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Motional Behavior within the Hard Domain of Segmented Polyurethanes: A ^{2}H NMR Study of a Triblock Model System

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Introduction

The degree of phase separation as well as the microstructure of the domains in block copolymers composed of incompatible rubber *soft segments* and rigid *hard segments* has received a lot of attention in order to establish structure-property relationships.[1-4] Deuteron (^{2}H) NMR, in combination with specifically labeled materials, can be used to detect both spatial variations in molecular mobility within microphases and the degree of phase separation in polyurethane block copolymers.[5-10] In order to obtain a better understanding of the behavior of multiblock copolymers, simple model systems have to be studied. Therefore, triblock polyurethanes (soft-hard-soft) with hard segments based on exactly five piperazine rings separated by butanediol chain extenders (BDO) and poly(oxytetramethylene) (POTM, M_n ca. 1000) soft segments have been prepared (compound 1). The samples were specifically deuterated in the piperazine rings, in either the outer rings (positions 1 and 5 of Chart I) or the central ring (position 3), employing a previously reported procedure.[9] In using these isotopically labeled samples, a study concerning motional processes that can occur within the crystalline hard domains of triblock polyurethanes, as compared to previous findings[9] on hard-segment oligomers and multiblock polymers of similar chemical compositions, has been performed and is reported here. The phase separation and packing of the hard segments of the soft-hard-soft triblock copolymers into domains are not hindered through constraints due to the connecting soft segments, as is the case of the multiblock copolymers. This would suggest that the triblock copolymers may undergo better phase separation than their multiblock counterparts and form hard domains that are more ordered and with sharper phase boundaries. Moreover, the specific labeling, along with ^{2}H NMR, has enabled us to make direct measurements of variations in segmental mobility from the core to the interface between the hard and soft domains. Not only does the study allow us to comment on the mechanism of the solidification process but it also facilitates the determination of the degree of phase separation. According to Krause,[11] the triblock copolymers should phase separate to a higher degree than their multiblock equivalents, and ^{2}H NMR ought to be sensitive to this difference. The chosen system is well suited for such a comprehensive study: (a) wide-angle X-ray scattering (WAXS) studies[4] have found no evidence of chain folding within the hard segments comprising the hard phase of polyurethanes of similar structure to those reported on here, and (b) On the basis of differential scanning calorimetry (DSC) and WAXS results,[4] a structure was postulated where hard segments are evenly stacked within crystallites. The proposed crystal structure, along with the connectivity between crystallizing moieties, permits accurate knowledge of the location of the isotopic labels within the crystal so that the solidification processes and differences in the segmental mobility of the deuterated sites can be followed precisely.

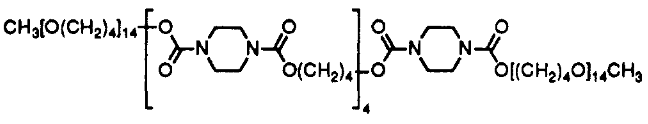

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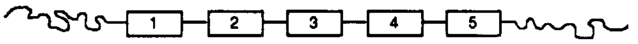
Chart I



Results and Discussion

The labeled polyurethanes were heated to temperatures above the melting point of the hard domains, T_m(hard) ca. 440 K, as determined by DSC (refer to Figure 1), and were slowly cooled. The ^{2}H NMR line shapes for both the outer- and center-labeled samples were recorded at various temperatures as described elsewhere[9,10] and are displayed in Figure 2. The spectra indicate changes in molecular mobility in a manner similar to that observed in the case of the comparably labeled multiblock polyurethanes[9] and yet display some interesting differences which can be related to differences in the solidification process and the degree of phase separation. At sufficiently elevated temperatures, $T > 410$ K, the spectra are completely motionally averaged, while at sufficiently low temperatures, $T \leq 240$ K, the spectra of both samples are very similar to that of the well-known powder pattern of a rigid solid (Pake diagram). At intermediate temperatures, the spectra can best be described as a superposition of broad and narrow components, and yet the spectral features are quite different for the two samples. The difference in the line shapes, and hence mobility, at the two sites is most evident upon inspection of spectra c and i of Figure 2, i.e., those of the outer- and center-labeled samples at 320 K, respectively. Unlike the spectrum of the center-labeled polyurethane, that of the outer-labeled sample has neither feet nor quadrupolar splitting peaks. It is necessary to go to subambient temperatures, i.e., where POTM is known to solidify, in order to observe such features in the spectra of the end-labeled sample (Figure 2d-f). As discussed elsewhere,[9,10] the dynamic glass transition, T_g, on the scale of the NMR experiments described here and the melting temperature of the crystalline POTM, T_m(soft), are so close that they cannot be distinguished. In either case, the solidification of the soft phase induces severe restrictions in the mobility at the interface of the hard segment, i.e., of the outer piperazine rings.

The spectrum of the polyurethane labeled in the central position of the hard segment has a broad component that closely resembles the rigid powder pattern with $\Delta\nu_Q$, the separation of the quadrupolar splitting as defined in Figure 3 of ref 9, as large as 117 kHz. Thus, large-angle motions, if any, are restricted to rates $\leq 10^4$ Hz.[12] In fact, this quadrupolar splitting is also detectable at elevated temperatures, i.e., up to 410 K, but, as was the case for comparably labeled hard-segment oligomers and multiblock polyurethanes, to the somewhat reduced value, 88 kHz, and with reduced relative intensity. This indicates substantial high-

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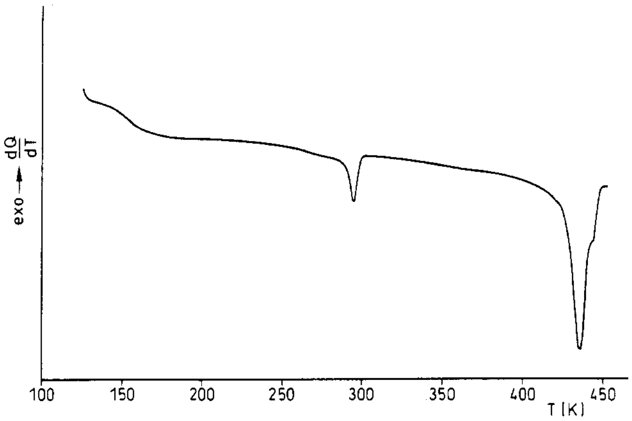

Figure 1. Differential scanning calorimetry trace of the triblock polyurethanes.

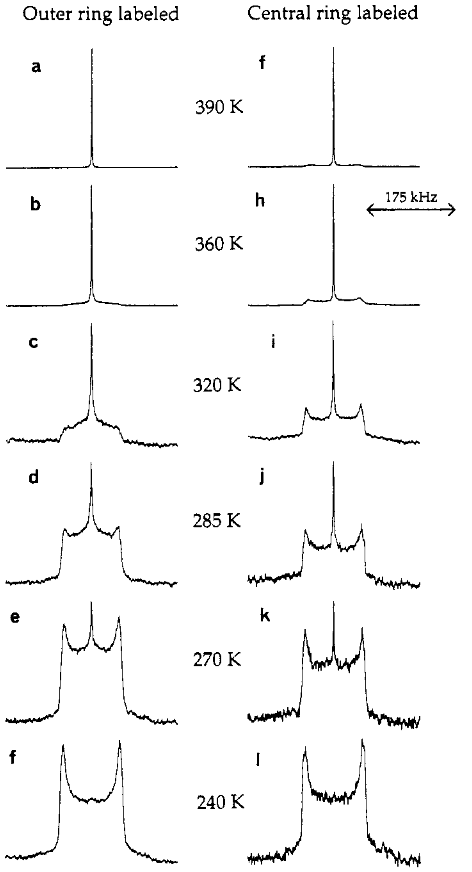

Figure 2. ^{2}H NMR spectra (46.07 MHz) of the piperazine-based triblock polyurethanes, selectively labeled in the hard segment. Spectra a–f were obtained from the sample labeled in the outer rings, and spectra g–l were obtained from the sample labeled in the central ring.

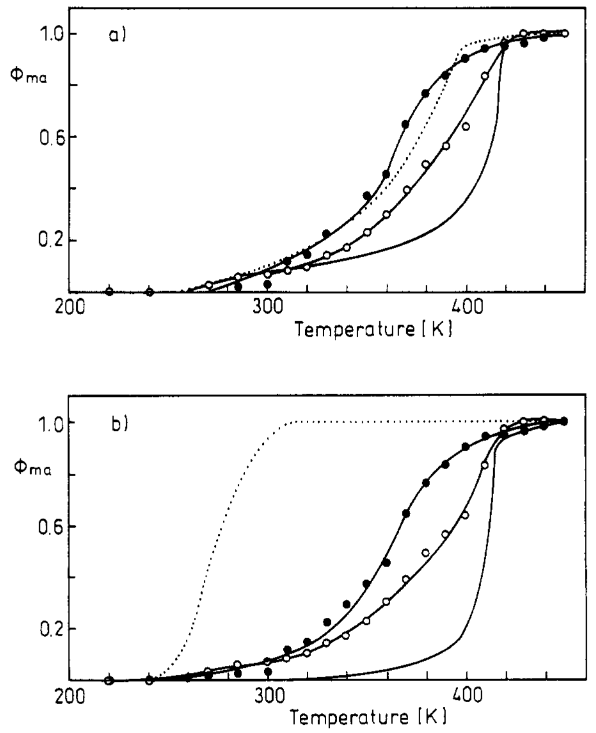

Figure 3. Fraction motionally averaged, Φ_{ma}, of the polyurethane triblocks: (●) outer-labeled triblock polyurethane; (○) central-labeled triblock polyurethane. (a) (—) Center-labeled multiblock polyurethane (reproduced from ref 9); (· · ·) outer-labeled multiblock polyurethane (reproduced from ref 9). (b) (—) Center-labeled hard-segment oligomer (reproduced from ref 9); (· · ·) polyurethane that is chain extended with individual piperazine rings (reproduced from ref 9).

frequency angular fluctuations, also observed in all hard-segment materials of MDI–BDO-based polyurethanes[6] and in other crystalline polymers.[13] Furthermore, the spectra of both the outer- and center-labeled triblock system are dominated by the narrow, motionally averaged peak (line width ca. 1 kHz at 300 K) at temperatures well below T_m(hard). In fact, for $410\ K < T < 440\ K$, the broad spectral features are not detected at all. From a comparison of melting enthalpies for the hard domains in the triblock polyurethanes and the crystalline hard-segment oligomer[9] an "overall" crystallinity of at least 70% is estimated. Thus, at most a 30% motionally narrowed signal can result from noncrystalline hard segments at temperatures above their T_g, estimated to be around 313 ± 10 K. The temperature dependence of the fraction of labels undergoing rapid motions for whose NMR signal is motionally averaged, Φ_{ma}, is plotted in Figure 3. For the central-labeled system (see Figure 3a), this limit is reached around 360 K already. Thus the narrow component must in part be attributed to hard segments undergoing quasi-isotropic motion within the crystallites, at least at elevated temperatures.

This quasi-isotropic motion with $\tau_c < 10^{-7}$ s may involve discrete jumps or diffusive motions or a combination of both. X-ray scattering investigations into the molecular structure and packing of the piperazine rings indicate that the angles formed by the D–C–D bonds do not deviate to a significant extent from the true tetrahedral angle,[14] and, hence, effective tetrahedral jumps are likely. This motional mechanism has indeed been shown to lead to ^{2}H NMR lines as narrow as 0.7 kHz in a low molar mass crystalline solid,[15] provided the jumps occur between all four sites.

The extent to which the mobility at the two labeled sites differs is evident upon inspection of Figure 3. At temperatures below 300 K or above 410 K, the values of Φ_{ma} at the two sites are indistinguishable. At temperatures in between these two extremes, however, Φ_{ma} is consistently larger for the outer-labeled sample than for the sample labeled at the center of the hard segment, indicating greater mobility at the surface of the crystal than at its center and that the onset of mobility within the crystals begins at the surface and proceeds inward. While the absolute value of Φ_{ma} will be affected by the degree of phase separation, the absolute difference of Φ_{ma} for the two samples is unaffected, so that it is related to the difference in the extent to which the motions are constrained, and has a maximum value of 0.27 ± 0.04 at 380 K, well below T_m(hard).

Dynamic coupling between the chains in the hard and soft domains is known to occur in block copolymers[17,18] so that the more rigid hard domains would restrict the mobility of the soft segments,[10,19] which in turn induce motions within the hard domains, especially at the interface and at elevated temperatures. Comparison of Φ_{ma} of the multi- and triblock polyurethanes suggests that the dynamic coupling between the two phases occurs to a significant extent. The value of Φ_{ma} for the central-labeled multiblock polymer is consistently below that of the equivalent triblock polymer at $T > 350$ K, and the plateau region in Φ_{ma} observed in the case of the multiblock copolymers is obscured in the case of the triblock polyurethanes (see Figure 3a). This suggests that there is greater dynamic coupling in the triblock copolymer. Such a phenomenon can be attributed to the difference in mobility of the soft segments comprising the two classes of polymers. Both ends of the soft segments are covalently bound to the hard segments in the multiblocks, whereas in the triblocks, only one end is linked to the hard segment while the other is free. The additional freedom permits the soft segment to induce motions within the hard domain of the triblock more easily. The effect is only observed once the ^{2}H NMR spectra of the hard-segment oligomers indicate the onset of motions at the center of the crystal, i.e., ca. 360 K, so that the onset of mobility within the ordered crystalline matrix facilitates the dynamic coupling with the more mobile soft segments.

Below 350 K, the central-labeled oligomer does not exhibit a motionally narrowed peak (see Figure 3b), so the presence of such a peak in the polymers can be attributed to incomplete phase separation. By comparison of Φ_{ma} of a non-phase-separating model system, i.e., a polymer where the soft segments are chain extended by individual labeled piperazine rings, and hard-segment oligomers, it was shown that the value of Φ_{ma} at temperatures ranging from 310 to 350 K for the polymer labeled in the central ring is equal to the fraction of hard segments dispersed in the soft phase.[9] For the triblock polyurethanes, this would correspond to a value of Φ_{ma} of 0.09 ± 0.02. This upper limit seems reasonable in light of the value reported by Kornfield et al., 0.15 ± 0.02, for the corresponding multiblock polyurethanes.

Conclusions

The motional behavior within the hard domain of the polyurethane triblock polymers can be divided into different temperature regimes. At $T < 300$ K, the soft phase has solidified to some extent and hinders the mobility of that part of the hard segments at the interface. Between 310 and 350 K the dual character of the ^{2}H NMR spectra is indicative of the heterogeneous nature of the system, and Φ_{ma} of the center-labeled sample indicates that 9 ± 2% of the hard segments are "dissolved" in the soft phase. Dynamic coupling between the two types of segments comprising the polymer is observed and occurs to an even greater extent between 360 and 400 K. Above 360 K, tetrahedral jumps can occur at a sufficient rate within the ordered hard phase so that the spectra are motionally averaged. Last, at $T > 440$ K, the hard segments are disordered.

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