

Improved Mechanical Properties of Shape-Memory Polyurethane Block Copolymers through the Control of the Soft-Segment Arrangement

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ABSTRACT: High-performance shape-memory polyurethane block copolymers, prepared with two types of poly(tetramethylene glycol) (PTMG) used as soft segments, were investigated for their mechanical properties. Copolymers with a random or block soft-segment arrangement had higher stresses at break and elongations at break than those with only one kind of PTMG. Random copolymers with fewer interchain interactions showed higher elongation than block copolymers. All the copolymers had shape-recovery ratios higher than 80%. In dynamic mechanical testing, the

glass-transition behavior clearly depended on the soft-segment arrangement: random copolymers had only one glass-transition peak, whereas block copolymers showed two separate glass-transition peaks. Overall, the control of the soft-segment arrangement plays a vital role in the development of high-performance shape-memory polyurethane. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2410–2415, 2004

Key words: copolymerization; mechanical properties; polyurethanes

INTRODUCTION

Shape-memory polymers have recently drawn the interest of researchers because of their superior properties and potential applications in medical, industrial, electronic, and textile fields.^{1–3} Although more advanced shape-memory polymers, such as shape-memory nanocomposites,^{4–8} have been reported, polyurethane (PU) block copolymers still play an important role in the area of shape-memory polymers. Basically, the shape-memory effect is known to originate from transitions from the glassy state to the rubbery state in soft segments and from phase separation among hard and soft segments. Therefore, researchers have focused on microphase- and macrophase-separation behavior and the corresponding impact on structural and physical properties. Shape retention, coming from interactions among hard segments via dipole–dipole interactions, hydrogen bonding, or crystallization, and shape recovery, coming from the reversible phase transformation of soft segments, are responsible for the shape-memory effect.

A two-step process or prepolymerization method is usually favored in the preparation of shape-memory

polyurethane (SMPU) because a more uniform distribution of the size and properties can be obtained than with the one-step method. Various methods of controlling the molecular structure and morphology of hard-segment and soft-segment domains have been already introduced to obtain higher performance SMPU. Examples include modifications of the chemical structure of the hard and soft segments, the segment length, the molecular weight of the soft segment, and the physical or chemical crosslinking method.^{9,10} In particular, control over interchain interactions such as hydrogen bonding has been determined to be the important factor. In this study, we tried to modify the soft-segment arrangement of SMPU in an attempt to improve the shape-memory properties, and the reasons for such high differences in the mechanical and thermomechanical properties were examined.

EXPERIMENTAL

4,4'-Methylene bis(phenyl isocyanate) (MDI; Junsei Chemical) and poly(tetramethylene glycol) (PTMG; molecular weight = 1800 or 1000 g/mol) were dried in a vacuum oven before use, and 1,4-butanediol (BD; Duksan Chemical) was stored on 4-Å molecular sieve. Synthesis was generally carried out in two steps as follows. In a 500-mL, four-necked cylindrical vessel equipped with a mechanical stirrer, calculated amount of MDI and PTMG in 100 mL of freshly distilled dimethylacetamide were stirred under nitrogen at

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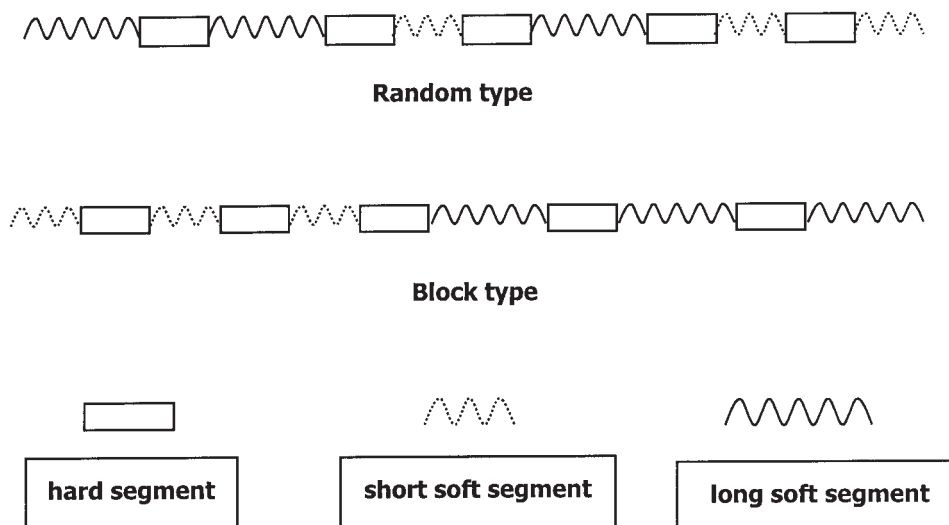


Figure 1 Stylized view of random and block copolymers.

80°C for 3 h to make prepolymer. In the second step, BD was added dropwise to the reaction mixture depending on the MDI/PTMG ratios. After the polymerization was over, SMPU was removed of solvent *in vacuo*, and further solidified by storing in an oven (100°C) for 24 h. Overall, three kinds of SMPU copolymers were prepared by the above method and same molar ratio of MDI/PTMG/BD = 2.1/1.0/1.1 was used in preparation of each sample, resulting in 30 wt % hard segment: (1) two PTMGs at 50/50 molar ratio were allowed to react with MDI in the first step; (2) low-molecular-weight PTMG at 50% molar ratio reacted first with part of MDI in the first step, and the remaining MDI coupled with high-molecular-weight PTMG at 50% molar ratio also in the first step; (3) blends of PUs having low-molecular-weight and high-molecular-weight PTMGs at 50/50 wt % were prepared via solution-mixing technique.

A Fourier transform infrared (FTIR) instrument (FTIR 300E, Jasco) equipped with attenuated total reflectance was used to record spectra of PU films. Tensile specimens molded to a 3-mm thickness at 160–230°C were freshly prepared before the tensile tests. Tensile tests were performed at room temperature with a universal testing machine (LR50K, Lloyd) with a dumbbell-type specimen, and the gauge length and crosshead speed were 25 mm and 10 mm/min, respectively. To measure the shape-memory effect, thermo-mechanical experiments were performed with a universal testing machine equipped with a controlled thermal chamber, and the relationship between the stress and strain at various temperatures was analyzed. Specifically, a deformation of up to 100% of the elongation was applied to a specimen at a constant crosshead speed of 10 mm/min at 20°C above the glass-transition temperature (T_g), and the specimen was then quickly cooled to 20°C below T_g with 100%

elongation. After remaining at that temperature for 5 min with the removal of the load, the specimen was heated to a temperature 20°C above T_g for the measurement of the recovery strain, and the shape recovery was calculated as follows:

$$\text{Shape retention (\%)} = (\text{Retention strain at } T_g - 20) \times 100 / (\text{Strain at 100\% elongation}) \quad (1)$$

$$\text{Shape recovery (\%)} = (\text{Strain at 100\% elongation} - \text{Recovery strain at } T_g + 20) \times 100 / (\text{Strain at 100\% elongation}) \quad (2)$$

RESULTS AND DISCUSSION

Copolymers prepared according to the aforementioned procedures resulted in quite different soft-segment arrangements. For a copolymer allowed to consume two PTMGs (low-molecular-weight and high-molecular-weight) together in the first step, the arrangement of the two PTMGs was random. How-

TABLE I
Molar Ratios of the Components for the Preparation of Random Copolymers

Sample code	Feed molar ratio				Hard segment (wt %)
	MDI	PTMG		BD	
		$M_n = 1000$	$M_n = 1800$		
100/0	1.5	1.0	0	0.5	30
70/30	1.8	0.7	0.3	0.8	30
50/50	2.1	0.5	0.5	1.1	30
30/70	2.2	0.3	0.7	1.2	30
0/100	3.0	0	1.0	2.0	30

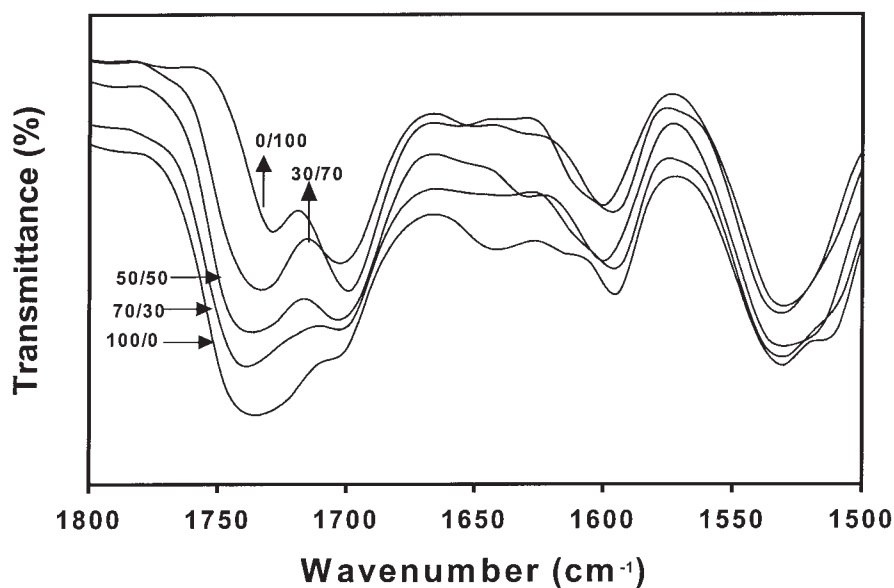


Figure 2 FTIR spectra of random copolymers.

ever, a copolymer made with the second method had a block distribution of two PTMGs along the polymeric chain. A stylized view of the soft-segment arrangement is presented in Figure 1. For convenience, copolymers prepared with the three different methods are designated as (1) random PU, (2) block PU, and (3) blend PU. In addition, PU-1 and PU-2 mean that the copolymers were prepared with one of the two PTMGs (low-molecular-weight or high-molecular-weight).

In addition to the mixing method reported in the Experimental section, an adjustment to the molar ratio of the two PTMGs in random PUs provided a greater selection of copolymers for comparison. Specific ratios are

presented in Table I. In the FTIR spectrum of a random PU (Fig. 2), clear differences in the phase-separation behavior, depending on the molar ratio of PTMG, can be observed. The characteristic absorption bands around 1700 and 1730 cm^{-1} are associated with the stretching mode of the carbonyl group in the hard segments.^{11,12} The former peak corresponds to carbonyl groups hydrogen-bonded to $-\text{NH}$ groups of neighboring hard segments, whereas the latter peak comes from the non-hydrogen-bonded carbonyl groups surrounded by soft segments. As a result, with increasing high-molecular-weight PTMG content, the absorption ratio of 1700 to 1730 cm^{-1} increases gradually, and this indicates that the phase separation is well developed.

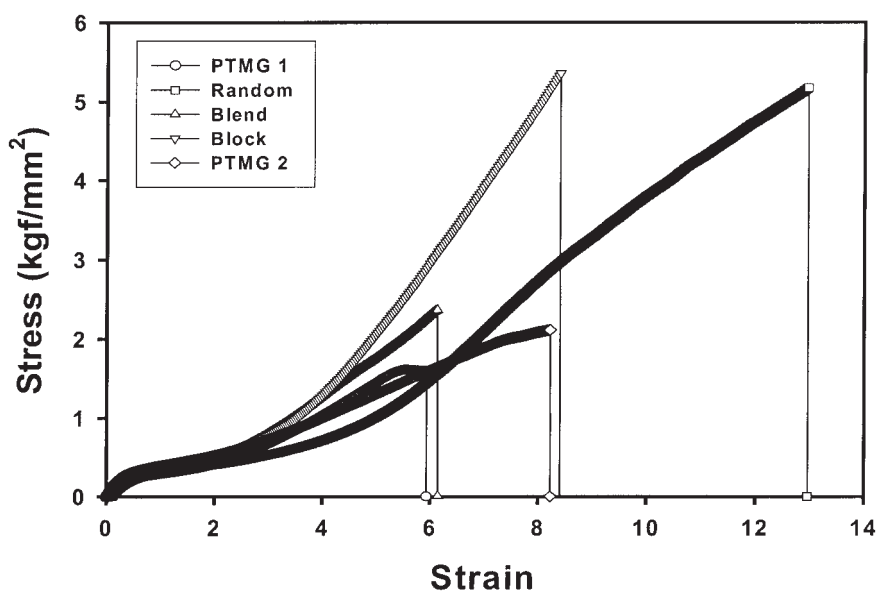


Figure 3 Stress-strain curves of the copolymers.

TABLE II
Modulus, Stress at Break, and Elongation at Break
Obtained from Tensile Tests

Sample code	PTMG1000/ PTMG1800 molar ratio	Modulus (kgf/mm ²)	Stress at break (kgf/mm ²)	Elongation at break (%)
Random	100/0	0.45	1.8	620
Random	70/30	0.54	5.0	1220
Random	50/50	0.48	2.2	1180
Random	30/70	0.55	0.7	910
Random	0/100	1.13	2.1	830
Blend	90/50	0.48	1.7	630
Block	50/50	0.83	4.9	840

Figure 3 shows stress-strain curves for five different kinds of copolymers: PU-1, PU-2, random PU, block PU, and blend PU. Although typical elastomeric behavior in the tensile tests was observed, apparent differences in the tensile modulus, strength at break, and elongation at break were observed. Noticeably, the block PU had a higher modulus than the random PU or blend PU (Table II). It seems that the uniform soft-segment distribution and the resultant effective interactions among the polymeric chains made the block PU harder to elongate than the other copolymers. In comparison with those of PU-1 and PU-2, higher strength at break and elongation at break were observed for both the block PU and random PU (Fig. 3). The blend PU, as expected, showed the lowest strength at break of the copolymers. The somewhat higher elongation at break of PU-2 was obviously due to the higher molecular weight of PTMG. As for the random PU, the highest breaking stress was observed at the molar ratio of 70/30 poly(tetramethylene glycol)-1000/poly(tetramethylene glycol)-1800, and the elongation at break followed a similar trend.

Various interactions can occur among copolymers, such as hydrogen-bonding, dipole-dipole, and induced dipole-dipole interactions, as shown in Figure 4.¹² Such interactions among hard segments significantly influence the phase separation of hard and soft segments. Therefore, a mismatch of hard segments by the random placement of soft segments among polymeric chains should result in a great reduction in the number of interactions, along with a low modulus and a high elongation at break. For regularly spaced copolymers such as PU-1 and PU-2, extensive interactions occurred, whereas copolymers such as the random PU and block PU had relatively weak interactions and, therefore, high elongation. Higher stress at break and elongation at break of the random PU and block PU indicate that mixed soft segments with different chain lengths can better absorb external stress and can be more elongated than PU-1 and PU-2. Combining these results, we find that the tensile properties of the copolymers are substantially influenced by the polymerization method and the chain length of the soft segment.

By analyzing the thermomechanical results of the stress and strain at various temperatures, we found that all of the copolymers with mixed soft segments had good shape retention and recovery higher than 80%, as shown in Figure 5. Specifically, shape retention was almost the same for all three copolymers, and the block PU was a little inferior to the other copolymers with respect to the shape recovery. Similar shape-memory results were observed for all three copolymers, although the tensile test results were quite different, depending on the type of copolymer, and this suggested that the shape-memory effect measured after elongation was not related to the tensile properties tested without elongation. High shape retention

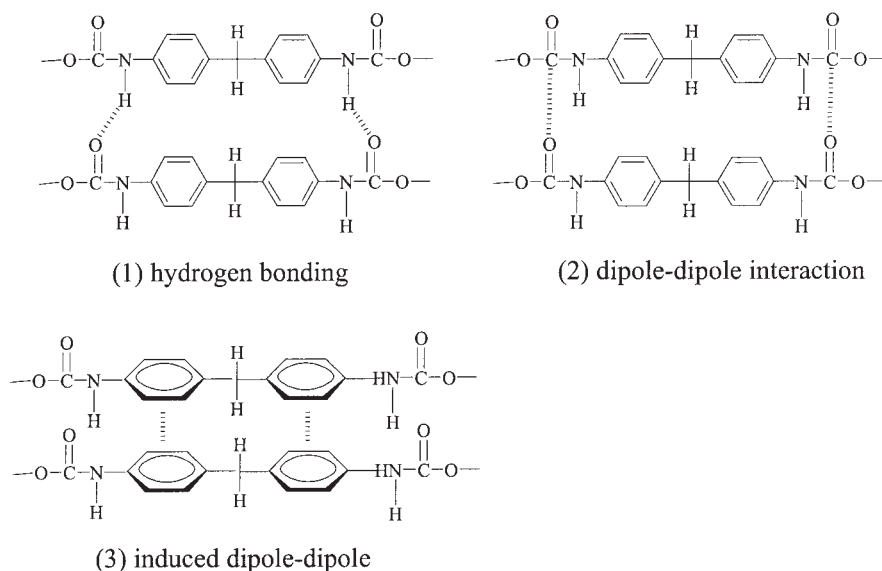


Figure 4 Possible interactions among copolymeric chains.

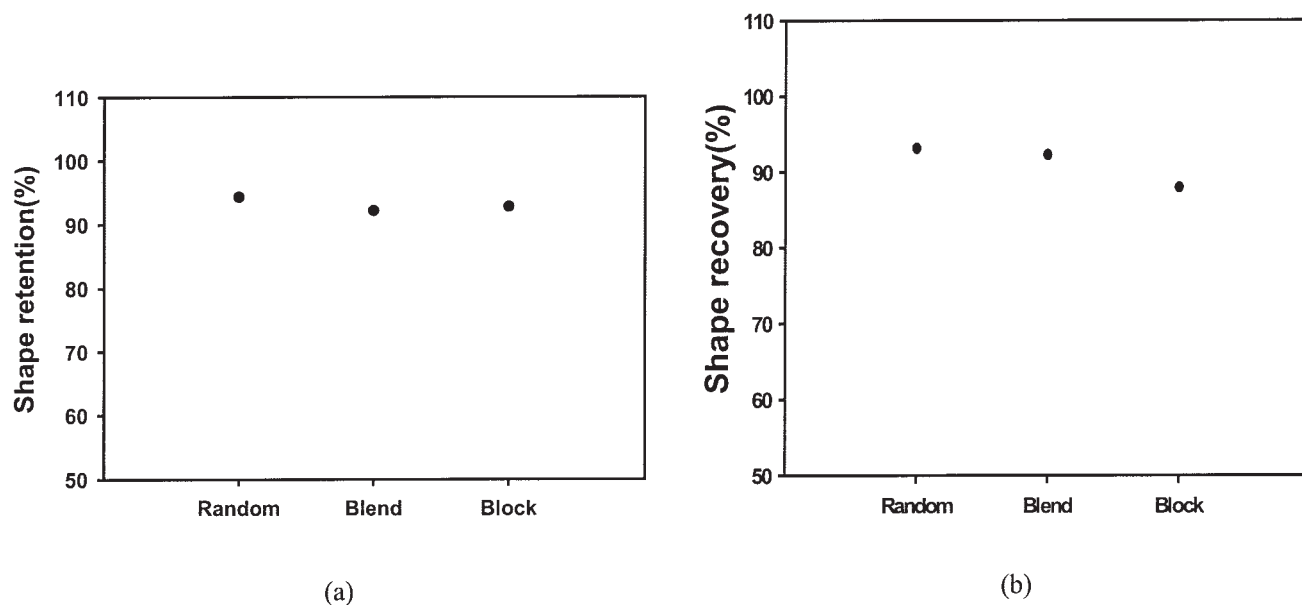


Figure 5 (a) Shape retention and (b) shape recovery of random, block, and blend copolymers.

and shape recovery, even after three cyclic tests, were attained.

The T_g values of the copolymers also depended on the polymerization method and molar ratio of PTMGs. Only one broad glass-transition peak appeared for the random PU, but the blend PU showed clear double peaks, as indicated in Figure 6. In contrast, the block PU had a minor transition peak at a low temperature and a major one at a high temperature. Therefore, we think that for the random PU, a mixed soft-segment arrangement from two PTMGs was made, and the block PU, although part of it, formed two different phase-separated soft-segment domains. The blend PU

obviously formed separate soft-segment domains, and this suggests that the blend copolymer was not as well intermingled as the random PU or block PU. Therefore, the control of the thermomechanical properties by the aforementioned technique will be very helpful to the development of advanced shape-memory polymers, such as shape-memory polymers with double-phase-transition capabilities.

The dependence of the mechanical properties (tensile modulus, stress at break, and elongation at break) on the molar ratio of PTMG for random PU was also investigated. PU-2 had the highest modulus, and those of the other copolymers, though quite low, were

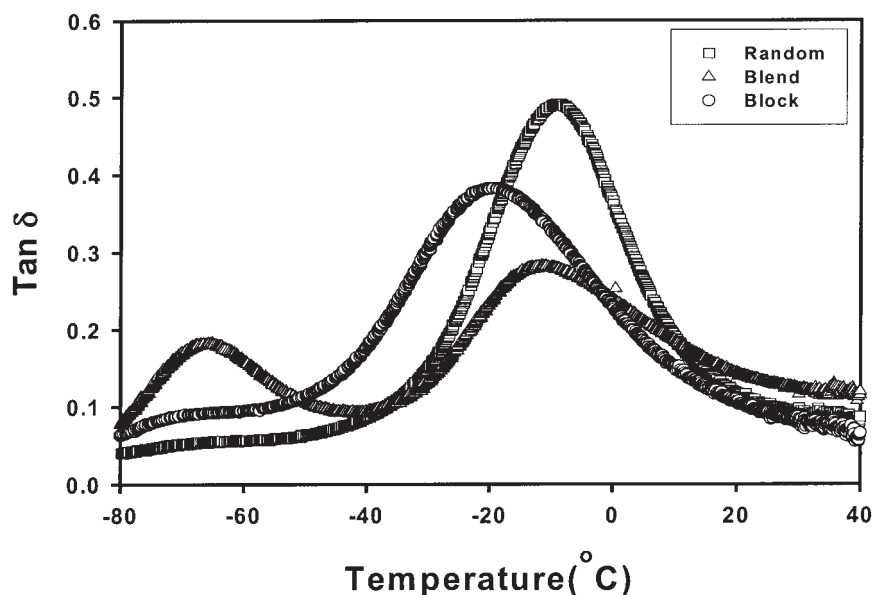
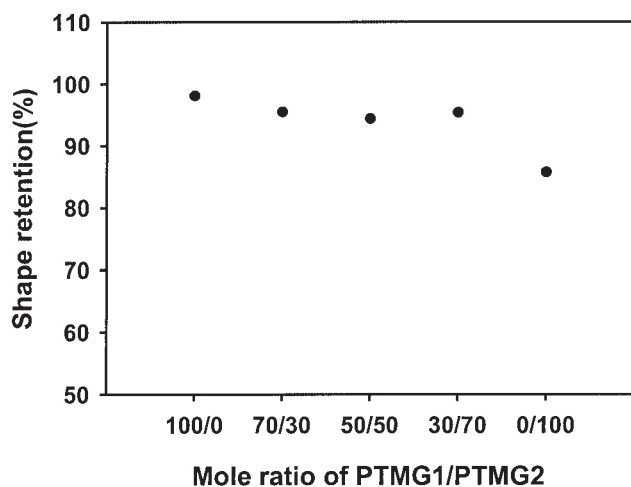
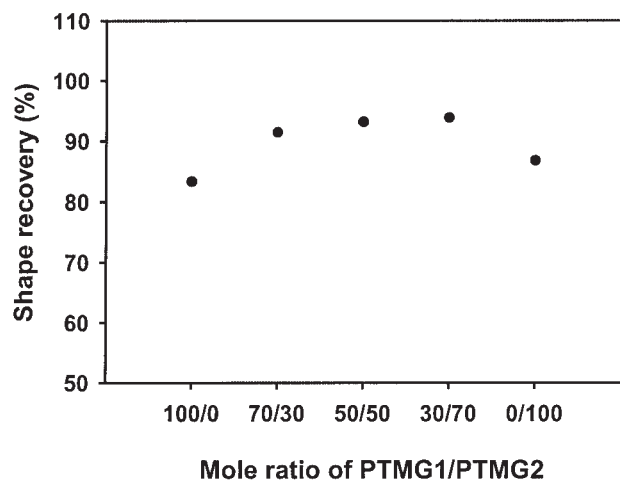


Figure 6 Profile of $\tan \delta$ versus the temperature for the three types of copolymers.



(a)



(b)

Figure 7 Comparison of the shape-memory effects of random copolymers: (a) shape retention and (b) shape recovery.

similar (Table II). Low-molecular-weight PTMG was responsible for the low modulus of PU-1, and a mixture of soft segments of different chain lengths was not effective for attaining a high modulus. Highly matched interchain interactions and high-molecular-weight PTMG accounted for the exceptionally high modulus of PU-2. However, higher elongation at break and stress at break could be obtained for the random PU with various soft-segment contents, in comparison with PU-1 and PU-2, at all molar ratios. The highest stress at break for the random PU was found at the molar ratio of 70/30 (low molecular weight/high molecular weight), as presented in Table

II. Such contrasting results can be explained by the fact that as the copolymer was extended further, the hard-segment domain of the random PU could be restructured because of relatively weak interactions among the hard segments, in contrast to PU-1 or PU-2, which had relatively stronger interactions.¹³ In a similar vein, the shape-memory effect of the random PU could be improved with a mixture of two PTMGs: a mixture of soft segments was effective in enhancing the shape recovery of PU, although the shape retention was not much different from that of PU-1 and PU-2 (Fig. 7). Consequently, the control of the soft-segment arrangement is clearly vital to the improvement of the shape-memory properties of SMPU.

CONCLUSIONS

Random and block PUs showed higher stress at break and elongation at break than copolymers with one kind of PTMG (PU-1 and PU-2) and blended PU. The introduction of two PTMGs together into the soft segment resulted in reduced interactions among the hard segments, and this made the copolymers easily elongated. Such copolymers presented relatively high shape-recovery ratio (>80%). The glass transition was dependent on the soft-segment arrangement: the random PU showed a single transition peak, and the block PU had a second peak in addition to a major one at a high temperature. Now we are assured that high-performance PUs with shape-memory effects can be tailor-made through the precise control of the soft-segment arrangement.

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