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# Effect of Hard-Segment Flexibility on Phase Separation of Segmented Polyurethanes

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## Introduction

Segmented polyurethanes are multiblock copolymers which consist of the so-called hard and soft segments.[1] Unlike A–B or A–B–A long-block copolymers, the blocks in segmented polyurethanes are usually very short. Consequently, there are many connecting points (chemical bonds) between the segments. By using small-angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC), we[2–6] were able to show that the system viscosity, the hard-segment mobility, and the hard-segment interactions were the three controlling factors for determining the structure of segmented polyurethanes. The phase-separation process of segmented polyurethanes was usually very slow and behaved like a relaxation process.[2,3] Earlier, Wilkes and co-workers also showed time-dependent mechanical properties.[7,8] Once the multiphase-separated structure had formed, posttreatments, such as annealing temperature, had only small effects.[4] Thermodynamically, phase separation is more complete with aromatic hard segments because of increased thermodynamic incompatibility between hard segments and aliphatic soft segments. However, from a kinetic viewpoint phase separation becomes more complete with aliphatic hard segments because of increased mobility.[2,3,5] Our experimental results[5] seem to support the kinetic viewpoint, which could also explain the annealing behavior and the spherulite growth of segmented polyurethanes.[6]

It is important to know whether the kinetic factors could be so significant that they could actually control the phase-mixed or phase-separated structure in segmented polyurethanes. Seefried et al.[9] observed a phase-mixed structure in the segmented polyurethanes with polycaprolactone (PCL) as the soft segment and a 80/20 blend by weight of 2,4-/2,6-toluenediyl diisocyanate isomers (TDI) with hydrogenated Bisphenol A (HBPA) as the hard segment. They attributed such phase mixing as due to the unsymmetrical structure of the isomeric TDI and suggested that the replacement of TDI by a symmetrical 4,4′-methylenebis(phenyl isocyanate) (MDI) could possibly create phase separation. However, from the kinetic viewpoint, the phase mixing of their samples was due mainly to the higher system viscosity and lower mobility of the hard segments. A replacement of TDI by MDI neither reduced the system viscosity nor increased the hard-segment mobility significantly. Consequently, we were still not able to observe any phase separation. To observe phase separation, a more flexible aliphatic hexamethylene diisocyanate (HDI) could be used to replace TDI, although the use of HDI would significantly reduce the difference in solubility parameters of the soft and the hard segments. The solubility parameter ($\delta$) of the components in the segmented polyurethanes are 10.6, 9.3, and 9.1 cal$^{1/2}$ cm$^{-3/2}$ for MDI, HDI, and PCL, respectively. The results presented in this paper clearly show that the kinetic process is predominant.

## Experimental Section

PCL glycol with a molecular weight of 2000 was purchased from Union Carbide, MDI from Dow Chemical, HBPA from TCI America, and HDI from Aldrich. HDI was distilled at 140 °C (20 mmHg) before use.

The two segmented polyurethane samples were synthesized by a one-step bulk polymerization. PCL was dehydrated and degassed in a 250-mL three-neck flask [100 °C (10 mmHg)] for 1 h. At 140 °C, HBPA was added with stirring. Then, a stoichiometric amount of MDI (or HDI) was added, stirred, and degassed for 1 min (15 min for HDI). The mixture was poured onto a mold which was preheated at 140 °C. Then, the sample was kept in an oven at 140 °C for 3 h (8 h for HDI). Each sample contained 42 wt % of the hard segment (MDI/HBPA or HDI/HBPA). The MDI-based and the HDI-based samples were denoted by UMDI and UHDI, respectively. Only as-reacted samples were used in this study.

The DSC data were obtained from a Thermal Analysis DSC station with a scanning rate of 20 °C/min. The SAXS experiments were performed by using a rotating-anode X-ray generator, a Kratky slit collimator, and a gas proportional counter. Desmearing was carried out by using a program based on the Lake algorithm.[10]

## Results and Discussion

Figure 1 shows DSC thermograms of UMDI and UHDI. UMDI gave rise to *only* a glass transition temperature ($T_g$) at about −16.0 °C, 44 °C higher than that of the pure PCL.[11] The increase in $T_g$ could be due to the presence of hard segments in the soft-segment phase and the restrictions introduced by the hard-segment domains where the two ends of the soft-segment chains were anchored. Camberlin and Pascault[12] showed that the chain-end restriction could raise the $T_g$ value by about 4 °C for a soft segment of 2280. Therefore, such a large increase in the $T_g$ value suggests that the soft-segment phase contains a substantial amount of hard segments MDI/HBPA. The $T_g$ value for UHDI was −55.8 °C. If the chain-end restriction effects are taken into account, it means that the phase separation in UHDI is nearly complete.

Crystallization of PCL in segmented polyurethanes was found under certain conditions.[11,13,14] The DSC curve of UHDI also shows a melting temperature of 48.8 °C for the soft-segmented crystals. For the soft segments to crystallize, the soft-segment phase must reach a certain degree of purity. Hu et al.[15] proposed that the crystallinity of soft segments could be used as a criterion for the degree of phase separation. A higher crystallinity of the soft segments implies a more complete phase separation. Therefore, the presence of the soft-segment melting peak in the DSC curve of UHDI also suggests a higher degree of phase separation.

UHDI also gives rise to a broad endotherm around 75.6 °C. Pure PCL has a crystal melting temperature of 60 °C.[11] Our preliminary wide-angle X-ray diffraction measurement of UHDI at 60 °C revealed no observable diffraction peaks. Therefore, this melting peak is attributed to the dissolution of the short-range-ordered, noncrystalline hard-segment domains.

Figure 2 shows the SAXS profiles of UMDI and UHDI at different temperatures. UMDI gave rise to very little scattered intensity, implying that the system was nearly homogeneous, while UHDI gave rise to a scattering peak at 23 °C. Since soft-segment crystals could contribute to the scattering peak, the SAXS measurements of UHDI

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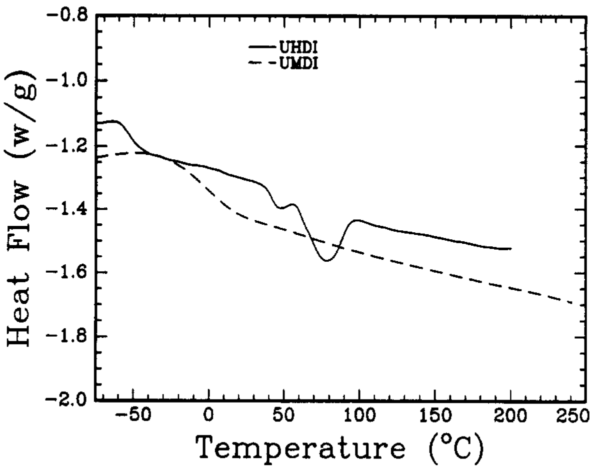

**Figure 1.** DSC thermograms of UMDI and UHDI.

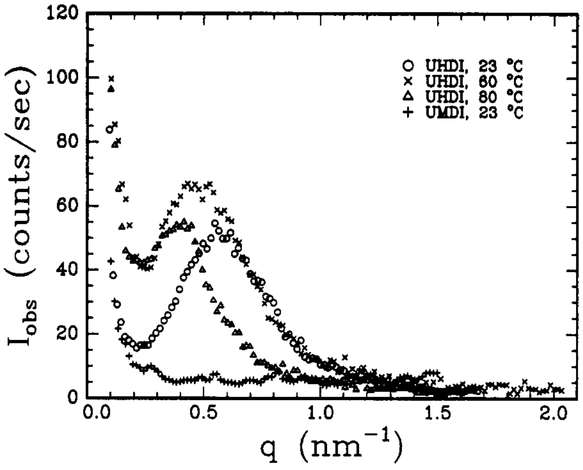

**Figure 2.** SAXS profiles of UMDI and UHDI at different temperatures.

were also performed at 60 and 80 °C which were above the melting temperature of the PCL crystals (48.8 °C). The scattering peak could indeed be observed in both cases, as shown in Figure 2, and thus confirmed the existence of phase-separated structure. At 120 °C, the scattering peak disappeared completely and the scattering profile was similar to that of UMDI, implying a phase-mixed structure.

For a two-phase system with diffuse interphase and thermal fluctuations, the scattered intensity $I(q)$ can be expressed by[16]

$$I_{obs}(q) = K_p q^{-4} \exp(-q^2\sigma^2) + I_b$$

where $I_{obs}(q)$, $q$, $K_p$, $\sigma$, and $I_b$ are respectively the measured scattered intensity, the magnitude of the scattering vector, a constant related to the area of interphase per unit volume, the diffuse-interphase thickness parameter, and the scattered intensity due to thermal fluctuations. $\sigma$ is related to the interphase thickness $E$ by $\sigma \approx (12)^{-1/2}E$. $I_b$ is assumed to be a constant in the Bonart method[16] because the SAXS curves did not reach very high $q$ values.

Figure 3 shows a plot of $I_{obs}q^4$ vs $q^4$ in order to obtain $I_b$. The curve of UMDI shows a straight line down to very small $q$ values, implying that the scattered intensity of UMDI was mainly due to thermal fluctuations.

The interphase thickness $E$ could be estimated by plotting $\ln[(I_{obs} - I_b)q^4]$ vs $q^2$, as shown in Figure 4. This procedure was difficult to be applied to UMDI due to its very small net scattered intensity ($I_{obs} - I_b$) over most of the $q$ values. It is interesting to note that the $E$ values of UHDI listed in Table 1 are all very small.

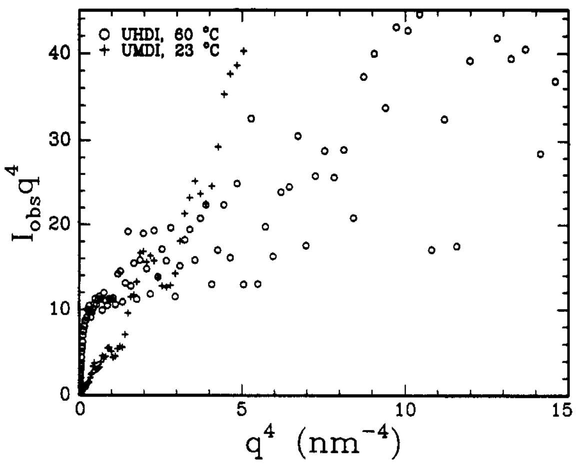

**Figure 3.** Typical plot for the determination of $I_b$ by the Bonart method.[16]

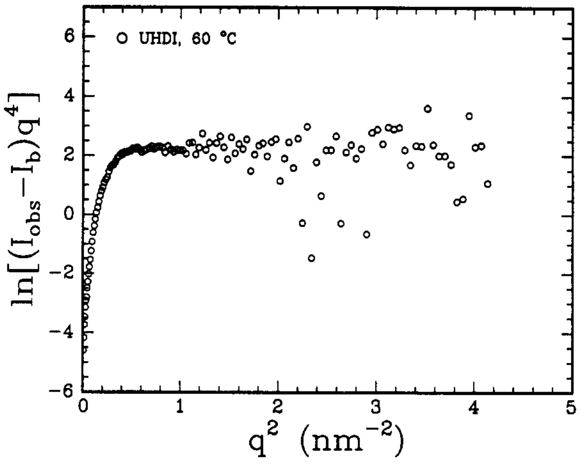

**Figure 4.** Typical plot for the determination of $E$.[16]

**Table 1. Structural Parameters of the Segmented Polyurethane Samples**

| sample | $Q$ (relative unit) | $d$ (nm) | $E$ (nm) | $I_b$ (counts/s) |
|---|---|---|---|---|
| UHDI | | | | |
| 23 °C | 15 | 9 | 0.4 | 0.5 |
| 60 °C | 16 | 10 | 0.3 | 2.4 |
| 80 °C | 8 | 14 | 0.3 | 1.2 |
| UMDI | | | | |
| 23 °C | ~0 | | | 6.3 |

The integrated scattered intensity $Q$ can be calculated by using[17]

$$Q = \int_0^\infty [I_{obs}(q) - I_b]q^2\, dq$$

while the interdomain spacing $d$ could be estimated by using the Bragg equation

$$d = 2\pi/q_{max}$$

where $q_{max}$ is the $q$ value of the first nonzero maximum in the $[I_{obs}(q) - I_b]q^2 \sim q$ plot. The $Q$ and $d$ values listed in Table 1 could be interpreted as due to the difference in thermal-expansion coefficients between the soft- and hard-segment phases and the melting of the soft-segment crystals as well as some of the hard-segment domains (at 80 °C).

## Concluding Remarks

This paper demonstrated that the kinetic factor (hard-segment mobility in this study) could control whether the structure in segmented polyurethanes was phase-mixed or phase-separated. UMDI has greater hard- and soft-segment incompatibility than UHDI according to the solubility parameters, while HDI/HBPA in UHDI has higher mobility than MDI/HBPA in UMDI due to the flexible HDI. The former did not give rise to any observable phase separation, while the latter gave rise to nearly complete phase separation.

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