Solid-State Carbon-13 NMR Studies of Model Urethane Elastomers

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Received April 27, 1989; Revised Manuscript Received October 26, 1989

ABSTRACT: Model urethane elastomers consisting of 4,4′-methylene diisocyanate, 1,4-butanediol, and a 2000 molecular weight poly(oxypropylenediol) were examined by solid-state carbon-13 NMR spectroscopy. $T_{1\rho}{}^{c}$ values were determined for the aromatic and butanediol carbons as a function of cross polarization field strength and temperature. The results for the aromatic carbons correlate well with observed high-temperature behavior of the elastomer as determined by dynamic mechanical spectroscopy. The biexponential decay of the butanediol resonances indicated that two types of motional populations can be associated with the phase-segregated portion of the hard segment. These results demonstrate the intimate connection between molecular motion and mechanical properties in urethane polymers. This understanding provides an important framework for optimizing physical properties in urethane polymers.

Introduction

Over the past few years carbon-13 $T_{1\rho}{}^{c}$ relaxation time measurements have been successfully applied to polycarbonate[1-3] and epoxy polymer systems[4-6] to determine molecular motion in the mid kilohertz frequency range. For polycarbonate the correlation between mid kilohertz molecular motions and observed mechanical behavior has not been straightforward. This has led to the conclusion that the mechanical behavior is dominated by correlated motions involving subunits larger than a single monomer.[7] For epoxy systems, mechanical relaxation results can be reconciled with the NMR results by presuming that the phenylene rings reorient by small diffusive steps.[6] In both of these polymer systems the complication of the spin–spin versus the spin–lattice contribution to the measured $T_{1\rho}{}^{c}$ value must be considered. Elegant methods of resolving this difficulty have been devised.[8]

Until now, little solid-state NMR work has been done on urethane elastomers. Nierzwicki and co-workers[9] have examined the microphase separation of 4,4′-methylene diisocyanate (MDI) polymerized with poly(tetramethylene oxide) and a variety of chain extenders by using the biexponential decay of the magnetization (free induction decay or FID) as a probe of the two-phase polymers. Eisenbach and Gronski[23] investigated phase separation in the MDI–butanediol–poly(tetramethylene oxide) system by examination of the ^{13}C CPMAS spectra and by observation of the cross polarization between a protonated soft segment and a deuterated hard segment. Assink and Wilkes[10] have conducted similar studies on other MDI–butanediol systems. Jelinski and co-workers[11,24] have used deuterium NMR to investigate phase segregation in urethanes containing an MDI–butanediol hard segment and a soft segment consisting of poly(propylene oxide) capped with poly(ethylene oxide) as well as systems consisting of only MDI–butanediol and TDI–butanediol. MDI–butanediol type urethane systems have been examined by a number of workers using X-ray, electron diffraction, and microscopy methods.[12-23] All of the above-mentioned studies made use of urethane polymers that contained a mixture of hard-segment lengths.

We report here the results of a solid-state carbon-13 $T_{1\rho}{}^{c}$ relaxation time study on two model urethane elastomers having precisely defined hard-segment lengths. Our results address the following questions: (1) How does hard-segment length affect the observed motion of the aromatic and butanediol carbons? (2) What is the effect of temperature on the hard-segment motion? (3) How do the observed motions correlate with the microdomain and dynamic mechanical properties of the polymers?

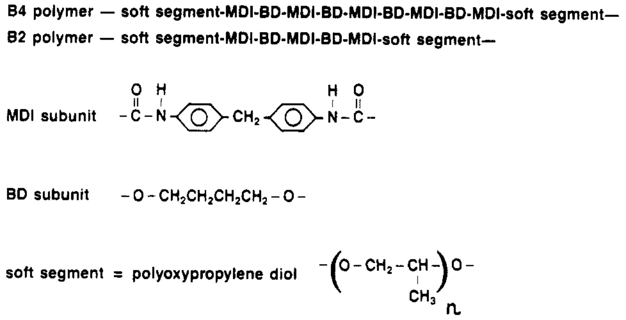

Figure 1. Structures and nomenclature for the polymers discussed in the text.

Experimental Section

Materials. The two polymers examined were solid urethane elastomers whose structures are shown in Figure 1. The synthetic route used to make these model polymers allows only well-defined hard-segment lengths to be obtained. As indicated by dynamic mechanical spectroscopy (DMS), the melting points of the B2 and B4 polymers were 98 and 175 °C, respectively. The peak molecular weights, as determined by gel permeation chromatography, were, for the B2 polymer, 150 000, and, for the B4 polymer, 220 000. Further details of the characterization of these polymers are contained in ref 26. No annealing of the polymers was performed on materials run at room temperature. Polymers run at 70 °C were cycled several times to remove any short-term annealing effects.

NMR. All data were taken by using a JEOL GX-270 spectrometer interfaced to Chemagnetics power amplifiers. Room-temperature data were acquired by using a Chemagnetics probe and Kel-F rotors. Seventy degree data were taken by using a Doty Scientific probe and Macor spinners. The pulse sequence was a bilevel standard cross polarization $T_{1\rho}{}^{c}$ sequence. Experiments were carried out at cross polarization field strengths of both 38 and 50 kHz. A cross polarization time of 900 μs was used for examination of the hard-segment resonances. Each spectrum of a relaxation curve consisted of 7100 scans with 8196 data points, 25 000 Hz sweep width, and 2.8-s recycle. Intensi-

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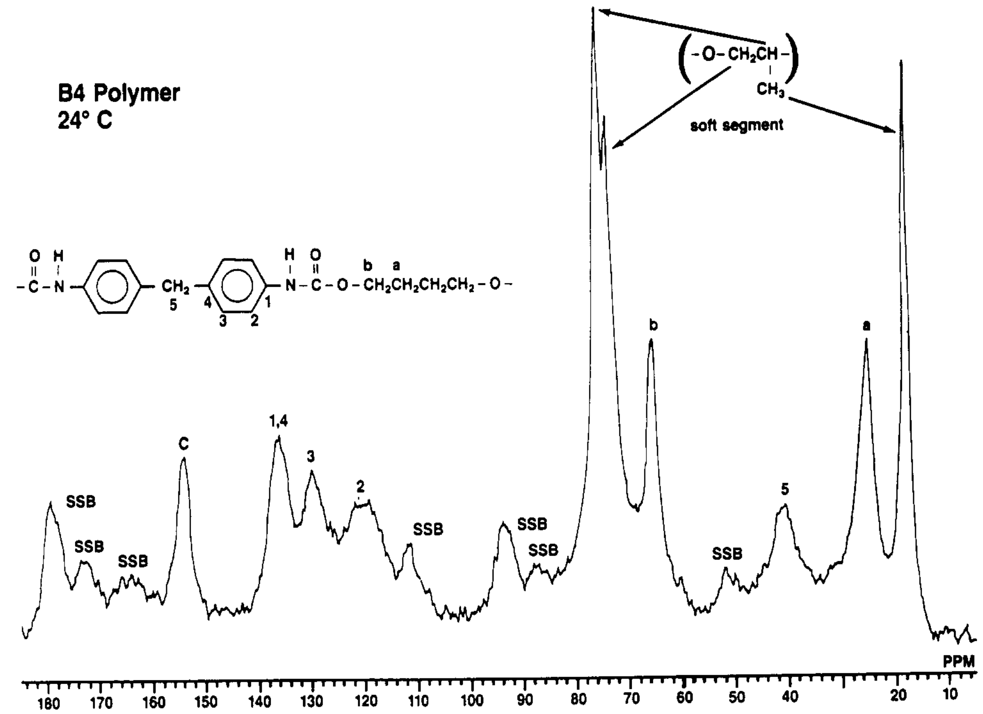

Figure 2. Solid-state ^{13}C CPMAS spectrum of the B4 polymer.

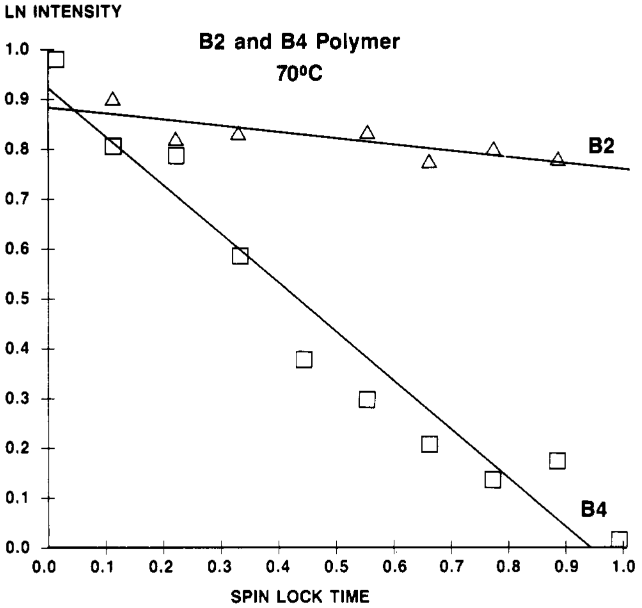

Figure 3. Decay of the magnetization of the 3,3′-carbons of MDI of B2 and B4 polymers at 70 °C.

ties were obtained by curve fitting the peaks to a Lorentzian line shape. A spinning speed of about 2950 Hz was employed for all spectra. Under these conditions sidebands are placed outside regions of interest. Sample temperature is the measured temperature of the spinner nitrogen in the immediate vicinity of the rotor. Samples were prepared by freezing in liquid nitrogen and grinding in a Janke & Kunkle Ikawerk blender. Adiabatic demagnetization in the rotating frame (ADRF) experiments were performed on a 100-MHz Chemagnetics M-1005 spectrometer that had been modified to allow the adiabatic removal of the H_1 field. A standard ADRF pulse scheme was used. Samples were run nonspinning with a spin lock field of 38 kHz and a spin lock period of 2 ms.

Results and Discussion

For a variety of reasons urethane elastomers are ideal systems to investigate by carbon-13 solid-state NMR. At room temperature, ADRF (adiabatic demagnetization in the rotating frame) experiments have shown that the spin-spin contribution to the relaxation rate is negligible, although below the soft segment glass transition of about −20 °C, this decay mechanism does become important.[25] The rapid decay of the aromatic resonances and the overall resolution obtainable for these polymers facilitate solid state C-13 studies. The correlation between the mechanical properties and the NMR results are also more straightforward than has been the case for other systems.

Results. The structures of the two urethane polymers investigated are shown in Figure 1. The material containing only two butanediol molecules per hard segment is referred to as B2. Similarly, B4 refers to four butanediols per hard-segment unit. For reference, Figure 2 shows a typical spectrum of the B4 polymer with assignments. Table I shows the measured values of $T_{1\rho}{}^{c}$ at both 38 and 50 kHz for both polymers. Relative to typical values obtained for materials such as polycarbonate, the aromatic resonance relaxation is quite rapid implying a great deal of motion in the rings at both 38 and 50 kHz. In general for both the butanediol and the aromatic resonances, increasing the spin locking field strength causes a slight increase in the $T_{1\rho}{}^{c}$ values. This implies that the motional spectral density distribution decreases slightly with increasing spin lock field strength over the range of 38–50 kHz. The measured rates reported here are slightly faster than those published previously.[26] We attribute this difference to the use of curve fitting to establish the peak intensities as opposed to the use of peak heights in our previous work. Aromatic ring motion can occur either by ring rotation or by an overall rocking of

Table I
$T_{1\rho}{}^{c}$ Values (ms) for the 2,3-Butanediol and 3,3′-Aromatic Resonances in the B2 and B4 Model Urethane Polymers at 24 °C

	38 KHz	50 KHz
B2 Aromatic	1.5	2.0
B2 Butanediol	6.4	7.9
B4 Aromatic	1.4	1.9
B4 Butanediol	4.7	5.5
	11.5	12.6

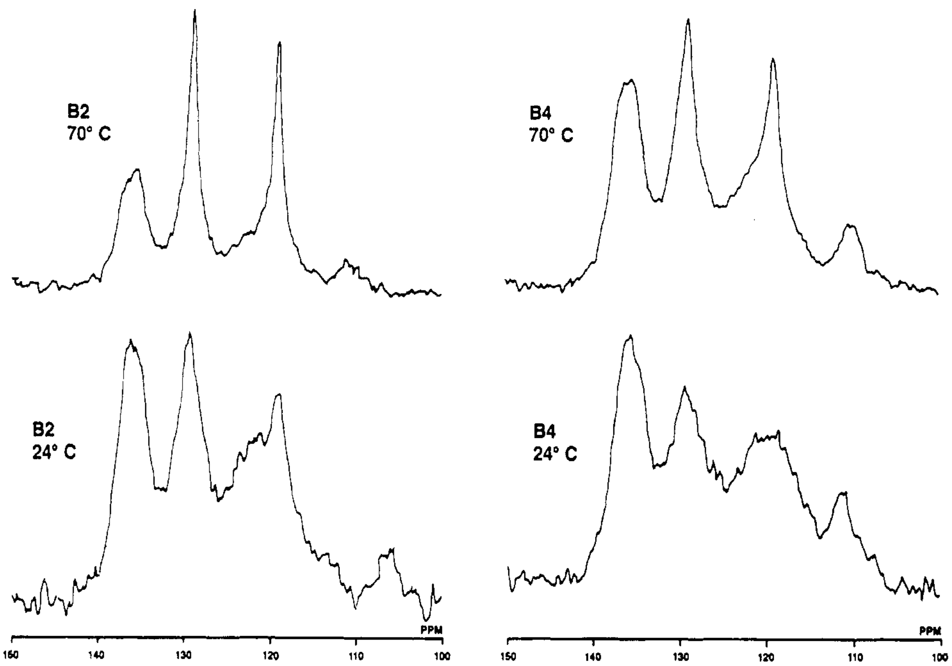

Figure 4. Aromatic region of the C-13 CPMAS spectra of B2 and B4 polymers at 70 °C.

the MDI group. Ideally, measurement of the bridge methylene $T_{1\rho}^{c}$ value would indicate the amount of rocking motion. Unfortunately since it is present in the lowest concentration, this peak shows the worst signal-to-noise ratio of the entire pattern and our relaxation curves exhibited correspondingly poorer fits. For B2 and B4 polymers at 24 °C and 38 kHz, we estimate $T_{1\rho}^{c}$ values of 6 and 5.5 (±2) ms, respectively.

The butanediol decay curves (peak a of Figure 2) for both B2 and B4 at 50 kHz and 24 °C are shown in parts A and B of Figure 5. Clearly there are at least two motionally nonequivalent populations of butanediol in the B4 polymer. This is not seen in the B2 material.

Discussion. Previously, by use of liquid-state techniques we showed that the onset of rapid (liquidlike on the NMR timescale) motion of the hard-segment aromatic carbons defined the upper useful temperature limit of the urethane polymer.[26] We have further confirmed this result by measuring the $T_{1\rho}^{c}$ values of the 3,3′-carbons of MDI at 70 °C for both B2 and B4 (Figure 3). At 70 °C the B2 polymer is nearing the temperature at which the dynamic mechanical spectroscopy (DMS) results indicate the onset of flow. At this temperature the B4 polymer is still within the rubbery plateau. The now greatly lengthened B2 relaxation time implies that most of the molecular motions are greater than 50 kHz, whereas the B4 hard-segment motions have not changed greatly. The increased temperature also results in a narrowing of the aromatic resonances for the B2 polymer. Although clearly present, the narrowing is less pronounced in the B4 polymer. Figure 4 shows spectra of the aromatic region of both polymers at 24 and 70 °C. Details of the aromatic ring motion remain to be investigated. However, a comparison of the $T_{1\rho}^{c}$ value at 24 °C for the bridge methylene carbons with the much smaller values obtained for the ring carbons also at 24 °C implies that substantial ring rotation is occurring in both the B2 and B4 polymers at room temperature.

The simplest explanation for two populations of butanediol carbons observed in the B4 polymer would be to attribute one of the components to the phase-mixed hard segment. This would imply, however, that the two polymers differ markedly in the amount of phase segregation present. The infrared results reported previously[26] for the maximum weight fraction of hard segment mixed with soft-segment phase for these two polymers was 44% for B2 and 38% for B4. These values are, however, the maximum possible amounts assuming that all non-hydrogen-bonded carbonyls are associated with the phase-mixed hard segment. The DMS results[26] also indicate that the B2 and B4 polymers have similar phase segregation. Electron microscopy results did, however, indicate spherulites in the B4 polymer that were not present in the B2 material. When the DSC results for these two polymers are compared to the heats of fusion for the capped hard segments alone, one can calculate approximately the percentage of hard segment that is present in the polymer as a crystalline form. For both polymers about 71% of the total hard segment was calculated to be crystalline. This is higher than the minimum amount of hydrogen-bonded hard segment as evidenced by the IR studies. All evidence thus suggests that a similar degree of phase segregation exists in both polymers.

By extrapolating the slow component of the $T_{1\rho}^{c}$ curve back to the intercept, we find that it is responsible for 59% of the initial peak intensity. This result is between the minimum amount of phase-segregated hard segment as evidenced by hydrogen bonding in the IR studies and the DSC crystallinity data, but the fact that only one hard-segment motional population is seen in the B2 polymer remains unexplained. That we do not observe two hard-segment phases in the B2 material in spite of the fact that the polymer is phase-segregated implies either that we are somehow greatly underrepresenting one component in the relaxation curves or that our view of the nature of the phase segregation in the polymers is incomplete. The optimum cross polarization time for the aromatic and butanediol resonances of both polymers was examined and found to be 900 μs. Also, these hard-segment carbons appeared to respond uniformly to variations in the cross polarization time. The intensities of the hard-segment carbons were also examined as a function of recycle time, and 2.8 s was found to be adequate for both polymers. Since the cross polarization dynamics of the aromatic and butanediol carbons of both polymers are similar, we do not believe that we are missing any significant portion of the available signal in our spectra.

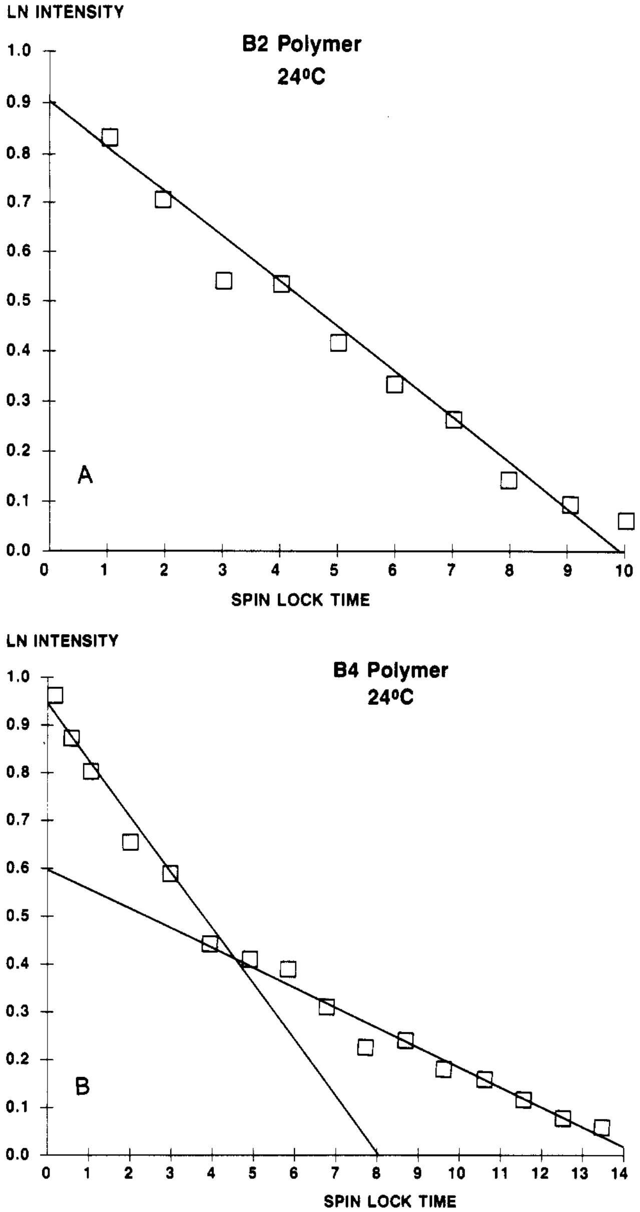

Figure 5. (A) Decay of the 2,3-butanediol resonance of B2 polymer at 24 °C. (B) Biexponential decay of the 2,3-butanediol resonance B4 polymer at 24 °C.

There are two possible explanations for the absence of biexponential decay in the B2 polymer. First, it is possible that the phase-mixed and phase-segregated butanediols have approximately the same degree of motion and therefore relax at the same rate. Second, the polymer may be essentially completely phase-segregated and no phase-mixed hard segment is present. Intuitively the first possibility is not appealing. One would expect the butanediols to reflect at least some of the motional restriction expected within a hydrogen-bound hard segment. However, the fact that the hard-segment length is short and the butanediol segment is flexible may allow some of the soft-segment motion to be reflected in the phase-segregated hard segment. This would tend to make the motions of the phase-segregated and phase-mixed butanediols similar. We feel that the second possibility (very little phase-mixed hard segment) is more likely. The electron microscopy results on the B2 polymer showed a complete absence of spherulites. This fact taken together with the evidence that both polymers are completely phase-segregated implies that phase segregation without spherulites is possible. The biexponential decay of the B4 polymer could, therefore, represent nonspherulitic as well as spherulitic phase-segregated hard segments. Since the degree of hard-segment crystallinity is similar for both polymers and since the DMS results indicate approximately equal phase segregation, it is clear even without the NMR results that there must be two types of phase-segregated hard segment present in the B4 polymer.

The assumption of complete phase segregation does not conflict with the infrared results discussed above. The non-hydrogen-bonded carbonyls are now assumed to result entirely from the nature of the packing of the chains. Blackwell[14,20] and co-workers have presented detailed X-ray structures of the packing of MDI–butanediol hard segments. For example, if one uses their structures and assumes complete phase segregation, one observes that some carbonyls remain non-hydrogen-bonded. In the B4 polymer the possibility of folding of the chain complicates this analysis. The spherulites in B4 are assumed to consist of an association of many chain clusters both folded and linear.

Discounting the possibility of a phase-mixed component for the reasons discussed above, there are two possible explanations for the biexponential decay observed in the B4 polymer. The first explanation, which we believe to be the most likely, is that one component is associated with spherulitic hard-segment butanediols and the other is associated with nonspherulitic phase-segregated butanediols. Since the rapid portion of the decay is most similar to that of the B2 polymer, we assign this portion of the curve to hard segments having nonspherulitic-type segregation. The slowly relaxing component would thus be due to butanediols associated with spherulites.

Recent work by Koberstein and co-workers[18,21] has shown that hard segments exist in kinked conformations where the chains are folded back upon themselves. The chain kinks necessary for this folding are most likely to be located in the flexible butanediol portion of the hard segment. In our model systems the B2 polymer is too short to fold in upon itself, whereas this folding is possible for the B4 polymer. The second component in our $T_{1\rho}{}^{c}$ results could, therefore, be associated with the kinked butanediols. Since this component is only observed in the B4 polymer where spherulites are also present, its presence suggests that the folded configuration may be associated primarily with the spherulites.

The second interpretation which at this time cannot be ruled out is that the butanediols closest to the soft segment are motionally different from those nearer the center of a hard segment. In the B2 polymer both butanediols are one MDI unit removed from the soft segment and would in this interpretation be motionally equivalent. For B4 there are two "inner" and two "outer" butanediols. These pairs could be motionally nonequivalent. This interpretation would imply that some of the soft-segment molecular motion is transmitted into the hard segment via an MDI unit.

The MDI–butanediol–polypropylene oxide system has been studied previously by Jelinsky and co-workers; however, the polymers used in their work are not strictly comparable to ours since their study made use of material that contained a distribution of hard-segment lengths[11] or contained no soft segment.[24] Our results indicate that in addition to different motional populations arising from butanediols which are phase-segregated and phase-mixed, one must consider different motional populations arising from within a phase-segregated hard segment. Since we would expect both populations to appear as broad components in a deuterium experiment, there is no conflict between our results and their calculation of phase mixing by deuterium NMR. Their finding of a phase segregation critical length consisting of three MDI units and two butanediols is in agreement with our observations. Moreover, in systems such as ours, hard segments of this length or longer appear to be rigorously excluded from the soft-segment phase.

Assink and Wilkes investigated an MDI–butanediol–adipic acid polyester urethane system by observation of the NMR free induction decay (FID). The shape of the FID can be related to the different motional populations present in the sample. They concluded that there was both a short-range and a long-range degree of phase mixing. Since their system contained a distribution of hard-segment lengths as well as phase-mixed material, correlation between their work and ours is difficult.

On the basis of the above discussion and our previous work, a model can be proposed for the behavior of the molecular motion in urethane elastomers as a function of temperature. Previous $T_{1\rho}{}^{c}$ measurements[26] as well as ADRF experiments[25] have shown that the soft-segment glass transition has a substantial effect on the relaxation properties of the hard segment. Raising the temperature through this transition allows increased hard-segment motion. Further increases in temperature do not cause large changes in the $T_{1\rho}{}^{c}$ value until one reaches temperatures at which flow can occur. The thermal energy presumably goes into increasing the frequency and amplitude of the soft-segment motions, although some of this motion is perhaps transmitted to the interfacial portions of the hard segment. At the point at which flow begins, mid kilohertz hard-segment motions concomitant with hydrogen bond disruption occurs. Logically, this would occur starting with those portions of the hard segment nearest the soft segment (interfacial) and proceeding inward. The presence of spherulites in the sample creates a second presumably restricted motional population that may give the polymer some additional thermal stability. Rotation of the phenyl rings, which is important in polymers such as epoxies and polycarbonates, appears to be extensive at room temperature but does not seem to play a major role in determining the mechanical properties of the polymer.

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