

# Structure and Viscoelastic Properties of Segmented Polyurethane Blends

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## SYNOPSIS

Structure and viscoelastic properties of segmented polyurethaneurea (SPU) blends were investigated. The glass transition temperature ( $T_g$ ) of poly(tetramethylene glycol) (PTMG) in a soft-segment block of the component SPU increased with decreasing molecular weight of PTMG. The blend samples showed two  $T_g$ s of PTMG in the temperature dispersions of the loss modulus ( $E''$ ) and loss tangent ( $\tan \delta$ ). The value of  $E'$  in the leathery region for the blend specimens was strongly affected by the morphology. The blends were considered to have a morphology where PTMG differing in molecular weight was localized.

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## INTRODUCTION

Segmented polyurethane (SPU) has been known as a multi-block copolymer composed of repeating units of hard- and soft-segment blocks. The film specimen prepared from the solution-cast method forms a two-phase structure comprising hard- and soft-segment domains.<sup>1-7</sup> The morphology of block copolymers is influenced by the primary chain structure and solvent power.<sup>8-10</sup> The mechanical and viscoelastic properties are affected by the primary chain structure through the morphology (higher-order structure).<sup>11-15</sup> It is very important to clarify the primary chain structure-morphology-property relationships for a detailed understanding of the mechanical and viscoelastic properties of the block copolymers. The morphology and mechanical and viscoelastic properties of SPUs have been widely examined by many researchers,<sup>1-6,16-18</sup> and the relations between structure and properties have become clear. However, there are few studies at present on the structure and mechanical and viscoelastic properties of blends of SPUs.<sup>17</sup> It is very interesting to investigate what kind of structure is formed and how the structure

affects the properties when samples are prepared by blending two different block copolymers. In this study, dynamic viscoelastic properties of SPUs as well as their blends were investigated. On the basis of the experimental results, the morphology of the blends in bulk was also estimated.

## EXPERIMENTAL

### Samples

Three types of segmented polyetherurethaneureas, which we abbreviate here as SPUs, were supplied as dimethylformamide (DMF) solutions from Toyobo Co., Japan. The prepolymer of the SPUs was composed of poly(tetramethylene glycol) (PTMG) and 4,4'-diphenylmethane diisocyanate (MDI). SPUs were prepared by chain-extending the prepolymers with 1,2-diaminopropane (DAP). The soft-segment block of the SPUs is composed of a sequence of PTMG and MDI, and the hard-segment block comprises MDI and DAP. The sample code, number-average molecular weight of PTMG ( $M_s$ ), and PTMG content ( $W_s$ ) are tabulated in Table I, together with those for the blend specimens. Here, the blend sample designated by SPU-1/5( $m/n$ ) ( $m, n = 1, 2$ ) indicates that the sample comprises SPU-1 and SPU-5, and the composition is  $m:n$  by weight.

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**Table I** Sample Code Name, Number-average Molecular Weight ( $M_n$ ) of PTMG and PTMG Content ( $W_s$ )

Sample	$M_n$	$W_s$
SPU-1	850	0.60
SPU-3	1350	0.70
SPU-5	2000	0.78
SPU-1/5(1/2)	1450	0.72
SPU-1/5(1/1)	1270	0.69
SPU-1/5(2/1)	1100	0.66

The blend samples were obtained by mixing the polymer solutions. The film specimens were prepared by the solution-cast method. The solutions were cast in a glass dish and then dried at 80°C. The films were dried further in a vacuum oven at 80°C. The film thickness was 100–300  $\mu\text{m}$ . The sample coded as SPU-1/5(1/1)H was made by laminating SPU-1 and SPU-5 films with almost the same thickness at 150°C for 3 min using a molding machine. We assumed that the  $M_n$  of SPU-1/5(1/1)H was identical to that of SPU-1/5(1/1).

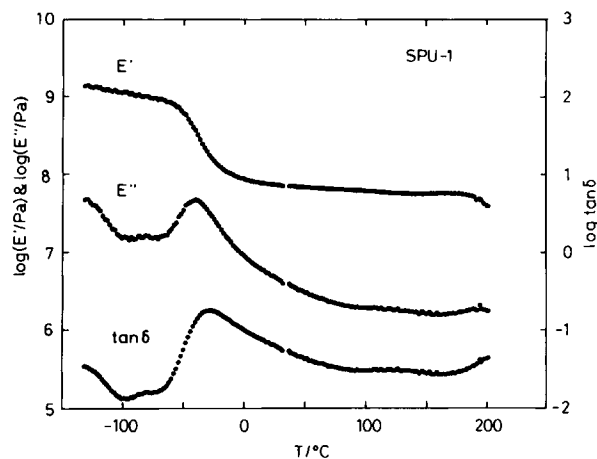
### Measurements

Temperature dispersions of the dynamic Young's modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) for the film specimens were measured using a Rheometrics solids analyzer (RSAII) upon increasing the temperature at an angular frequency ( $\omega$ ) of 10  $\text{s}^{-1}$  after the samples were cooled to low temperatures in the chamber of the equipment. The strain amplitude of the dynamic measurements ( $\epsilon_0$ ) was fixed at  $5 \times 10^{-3}$ . Differential scanning calorimetry (DSC) measurements of SPU samples were carried out using a Shimadzu DSC-50 with a heating rate of 20°C/min after rapid cooling.

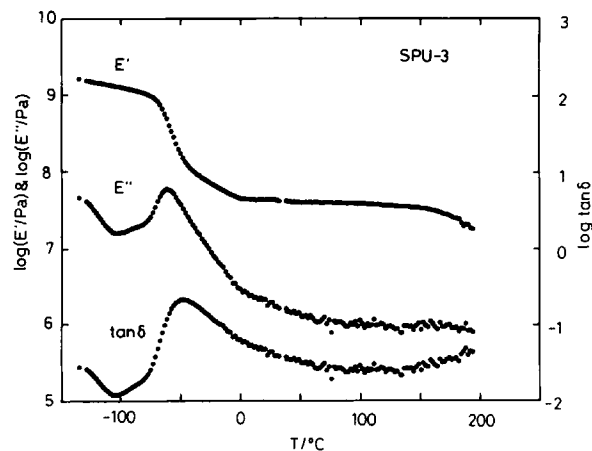
## RESULTS

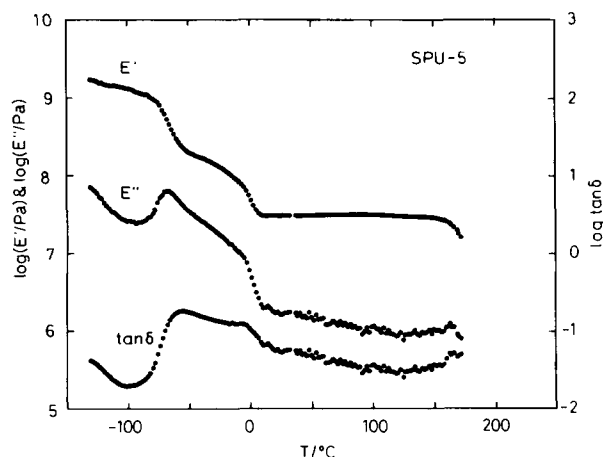
### Temperature Dispersions of $E'$ , $E''$ , and $\tan \delta$ for Component SPUs

Figure 1 shows temperature dispersion curves of  $E'$ ,  $E''$ , and  $\tan \delta$  for SPU-1. At low temperatures,  $E'$  shows a high value of the order of  $10^9$  Pa, showing that the sample is in the glassy state.  $E'$  starts to drop at about  $-60^\circ\text{C}$  on increasing the temperature and  $E'$  reaches almost a constant value around  $0^\circ\text{C}$ . At higher temperatures, a plateau region is observed in the  $E'$  vs. temperature ( $T$ ) curve. The decrease

**Figure 1** Temperature dispersions of the dynamic Young's modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) of SPU-1.

in  $E'$  is again observed around  $200^\circ\text{C}$ . A peak is observed around  $-40^\circ\text{C}$  in the  $E''$  curve and a peak also appears at about  $-30^\circ\text{C}$  in the  $\tan \delta$  curve. We regarded the peak temperature in the  $\tan \delta$  curve as the glass transition temperature ( $T_g$ ) of SPU-1 determined by the viscoelasticity measurement. Similar plots for SPU-3 are shown in Figure 2. The shapes of the dispersion curves are similar to those of the curves for SPU-1. However, the peak temperatures in the  $E''$  curve and the  $\tan \delta$  curve for SPU-3 are different from those for SPU-1; the peak is located around  $-60^\circ\text{C}$  in the  $E''$  curve and around  $-50^\circ\text{C}$  in the  $\tan \delta$  curve for SPU-3, while the corresponding peaks for SPU-1 are observed around  $-40$  and  $-30^\circ\text{C}$ . In Figure 3, similar plots for SPU-5 are shown. In the  $E'$  curve, a broad shoulder is

**Figure 2** Temperature dispersions of the dynamic Young's modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) of SPU-3.



**Figure 3** Temperature dispersions of the dynamic Young's modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) of SPU-5.

observed in the temperature region of  $-50$  to  $0^\circ\text{C}$ . A peak around  $-70^\circ\text{C}$  and a shoulder appear in the  $E''$  curve. Similarly, the  $\tan \delta$  curve shows a peak and a shoulder. The peak is located around  $-55^\circ\text{C}$ .  $T_g$ s of the component SPUs determined by the viscoelasticity measurements are summarized in Table II. The  $T_g$  determined by the viscoelasticity measurements increased with decreasing  $M_s$ .

#### Temperature Dispersions of $E'$ , $E''$ , and $\tan \delta$ for SPU-1/5 Blends

Figure 4 represents the temperature dispersion curves of  $E'$ ,  $E''$ , and  $\tan \delta$  of SPU-1/5(2/1). Two peaks are observed in the low-temperature region of the  $E''$  curve, and a peak and a shoulder also appear in the  $\tan \delta$  curve. A peak and a shoulder are observed in the  $E''$  curve of SPU-1/5(1/1) shown in Figure 5. The  $\tan \delta$  curve in the figure also has a

peak and a shoulder at low temperatures. Figure 6 shows similar plots for SPU-1/5(1/2). The temperature dispersion curve of  $E'$  in the region of the glass-to-leather transition is apparently divided into two parts: One of them at lower temperatures has a steeper slope and the other, a gentle one. A peak and a shoulder are also observed in the  $E''$  curve, and a flat band with high values exists in  $\tan \delta$  curve. In Figure 7, similar plots for a laminated specimen SPU-1/5(1/1)H are shown. This sample clearly shows two peaks in the  $E''$  vs.  $T$  curve and a peak and a shoulder in the  $\tan \delta$  vs.  $T$  curve. The temperatures at which the peak and shoulder were located in the  $\tan \delta$  curve were regarded as  $T_g$ 's of the blend and laminated specimens, and the values of the  $T_g$ 's are listed in Table II.

#### DSC Measurements

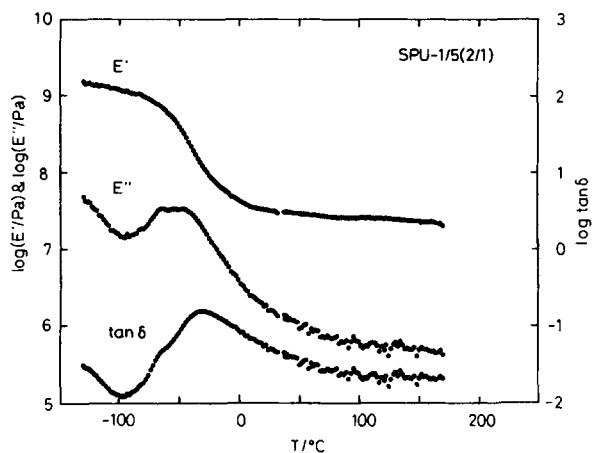
Figure 8 shows the DSC thermograms of the component SPUs as well as SPU-1/5 blends. An endothermic peak is observed in the temperature range of  $-15$  to  $0^\circ\text{C}$  for all samples except for SPU-1 and becomes larger with increasing  $M_s$  for the component SPUs. As will be discussed in detail later, the peak corresponds to the melting of the soft-segment PTMG,<sup>5,19-21</sup> and the peak temperature was regarded as the melting temperature ( $T_m$ ) of PTMG. At low temperatures, two turning points of the slope, which are shown by arrows in the figure, are observed in each thermogram. The temperature region between the two turning points is relatively narrow for SPU-1 and SPU-5, but is broad for SPU-3, as can be seen from the figure. The transition region for the three blend specimens is also broad. From the DSC measurements, we determined the  $T_g$  of each sample as a midpoint between two turning points in a thermogram. Although we could see two glass transitions

**Table II** Glass Transition Temperature ( $T_g$ ), Melting Temperature ( $T_m$ ), Heat of Fusion ( $\Delta Q$ ), and Degree of Crystallinity ( $X_s$ ) of Soft-segment PTMG

Sample	$T_g$ ( $^\circ\text{C}$ )	$T_m$ ( $^\circ\text{C}$ )	$\Delta Q$ (kJ/kg)	$X_s$ (%)
SPU-1	$-29^a$	$-47^b$	—	—
SPU-3	$-49^a$	$-59^b$	1.00	0.69
SPU-5	$-56^a$	$-66^b$	11.12	7.0
SPU-1/5(1/2)	$-32^a, -66^a$	$-62^b$	4.33	2.9
SPU-1/5(1/1)	$-31^a, -64^a$	$-61^b$	4.43	3.1
SPU-1/5(2/1)	$-38^a, -63^a$	$-63^b$	2.28	1.7
SPU-1/5(1/1)H	$-32^a, -65^a$	—	—	—

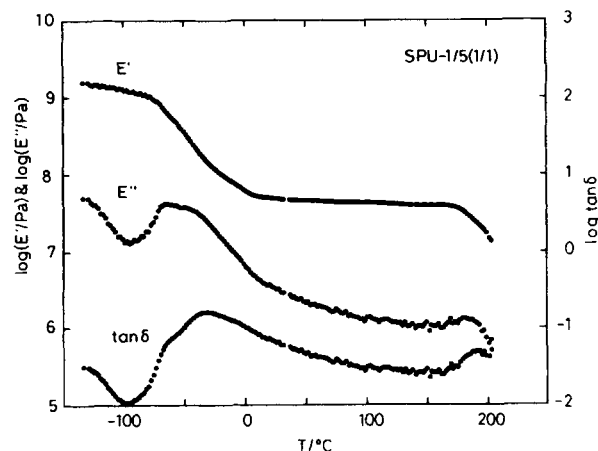
<sup>a</sup> Determined by viscoelasticity measurements.

<sup>b</sup> Determined by DSC.

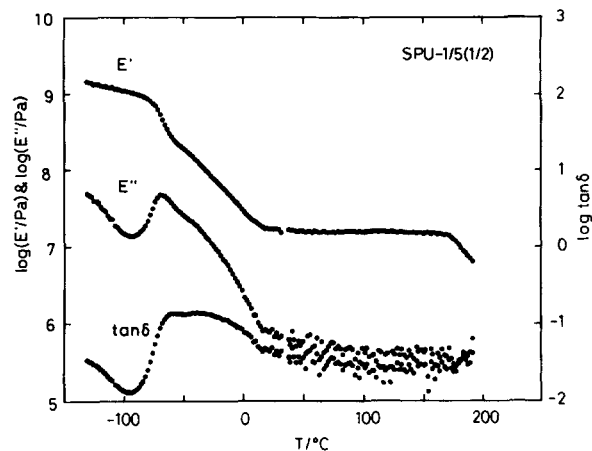


**Figure 4** Temperature dispersions of the dynamic Young's modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) of SPU-1/5(2/1).

of PTMG appearing as a peak and shoulder in the  $\tan \delta$  curve and two peaks in the  $E''$  dispersion curves for the blends by viscoelasticity measurements, as will be discussed later, we could not distinguish the two glass transitions by DSC.  $T_g$ ,  $T_m$ , heat of fusion ( $\Delta Q$ ) of PTMG, and degree of crystallinity ( $X_s$ ) of PTMG for the samples are listed in Table II. The value of the  $T_g$  obtained by DSC increases with decreasing  $M_s$  for the component SPUs, but those for the blends are almost constant. The  $T_m$  of SPU-5 is higher than that of SPU-3, and those for the blends are almost identical. The  $\Delta Q$  and  $X_s$  of SPU-5 are larger than those of SPU-3. SPU-1/5(1/1) shows larger values of  $\Delta Q$  and  $X_s$  compared with those for SPU-1/5(1/2) and SPU-1/5(2/1).



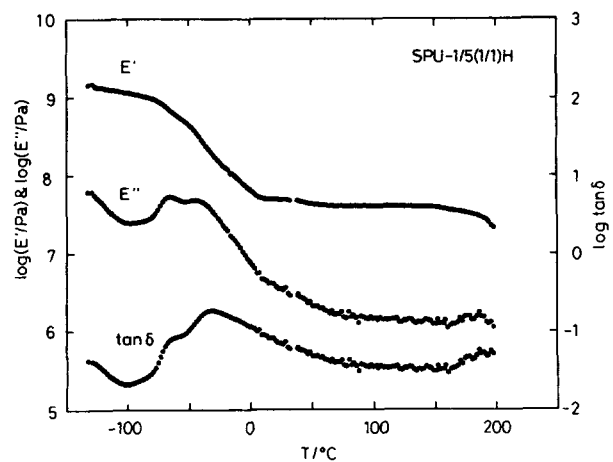
**Figure 5** Temperature dispersions of the dynamic Young's modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) of SPU-1/5(1/1).



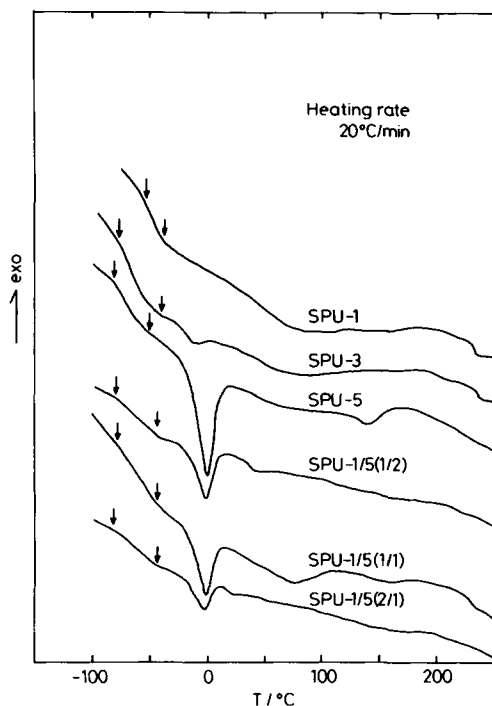
**Figure 6** Temperature dispersions of the dynamic Young's modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) of SPU-1/5(1/2).

## DISCUSSION

The temperature-dispersion curves of  $E''$  and  $\tan \delta$  for the component polymers showed a peak at low temperatures. We determined  $T_g$  as a peak temperature in the  $\tan \delta$  curve, as stated before.  $T_g$  was also determined by the DSC measurements. The  $T_g$  for the component SPUs determined by viscoelasticity measurement is slightly higher than that obtained by DSC, as can be seen in Table II.  $T_g$  obtained by viscoelasticity measurements decreases in the same way with increasing  $M_s$ , as  $T_g$  determined by DSC does. Since the  $T_g$  of the PTMG homopolymer has been reported to be  $-85^\circ\text{C}$ ,<sup>19</sup> the data show that the value of the  $T_g$  of PTMG in SPUs approaches that of the homopol-



**Figure 7** Temperature dispersions of the dynamic Young's modulus ( $E'$ ), loss modulus ( $E''$ ), and loss tangent ( $\tan \delta$ ) of SPU-1/5(1/1)H.



**Figure 8** DSC thermograms of the component SPUs and blends.

mer with increasing  $M_s$ . Since the film of SPU has a two-phase structure, the decrease of  $T_g$  with increasing  $M_s$  is attributed to the decrease of the miscibility between soft and hard segments: The increase of the degree of the phase mixing between soft and segment phases increases the  $T_g$  of the soft-segment block.<sup>3-6,17-20</sup>

As stated previously (Fig. 8), the endothermic peak was observed in the DSC thermograms of SPU-3 and SPU-5, but no peak was observed in the curve of SPU-1. The peak is due to the melting of microcrystalline domains of soft-segment PTMG, which were formed by cooling prior to the measurements. The temperature-dispersion curves of  $E'$ ,  $E''$ , and  $\tan \delta$  of SPU-5 are clearly affected by the melting, but those for SPU-3 are not clearly affected in spite of the occurrence of melting. This may be because the viscoelasticity measurement is not as sensitive for detecting the melting of the microcrystalline domains of PTMG in comparison with the DSC measurement. As can be seen from Table II, the  $T_m$ s of PTMG for SPU-3 and SPU-5, which were determined as a peak temperature in the DSC thermograms, are, respectively,  $-12.5$  and  $0.1^\circ\text{C}$ , while that of the PTMG homopolymer is reported to be  $44^\circ\text{C}$ .<sup>21</sup> The lowering of the  $T_m$  of PTMG may be due to the small size of the microcrystalline PTMG domains. The  $\Delta Q$  of PTMG in SPU-3 is smaller than that in

SPU-5, and the melting of PTMG in SPU-1 was not determined by DSC measurements. The decrease of  $\Delta Q$  is due to the decrease of crystallinity with decreasing  $M_s$ . By using the data of  $\Delta Q$  in Table II and  $W_s$  in Table I, the crystallinity of PTMG ( $X_s$ ) was determined by assuming that the  $\Delta Q$  of the homopolymer of PTMG was  $206 \text{ kJ/kg}$ .<sup>21</sup> The value of  $X_s$  of SPU-1 is almost zero. The  $X_s$  of SPU-5 is larger than that of SPU-3, but is highest at 7.0 wt %.

The temperature-dispersion curves of the  $\tan \delta$  of SPU-1/5(1/1) (Fig. 5) and SPU-1/5(1/1)H (Fig. 7) showed a peak and a shoulder. By comparing the dispersion curve of SPU-1/5(1/1)H with that of SPU-1/5(1/1), the peak temperature and the position of the shoulder are almost the same. Since SPU-1/5(1/1)H has a double-layer structure, it is clear that the peak and shoulder correspond to the  $T_g$ s of PTMG of each component SPU. Actually, the peak temperature agrees well with that of SPU-1, and the temperature at which the shoulder appears is close to the peak temperature of SPU-5. The similarity in the shapes of the dispersion curves of SPU-1/5(1/1) and SPU-1/5(1/1)H, which are also the same in composition, suggests that the blend sample has a higher-order structure in which the soft-segment chains differing in  $M_s$  are localized. One of the possible structures for the blend is the double-layer structure such as the structure for SPU-1/5(1/1)H. In this case, the two surface regions of the film specimen have different PTMG contents. However, infrared absorption spectra for the two surface regions were almost identical,<sup>22</sup> indicating that the localization of PTMG occurs not at the macroscopic level but at the microscopic level. The  $\tan \delta$  curve of SPU-1/5(1/2) also showed a shoulder and a peak in the low-temperature region. The appearance of a peak and a shoulder in the  $\tan \delta$  curves of SPU-1/5(1/2) also shows that the systems contain two types of PTMG. The lower  $T_g$  originates from the soft segments of SPU-5, and the higher one, from that for SPU-1. For the temperature-dispersion curve of  $\tan \delta$  for SPU-1/5(2/1), a flat dispersion band was observed. The band occurs from the overlapping of the two  $T_g$ s of PTMG of the component SPUs.

The results of the viscoelasticity measurements clearly show that at low temperatures soft segments are microscopically localized, although the information is limited to the localization at low temperatures. The localization may be realized even for homogeneous blends at high temperatures where  $E'$  shows a plateau value, because the soft-segment chains of SPU-5 can crystallize and the

crystallization of the chains excludes the soft-segment chains of SPU-1 when the specimens are cooled. When the soft-segment chains of both SPU-1 and SPU-5 are delocalized at high temperatures (e.g., at room temperature), the  $X_s$  of the blends will be much reduced in comparison with the values obtained by assuming that the crystallization of PTMG of SPU-5 is not affected by the existence of SPU-1 (2.7% for 2/1 blend, 3.9% for 1/1, and 5.0% for 1/2), because the PTMG of SPU-1 prevents the PTMG of SPU-5 from crystallization. The  $X_s$  of the 1/1 blend is high and reaches about 79% of the expected value. The values of  $X_s$  for the 1/2 and 2/1 blends are not so low compared with the expected values. These may indicate that the localization occurs even at high temperatures for the blends, although there will be some extent of delocalization. The relatively large reduction of the values of  $X_s$  for the blends with unequal compositions (the 1/2 and 2/1 blends) is attributed to the increase of the degree of delocalization of the PTMG of SPU-1 and SPU-5 in the film preparation stage where microphase separation occurs. We do not know from the experiments whether the hard-segment domains are also localized, because the melting behavior of the hard-segment domains was not clear by the viscoelasticity and DSC measurement results.

The plateau values of  $E'$  of the component SPUs decrease with increasing  $M_s$ . Comparing  $E'$  of SPU-1/5(1/1)H with that of SPU-1/5(1/1), we can see that the values are almost identical. The values are also close to that for SPU-3. The plateau value of  $E'$  for SPU-1/5(2/1) is almost identical to that of SPU-5 in spite of the difference in  $M_s$ , and the value of  $E'$  for SPU-1/5(1/2) is lower compared with that for SPU-5. This indicates that the  $E'$  value for the SPU blends cannot be determined only by  $M_s$ , and the coincidence of  $E'$  values for the three samples with almost the same  $M_s$  (SPU-1/5(1/1), SPU-1/5(1/1)H, and SPU-3) is only incidental. Since morphology is closely related to the mechanical and viscoelastic properties of the specimens, the above results strongly suggest that the morphology of the blends is different from that for the component SPUs. We think that there is localization of PTMG differing in  $M_s$  even at high temperatures.

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