, 455–436 K; S_A–S_E, 426–414 K. (b) Heating curve: S_E–S_A, 425–436 K; S_A–I, 441–467 K. No detectable change in the heat capacity of the sample was observed between the S_E and glass phases. These data cannot be compared directly to NMR results obtained for samples containing a probe molecule because the presence of the probe generally lowers the transition temperatures. Because of this, an attempt was made to measure DSC curves on a sample containing 10 wt % benzene-d_6. However, because the sample could not be measured in a container in which the partial pressure of benzene above the sample could be controlled, considerable evaporation of the benzene in the sample occurred at higher temperatures, leading to a change in concentration during the course of the experiment. Thus, for this sample we have not been able to obtain reliable transition temperatures. In the initial heating curve two small steps are observed at 233 and 258 K. In this temperature range the effects of evaporation are small and the peaks are likely associated with the glass transition. However, their exact origin is unclear, and they only give a rough estimate of T_g.

In Figure 2, selected ^{2}H NMR spectra of benzene-d_6 dissolved in PMFS are shown as a function of temperature between 16 and 434 K. At temperatures greater than 434 K, the polymer is in the isotropic phase and a narrow single line spectrum (not shown) from the rapidly and isotropically tumbling benzene molecules is observed. Between 434 and 244 K (Figure 2I) the polymer matrix is

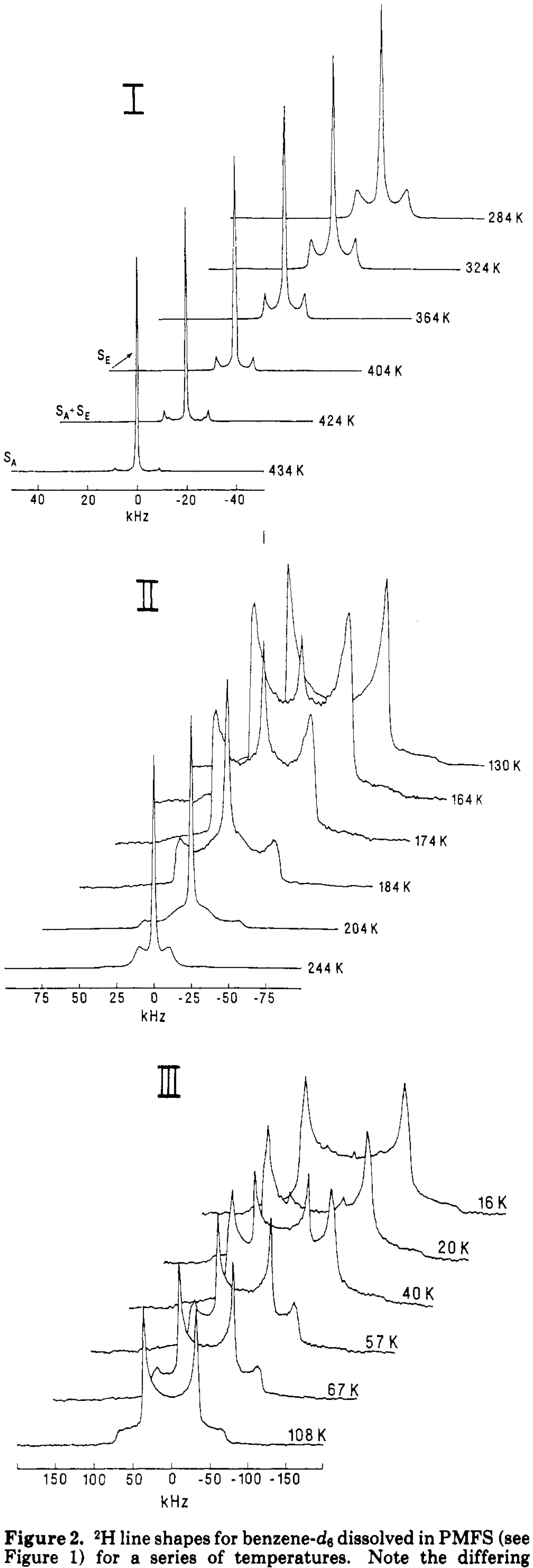

Figure 2. ^{2}H line shapes for benzene-d_6 dissolved in PMFS (see Figure 1) for a series of temperatures. Note the differing frequency scales in I–III.

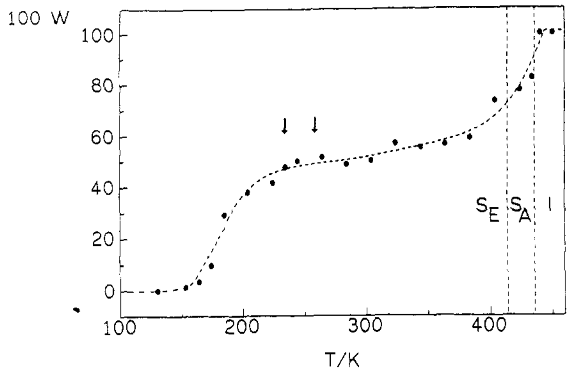

Figure 3. Benzene-d_6 in PMFS: fractional contribution, W, to the total ^{2}H NMR signal intensity from rapidly and isotropically tumbling molecules as a function of temperature. The two arrows indicate the temperatures at which features in the DSC heating curve associated with the glass transition are observed. The vertical dotted lines indicate the phase-transition temperatures from the S_E phase to the $S_E + S_A$ two-phase region and from the S_A phase to the S_A + I two-phase region.

in the smectic phase, and in addition to the narrow isotropic peak a doublet from rapidly but anisotropically tumbling benzene molecules appears. At 424 K where the transition from smectic A to smectic E occurs, both phases are present and two doublets are observed. At lower temperatures (244 K > T > 130 K, Figure 2II, the reorientational motion of the benzene probe becomes slow as the polymer enters the glass phase and the sharp peaks broaden to form a Pake spectrum in the limit of rapid rotations about the 6-fold axis. It is important to point out that the glass transition is not a phase transition in the usual sense and that the molecular motions become slow without an accompanying change in the order of the system such as that which occurs when a crystalline solid is formed. Thus, it is somewhat surprising that the order evident in the spectra in the smectic phase is not apparent in glass. The "freezing out" of the reorientational motion occurs over a wide temperature range, and at intermediate temperatures spectra due to rapidly (central line) and slowly (Pake-like spectra) tumbling benzene molecules are observed simultaneously. For T < 130 K (Figure 2III) the rotation of the benzene molecule about its 6-fold axis freezes out, resulting in a Pake spectrum that is a factor of 2 wider in the rigid limit at 16 K. Again, this occurs over a wide temperature range, and at intermediate temperatures a weighted sum of the two Pake spectra is observed.

We will now consider several features of these spectra in more detail. Of particular interest is the coexistence of the central peak and components due to ordered and/or slowly tumbling benzene molecules over a temperature range of approximately 300 K. In Figure 3 we have plotted the fractional contribution of the central peak, W, to the total signal intensity as a function of temperature. The phase-transition temperatures as obtained by DSC are also shown. As can be seen, the contribution from the central peak falls off sharply in the smectic A phase and then remains roughly constant in the smectic E phase even though considerable broadening of the remainder of the spectrum is observed in Figure 2I. This suggests that the benzene molecules reside in two distinct environments with differing orientational and dynamic properties. Below 250 K the central peak begins to freeze out, and its contribution to the total intensity falls off as the polymer matrix enters the glass phase.

In order to understand this behavior it is important to locate the glass transition temperature, T_g. This is most easily estimated from relaxation measurements. In the smectic phase the relaxation is described by a single exponential whereas in the glass it becomes pronoucedly nonexponential. In both cases it is determined by the rotation of the benzene molecule about its 6-fold axis.

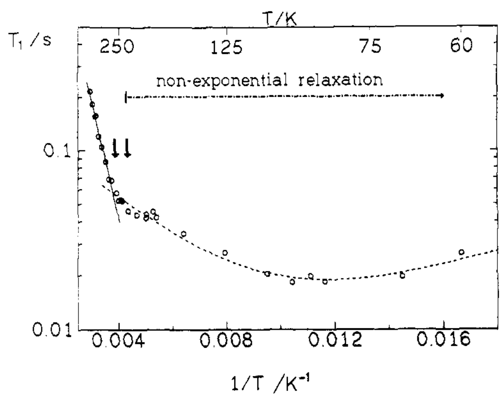

Figure 4. Benzene-d_6 in PMFS: ^{2}H spin–lattice relaxation time, T_1, versus the inverse of the absolute temperature. The values of T_1 have been obtained from the initial slope of the relaxation curve at each temperature. The two arrows indicate the temperatures at which features in the DSC heating curve associated with the glass transition are observed. The dashed/dotted line above the data points indicates the temperature range in which the relaxation is nonexponential. The solid and dashed curves through the points describe the temperature dependence of T_1 in the smectic E and glass phases, respectively.

Qualitatively, below T_g the polymer system is trapped in a nonequilibrium state of the liquid-crystalline phase because it is kinetically blocked from reaching equilibrium. The nonexponential relaxation results from the fact that in the extremely viscous glass phase no molecular motion averages the distribution of local environments that the deuterons experience. The static density fluctuations in the glass are thus probed by the mobile benzene molecules, which leads to inhomogeneous relaxation. This is equivalent to a breakdown of the mean-field theory generally used for the description of liquid solutions. Assuming a distribution of relaxation rates, $f(R^i)$ with $R^i = 1/T_1{}^i$, we describe the normalized recovery function by a convolution of $f(R^i)$ with an exponential decay[9]

$$\frac{M_0 - M(t)}{M_0} = \Phi(t) = \int_0^\infty f(R^i)\exp(-tR^i)\,\mathrm{d}R^i \qquad (1)$$

Expanding this for short times yields

$$\lim_{t\to 0}\Phi(t) \approx 1 - \int_0^\infty f(R^i)\,\mathrm{d}R^i = 1 - \left\langle \frac{1}{T_1{}^i} \right\rangle t \qquad (2)$$

Thus, we have defined a spin–lattice relaxation time by $T_1 \equiv \langle 1/T_1{}^i \rangle^{-1}$, which is given by the initial slope of the nonexponential relaxation curves.

At temperatures higher than T_g the motions of both the guest and host are sufficiently rapid that all guest molecules experience the same mean environment and the relaxation is exponential. The value of T_1 corresponding to the mean environment is also given by the initial slope of the relaxation curves.

In Figure 4 we have plotted T_1 against the inverse of the absolute temperature. Also indicated in the plot is the temperature at which the transition from exponential to nonexponential relaxation occurs. At this temperature a sharp change in the temperature dependence of T_1 also occurs. These two effects have been observed in other glass/probe systems by NMR[10] and tracer diffusion measurements[11] and are general features of the glass transition. Above T_g, an apparent Arrhenius type behavior is observed for T_1 and we obtain a value of 13.1 ± 0.4 kJ/mol for the activation energy for rotations about the 6-fold axis. The observed temperature of 254 K for the crossover in the temperature dependence of the relaxation times is in good agreement with the temperature range for T_g obtained from DSC measurements.

If we now compare this temperature with Figures 2 and 3, it is apparent that at temperatures below the glass transition the isotropic peak is still observed. This means that although the motions of the polymer matrix are frozen out at least a fraction of the benzene guest molecules is still able to tumble freely. Such behavior is typical of polymer glasses containing low molecular weight additives and is not a function of the liquid crystallinity of the polymer.[7,12] The fact that the isotropic line freezes out over a fairly wide temperature range is again a result of the fact that no averaging over the distribution of local environments occurs so that a distribution of temperatures at which the reorientational motions of the benzene guest become slow on the NMR time scale is observed. In several other systems it has been shown that no rapid reorientation of the additive persists below its glass transition temperature.[8] Accordingly, the central peak is no longer observed below 131 K, which is reported as the glass transition temperature of benzene.[13]

The main motivation for choosing benzene as a probe molecule is that the rotation about the 6-fold axis provides an effective spin-lattice relaxation mechanism, which remains operative down to very low temperatures. Further, because the activation energy for the rotation is sensitive to the local environment, the NMR spectra and relaxation curves in the glass reflect the structural disorder of the amorphous system. The freezing out of the 6-fold rotation is evident in Figure 2III. This occurs over a wide temperature range, and at intermediate temperatures spectra that are weighted sums of the two limiting case spectra are observed. This is again a result of the fact that a broad, nonaveraged distribution of local environments is present in the sample. This is to be contrasted with the NMR line-shape behavior in crystalline solids where a very narrow distribution of local environments is present and more complex spectra due to partial averaging over the molecular motions are observed.[14] An analysis[8] of the spectra in Figure 2III yields the fraction of molecules rotating rapidly about the 6-fold axis at each temperature, $F(T)$. If it is assumed that the reorientation of the benzene molecules is determined by an Arrhenius type process, then the distribution function, $g(E)$, of the activation energy for rotations about the 6-fold axis is given by $\mathrm{d}F(T)/\mathrm{d}T$. This function is plotted in Figure 5 (solid curve). For comparison, the curve for the rotation of hexamethylbenzene-d_{18} in polystyrene is also shown (dotted curve). The form of the two curves is very similar and is typical of the 6-fold rotation of guest molecules in polymer glasses.[8] Thus, the liquid crystallinity of the polymer apparently plays no significant role in determining the distribution of activation energies.

The observation of a single spin-lattice relaxation time above T_g is in apparent contradiction to the fact that in the spectra both isotropically and anisotropically tumbling benzene molecules and hence two populations are observed in the smectic phase. This may be a result of the fact that the spectrum is sensitive to motions on a time scale on the order of 10 μs whereas the spin-lattice relaxation occurs on a time scale of several milliseconds. The implication here is that exchange between the two environments occurs on a time scale that is faster than several milliseconds but slower than several microseconds. A more likely explanation of this behavior is that the spin-lattice relaxation and the spectrum are sensitive to different parts of the total rotational potential. The spin-lattice relaxation is determined essentially by the rotation of the benzene molecule about its 6-fold symmetry axis whereas the spectrum is sensitive to reorientational motion of the symmetry axis. If we assume that no exchange between the two environments occurs, then they must have the same mean potential for rotation about the 6-fold axis but show differences in the mean potential for reorientation of the symmetry axis. This is reasonable, since as will be shown in the following section the differences in the mean reorientational potential are very small.

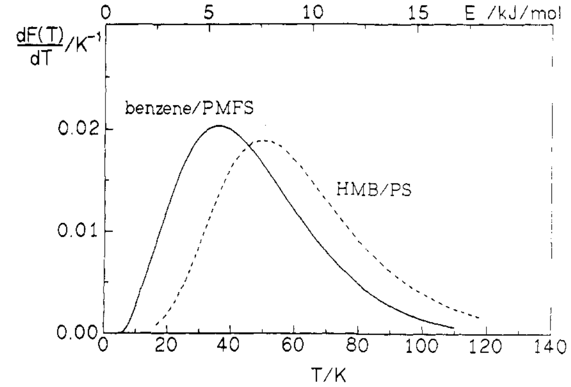

Figure 5. Activation energy distribution for 6-fold rotations of benzene and hexamethylbenzene in polymer glasses. Solid curve: benzene-d_6 in PMFS. Dotted curve: hexamethylbenzene-d_{18} in polystyrene.

We will now consider the degree of ordering of the benzene probe, which is reflected in its NMR spectra and is an indirect measure of the ordering of the polymer matrix. Our sample has been cooled slowly from the isotropic phase in the presence of a 7-T magnetic field and is completely aligned macroscopically. Thus, as in monomeric liquid-crystalline solutions the spectrum of the solute arises from the average over an anisotropic orientational distribution and is a function of the scalar, dipolar, and quadrupolar couplings as well as the chemical shift anisotropy. However, for benzene-d_6 chemical shift effects may be safely ignored, and the scalar and dipolar couplings are not resolved. Thus the spectrum consists of a doublet whose splitting is given by[15]

$$\Delta\nu = \frac{3}{2}\frac{e^2Q}{h}q_{cc}\left(S_{cc} + \frac{1}{3}\eta(S_{aa} - S_{bb})\right) \tag{3}$$

where a, b, and c refer to the principal axes of the electric field gradient tensor at the site of the deuteron; c is parallel to the C–D bond, a is in the plane of the aromatic ring, and b is perpendicular to a and c. S_{aa}, S_{bb}, and S_{cc} are the diagonal elements of the order matrix in this axis system. $1.5e^2Qq_{cc}h^{-1}$ is the quadrupolar coupling constant of the deuterons, and η is the asymmetry parameter of the electric field gradient tensor. For benzene $S_{zz} = S_{bb} = -2S_{aa} = -2S_{cc}$, where z is the 6-fold symmetry axis, and eq 3 can be rearranged to give

$$S_{zz} = \frac{-4\Delta\nu h}{3e^2Qq_{cc}(1+\eta)} \tag{4}$$

In Figure 6 we have plotted S_{zz} as a function of temperature. Here we have used a value of 180.7 kHz for $e^2Qh^{-1}q_{cc}$ and 0.041 for η.[16] The DSC cooling curve for the pure polymer is also shown. In the smectic A–isotropic two-phase region no spectrum from ordered benzene could be detected. This suggests that if no change in the ratio of

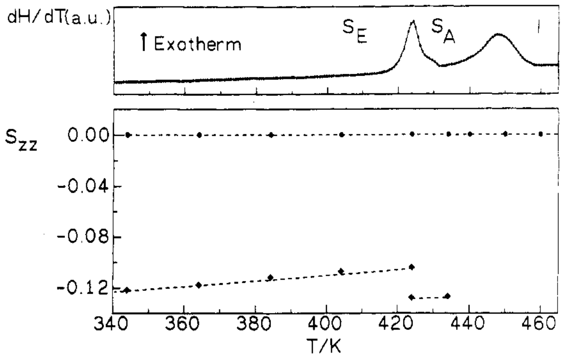

Figure 6. Order parameter, S_{zz}, of the symmetry axis of benzene-d_6 in PMFS as a function of temperature. S_{zz} has been obtained from the measured quadrupolar splittings using eq 4, a value of 180.7 kHz for the quadrupolar coupling constant and 0.041 for the asymmetry parameter η.[11] The DSC cooling curve for the pure polymer is also shown.

ordered to disordered domains in the sample occurs, then the benzene guest is apparently preferentially dissolved in the isotropic regions of the sample and as can be seen in Figure 3 its concentration in the ordered regions increases rapidly with decreasing temperature. It is also apparent that the S_A–S_E phase transition is accompanied by a decrease in the ordering of the benzene probe. This is somewhat surprising since the ordering within the liquid-crystalline domains is higher in the S_E phase. Similar behavior has been observed in several monomeric liquid crystals[17,18] and has been explained as the result of a purging of the solute from the aromatic core regions of the liquid crystal to the less ordered aliphatic regions. However, it is known[19] that in many liquid crystals the ordering of solutes is partly determined by the interaction between the molecular quadrupole moment of the solute and an external electric field gradient due to the liquid-crystalline environment.[20] This contribution to the ordering of the solutes is not correlated to the ordering of the liquid crystal itself, and its sign, magnitude, and temperature dependence vary from one liquid crystal to another. It is entirely possible that this contribution to the ordering of benzene is smaller in the S_E phase than in the S_A phase. The magnitude of the electric field gradient has only been determined in a few nematic phases to date, and its contribution to the ordering in the present system is unknown.

It is known[1-4] that the ordering of the polymer matrix is retained in the glass phase; thus, one would expect that the benzene ordering observed in the smectic E phase should also be retained in the glass. This applies to the ordering within the liquid-crystalline domains (microscopic ordering) as well as to the ordering of the domains themselves (macroscopic ordering). From a linear extrapolation of the temperature dependence of the order parameters in the smectic phase, we obtain a value of −0.14 for S_{zz} and at T_g = 254 K. This value can be used to calculate the orientational distribution from which the slow motion spectra can be calculated. To do this, however, assumptions must be made about the form of the distribution. Here, we assume that it is determined by the orientation potential or "potential of mean torque".[21] For a molecule with C_3 or higher symmetry this can be written[22] as

$$U(\Theta) = G\beta\left(\frac{3}{2}\cos^2\Theta - \frac{1}{2}\right) \qquad (5)$$

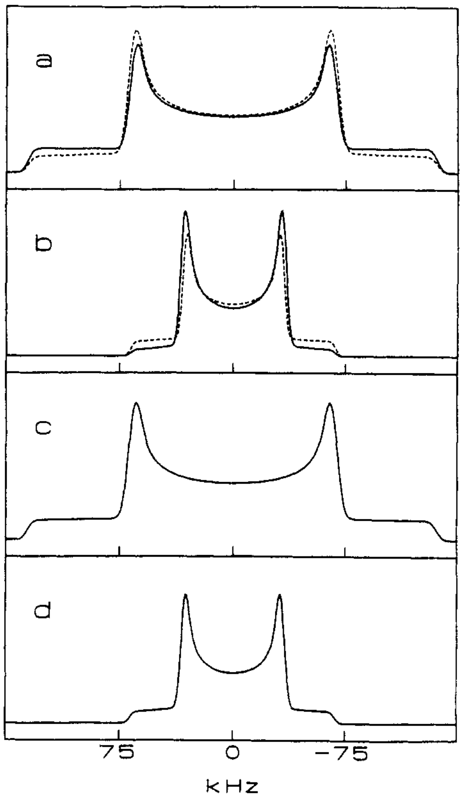

Figure 7. Calculated spectra for benzene-d_6 in the limit of slow reorientation of the 6-fold axis. (a) Solid curve: partially ordered benzene in the limit of slow rotation about the 6-fold axis. The spectrum has been calculated by using a value of $G\beta = -3.9 \times 10^{-21}$ J in eq 5, a line width of 3.0 kHz and T = 130 K. The value of $G\beta$ yields S_{zz} = −0.14 in agreement with the value obtained from a linear extrapolation of the curve in Figure 6 to T_g = 254 K. Dashed curve: randomly distributed benzene. The spectrum has been calculated by using the same parameters as for the solid curve except with $G\beta$ = 0.0. (b) Spectra in the limit of rapid rotations about the 6-fold axis. All parameters are the same as those used for the spectra in a. (c and d) Weighted sums of the spectra in a and b, respectively. Weighting factors: ordered benzene (solid curves), 0.4; disordered benzene (dashed curves), 0.6.

G describes the mean field due to the liquid-crystalline environment, and β is some molecular property that interacts with the mean field. The product $G\beta$ is thus the strength of the interaction of the molecule with its environment. We obtain a value of -3.9×10^{-21} J for $G\beta$ from a fit to the order parameter. Using this value, we can now calculate the contribution to the glass phase spectra from the ordered benzene molecules. The results of this calculation are shown in parts a and b of Figure 7 (solid curves) for slow and rapid rotation about the 6-fold axis, respectively. For comparison, the corresponding isotropic Pake spectra are also shown (dashed curves). It is immediately apparent from these plots that the value of S_{zz}, and hence $G\beta$, represents a very small deviation from an isotropic distribution. Careful inspection of Figure 7a shows a small increase in the intensity of the wings of the oriented spectrum, whereas in Figure 7b the intensity in the wings of the oriented spectrum is slightly decreased. If no change in the relative populations of ordered and disordered benzene occurs during the phase transition, then the observed spectra should be weighted sums of the spectra in Figure 7a for slow rotations and in Figure 7b for rapid rotations. Such spectra are shown in parts c and d of Figure 7 where the weighting factors 0.4 and 0.6 for the ordered and disordered spectra, respectively, have been estimated from Figure 3. These plots are virtually indistinguishable from isotropic Pake spectra, which is in agreement with the fact that the observed spectra in Figure 2III are described well as weighted sums of the two limiting case isotropic Pake spectra.

For larger, more highly ordered guests, the deviations from an isotropic Pake spectrum will be larger and thus more easily observed. For such guest molecules it should also be possible to observe the effects of the distribution of local environments in the glass phase. These systems present a unique opportunity for the study of the mechanisms that lead to the ordering of the guest. Because it is possible to experimentally determine the form of the orientational distribution function,[23] they present a more stringent test of proposed orienting mechanisms than the spectra in low molecular weight liquid crystals where only the order parameters that are averages over the distribution function are observed. Work is in progress using larger guests such as coronene and anthracene, where the degree of ordering is expected to be much larger and thus more easily observed in the glass phase.[24] Initial results show a very high degree of ordering for both solutes; however, the relaxation times for anthracene become prohibitively long in the glass phase, and coronene is apparently insoluble in the S_E phase.

Conclusions

We have shown that the NMR spectra and relaxation data of benzene in PMFS yield information about the macroscopic and microscopic properties of the polymer/probe system. The use of a mobile probe molecule such as benzene allows all phases, including the glassy state, of the system to be investigated. At higher temperatures, where averaging over the distribution of local environments occurs, a single mean environment is observed for rotations about the 6-fold axis, whereas two distinct average environments exist for the reorientation of the 6-fold axis. From the relaxation data, the glass transition temperature is easily identified and it is apparent that in the glass phase an averaging over the distribution of local environments does not occur. The observed behavior is typical of polymer glasses and is not strongly affected by the liquid crystallinity of PMFS.

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References and Notes

(1) Proceedings of the International Conference on Liquid Crystal Polymers. *Mol. Cryst. Liq. Cryst.* 1988, *153*, Part A; 1988, 155, Part B.

(2) Finkelmann, H.; Rehage, G. Liquid Crystal Polymers, Vol. II/III. *Adv. Polym. Sci.* **1984**, *60/61*, 99.

(3) Ciferri, A.; Krigbaum, W. R.; Meyer, R. B. *Polymer Liquid Crystals*; Academic Press: New York, 1982.

(4) Müller, K.; Wassmer, K.-H.; Kothe, G. *Adv. Polym. Sci.* **1990**, *95*, 1; Polymer Liquid Crystals. *Faraday Discuss. Chem. Soc.* **1985**, 79.

(5) Schmidt, H. W. *Angew. Chem., Adv. Mater.* **1989**, *101*, 964.

(6) Kossmehl, G.; Schulz, M.; Vieth, H.-M. *Makromol. Chem.* **1990**, *191*, 3107.

(7) Rössler, E.; Sillescu, H.; Spiess, H. W. *Polymer* **1985**, *26*, 203.

(8) Rössler, E.; Taupitz, M.; Börner, K.; Schulz, M.; Vieth, H.-M. *J. Chem. Phys.* **1990**, *92*, 5847.

(9) Rössler, E.; Taupitz, M.; Vieth, H.-M. *J. Phys. Chem.* **1990**, *94*, 6879.

(10) Ehlich, D.; Sillescu, H. *Macromolecules* **1990**, *23*, 1600.

(11) Börner, K. Diploma Thesis, Freie Universität, Berlin, 1990. Börner, K.; Rössler, E.; Vieth, H.-M., in preparation.

(12) Rössler, E. *Lecture Notes in Physics*; Springer: Berlin, 1987, Vol. 277.

(13) Wong, J.; Angell, C. A. *Glass Structure by Spectroscopy*; Dekker: New York, 1976.

(14) Spiess, H. W. *Chem. Phys.* **1974**, *6*, 217. Spiess, H. W.; Grosescu, R.; Haeberlen, U. *Chem. Phys.* **1974**, *6*, 226.

(15) Emsley, J. W.; Lindon, J. C. *NMR Using Liquid Crystalline Solvents*; Pergamon Press: Oxford, 1975.

(16) Barnes, R. G.; Bloom, J. W. *J. Chem. Phys.* **1972**, *57*, 3082.

(17) Vaz, N. A. P.; Doane, W. *J. Chem. Phys.* **1983**, *79*, 2470.

(18) Moseley, M. E.; Loewenstein, A. *Mol. Cryst. Liq. Cryst.* **1982**, *90*, 117.

(19) Burnell, E. E.; van der Est, A. J.; Patey, G. N.; de Lange, C. A.; Snijders, J. G. *Bull. Magn. Reson.* **1987**, *9*, 4. van der Est, A. J.; Kok, M. Y.; Burnell, E. E. *Mol. Phys.* **1987**, *60*, 397. van der Est, A. J. Ph.D. Thesis, University of British Columbia, 1987. Weaver, A.; van der Est, A. J.; Rendell, J. C. T.; Hoatson, G. L.; Bates, G.; Burnell, E. E. *Liq. Cryst.* **1987**, *2*, 633. Kok, M. Y.; van der Est, A. J.; Burnell, E. E. *Liq. Cryst.* **1988**, *3*, 485.

(20) Patey, G. N.; Burnell, E. E.; Snijders, J. G.; de Lange, C. A. *Chem. Phys. Lett.* **1983**, *99*, 271. van der Est, A. J.; Burnell, E. E.; Lounila, J. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84*, 1095.

(21) Emsley, J. W.; Hashim, H.; Luckhurst, G. R.; Shilstone, G. N. *Liq. Cryst.* **1986**, *1*, 437.

(22) Burnell, E. E.; de Lange, C. A.; Snijders, J. G. *Phys. Rev. A* **1982**, *25*, 2339. Snijders, J. G.; de Lange, C. A.; Burnell, E. E. *J. Chem. Phys.* **1982**, *77*, 5386. Snijders, J. G.; de Lange, C. A.; Burnell, E. E. *J. Chem. Phys.* **1983**, *79*, 2964. Snijders, J. G.; de Lange, C. A.; Burnell, E. E. *Isr. J. Chem.* **1983**, *23*, 269. de Lange, C. A.; Snijders, J. G.; Burnell, E. E. In *Nuclear Magnetic Resonance of Liquid Crystals*; Emsley, J., Ed.; D. Reidel Publishing Co.: Dordrecht, The Netherlands, 1985.

(23) Spiess, H. W. In *Developments in Oriented Polymers*; Ward, I. M., Ed.; Applied Science Publishers: Barking, U. K., 1981; Vol. 1.

(24) Kossmehl, G.; Schulz, M.; Vieth, H.-M.; van der Est, A. Proceedings of the 8th Liquid Crystals Conference of Socialist Countries. *Mol. Cryst. Liq. Cryst.* **1990**, *193*, 171.

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