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Investigation of the Phase Separation Behavior of Polyurethane Elastomers by Two-Dimensional Wide-Line-Separation Nuclear Magnetic Resonance Spectroscopy

Hun-Jan Tao, David M. Rice,[†]
William J. MacKnight, and Shaw L. Hsu*

Department of Polymer Science and Engineering and
The Materials Research Science and Engineering Center,
University of Massachusetts, Amherst, Massachusetts 01003

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Introduction

It is well-known that polyurethane elastomers exhibit a phase-separated structure.[1] Although various techniques have been employed to assess phase composition, a quantitative analysis is difficult to achieve.[2] For example, DSC measurements associated with the Fox equation or its modified form are commonly utilized for determination of phase composition based on changes in glass transition temperature (T_g) as well as changes in the heat capacity of soft segments. With this method, however, phase compositions remain inaccessible unless the cross-linking effect is specifically taken into account. It is well documented that the confinement of polymer chain ends will dramatically alter glass transition temperature[3,4] and the heat capacity change (cross-linking effect).[3−5] For instance, the glass transition temperatures of cross-linked poly(propylene glycols) deviate from their linear forms by 56.15 and 27.4 °C for molecular weights of 1000 and 3000, respectively.[3] Soft segments in phase-separated structures exhibit similar behavior. The application of commonly used thermal analysis for analyzing phase composition therefore merits additional detailed considerations, and alternative techniques should be developed.

Several methods associated with solid-state NMR have been used to investigate the phase separation behavior of polyurethane elastomers.[6−12] The recently developed two-dimensional wide-line-separation nuclear magnetic resonance spectroscopy (WISE-NMR) provides a particularly interesting alternative tool for determination of the phase composition of polyurethane elastomers.[13,14] With this experiment, a correlation has been established between chemical structure and segmental mobility as reflected in ^{13}C chemical shifts and ^{1}H line shapes, respectively. Segments dispersed in the hard-segment-rich domain are immobilized, resulting in broad components in the ^{1}H spectra. The fraction of hard/soft segments distributed in each phase can therefore be calculated from the resolved ^{13}C spectrum. Utilizing this technique, the degree of phase separation in piperazine-based polyurethanes has been established.[9,14]

The results of our investigation on the phase separation behavior of a model polyurethane elastomer by two-dimensional wide-line-separation nuclear magnetic resonance spectroscopy are presented in this paper. A comparison of results obtained by other techniques is also provided.

Experimental Section

Materials. To avoid complexities arising from polydispersity in hard segments, we employed a model polyurethane with monodisperse hard-segment length, B4 polymer, kindly provided by Dow Chemical Corp.[15] The hard segment of B4 polymer contains five MDI [4,4′-methylenebis(phenyl isocyanate)] and four BD (butanediol) units. The soft segment is monodisperse PPG [poly(propylene glycol)] with a molecular weight of 2000. B4 polymer consists of 45 wt % hard segments. The structure is presented in Figure 1.

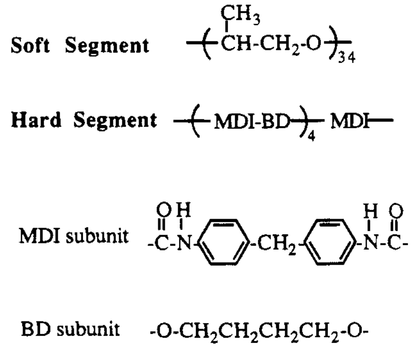

Figure 1. Structures of the soft segment and hard segment for B4 polymer.

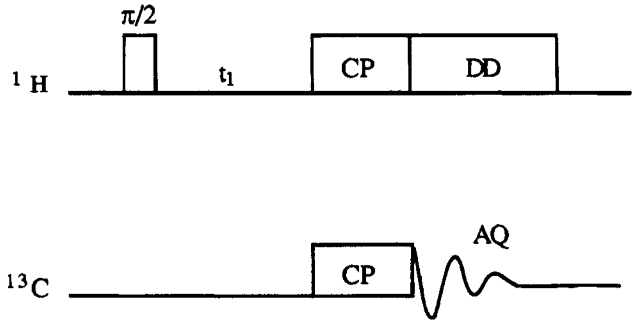

Figure 2. Pulse sequence of WISE-NMR experiment used in this work with proton evolution, cross polarization (CP), and ^{13}C acquisition (AQ) with dipolar decoupling (DD) of protons.

Measurements. The basic version of WISE-NMR measurement[13] has been adopted in this study without incorporation of a TOSS sequence[16,17] for suppressing ^{13}C spinning side bands. A detailed description regarding the principle, pulse sequence, and applications has been published previously.[13,18] Spectra were obtained at 25 °C by a Bruker MSL-300 spectrometer with magic angle spinning at 4.0 kHz. A sample of about 200 mg was prepared by grinding under liquid nitrogen followed by packing in a sapphire rotor with Kel-F end caps. A cross polarization time of 1000 μs and 128 t_1 increments with a dwell time t_1 of 4 μs were employed (Figure 2).

Heat capacity change measurements were obtained with a TA Instruments DSC-2910 purged with dry nitrogen. Runs were conducted on polymer samples of about 10 mg at a heating rate of 10 °C/min from −100 to +30 °C. The temperature was calibrated by cyclohexane at −87 °C associated with crystal−crystal transformation.

Results and Discussion

The WISE spectrum for B4 polymer at 25 °C is shown in Figure 3a. The ^{13}C chemical shifts associated with soft segments are 18 and 75 ppm corresponding to the PPG methyl and methylene groups, respectively. For hard segments, the chemical shifts of phenyl rings are located in the 115−140 ppm region, those of butanediol methylenes at 25 and 66 ppm, and those of the carbonyl at 155 ppm.[10] To evaluate the fraction of mobile soft segments, the cross section of the WISE spectrum along 75 ppm for methylenes of the soft segment is shown in Figure 3b. Only one mobile component with a bandwidth (fwhh, full width at half-height) of 3.2 kHz was

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* To whom correspondence should be addressed.

[†] Present address: Varian NMR Instruments, 3120 Hansen Way M/S D-298, Palo Alto, CA 94304-1030.

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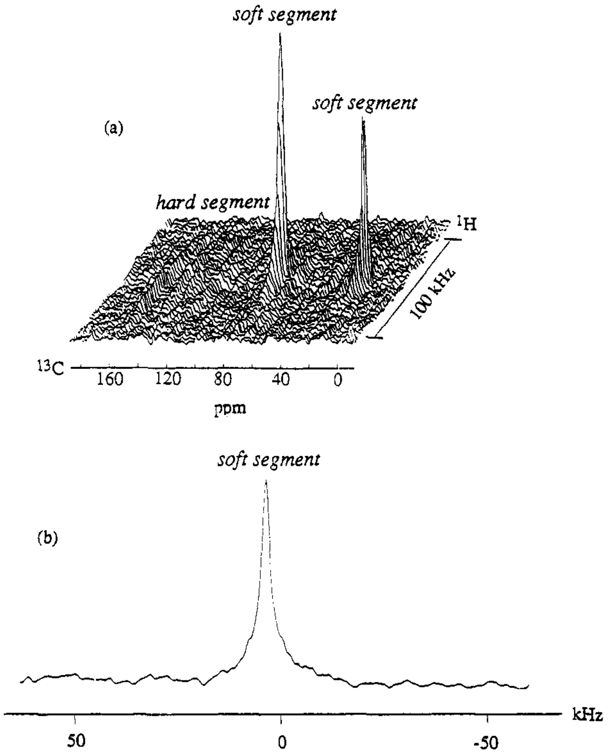

Figure 3. WISE-NMR spectra of B4 polymer (a) and its cross section along 75 ppm (b).

found. We found no evidence for soft segments to be dissolved into the hard domains. The dipolar line width for the immobile CH or CH_2 of the soft segments units is known to be 50 kHz. This immobile component cannot be measured accurately, however. This result is consistent with the finding of piperazine-based polyurethane with monodisperse hard-segment length by deuteron NMR measurement.[9,14] For that system, the degree of phase separation was measured as high as 85%.[14] On the other hand, the $(\Delta C_p/W_s)/\Delta C_p{}^\circ$ value measured by thermal analysis is 78% which is frequently referred to as the fraction of soft segments dispersed in the hard-segment-rich domains,[2,19] where ΔC_p, W_s, and $\Delta C_p{}^\circ$ represent the heat capacity change for polyurethane elastomers at the glass transition temperature of the soft segment, the weight fraction of the soft segments in the elastomers, and the heat capacity change for un-cross-linked neat soft segments at its T_g, respectively. The $(\Delta C_p/W_s)/\Delta C_p{}^\circ$ value is lower than the WISE result probably due to the extra contribution from the cross-linking effect which can also decrease the heat capacity change.[4,5] It is therefore inadequate to taken the heat capacity change value as the fraction of soft segments dispersed in the hard domains or in the interfaces without explicitly extracting the cross-linking effect.

Because of the very weak intensity in the 115−140 ppm region, it is difficult to estimate the exact distribution of hard segments in two phases.[10] Figure 3a indicates that there is no detectable amount of the mobile hard-segment component. On the basis of this result, we believe that the degree of phase separation for B4 polymer is extremely high. $T_{1\varrho}{}^{C}$ measurement of the B4 polymer investigated previously indicated that the polymer is very likely to completely phase separate.[10] Our WISE measurement is consistent with this conjecture. Further experiments for enhancing the WISE signal in the 115−140 ppm region will be conducted in the near future.

The glass transition temperature change and infrared measurements have also previously been utilized the degree of phase separation for B4 polymer.[15] The degree of phase separation was defined as the fraction of hard segments distributed in the hard domains. By DSC measurements, the reported degree of crystallinity of B4 polymer is 73%.[15] As the hard domains are not necessarily composed of perfectly crystalline structure, the actual degree of phase separation should be higher than the degree of crystallinity. On the other hand, the composition of the soft-segment-rich phase was previously proposed to be estimated by the following generalized Fox equation[19]

$$\frac{w_1 + (1 - w_1)k}{T_g} = \frac{w_1}{T_{g1}} + \frac{k(1 - w_1)}{T_{g2}} \qquad (1)$$

where T_g, T_{g1}, and T_{g2} represent the glass transition temperature for the soft segments in the phase-separated structure, the pure linear soft segments, and the hard domains, respectively. w_1 in eq 1 is the weight fraction of soft segments in the soft-segment-rich phase. The parameters used in this calculation are $T_g = -32$ °C, $T_{g1} = -69$ °C, $T_{g2} = 109$ °C, and $k = 1.18$.[15,19] According to this calculation, the soft-segment-rich phase consists of 29% hard segments. The associated degree of phase separation determined is then unreasonably low. It is believed that the effect of cross-linking on T_g prohibits its applicability for determination of phase composition. Finally, the degree of phase separation estimated by the infrared carbonyl region is about 70% assuming that the carbonyl groups in the hard domains are all hydrogen-bonded and free from hydrogen bonding outside the hard domains.[15] The cross-linking effect does not perturb the carbonyl stretching region. Nevertheless, the degree of phase separation determined by the infrared method might still be less than its true value due to two reasons. First, the carbonyl groups in the interfaces might not show hydrogen-bonded features. Second, as the hard domains are not necessarily composed of perfect crystalline structure, and even if they do, based on Blackwell's model some carbonyl groups still cannot form hydrogen bonds.[10,20,21]

Conclusions

Our finding by WISE-NMR measurements indicates that the B4 polymer is likely to phase separate completely and form a relatively pure hard-segment-rich phase and soft-segment-rich phase. It is difficult to explicitly calculate phase composition by thermal analysis due to the complexity of cross-linking effects. Phase separation behavior measured by infrared relies on the relative intensity of various features sensitive to hydrogen bonds formed. Even though the degree of phase separation measured by infrared may not accurately reflect the true value (lower than NMR measurements), it represents a more reliable tool than thermal analysis for determination of the relative degree of phase separation for different chain lengths in hard/soft segments. This conclusion is based on the fact that infrared measurements are free from complications of the cross-linking effect.

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