rigid-amorphous fraction. Not only must the glass transition be characterized by T_g but also information on its breadth and hysteresis is valuable to specify strain on the amorphous portions. Such detailed analysis is possible by separation of the heat capacity known from independent analysis from the overall thermal effects. All of the crystals (and the rigid-amorphous fraction) are metastable, and their change during analysis due to reorganization, perfection, and recrystallization must be assessed. A slightly higher heat capacity at constant pressure of amorphous PEEK below T_g cannot be fully assigned at present.

Much further work, especially on the time dependence of crystallization and annealing as well as on different crystallization conditions, is possible to reach the degree of specification needed for reproducible and reliable application of PEEK as composite matrix.

Acknowledgment. This research was supported by a NASA Institute Grant No. NGL32-018-003 and by the National Science Foundation, Polymers Program, Grant No. DMR 83-17097.

Registry No. PEEK, 31694-16-3.

References and Notes

(1) Cheng, S. Z. D.; Lim, S.; Judovits, L.; Wunderlich, B. *Polymer* to be published.
(2) Cheng, S. Z. D.; Wunderlich, B. *J. Polym. Sci., Polym. Phys. Ed.*, to be published.
(3) Blundell, D. J.; Osborn, B. N. *Polymer* **1983**, *24*, 953.
(4) Dawson, P. C.; Blundell, D. J. *Polymer* **1980**, *21*, 577.
(5) Rueda, D. R.; Ania, F.; Richardson, A.; Ward, I. M.; Balta Calleja, F. J. *Polym. Commun.* **1983**, *24*, 258.
(6) Wakely, N. T. *Polym. Commun.* **1984**, *25*, 306.
(7) Lovinger, A. J.; Davis, D. D. *J. Appl. Phys.* **1985**, *58*, 2843.
(8) Lovinger, A. J.; Davis, D. D. *Polym. Commun.* **1985**, *26*, 322.
(9) Attwood, T. E.; Dawson, P. C.; Freeman, J. L.; Hoy, L. R.; Rose, J. B.; Staniland, P. A. *Polymer* **1981**, *22*, 1096.
(10) Bishop, M. T.; Karasz, F. E.; Russo, F. E.; Langley, K. H. *Macromolecules* **1985**, *18*, 86.
(11) Gaur, U.; Wunderlich, B. *Macromolecules* **1980**, *13*, 445.
(12) Suzuki, H.; Wunderlich, B. *Makromol. Chem.* **1985**, *189*, 1109.
(13) Wunderlich, B. *Macromolecular Physics, Crystal Melting*; Academic: New York, 1980; Vol. III.
(14) Wunderlich, B. In *Thermal Analysis in Polymer Characterization*; Turi, E., Ed.; Wiley/Heyden: New York, 1981; p 1. See also: Wunderlich, B.; Menczel, J. *Prog. Calorimetry Thermal Anal.* **1984**, *2*, 81.
(15) Wunderlich, B.; Bopp, R. C. *J. Thermal Anal.* **1974**, *6*, 335. See also: Mehta, A.; Bopp, R. C.; Gaur, U.; Wunderlich, B. *J. Thermal Anal.* **1978**, *13*, 197.
(16) Ginnings, D. C.; Furukawa, G. T. *J. Am. Chem. Soc.* **1953**, *75*, 522.
(17) See, for example; Wunderlich, B.; Baur, H. *Adv. Polym. Sci.* **1970**, *7*, 151.
(18) Ferry, J. D. *Viscoelastic Properties of Polymers* , 3rd ed.; Wiley: New York, 1980.
(19) Cheng, S. Z. D.; Wunderlich, B., to be submitted.
(20) Gaur, U.; Lau, S.-F.; Wunderlich, B. *J. Phys. Chem. Ref. Data* **1983**, *12*, 91.
(21) Sasuga, T.; Hagiwara, M. *Polymer* **1985**, *26*, 501.
(22) Wunderlich, B. *J. Chem. Phys.* **1962**, *37*, 2429.
(23) Wunderlich, B. *Macromolecular Physics, Crystal Nucleation, Growth, Annealing*; Academic: New York, 1976; Vol. II.
(24) Suzuki, H.; Wunderlich, B. *Makromol. Chem.* **1985**, *189*, 1109.
(25) Grebowicz, J.; Lau, S. F.; Wunderlich, B. *J. Polym. Sci., Polym. Symp.* **1984**, *71*, 19.
(26) Wunderlich, B.; Bodily, D. M.; Kaplan, M. H. *J. Appl. Phys.* **1964**, *35*, 95.
(27) Wolpert, S. M.; Weitz, A.; Wunderlich, B. *J. Polym. Sci., Part A-2* **1971**, *9*, 1887.
(28) Menczel, J.; Wunderlich, B. *J. Polym. Sci., Polym. Lett. Ed.* **1981**, *19*, 261.
(29) Wunderlich, B.; Melillo, L.; Cormier, C. M.; Davidson, T.; Snyder, G. *J. Macromol. Sci., Phys.* **1967**, *B1*, 485.

Complex Molecular Motions in Bulk Hard-Segment Polyurethanes: A Deuterium NMR Study

Agustin Kintanar and Lynn W. Jelinski*
AT&T Bell Laboratories, Murray Hill, New Jersey 07974
Irena Gancarz and Jeffrey T. Koberstein
Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544.
Received September 25, 1985; Revised Manuscript Received April 23, 1986

ABSTRACT: Solid-state deuterium NMR spectroscopy is used to characterize molecular motion in two specifically deuterated polyurethane hard-segment polymers. The polyurethanes consist of bis(4-isocyanophenyl)methane (MDI), chain extended with butanediol-2,2,3,3-d_4 (BDO), and 2,4-toluenediyl diisocyanate (TDI), chain extended with butanediol-2,2,3,3-d_4. Line shape and relaxation (T_1) data were obtained as a function of temperature. The results indicate a broad distribution of motional correlation times in both materials. In the semicrystalline MDI–BDO polymer, the distribution divides cleanly into two components that are attributable to the crystalline and amorphous regions of the material. In the TDI–BDO polymer, there is only a single broad distribution, in keeping with the completely amorphous nature of this material. The results also show that the predominant large-scale motion of the alkyl chain is a gauche–trans conformational hop. The central methylene carbons of the butanediol undergo librations about their equilibrium positions, in addition to the large-scale conformational transitions. Above ~60 °C, additional larger scale diffusion of the entire butanediol moiety occurs within a cone of semiangle ~15°. The results are consistent with the existence of kinked conformations in the alkyl chain of this material.

The morphology and physical properties of polyurethane block copolymers have been areas of considerable interest for at least 20 years. Studies of these thermoplastic elastomers have focused primarily on the microphase separation of the hard and soft segments into domains, to which the unique properties of these materials may be directly ascribed.

We have recently demonstrated the viability of solid-state deuterium (^{2}H) NMR as a technique for evaluating phase separation and phase mixing in polyurethanes[1] and in another segmented copolymer system, the Hytrel copolyesters.[2,3] The NMR method is based on differential segmental mobilities of ^{2}H-labeled moieties in the hard and soft domains and at the domain interfaces.

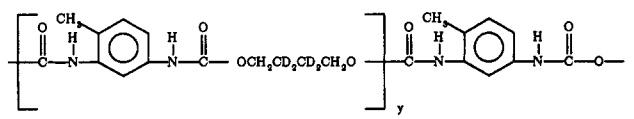
Solid-state ^{2}H NMR is a powerful tool for characterizing molecular motion in polymers.[4,5] In a rigid lattice powder, where the orientation of a selected C–D bond is random and the motions of this bond are slow on the ^{2}H NMR time

0024-9297/86/2219-1876$01.50/0

scale ($\tau_c \gtrsim 10^{-3}$ s), the ^2H NMR spectrum consists of a Pake doublet that has a quadrupole splitting, $\Delta\nu_0$, of ~128 kHz. The broad spectrum arises from the interaction of the quadrupole moment of the deuteron and the electric field gradient around the nucleus. The electric field gradient tensor is axially symmetric and has its maximal component along the C–D bond axis. Because of this, the interpretation of ^2H NMR line shapes in the presence of motion is straightforward. The spectra are sensitive to the nature of the motion (e.g., diffusive or discrete hops), the geometry of the motion, and the correlation time of the motion when the correlation time is in the intermediate exchange regime ($10^{-7} < \tau_c < 10^{-4}$ s).[4,5] Therefore, temperature-dependent solid-state ^2H NMR spectra can provide information concerning the rate, angular range, and nature of the motion. It is clear that information of this type is essential to obtaining a precise correlation of polymer molecular structure and observed macroscopic properties.

We report here results of a ^2H NMR study of molecular motion in two polyurethanes consisting entirely of hard segments. The materials are bis(4-isocyanophenyl)-methane (MDI), chain extended with butanediol-*2,2,3,3-d*$_4$, and 2,4-toluenediyl diisocyanate (TDI), chain extended with butanediol-*2,2,3,3-d*$_4$. The structures are shown below.

MDI - BDO



TDI - BDO

The deuterium label is located only on the center methylene carbons of the butanediol residues, and thus our study probes local motions in the vicinity of the label. Earlier studies of poly(butylene terephthalate), which contains the same labeled butanediol moiety, have shown that the predominant motion of the alkyl segment is of a three-bond type, resulting in a fast gauche-trans conformational reorientation of the interior methylenes.[2,6,7] These studies further showed that the terephthalate residues are moving slowly on the ^2H NMR time scale.

In this paper we address the details of molecular motion of the butanediol portion of the polyurethane hard segment. Such experiments are relevant in view of recent SAXS studies on segmented polyurethanes by Koberstein and co-workers.[8,9] Their experiments suggest that the hard segments exist in kinked conformations and that the hard-segment chains are able to fold back on themselves in the solid state, thereby filling space efficiently. The kinks would likely be located at the butanediol moiety, which is the most flexible portion of the hard segment chain.

Furthermore, Dumais et al.[1] have used deuterium NMR spectra of the MDI–BDO material as a control sample for observing and quantifying the interfacial hard segments in a series of polyurethane copolymers containing 70, 60, and 50 wt % MDI–BDO hard segment. They observed that the all-hard-segment material exhibits a motionally averaged deuterium NMR line shape at room temperature, and it was assumed that the molecular motions of the all-hard-segment material are similar to those of the hard-segment-rich microdomains in the copolymers. However, the details of the hard-segment motion were not investigated.

Here we provide experimental data that bear on the following questions related to molecular motion of the butanediol portion of the polyurethane hard segments: (1) What are the predominant modes of molecular motion of the alkyl residues? (2) Are these motions characterized by a single correlation time or rather by a distribution of characteristic frequencies? (3) How do the dynamics of the butanediol residues in MDI–BDO and TDI–BDO compare? (4) Are these results consistent with the proposed model of a kinked conformation for the butanediol group?

Experimental Section

Samples. The selectively labeled hard-segment polyurethane samples were prepared in THF solution according to literature methods,[10] using butanediol-*2,2,3,3-d*$_4$ (Merck) as the starting diol and the appropriate diisocyanate (MDI or TDI). The polymer was characterized by DSC measurements and by solution-state ^2H NMR spectroscopy.

The DSC measurements of the MDI–BDO sample (heating rate 20 °C/min) reveal a small high-temperature endotherm at ~213 °C which is due to melting of the crystalline component.[11] We did not observe a clear glass transition temperature, although this has been reported to be 109 °C.[12] The TDI–BDO polymer is known to have a T_g of 101 °C.[12]

NMR Measurements. Solution-state ^2H NMR analyses were performed on both Varian XL-200 and JEOL GX-500 spectrometers. The samples were dissolved in Me_2SO, and spectra were obtained both at room temperature and at 90 °C. The results attest to the integrity of the labeling pattern and indicate a number-average degree of polymerization of ~20 for MDI–BDO and ~22 for TDI–BDO.

Solid-state ^2H NMR spectra were obtained on a home-built spectrometer operating at 8.5 T, corresponding to a ^2H resonance frequency of 55.26 MHz. The spectrometer has been described previously.[2] The sample temperature was regulated by using either a heated air flow or a liquid nitrogen boil-off system. The temperature was measured next to the sample by means of a digital thermometer (Omega 2176A) equipped with a copper–constantan thermocouple. Temperatures are considered accurate and stable to ±1 °C.

Spectra were obtained in quadrature with the quadrupolar echo pulse sequence ($90_{\pm x}$–τ_1–90_y–τ_2)[13] or some variation thereof.[14] The 90° pulse width was typically 3.3 μs. A total of 4K data points was collected with a digitization rate of 100 ns/point. Unless specified otherwise, the delay between the quadrupole pulse pair was set at 30 μs, which was ample time for the probe and receiver to recover after the pulses.

Variations of the quadrupole echo pulse sequence were used for spin–lattice relaxation time determinations and for selective observation of a fast (short-T_1) component. The amorphous quadrupole echo pulse sequence.[14] was used for progressive saturation T_1 measurements and for selectively observing the fast component. This sequence consists of a train of 90° pulses to saturate the entire spin system, followed by a delay (t_s), followed by the quadrupole echo pulse pair. The delay (t_s) was varied over several orders of magnitude for the progressive saturation T_1 experiments and was set at 100 ms (~5T_1 of the fast component) otherwise. The amorphous inversion–recovery quadrupole echo pulse sequence[14] was used to measure the spin–lattice relaxation time of the short-T_1 component. The pulse sequence consists of a saturating train of 90° pulses, followed by a delay to allow the magnetization of the rapidly relaxing amorphous component to recover, followed by a 180° pulse to invert the fast-component magnetization, followed by a variable delay, followed by the quadrupole echo pulse pair.

Data Analysis. Typically 12–20 points were obtained for either progressive saturation or inversion–recovery relaxation experiments. Data out to 100 ms (5T_1 of fast component) were reasonably linear and were analyzed with a nonlinear three-pa-

Table I
Percent of Polyurethane Samples Observed by Different NMR Pulse Delays

MDI-BDO			TDI-BDO		
temp, °C	% in rapid motion[a]	% in slow motion[b]	temp, °C	% in rapid motion[a]	% in slow motion[b]
−45	48[c,e]	52[d,e]	−53	48[c,e]	52[d,e]
−2	64[f]	36[f]	−6	69	31
22	69	31[d]	22	79	21
55	70	30	40	84	16
73	71	29	78	95	5
123	67	33	93	100	0

[a] Measured with the amorphous quadrupole echo pulse sequence, t_a = 100 ms except as noted, estimated uncertainty ±2%. [b] Obtained by difference methods. Quadrupole delay time t_a = 2 s, unless noted otherwise. [c] t_a = 160 ms. [d] t_a = 4 s. [e] Estimated uncertainty ±8%. [f] Estimated uncertainty ±4%.

rameter fit routine on a Nicolet 1180E computer system, using the NMC program. In some cases linearity was checked by casting the inversion–recovery data in semilogarithmic form. The intensity at each delay time was obtained from the height of the echo or from integration of the entire line shape. The results obtained by either method were the same, within experimental error.

The total equilibrium ^{2}H NMR spectral intensity data were corrected for the variation of the probe signal intensity response with temperature. The probe response was calibrated by obtaining a fixed number of scans on a sample of L-alanine-d_3 under equilibrium conditions at a variety of temperatures.

Calculated solid-state ^{2}H NMR spectra were obtained according to the methods described by Mehring.[15] The calculated spectra have been corrected for the effects of pulse power fall-off[16] and for the effects of motions that occur during the quadrupole echo delay time.[17]

Results

^{2}H NMR Spectra of MDI-BDO. The ^{2}H NMR spectra of the bulk MDI-BDO polymer reflect a very broad distribution of motional correlation times at all temperatures observed (−59 to +95 °C). This is clearly demonstrated in Figure 1, where we show spectra obtained with the amorphous quadrupole echo pulse sequence at several representative temperatures. The top row of line shapes was obtained with an equilibrium delay time of 2–4 s between the saturating pulse train and the quadrupole echo pulse pair. From separate progressive saturation spin–lattice relaxation time (T_1) experiments (see below), we estimate that we are observing approximately 90% of the deuterons in the MDI-BDO sample at an equilibrium delay time of 2 s at room temperature.

In the second row, we show spectra that were obtained also with the amorphous quadrupole echo pulse sequence, except that the delay between the saturating pulses and the observe pulses is shortened to 100 ms (160 ms for the −45 °C spectrum). These line shapes are plotted on the same vertical scale as the corresponding top row spectra, and it is apparent that there is a considerable loss of intensity due to the saturation of deuterons with relatively long T_1 values. Integration of these spectra shows that at room temperature and above (data up to 123 °C, spectrum not shown), approximately 70% of the deuterons contribute to the short-T_1 component. At −2 °C, the short-T_1 component has only ~64% of the intensity of the equilibrium recycle spectrum, and at −45 °C this value has decreased to ~48%. The relative intensity data are listed in Table I. We note that the total intensity (obtained by integration of the spectra, top row, Figure 1) remains approximately constant from −2 to +73 °C. We observe only a slight decrease in total intensity at 123 °C.

Subtraction of the middle-row spectra from the corresponding top-row spectra affords the line shapes of the long-T_1 component. These difference spectra are shown in the bottom row. The line shape at −45 °C can be fit to a calculated rigid-lattice Pake doublet with a quadrupole

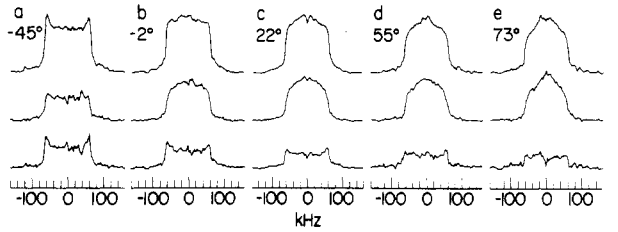


Figure 1. Solid-state ^{2}H NMR spectra (55.26 MHz) of the hard-segment MDI-BDO polymer obtained with the amorphous quadrupole echo pulse sequence. Top row: spectra obtained with an equilibrium delay time of 2–4 s after the saturating "comb" of pulses. Middle row: spectra obtained with a delay time of 100–160 ms. Bottom row: difference spectra of the equilibrium and fast-recycle spectra. Spectra within a column (a–e) were obtained at the same temperature. The experimental temperatures are (a) −45 °C, (b) −2 °C, (c) 22 °C, (d) 55 °C, and (e) 73 °C.

splitting, $\Delta\nu_q$, of 125 kHz. The difference spectra at −2 and +22 °C fit somewhat less well to a rigid-lattice pattern, as there is too much intensity at the center of the experimental line shape, especially at the higher temperature. As the temperature is increased further, to 55 and 73 °C, the centers of the staticlike powder patterns (Figure 1, bottom row) continue to fill in (giving rise to a flat-topped spectrum at 73 °C), while the overall breadth at half-height remains the same. This kind of behavior is observed when the methylene groups undergo gauche–trans conformational transitions (such that the C–D bonds hop between two sites separated by a projected (Newman) angle of ~120°) at a rate that is intermediate on the NMR time scale ($10^{-4} > \tau_c > 10^{-7}$ s).[2,15] A projected Newman angle of 120° corresponds to a dihedral (jump) angle between sites of ~109°.

Motion of the Fast Component of MDI-BDO. In Figure 2 we show ^{2}H NMR spectra of the fast component only, obtained with the amorphous quadrupole echo pulse sequence with a delay of 100 ms, at various temperatures. The line shapes indicate that the motionally averaged electric field gradient tensor is axially asymmetric, suggesting that the motional process leading to collapse of the static powder pattern has twofold symmetry.[2,15,18] Furthermore, the overall breadth of the room temperature spectrum is ~120 kHz; which implies that the proposed twofold hopping motion involves a C–D bond reorientation with a dihedral (jump) angle of ~109°. Such a line shape can arise from a gauche–trans conformational transition.[18,19]

Concentrating first on a simulation of the room temperature experimental spectrum, we varied the dihedral (jump) angle from 102° to 118° and allowed the correlation time to go from the intermediate exchange regime to the rapid-motion limit ($\tau_c \lesssim 10^{-8}$ s). We assumed a quadrupole splitting of 120 kHz which we determined from the breadth at half-height of the spectrum. This decrease from the

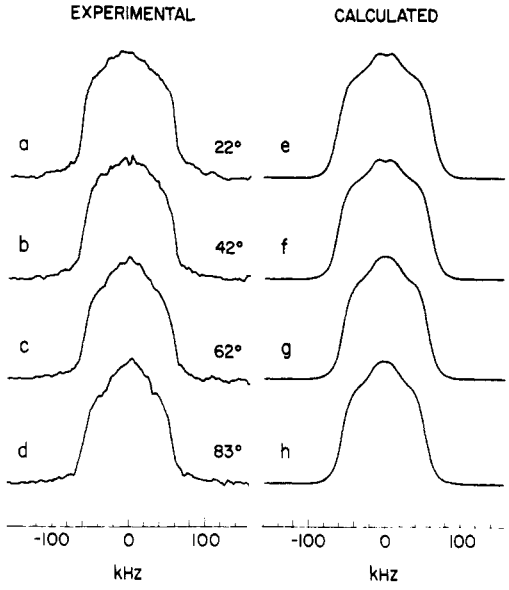


Figure 2. Experimental (a–d) and calculated (e–h) solid-state ^2H NMR spectra of the short-T_1 component of the MDI–BDO polymer. Spectra a–d were obtained with the amorphous quadrupole echo pulse sequence with an amorphous delay time, t_a, of 100 ms at 22, 42, 62, and 83 °C, respectively. Spectra e–h were calculated as described in the text using quadrupole splittings of 120, 118, 107, and 105 kHz, respectively.

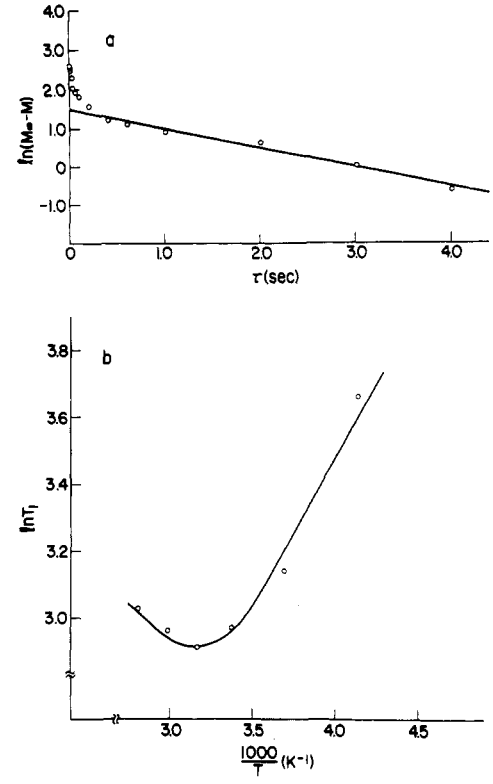


Figure 3. Representative ^2H NMR spin–lattice relaxation data of MDI–BDO. (a) Semilogarithmic plot of the magnetization recovery vs. the delay time showing the nonexponential and biphasic nature of the data. The progressive saturation data were obtained with the amorphous quadrupole echo pulse sequence at 22 °C. The amorphous delay time was varied from 1 ms to 8 s, by which time magnetization recovery was complete. (b) Arrhenius plot of the natural logarithm of the spin–lattice relaxation time (of the short-T_1 component) vs. the reciprocal of the absolute temperature. The data were obtained with the amorphous inversion–recovery quadrupole echo pulse sequence with a 100–160-ms delay after the saturation pulses.

rigid lattice value of 125 kHz is expected to arise from a fast libration of the methylene groups about their equilibrium positions. (We use *libration* to indicate a low-amplitude, high-frequency molecular motion.) These librational motions consist of a small torsional oscillation (±10°) of the methylene group about a C–C bond. With this single-correlation-time, single-angle model, the best calculated line shape is obtained with a jump angle of ~114° with a correlation time in the rapid-motion limit. Similar conditions obtain for the spectra at higher temperatures. The agreement between the calculated and experimental spectrum is good, given the simplicity of the model. However, note that the simulated spectrum has a small dip in the center and the shoulders are too narrow near the top. Differences between the calculated and observed spectra are attributed to distributions in the frequencies of motion (vide infra).

We now address the line shapes obtained at elevated temperatures. The line shape obtained at 42 °C (Figure 2b) is essentially identical with the room temperature spectrum except for a slight narrowing of ~2 kHz. At 62 °C, however, we observe further significant narrowing of the overall breadth of the pattern, which becomes even more pronounced at 83 °C, where the breadth (at half-height) of the spectrum is only ~105 kHz. This additional narrowing is attributed both to increasingly larger amplitude librations of the methylene groups about their equilibrium positions and to diffusion of the entire butanediol chain about its equilibrium position.[20]

The respective calculated spectra were obtained by including a fast, small-amplitude diffusion of the butanediol chain in addition to the aforementioned gauche–trans conformational hops and small-angle librations of the methylenes. The first and third motional modes cause a reduction in the breadth of the spectrum, while the second motional mode affects mainly the line shape. We obtain reasonably good agreement between the observed and calculated spectra at 62 and 83 °C if we assume that the butanediol moiety is diffusing within a cone whose semi-angle increases with increasing temperature and that the C–D bond hops between two equally populated sites with a dihedral angle of 114°, via a gauche–trans conformational transition. We require cone angles of ~12° and ~16° to adequately fit the spectra at 62 and 83 °C, respectively (Figure 2c,d).[21]

We now consider the line shapes of the fast component at reduced temperatures. These spectra have already been shown in the middle row of Figure 1, parts a and b. The line shape at −2 °C is essentially identical with the room temperature spectrum, indicating that the deuterons contributing to this component are undergoing motion in the fast limit at −2 °C. At −45 °C, however, the pattern has a characteristic flat top, suggesting that the hopping motion has a correlation time in the intermediate-exchange regime.

Spin–Lattice Relaxation Times of MDI–BDO. Further evidence that there is a broad distribution of motional correlation times in the MDI–BDO material is provided by progressive saturation T_1 results obtained at several temperatures, using a variable delay that spanned some 5 decades (10 s to 100 μs). Representative data are shown in Figure 3a. In all cases, we were unable to adequately fit the entire magnetization recovery curves to either a single- or a double-exponential decay, even though the curves appear to be biphasic.

We have obtained very precise T_1 measurements of the fast component at a variety of temperatures with the amorphous inversion–recovery quadrupole echo pulse sequence.[14] These experiments represent the rapidly decaying portion of the magnetization recovery curve, which data is reasonably linear out to 100 ms. The T_1 values are

Table II
Spin-Lattice Relaxation Times[a] for Polyurethane Hard Segments

MDI-BDO			TDI-BDO		
temp, °C	T_1[b] fast component, ms	T_1[c] slow component, ms	temp, °C	T_1[b] fast component, ms	T_1[c] slow component, ms
-32	39		-53	49	
-3	23				
22		2000	-7	28	
23	19.4		22		200
42	18.3		23	21	
62	19.3		40		60
75		900			
83	20.7				

[a] Measured at 55.26 MHz for deuterium. [b] Measured by inversion-recovery. [c] Measured by progressive saturation. Estimated uncertainty ±20%.

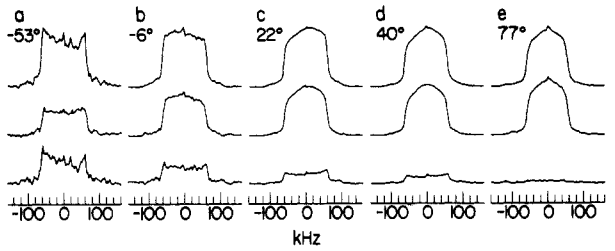


Figure 4. Solid-state ^2H NMR spectra (55.26 MHz) of the hard-segment TDI-BDO polymer obtained with the amorphous quadrupole echo pulse sequence. Top row: spectra obtained with an equilibrium delay time of 2–4 s after the saturating pulse train. Middle row: spectra obtained with a delay time of 100–160 ms. Bottom row: difference spectra of the equilibrium and fast-recycle line shapes. Spectra within a column (a–e) were obtained at the same temperature. The experimental temperatures are (a) -53 °C, (b) -6 °C, (c) 22 °C, (d) 40 °C, and (e) 77 °C.

summarized in an Arrhenius plot in Figure 3b. The plot shows a T_1 minimum at ~45 °C. Since the T_1 minumum occurs when $\omega_0\tau_c \sim 1$, this suggests that there are motions occurring with an average correlation time of ~2 ns at this temperature. A number of motional modes could contribute to the efficient spin-lattice relaxation. The calculated spectra at this temperature (vide supra) require both the large-scale conformational transition and a lower amplitude libration for adequate simulation. The T_1 data are summarized in Table II.

^2H NMR Spectra of TDI-BDO. The ^2H NMR spectra of the TDI-BDO polymer also reveal a broad distribution of correlation times at temperatures from -55 to 40 °C (the glass transition temperature). This is demonstrated in Figure 4, where we show spectra of TDI-BDO obtained with the amorphous quadrupole echo pulse sequence at several representative temperatures. The top row of line shapes was obtained with an equilibrium delay time of 2 s (4 s for the -53 °C spectrum) between the saturating pulse train and the quadrupole echo pulse pair. Separate progressive saturation spin-lattice relaxation time (T_1) experiments (vide infra) indicate that we are observing all the deutrons in TDI-BDO with this delay time at room temperature. In the second row, we show line shapes obtained with the same pulse sequence except the delay time is shortened to 100 ms (160 ms for the -53 °C spectrum). These spectra are plotted on the same vertical scale as the top-row line shapes, and as we observed for MDI-BDO polymer, there is again a loss in intensity at the shorter delay time because of saturation of deuterons with long spin-lattice relaxation times. The relative intensity of the short-T_1 component is obtained by integration of the top- and middle-row spectra, and the results are summarized in Table I. The fraction of deuterons contributing to the short-T_1 component increases monotonically until ~20 °C above the glass transition, when essentially 100% of the deutrons are observed with a delay time of 100 ms. This is in sharp contrast to the behavior of the MDI-BDO material, where the fraction of deutrons contributing to the short-T_1 component was constant at ~70% from 20 to 73 °C.

In the bottom row, we show difference spectra of the corresponding top- and middle-row line shapes. These difference spectra represent the line shapes of the long-T_1 component of the distribution. At -53 °C, the spectrum fits reasonably well to a rigid-lattice Pake doublet with a quadrupole splitting $\Delta\nu_q$ ~125 kHz. As the temperature is increased, the center of the pattern fills in to give a nearly flat-topped spectrum at 22 °C. At 77 °C, there is essentially no intensity in the difference spectrum as nearly all the deuterons have very short T_1 values and relax within 100 ms. The overall pattern of change in the difference line shapes is similar to that of the MDI-BDO polymer, although the changes occur at lower temperatures for the TDI-BDO material. This suggests that as in the MDI-BDO material, the predominant motion of the butanediol residues in TDI-BDO is a twofold hop between sites separated by a dihedral angle of ~114 °C, consistent with a gauche–trans conformational transition of the interior methylenes.

This interpretation is supported by the line shapes of the short-T_1 component (Figure 4, middle row), obtained with a delay time of 100 ms (160 ms for the -53 °C spectrum). At -53 °C, the spectrum is nearly flat-topped but retains nearly the same spectral breadth (~120 kHz). As the temperature is increased, the center of the pattern becomes domelike, indicating that the average rate of the large-amplitude twofold hop is in the fast limit of the ^2H NMR time scale ($\tau_c \leq 10^{-7}$ s). At the highest temperature (77 °C), the spectrum narrows significantly so that the breadth at half-height is ~110 kHz. The ^2H NMR spectra of the fast-T_1 component in TDI-BDO and MDI-BDO are very similar. In fact at ~20 and ~40 °C, the line shapes from the two materials are virtually identical and fit reasonably well to the same calculated spectrum (Figure 4, middle row, and Figure 2a,b). Thus, at least at these temperatures, and for the fast component of the distribution, the butanediol residues undergo the same type of motion in TDI-BDO and MDI-BDO. That is, the predominant motion is a twofold hop between sites of equal probability separated by a dihedral angel of ~114°. The average correlation time of this motion is in the fast limit of the ^2H NMR time scale ($\tau_c \leq 10^{-7}$ s) above 20 °C. Superimposed on the large-amplitude motion is a small-amplitude libration of the methylene groups, which accounts for the observed motionally narrowed breadth of these spectra (~120 kHz) from the rigid-lattice value. The additional narrowing of the spectrum at 77 °C is attributed both to larger amplitude librations of the methylene groups about their equilibrium positions and to diffusion of the entire butanediol chain within a narrow cone of semiangle ~10°.[20]

We also note that the variation of the total spectral intensity with temperature (obtained by integration of the equilibrium delay spectra) appears markedly different in the TDI-BDO polymer than in the MDI-BDO material. This effect is related to the T_g of the polymer and is shown graphically in Figure 5. It appears that the large-scale motions that occur above T_g prevent proper refocusing of the quadrupole echo signal, leading to marked reductions in echo amplitude.

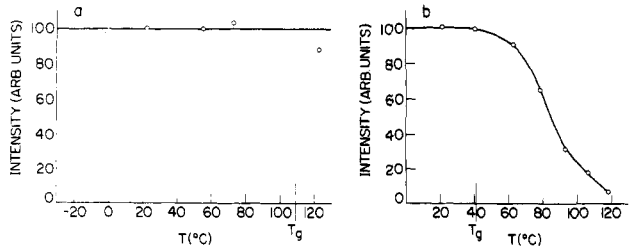


Figure 5. Plot of the total equilibrium ^2H NMR spectral intensity (obtained by integration of the line shapes) vs. the temperature: (a) MDI–BDO, (b) TDI–BDO. The intensity data were corrected for the signal intensity response of the probe as described in the text.

Spin–Lattice Relaxation Times of TDI–BDO. Further evidence that there is a broad distribution of correlation times is provided by progressive saturation T_1 results obtained at room temperature, using a variable delay that spanned some 4 decades (2 s to 1 ms). The data, shown in Figure 6a, clearly describe a nonexponential recovery. There are deuterons in some environments that take up to 1 s to relax, whereas a good proportion of deuterons are fully relaxed by 100 ms. In contrast, progressive saturation data obtained at 60 °C (not shown) indicate that all deuterons attain equilibrium in 200 ms and the nonexponential nature of the magnetization recovery is not as evident.

We have also obtained T_1 results of the fast component only with the amorphous inversion–recovery quadrupole echo pulse sequence at −55, −17, and +23 °C. (These are temperatures at which intensity losses are not a problem.) In these experiments, the magnetization recovery was reasonably linear up to the longest delay time used (100–160 ms, $\sim 4T_1$). The results are shown in an Arrhenius plot in Figure 6b. The T_1 data are summarized in Table II. Note that the T_1 values of the fast component in TDI–BDO and MDI–BDO are quite similar. Thus, in addition to the similarity in types of motion of the fast component in both polymers, the rates of motion are quite similar as well.

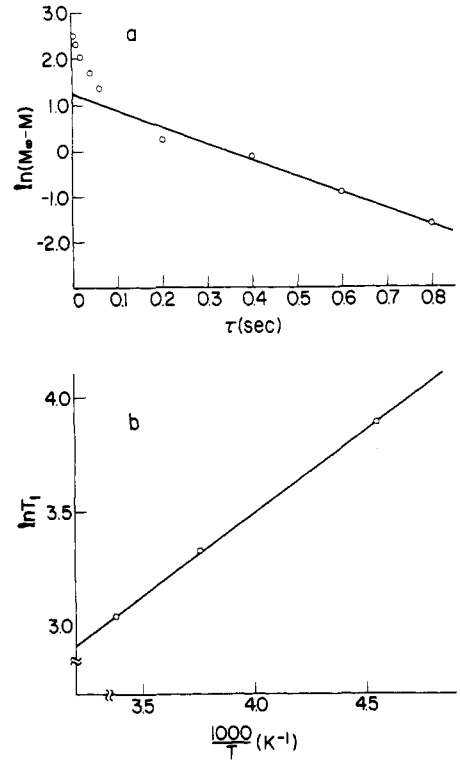


Figure 6. Representative ^2H NMR spin–lattice relaxation data of TDI–BDO. (a) Semilogarithmic plot of the magnetization recovery vs. the delay time showing the nonexponential nature of the data. The progressive saturation data were obtained with the amorphous quadrupole echo pulse sequence at 22 °C. The amorphous delay time was varied from 1 ms to 2 s, by which time magnetization recovery was complete. (b) Arrhenius plot of the natural logarithm of the spin–lattice relaxation time (of the short-T_1 component) vs. the reciprocal of the absolute temperature. The data were obtained with the amorphous inversion–recovery quadrupole echo pulse sequence with a 100–160-ms delay after the saturating pulse train.

Discussion

Nature of the Distribution of Motional Correlation Times in MDI–BDO and TDI–BDO. The evidence presented in the previous section clearly indicates that there is a broad distribution of motional correlation times in both MDI–BDO and TDI–BDO. The nature of the distribution in the two polymers is quite different, however. First, there are slower motions occurring in MDI–BDO than in TDI–BDO. The spin–lattice relaxation indicate that there are deuterons with much longer T_1 values in MDI–BDO than in TDI–BDO. Second, the distribution of motion in MDI–BDO divides clearly into two major components, while that of TDI–BDO does not. This is indicated by the relative intensities of the equilibrium and fast recycle spectra (Figures 1 and 4 and Table I). At low temperatures, both polymer systems have ~50% of the deuterons contributing to the short-T_1 component. As the temperature is increased, the percentage of deuterons contributing to the fast component increases on both systems. At room temperature the relative intensity in the short-T_1 component starts to plateau at 70% in the MDI–BDO system and remains at this value even above the glass transition. In the TDI–BDO system, however, the relative intensity of the fast recycle spectra increases monotonically to a value of 100% at about 60 °C.

The differences in the distribution of motion in the two polymers can readily be explained by the fact that MDI–BDO is semicrystalline while TDI–BDO is completely amorphous. The slower moving deuterons with long T_1 values observed in the MDI–BDO material are likely located in the crystalline domains. In these domains, the packing is ordered and consequently denser, making the large amplitude (twofold hop) motion less likely to occur. The existence of crystalline regions in MDI–BDO also explains the constant long-T_1 component (30%) that is observed over a wide range of temperatures. At low temperatures (~ −40 °C) deuterons in both the crystalline and amorphous domains of MDI–BDO contribute to the long-T_1 component as the motions are slow in both regions. At higher temperatures (~20 °C), the motional constraints in the amorphous regions are readily relaxed so that essentially all the deuterons in this domain contribute to the fast recycle spectrum. However, deuterons in the crystalline domains are still packed tightly and therefore move slowly and contribute to the long-T_1 component. Our relative intensity results indicate that our MDI–BDO sample is ~30% crystalline. Although it is difficult to obtain reliable quantitative results from our DSC measurements, 30% crystallinity is not inconsistent with these results. Morevoer, it is well-known that crystallinity of 30% can be routinely obtained in MDI–BDO.[11]

It is clear that even in amorphous domains of these polymers, there is a very broad distribution of motional correlation times. This is demonstrated most clearly by the ^2H NMR line shapes of TDI–BDO (Figure 4). From the line shapes and the T_1 data, we estimate that the distribution of motional correlation times in the amorphous

regions of MDI–BDO and TDI–BDO spans some 5 orders of magnitude. Even at high temperatures, when the deuterons in the amorphous regions contribute only to the fast recycle (short-T_1) spectra, there is still a distribution of motions. This is evident in the imperfections of the fit of the calculated spectra to a single-correlation-time model. Moreover, ^{2}H NMR spectra obtained with different delays between pulses (not shown) have different line shapes, again indicating that even in the fast recycle spectra not all the deuterons are moving at rates in the fast limit of the ^{2}H NMR time scale.[17]

The distribution in the characteristic frequencies of motion of the labeled methylene groups in the amorphous regions of the polymer are likely due to variation in the local packing density due to the irregular packing of the polymer in these domains. These variations are on a molecular-length scale and change with changing temperature. Alternatively, or in addition to the above reasons, the slower components in the distribution may be attributed to butanediol residues that are in constrained conformations because they are the sites of twists and turns of the polymer chains. We note, however, that the observed broad range of motional correlation times probably represents distributions in both the characteristic frequencies and amplitudes of several motional modes (e.g., a large-amplitude twofold hop and a small-angle vibration). Finally, we note that the constraints resulting in the broad range of correlation times in the amorphous region relax readily with temperature, permitting a facile shift of the entire distribution of motion to higher frequencies.

Details of Molecular Motion in the Fast Component. The ^{2}H NMR spectra of the fast (amorphous) component of the MDI–BDO and TDI–BDO polymer are consistent with the occurrence of gauche–trans isomerization in the butanediol moiety. Librations of the methylene groups are superimposed on this motion, and, at high temperatures, diffusion of the entire butanediol chain may also occur.

This motional model is supported by the T_1 data. The magnitude of the T_1 minimum (~20 ms) of the amorphous component in MDI–BDO suggests that more than one motion contributes to relaxation, since we would expect a much higher or lower T_1 value at the minimum if one process were dominant.[22]

The predominant motion affecting line shapes is the large-amplitude twofold hop of the labeled methylene groups. The motion results from a gauche–trans conformational transition of the labeled methylene group. In Figure 7a, we show in a Newman projection (down the center bond of the butanediol moiety) how this motion occurs. As diagrammed, this motion requires a large-scale reorientation of the ends of the polymer chain which would be energeticaly unfavorable. Several motional models involving cooperative motion about several bonds have been proposed that avoid this situation. Two of the models, involving motion about three bonds, are shown schematically in Figure 7b. These motions have been shown to occur in poly(butylene terephthalate).[2,6] Similar motions probably occur in these polyurethane systems as well.

The observed gauche–trans conformational transitions in these polyurethanes are quite similar to those observed in poly(butylene terephthalate). There are, however, some important differences. The spectra we observe here are best fit to a calculated line shape obtained with a dihedral angle of ~114°; as opposed to the 102° angle that was reported for poly(butylene terephthalate).[2] We note that there is some uncertainty in the determination of this angle in the present study because of the broad distribution of

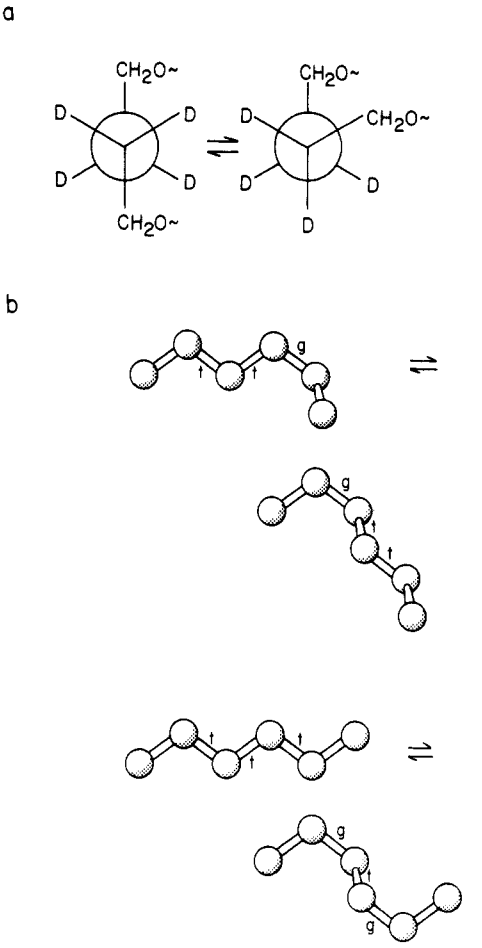


Figure 7. Schematic representation of mechanisms for trans–gauche conformational transitions in the butanediol residues of MDI–BDO or TDI–BDO. (a) Newman projection showing a discrete isomerization about the central bond in the alkyl moiety. (b) Helfand-type models of motion about three bonds, involving gauche migration ($ttg^{\pm} \rightleftarrows g^{\pm}tt$) and pair–gauche production ($ttt \rightleftarrows g^{\pm}tg^{\mp}$).

motional correlation times (vide supra). Moreover, the conformational hops occur at a much faster rate in the polyurethane system than in poly(butylene terephthalate). The present results indicate that the average correlation time for this motional process is in the fast-exchange limit above −2 °C. In poly(butylene terephthalate) the fast-exchange limit for this motional process occurs at ~85 °C. Furthermore, the results for poly(butylene terephthalate) indicate a much narrower distribution of correlation times than what we observe here for MDI–BDO and TDI–BDO.

The most obvious difference between the two systems is the presence of fast butanediol chain diffusion that occurs in the polyurethane hard-segment polymers and results in significantly narrowed spectra at high temperature. The ^{2}H NMR spectra of poly(butylene terephthalate) up to 85 °C suggest that little such motion is occurring in this polymer.[2]

There is indirect IR spectroscopy evidence that the butanediol chain diffusion occurs at elevated temperatures in MDI–BDO polyurethane.[23,24] The evidence consists of quantification of the free and hydrogen bonded NH groups and is based on their different vibrational frequencies and extinction coefficients. The results reveal an increase in the amount of free NH groups starting at about 75 °C. Large-amplitude diffusion of the butanediol moiety would require disruption of the hydrogen bonds of the NH groups on one chain with the oxygen atoms on the ester groups of adjacent chains. A recent communication has ques-

tioned the validity of these IR experiments, however, noting that the IR line shape changes may be accounted for by frequency shifts and reduction of the extinction coefficients of the hydrogen bonded NH group IR band.[26] These workers attribute the changes in extinction coefficient to a change in the "strength" of the hydrogen bond. It is clear, however, that the stretching of hydrogen bonds due to the proposed diffusion of the butanediol chain in a cone would be expected to modulate the IR properties of the NH region.

Motion in TDI–BDO above T_g. We now address the large decrease in absolute ^2H NMR spectral intensity that we observe in the TDI–BDO material above its glass transition temperature. This intensity decrease is likely due to the onset of C–H bond rotations that accompany translational motions of the polymer chain.

An understanding of this effect requires a more thorough understanding of the quadrupole echo sequence. During the first radio-frequency pulse, the spin magnetization is tilted away from alignment with the static field (B_0) until it is in a plane perpendicular to B_0. After the pulse, the magnetization precesses in the plane under the influence of the quadropolar interaction. Since every spin "sees" interactions with different magnitudes, the spins dephase. The second radio-frequency pulse causes the dephasing to change direction, and the spins refocus to form an echo. Chain motions that occur while the spins are dephasing or refocusing result in a scrambling of the quadropole interaction that each spin "sees". Therefore, refocusing is incomplete and we see echoes with reduced intensity. The spectral intensity decreases with increasing temperature because as the motion speeds up, there is an increased probability that more portions of the polymer chain move and therefore more spins are "scrambled".

Summary

These ^2H NMR results show the existence of a broad distribution of motional correlation times in the hard-segment (butanediol-labeled) polyurethane polymers. In semicrystalline MDI–BDO, the distribution is divided into two major components corresponding to crystalline and amorphous regions of the polymer. In the crystalline region, the C–D bonds may be considered static on the ^2H NMR time scale at room temperature. However, relaxation data indicate that there are high-frequency librational motions of the labeled methylene groups in these relatively rigid domains. The motional constraints in the crystalline region are not easily relaxed at higher temperatures and the distribution shifts only slowly to higher frequencies with increasing temperature.

In the amorphous regions of MDI–BDO and in the amorphous polymer TDI–BDO, there is a broad range of motional correlation times, extending over 5 orders of magnitude. Motion in these domains is considerably faster than in the crystalline domains at room temperature. The correlation times range from $\sim 10^{-5}$ to 10^{-9} s. The constraints responsible for the distribution of motion in the amorphous domains are likely differences in local packing density. These constraints vary readily with temperature so that the distribution moves easily to lower or higher frequencies of motion. Thus at −50 °C, some of the deuterons in the amorphous region are moving as slowly as those in the crystalline regions, while at about 70 °C, most of the deuterons in the amorphous domain are moving at rates very much faster than in the crystalline domain and in the fast limit of the ^2H NMR time scale ($\tau_c < 10^{-7}$ s).

The ^2H NMR spectra of the amorphous component (obtained with a short delay time) are consistent with the occurrence of gauche–trans conformational transitions as the major motional mode. The motion consists of hops of the C–D bonds between two equally populated sites separated by a dihedral angle of ~114°. Observation of this motional mode is consistent with the existence of kinked conformations of the alkyl segment in MDI–BDO and TDI–BDO. Low-amplitude high-frequency librations of the methylene groups about their equilibrium position may also occur to account for the small observed narrowing of the quadrupole splitting from the rigid-lattice value. This motional model is consistent with the observed magnitude of the T_1 minimum in the amorphous component of MDI–BDO, which indicates that more than one motional mode is contributing to relaxation.

Above ~60 °C, we observe further significant narrowing of the ^2H NMR line shapes, which indicates the onset of an additional mode of motion. This motion is modeled by diffusion of the butanediol chain within a cone of small semiangle (10–20°). The amplitude of the diffusion and thus the semiangle of the cone is assumed to increase with increasing temperature.

Finally, in the amorphous TDI–BDO polymer we observe the onset of large-scale C–D bond motions at rates greater than 10^5 s^{-1} at ~20 °C above the glass transition temperature ($T_g \sim 41$ C), which results in a decrease in intensity of the quadropole echo.

Registry No. (MDI)-(BDO) (SRU), 25868-09-1; (MDI)-(BDO) (copolymer), 25805-16-7; (TDI)-(BDO) (SRU), 54633-10-2; (TDI)-(BDO) (copolymer), 25867-01-0.

References and Notes

(1) Dumais, J. J.; Jelinski, L. W.; Leung, L. M.; Gancarz, I.; Galambos, A.; Koberstein, J. T. *Macromolecules* **1985**, *18*, 116.
(2) Jelinski, L. W.; Dumais, J. J.; Engel, A. K. *Macromolecules* **1983**, *16*, 492.
(3) Jelinski, L. W.; Dumais, J. J.; Engel, A. K. *ACS Symp. Ser.* **1984**, *247*, 55.
(4) Spiess, H. W. *Colloid Polym. Sci.* **1983**, *261*, 193.
(5) Torchia, D. A. *Annu. Rev. Biophys. Bioeng.* **1984**, *13*, 125.
(6) Jelinski, L. W.; Dumais, J. J.; Engel, A. K. *Macromolecules* **1983**, *16*, 403.
(7) Jelinski, L. W.; Dumais, J. J.; Watnick, P. I.; Engel, A. K.; Sefcik, M. D. *Macromolecules* **1983**, *16*, 409.
(8) Koberstein, J. T.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 1439.
(9) Leung, L. M.; Koberstein, J. T. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1883.
(10) Lyman, D. J. *J. Polym. Sci.* **1960**, *45*, 49.
(11) Kajiyama, T.; MacKnight, W. J. *Polym. J. (Tokyo)* **1970**, *1*, 548.
(12) Schneider, N. S.; Paik Sung, C. S.; Matton, R. W.; Illinger, J. L. *Macromolecules* **1975**, *8*, 62.
(13) Davis, J. H.; Jeffrey, K. R.; Bloom, M.; Valic, M. I.; Higgs, T. P. *Chem. Phys. Lett.* **1976**, *42*, 390.
(14) Cholli, A. L.; Dumais, J. J.; Engel, A. K.; Jelinski, L. W. *Macromolecules* **1984**, *17*, 2399.
(15) Mehring, M. *High Resolution NMR in Solids*, 2nd ed.; Springer-Verlag: New York, 1983.
(16) Bloom, M.; Davis, J. H.; Valic, M. I. *Can. J. Phys.* **1980**, *58*, 1510.
(17) Spiess, H. W.; Sillescu, H. *J. Magn. Reson.* **1981**, *42*, 381.
(18) Huang, T. H.; Skarjune, R. P.; Wittebort, R. J.; Griffin, R. G.; Oldfield, E. *J. Am. Chem. Soc.* **1980**, *102*, 7377.
(19) Rosenke, K.; Sillescu, H.; Spiess, H. W. *Polymer* **1980**, *21*, 757.
(20) It is theoretically possible to account for the observed decrease in quadrupole splitting at high temperature by a model of only large amplitude (~ ±30°) librations of the methylene groups about their equilibrium position. Such a model, however, introduces additional asymmetry into the electric field gradient tensor and results in a line shape substantially different from that observed experimentally.
(21) We assume that the rigid lattice quadrupole splitting (125 kHz) was reduced to ~120 kHz by librations of the methylene groups about their equilibrium positions. The quadrupole splittings were further narrowed by assuming a libration of the entire butanediol chain within a cone of semiangle θ_L. The reduction factor is given by $(3 \cos^2 \theta_L - 1)/2$.
(22) We have calculated the spin–lattice relaxation time vs. the correlation time for a twofold jump motional model using the

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.

(23) MacKnight, W. J.; Yang, M. *J. Polym. Sci., Polym. Symp.* **1973**, *No. 42*, 817.
(24) Seymour, R. W.; Cooper, S. L. *Macromolecules* **1973**, *6*, 48.
(25) Torchia, D. A.; Szabo, A. *J. Magn. Reson.* **1982**, *49*, 107.
(26) Coleman, M. M.; Skrovanek, D. J.; Howe, S. E.; Painter, P. C. *Macromolecules* **1985**, *18* 299.

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

J. J. Dumais, A. L. Cholli,† and L. W. Jelinski*

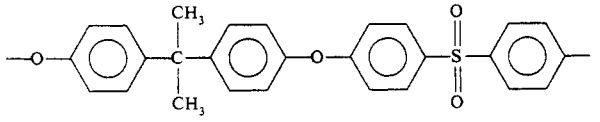
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

J. L. Hedrick‡ and J. E. McGrath

Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061.
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.

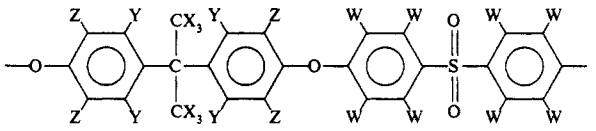


I

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.

† Present address: BOC Corporation, Murray Hill, New Jersey 07974.
‡ Present address: IBM Research Laboratory, San Jose, California 95193.

0024-9297/86/2219-1884$01.50/0