expression of Torchia and Szabo.[25] For a gauche–trans conformational transformation, we expect a T_1 value of 5 ms at the minimum ($\tau_c \sim 2$ ns). For a low-amplitude (±10°) libration, the predicted T_1 at the minimum is 33 ms. Contributions to relaxation by other motions would decrease the observed T_1 value. Since we observe a minimum T_1 of ~20 ms (42 °C), we conclude that fast librations are the dominant motional mode for relaxation at this temperature, with significant contributions from fast ($\tau_c \sim 5 \times 10^{-8}$ s) gauche–trans conformational hops.

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Molecular Basis of the β-Transition in Poly(arylene ether sulfones)

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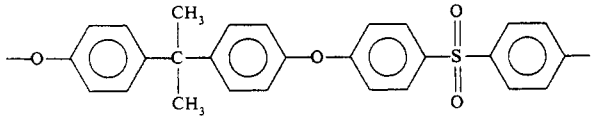
Received October 17, 1985; Revised Manuscript Received April 23, 1986

ABSTRACT: The molecular basis for the β-relaxation in poly(arylene ether sulfones) has been established by deuterium NMR studies on specifically deuterated structures such as I. The primary mode of motion of the aromatic rings in these polymers is 180° phenyl ring flips. These flips occur with a broad distribution of characteristic frequencies (ca. 10^2–10^7 s^{-1}). Added antiplasticizers decrease the magnitude of the β-relaxation and lead to a significant loss in ductile mechanical properties. Antiplasticizers also markedly reduce the rate of phenyl ring flips, thereby establishing this type of phenyl motion as a molecular-level process contributing to the β-relaxation. Other details of motion in these polymers are also addressed.

Poly(arylene ether sulfones) such as I are prepared by the step-growth polymerization of bisphenol A and 4,4′-dichlorodiphenyl sulfone[1-3] and are an important family of modern thermoplastics. These materials are generally oxidatively stable at relatively high temperatures and also are quite resistant to acidic and basic aqueous environments. Polysulfones have therefore enjoyed widespread use under demanding service conditions.

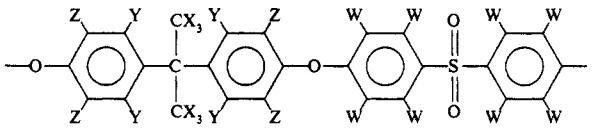


I

The dynamic mechanical behavior of poly(aryl ethers) and related macromolecules is a subject of controversy and has been extensively studied and reviewed.[4] The vast amount of existing experimental data can be summarized by the following generalizations: (1) poly(aryl ethers) exhibit a broad, prominent secondary relaxation, the β-relaxation, at −100 °C (1 Hz); (2) this dynamic mechanical relaxation is enhanced by water sorption but only in those poly(aryl ethers) that contain polar groups;[5] and (3) the β-relaxation is diminished by the addition of low molecular weight antiplasticizers. On the basis of these findings, the molecular-level process responsible for the β-transition in polysulfones has been attributed to a superposition of two relaxations.[4] One involves rotation of the aryl–ether bond; the other arises from relaxation of the sulfone–water complex.

We present data here that bear directly on the molecular-level processes responsible for the β-relaxation. In particular, we show (1) that 180° flips of the aromatic rings are the primary mode of molecular motion; (2) that the flips occur over a broad range of characteristic frequencies (ca. 10^2–10^7 s^{-1}); (3) that antiplasticizers cause the ring motions to become slower; and (4) that the presence of water does not affect the phenyl ring flip process.

Solid-state deuterium NMR is employed to probe molecular motion in the following three selectively labeled polysulfones:[6,7]



II W = ^{2}H; X = Y = Z = ^{1}H

III W = Z = ^{1}H; Y = ^{2}H

IV W = Y = ^{1}H; X = ^{2}H

Although most of the data were obtained on the polymer bearing deuterons on the aromatic rings flanking the sulfone group, II, the other two polymers serve to confirm the conclusions. For example, the bisphenol-A-labeled polymer III was used to ensure that the two types of phenyl rings do not undergo widely different motions. The methyl-labeled material IV is sensitive to motions occurring about an axis other than the main-chain backbone.

The specific polysulfone I is completely amorphous, in contrast to the semicrystalline morphologies often encountered in other polymers and, indeed, in certain other poly(arylene ether sulfones).[3] Crystallization in I is prohibited by virtue of both the tetrahedral *gem*-dimethyl group and the tetrahedral sulfone group. These centers restrict the regular chain packing needed for crystallization.

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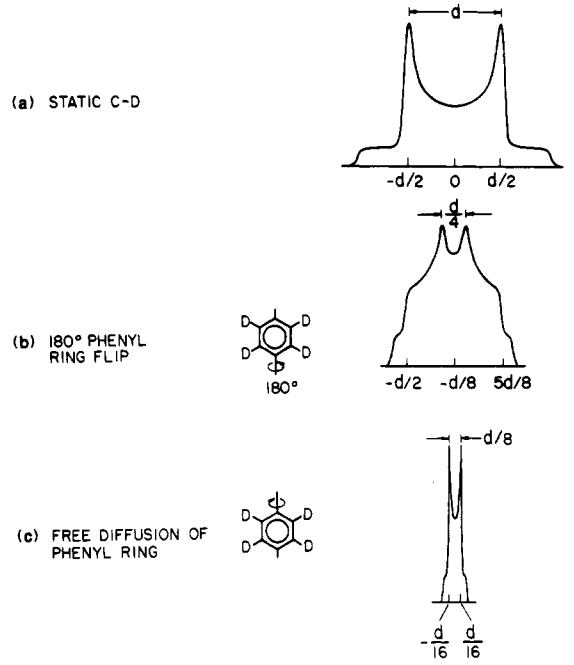


Figure 1. Calculated solid-state deuterium NMR spectra for three models of phenyl group motion: (a) static; (b) rapid 180° flips about the 1,4-phenylene axis; (c) rapid diffusion about the 1,4-phenylene axis.

This amorphous polysulfone system therefore provides an opportunity to contrast the phenyl ring behavior observed here with that of semicrystalline polymers. This comparison is particularly relevant in light of recent work that suggests that the phenyl ring is a sensitive probe of the local conformational space surrounding it.[8,9]

Deuterium NMR has recently provided much detailed information concerning the amplitude and frequency of local motions in a number of polymers.[10-17] The deuterium NMR lines shape is sensitive to motions with correlation times between 10^{-4} and 10^{-7} s, and at ambient temperatures many amorphous polymers have large-amplitude motions in this regime.

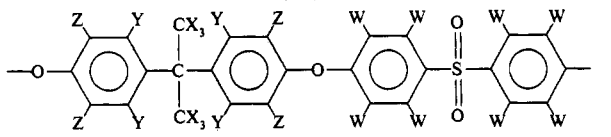
Figure 1 shows the explicit line shapes that are calculated for three simple types of phenyl group motion. In Figure 1a the rings are static on the deuterium NMR time scale, whereas in Figure 1b the rings are flipping rapidly by 180° about the 1,4-phenylene axis. The discrete 180° flipping motion shown in Figure 1b is readily distinguished from the situation shown in Figure 1c where the rings undergo rapid diffusion about the 1,4 axis.

Although employed only indirectly in this report, several techniques can broaden the 10^{-4}–10^{-7} s deuterium correlation time window. Spin alignment techniques can extend the measurements to slower motions,[18] and spin–lattice relaxation measurements are sensitive to faster motions.[19] Deuterium NMR also has the advantages that the molecular geometry of the electric field gradient tensor is known and that the maximal component of the tensor is along the carbon–deuterium bond. Quadrupolar relaxation is dominant, and the deuterium nucleus serves as a probe of motion only in its local environment, being insensitive to long-range translational motions.

Materials and Methods

Samples. Syntheses of the selectively labeled samples employed in this report have been described previously.[6,7] The monomers were characterized by mass spectroscopy, infrared spectroscopy, thin-layer chromatography, and proton NMR spectroscopy. The polymers were characterized by thermal measurements, intrinsic viscosity measurements, and high-resolution solution-state carbon and deuterium NMR spectroscopy. These results, which have been previously reported, showed that the labeled polymers are of high molecular weight.[7] Deuterium exchange occurred during the syntheses of polymers III and IV but not for II. The extent and mechanisms of the exchanges have been described previously.[7] We repeat here in Table I the amount and location of the deuterium atoms in each sample. X-ray diffraction measurements showed the samples to be completely amorphous.

Table I



	% monomer units containing deuterium			
sample	W	X	Y	Z
II	5	*a*	*a*	*a*
III	*a*	7	13	*a*
IV	*a*	13	*a*	7

[a] Indicates no measurable amount of deuterium at this site.

Three general types of samples were prepared for NMR measurements: (1) samples equilibrated with atmospheric moisture; (2) rigorously dried samples; and (3) samples blended with 40 wt % 4,4′-dichlorodiphenyl sulfone (DCDPS). DCDPS has previously been reported to be an antiplasticizer for I.[2]

The rigorously dried sample was obtained by drying polymer II under vacuum (<1 torr) for 24 h at room temperature and then heating it to 150 °C over a period of 8 h. The sample was held at 150 °C for 48 h and was cooled to room temperature under vacuum. The thin, transparent film was cut in a dry nitrogen atmosphere and sealed in an NMR tube in the drybox.

After completion of the NMR experiments on the dried polymer, the sample was placed in a high-humidity chamber for 64 h to obtain the samples equilibrated with atmospheric moisture.

The blends were prepared by physically mixing the polymer and the DCDPS and then compression molding the mixture at 330 °C between ferrotype plates. The resulting transparent blend was cooled under pressure, cut into small pieces, compression molded again at 330 °C and cooled under pressure. These samples were then annealed at 80 °C for 24 h under vacuum. In all cases, approximately 100–130 mg of the polymer was packed into 5 × 15 mm (o.d.) sample tubes.

Solution NMR Measurements. Solution-state deuterium NMR measurements were performed on 10% (w/v) solutions of the polymers in $CHCl_3$ with a small amount of dioxane-d_4 as reference. Spectra were obtained at both 25 and 50 °C on a Varian XL-200 spectrometer operating at 30.7 MHz for deuterium. A minimum of 80 transients was obtained for each spectrum. The standard inversion–recovery pulse sequence was used for T_1 measurements.[20]

Solid-State NMR Measurements. Solid-state NMR experiments were performed on a home-built spectrometer operating at 55.26 MHz for deuterium. The spectrometer has been described previously.[17] The 90° pulse width was 3.3 μs. Data were collected in quadrature using 4K data points and a sampling rate of either 100 or 200 ns/point. The quadrupole splitting for the methyl group was determined with a sampling rate of 1 μs/point. The free induction decays were zero-filled prior to Fourier transformation.

Three pulse sequences were employed to selectively observe different types of molecular motions. These pulse sequences have been described previously[8] but will be discussed briefly here.

The quadrupole echo pulse sequence[21-23] ($90^{\pm}_x$–t_1–90_y–t_2–acquire–T) refocuses the inhomogeneously broadened NMR signal. The delay times t_1 and t_2 were typically set at 30 and 33 μs, respectively. The free induction decay was left-shifted so that the portion of the signal that was Fourier transformed began at exactly the top of the echo maximum. T, the time between pulses, was typically varied between 1 and 10 s.

The amorphous quadrupole echo pulse sequence ((90–2 ms)$_5$–t_a–$90_{\pm x}$–t_1–90_y–t_2–acquire–T) allows selective observation

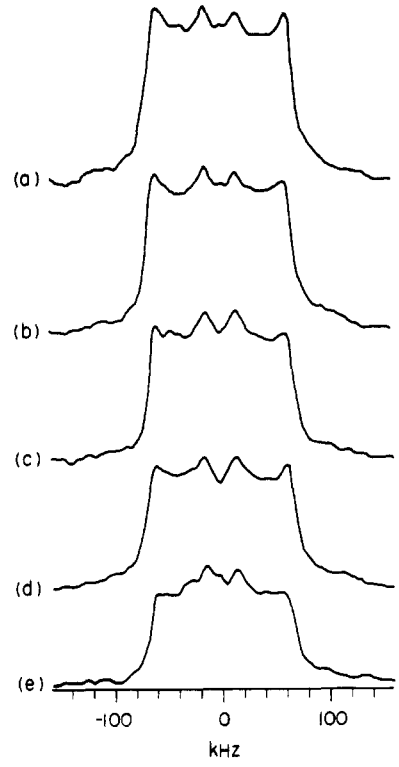


Figure 2. Solid-state deuterium NMR spectra of polysulfone II obtained at 23 °C and 55.26 MHz with the quadrupole echo pulse sequence. The delay between sequences, T, was set at (a) 10 s; (b) 5 s; (c) 3 s; (d) 2 s; (e) 1 s.

of the most mobile components of the sample. The delay, t_a, was typically set at 300 ms.

A modification of the above sequence, $((90\text{–}2\text{ ms})_5\text{–}t_a\text{–}180\text{–}\tau\text{–}90_{\pm x}\text{–}t_1\text{–}90_y\text{–}t_2\text{–acquire–}T)$, was used to obtain inversion–recovery spin–lattice relaxation data for the mobile components.

Data Analysis. Peak heights were used for the solution-state deuterium T_1 measurements. The solid-state progressive saturation data were analyzed both by total integrated intensity and by using the height of the peak corresponding to the perpendicular orientation of the C–D bond vector with respect to the static magnetic field. The solid-state inversion–recovery data were analyzed on the basis of peak area. The solid-state relaxation data were treated as arising from a single decay process and should be considered as estimates.

Results

General Description of Spectra. Figure 2 shows typical quadrupole echo solid-state deuterium NMR spectra of polysulfone II. The spectra were obtained with recycle delay times ranging from 10 (Figure 2a) to 1 s (Figure 2e) and are scaled so that the intensities can be meaningfully compared. These spectra do not match either the slow-motion or fast-motion limit spectra shown in Figure 1. Instead, as further data and calculations will show, they represent the sum of spectra reflecting a broad distribution of 180° phenyl ring flip rates. The spectra of Figure 2 show that essentially all of the signal is observed at the 10-s recycle delay.

The data show that not all of the aromatic rings in the sample have motions that are identical in rate. The differences in ring motions are attributed to local fluctuations in chain packing density (see below). The most mobile regions of the material can be selectively observed with the amorphous quadrupole echo pulse sequence. The spectrum corresponding to the most mobile rings is shown in Figure 3c, where it is compared to the spectrum reflecting the entire sample (a) and to the spectrum obtained with a rapid recycle delay (b). The spectrum in Figure 3c

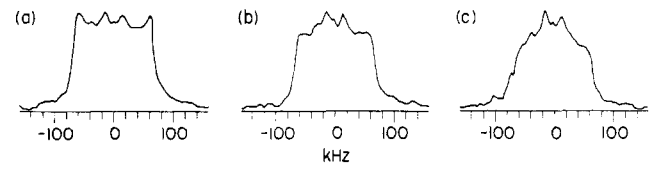


Figure 3. solid-state deuterium NMR spectra of polysulfone II obtained at 23 °C and 55.26 MHz. Spectra a and b were obtained with the quadrupole echo pulse sequence, using recycle delays of 10 and 1 s, respectively. Spectrum c was obtained with the amorphous quadrupole echo pulse sequence.

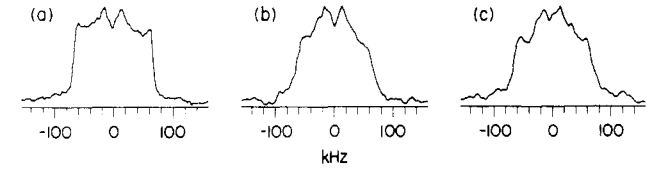


Figure 4. Solid-state deuterium NMR spectra of polysulfone II obtained at 55.26 MHz using the amorphous quadrupole echo pulse sequence with a recycle delay of 2 s. (a) 23 °C; (b) 46 °C; (c) 74 °C.

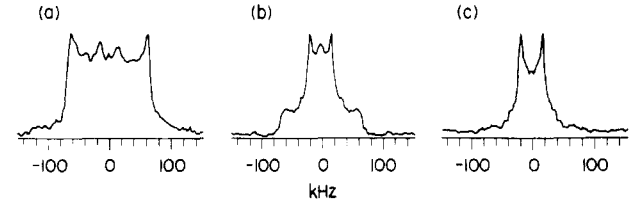


Figure 5. Comparison of the solid-state deuterium NMR spectra of polysulfones II (a), III (b), and IV (c). All spectra were obtained at 23 °C and 55.26 MHz with the quadrupole echo pulse sequence with a recycle delay of 10 s.

corresponds to rapid 180° phenyl ring flips (cf. Figure 1b). It is estimated that approximately 45% of the rings in the sample belong to this fraction. The spectra in Figure 3 further show the distributed nature of the aromatic ring motions in polysulfone II.

The spectra of Figure 4 show the effects of temperature on the phenyl ring motions in polysulfone II. As the temperature is increased from 23 (a) to 46 °C (b), the spectrum goes from one in which only part of the rings undergoes ring flips that are rapid on the deuterium NMR time scale to one in which all of the rings are flipping with $\tau_c < 10^{-7}$ s. That the constraints inhibiting rapid ring flips are so readily relaxed is an unexpected result but has been seen previously in polycarbonate.[10] Figure 4c shows that an increase in temperature to 74 °C causes no further change in the line shape. The gross character of these temperature-induced changes in the line shape are immediately reversible with temperature, but several days are required for the line shapes to become fully reversible in detail. This result suggests that phenyl ring motions may be involved in polymer aging processes.

In Figure 5 we compare the solid-state deuterium NMR spectra of polysulfones II, III, and IV. Polysulfone III contains deuterated methyl groups in addition to the deuterated bisphenol A rings (see Table I). The methyl group line shape is reduced in width over the aromatic ring line shapes by virtue of rapid threefold rotation about the C–CD_3 bond. Although the methyl groups partially obscure the line shape from the aromatic deuterons in Figure 5b, the aromatic line shapes of polysulfones II and III appear to be similar. The similarity between the aromatic line shapes for polysulfones II and III is further indicated by difference spectra. Subtraction of the spectrum of Figure 5a from 5b gives a clean methyl pattern and a good null for the aromatic region (not shown). Figure 5c shows

Table II
Solution-State Deuterium NMR Spin-Lattice Relaxation Time Data for Polysulfones II, III, and IV[a]

group	25 °C (ms)	50 °C (ms)
CD_3		
II	21	34
IV	22	35
Aromatic		
II[b]	20, 20	33, 33
III	18	30
IV	18	29

[a] Determined by inversion-recovery at 30.7 MHz; esimated uncertainty ±10%. [b] Contains magnetically inequivalent aromatic deuterons.

Table III
Solid-State Deuterium NMR Relaxation Times[a] for the Aromatic Deuterons in Polysulfone II

	T_1, ms	fraction of sample
mobile component	25 ± 3 ms[b]	45%
rigid component	1200 ± 200 ms[c]	55%

[a] 55.26 MHz, 23 °C. [b] Measured by inversion-recovery. [c] Measured by progressive saturation.

the spectrum for polysulfone IV. (The aromatic groups appear mainly as wings in the spectrum because of the narrowed filters intentionally used to acquire the methyl region in this spectrum.) The methyl groups have a quadrupole splitting, $\Delta\nu_q$, of 36.9 kHz. Such a splitting is typical of methyl groups on polymer main chains when there is no substantial averaging of the methyl line shape by large scale main-chain reorientation.[24-26]

Relaxation. Solution-state deuterium NMR relaxation times for polysulfones II, III, and IV are reported in Table II. The T_1 values increase with increasing temperature, indicating that the polysulfone motions in solution are on the fast correlation-time side of the T_1 minimum. Furthermore the spin–lattice relaxation times for all of the aromatic deuterons are the same, within experimental error. This latter finding illustrates that there are no major differences between the bisphenol-A and sulfone aromatic groups in solution.

Solid-state deuterium NMR relaxation data for polysulfone II are listed in Table III. Separate average relaxation times were measured for the mobile and rigid fractions. The percent of sample in each of these fractions is also listed in Table III. These data represent averages of a best fit to a single-exponential decay, although some nonlinearity was observed in the data. It should be noted that separation of the spectra into mobile and rigid components is artifical. The nonsingle exponential character of the relaxation and the complicated line shapes suggest that the true situation is best described as a distribution of 180° phenyl ring flip rates. The source of the seemingly bimodal behavior of the data arises from intensity distortions that occur when the time between the two pulses in the solid echo sequence is comparable to the motional correlation time.[27] These intensity losses arise from homogeneous broadening mechanisms. When motions occur whose characteristic frequencies are comparable to the quadrupole echo decay time, t_1 and t_2, the echo will not be properly refocused, leading to a loss in signal intensity.

Effect of Sorbed Water on Solid-State Deuterium NMR Spectra of Polysulfone II. The presence or absence of water does not perceptibly affect the observed solid-state deuterium NMR spectra of polysulfone II.

Addition of Antiplasticizers. Figure 6 compares the spectra with and without the antiplasticizer 4,4′-dichlorodiphenyl sulfone (DCDPS) added at 40% by weight

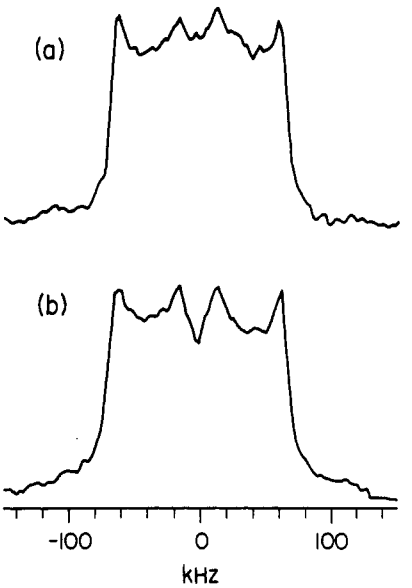


Figure 6. Comparison of the solid-state deuterium NMR spectra of polysulfone II with DCDPS added at 40% by weight (a); with polysulfone II (b). These spectra were obtained at 23 °C and 55.26 MHz with the quadrupole echo pulse sequence with a recycle delay of 2 s.

to polysulfone II. The spectrum in Figure 6b was obtained in the absence of added antiplasticizer. We have already seen that this spectrum represents the composite line shape from rings that are static on the deuterium NMR time scale and those that are flipping. The spectrum in Figure 6a was obtained with the antiplasticizer. The characteristic 32-kHz splitting (see Figure 1b) is largely gone and the center of the pattern is filled in. This suggests that the ring-flip process has been substantially slowed by this small-molecule antiplasticizer.

Discussion

Description of Motions in Unplasticized Polysulfones. Several lines of evidence indicate (1) that the primary mode of motion of the aromatic rings in the polysulfones is 180° phenylene ring flips; and (2) that these motions are best described by a broad distribution (ca. 10^2–10^7 s^{-1}) of characteristic frequencies. These two major findings will be addressed separately.

That the primary mode of motion in polysulfone II arises from 180° phenylene ring flips can best be seen from the spectrum shown in Figure 3c. The experimental conditions used to obtain this spectrum select for that fraction of the sample involved in rapid motions. The spectrum of Figure 3c matches one calculated for rapid ($\tau_c < 10^{-7}$ s) 180° phenylene ring flips. Furthermore, the spectra of Figure 2 are consistent with 180° rings that have flip rates ranging from static to intermediate to rapid. This distribution in ring-flip rates is attributed to molecular-level fluctuations in chain packing. Other large-amplitude main-chain motions can be ruled out by inspection of the spectra for the methyl-labeled polymers (Figure 5b,c). The quadrupolar splitting, $\Delta\nu_q$, for the methyl groups is 36.9 kHz. Such a splitting is expected for methyl groups that undergo threefold rotation about the C–CD_3 bond. Additional main-chain motion would cause this quadrupolar splitting to be narrowed further.

The temperature-dependent spectra of Figure 4 indicate that the constraints responsible for the inhibition of phenyl ring flips are readily relaxed at temperatures well below the DSC T_g of 189 °C. It is assumed that these constraints arise form local chain packing heterogeneities, perhaps

caused by the chains coiling upon themselves. That the constraints preventing rapid 180° phenyl ring flips in the polysulfones are readily relaxed can be contrasted to the situation encountered in semicrystalline polymers. The phenyl rings in the amorphous regions of both poly(butylene terephthalate)[8] and polystyrene[10] undergo 180° flips. However, the constraints that inhibit free flipping of the rings in these semicrystalline polymers arise from the intimate presence of crystalline regions. These semicrystalline polymers must be heated well above T_g in order to obtain the situation where all the rings are involved in flips that are rapid on the deuterium NMR time scale.

It is appropriate to compare the results presented here with other strictly amorphous polymers.[10-12] For polycarbonate, *all* of the phenyl rings undergo rapid 180° ring flips at or above room temperature, in contrast to the situation in the polysulfones, where a sizable fraction (ca. 50%) of staticlike rings are observed at room temperature. This latter result is expected, as the sulfone group is known to impart a stiffness to the polymer chain. It is only below room temperature that staticlike rings are observed for polycarbonate, in conjunction with rings that continue to flip rapidly. For polycarbonate the number of rings that flip rapidly decreases with decreasing temperature. The polycarbonate results are attributed to differences in molecular-level packing.[9-12]

Several lines of evidence argue for a broad distribution of phenyl ring-flip rates, rather than a bimodal one. First, the relaxation data are not strictly single exponential in character. Second, the solid-state relaxation time (see Table III) for the less mobile component is 1.2 s, which corresponds to a correlation time of approximately 10^{-6} s, assuming a single correlation time. Finally, the spectrum calculated for a single correlation time of 10^{-6} s does not correspond to the observed spectrum; it shows considerably more motional narrowing.

It is again appropriate to compare the present bisphenol A polysulfone results with those for the somewhat analogous bisphenol A polycarbonate. Jones and co-workers have used proton and carbon NMR spectroscopy to study phenyl ring motions in various types of polycarbonates.[28-30] Early proton second-moment studies[28] showed some evidence for bimodal behavior. However, more recent T_1 and $T_{1\rho}$ data fit well to correlation functions involving a distribution of phenyl ring flips. Furthermore, Schaefer and colleagues, using dipolar rotational spin-echo carbon NMR spectroscopy, have demonstrated that at room temperature there is but one dynamic ring population in polycarbonate.[31] Garroway and co-workers[32] found a "fast fraction" and a "slow fraction" when studying phenyl ring motions in a piperidine-cured epoxy resin. In this case, the temperature dependence of the line shapes could be analyzed with either an inhomogeneous distribution of single-exponential processes or with a homogeneous distribution involving a nonexponential autocorrelation function.

Effect of Added Water and Antiplasticizers. It is well known that low molecular weight antiplasticizers such as 4,4′-dichlorodiphenyl sulfone restrict molecular motion and cause a decrease in the tan δ of the β-relaxation.[4,33,34] The ductile mechanical properties of the polysulfone are concommitantly lost.[4]

It has furthermore been shown that whether a phenyl ring in a polymer is able to undergo a 180° flip appears to be a sensitive reporter of the conformational space surrounding the ring.[8,35] If the phenyl ring motions are responsible for the β-relaxation, one would predict that the effect of added antiplasticizers (i.e., association of the low molecular weight compound with the phenyl rings) would cause the average phenyl motions to become slower. As Figure 6 illustrates, this is precisely the case. It is therefore appropriate to associate phenyl ring flips with a molecular-level process associated with the β-relaxation. It is likely that the phenyl ring-flip process is also important in systems where aging-induced embrittlement occurs.

The addition or removal of water does not produce a perceptible change in the deuterium NMR line shape for the phenyl rings. Such a result provides neither positive or negative information concerning the role of water in β-transition. Instead, it simply indicates that water appears to have no major effect on the rate of the phenyl ring flips.

Conclusions

The main conclusion established here is that 180° flips of the phenyl rings are the primary mode of molecular motion of the aromatic rings in polysulfone and that these ring flips occur over a broad range of characteristic frequencies. We have further shown that these ring flips are a molecular-level process related to the β-relaxation. Data from the methyl-labeled polysulfone indicate that additional large-amplitude main-chain motions do not occur at room temperature. Antiplasticizers cause these phenyl ring motions to become slower, whereas water appears to have no perceptible effect on phenyl ring motions.

Studies such as these show much promise for unraveling the details of molecular-level motions in polymers and for establishing their relationship to dynamic mechanical and dielectric relaxation phenomena.

Acknowledgment. We are grateful to Dr. A. J. Lovinger for obtaining the X-ray diffraction data and to Drs. H. D. Keith, A. E. Tonelli, and E. Helfand for helpful discussions.

Registry No. II (copolymer), 102438-61-9; II (SRU), 102438-57-3; III (copolymer), 102438-63-1; III (SRU), 102438-58-4; IV (copolymer), 102438-64-2; IV (SRU), 102438-59-5; H_2O, 7732-18-5; DCDPS, 80-07-9; (bisphenol)·(DCDPS) (copolymer), 25154-01-2; (bisphenol A)·(DCDPS) (SRU), 25135-51-7.

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Characterization of Polymer Blends by Selective Proton Spin-Diffusion Nuclear Magnetic Resonance Measurements

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ABSTRACT: Spin diffusion in proton nuclear magnetic resonance has been used to study binary blends of polystyrene and poly(vinyl methyl ether). By means of a selective excitation technique, it was possible to detect the coexistence of pure and mixed domains. Within the framework of a simple three-phase model, the total amount of polymer contained in the mixed phase and its composition could be determined.

I. Introduction

The blending of polymers offers the possibility of tailoring new technically important materials with specified physical properties.[1-3] Only a small number of polymer combinations leads to thermodynamically stable blends. In most cases the artificially enforced mixtures are far from thermodynamic equilibrium and unstable. Because of low translational mobility in macromolecular systems, equilibration may proceed very slowly. The distinction between compatible and incompatible blends is in many cases not trivial. It is therefore of importance to have available analytical tools for studying phase separation on a microscopic scale. Several techniques have been applied so far, in particular, diffraction methods,[4-8] thermal analysis,[9] and electron microscopy.[10] Compatible blends exhibit a single glass transition temperature T_g while for incompatible blends the glass transitions of the individual homopolymer components can be detected. Standard methods for the determination of T_g are differential scanning calorimetry (DSC),[11,12,27] dilatometry,[13] dynamic mechanical relaxation,[14,15] and dielectric relaxation measurements.[16,17] It has also been recognized by several researchers that spin diffusion in nuclear magnetic resonance can provide information on heterogeneity.[18-25]

In a recent study, two-dimensional (2D) NMR spectroscopy was used for obtaining revealing plots that qualitatively allow the distinction between compatible and incompatible mixtures.[26] To describe a binary mixture of two distinct polymers, a three-phase model has been proposed with two pure polymer phases and a mixed phase. By 2D spin-diffusion measurements, it was possible to deduce bounds for the composition of the mixed phase. However, it turned out to be a priori impossible to determine the exact composition of the mixed phase by 2D or by transient 1D measurements.

It will be demonstrated in this paper that one-dimensional (1D) saturation-transfer experiments allow immediate access to the composition of the mixed phase. Transient spin-diffusion measurements can be used for the determination of spin-diffusion rate constants, which provide information on the size of the domains and on molecular mobility. The measurements reported here focus on proton spin diffusion, which is particularly informative as it proceeds at a high rate and is not much impeded by competing relaxation processes.

II. Samples

Binary polymer blends consisting of atactic polystyrene (PS) (supplied by BASF) and atactic poly(vinyl methyl ether) (PVME) (Aldrich-Chemie, Steinheim, BRD) were used. Both polymers have a distribution of molecular weights. The sample of PS is characterized by $\bar{M}_\eta = 279\,000$ (toluene, 25 °C) and $\bar{M}_w/\bar{M}_n = 2.5$ and the sample of PVME by $\bar{M}_\eta = 53\,500$ (benzene, 30 °C) and $\bar{M}_w/\bar{M}_n \simeq 2.0$ as estimated from gel permeation chromatography (GPC) measurements. The blending was effected by precipitation from a homogeneous solution of the two polymers in toluene or chloroform (containing 2.5% of each polymer) by adding a large excess of petroleum ether cooled to −60 °C. The precipitate was filtered off and vacuum dried for 48 h at room temperature. Samples of 50 mg were necessary for the NMR measurements.

It is well-known from thermal analysis[27,28] and from proton NMR relaxation studies[29] that the physical properties of this particular blend depends on the solvent from which it is precipitated. Some indication of this behavior could already be deduced by visual inspection of the two blends. The blend cast from toluene (B_T) appeared more transparent than the blend cast from chloroform (B_C). The blend B_T remained unaltered even after storing for 6 months at room temperature while the blend

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0024-9297/86/2219-1889$01.50/0