

Study on Shape-Memory Behavior of Polyether-Based Polyurethanes. II. Influence of Soft-Segment Molecular Weight

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ABSTRACT: Polyurethanes (PUs) of a suitable molar ratio of monomers were found to have shape-memory behavior. In this study, four series of PUs were synthesized by 4,4'-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BD), and various molecular weights of poly(tetramethylene oxide)glycol (PTMO) to study the influence of the soft segment (PTMO) on the shape-memory behavior of PUs. The investigation on thermal and dynamic mechanical properties was performed using DSC and DMA; then, the morphology of the PUs was directly observed by TEM. At the range of the individual glass transition, a similar recovering behavior was found from the deformed specimen that contained the same composition but different molecular weights of PTMO. However, the phase separation between the soft and the hard segments of the PUs would influence their shape-memory behavior. On the other hand, a large number of the dispersed phase of the PUs would delay the recovery rate of the deformed specimens using a high molecular weight PTMO. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1575–1586, 1998

Key words: polyether-based polyurethanes; shape memory behavior; morphology; thermal properties; dynamic mechanical properties; soft segment

INTRODUCTION

The investigation of the characteristics of a shape-memory alloy¹ has promoted the development of shape-memory polymers. Many kinds of shape-memory polymers were found.^{2–9} For polymers which displayed the mechanical behavior of shape memory, the morphology of shape-memory polymers should contain two phases⁴: One is the reversible phase, and the other is the fixed phase. The reversible phase shows a phase-transition

temperature that is a little higher than the operating temperature and could fix the deformation after cooling. However, the fixed phase consists of a phase with a high transition temperature or a crosslinking structure point. Thus, it could act the same as does rubber recovering from deformation. Consequently, the shape-memory behavior of polymers is influenced by the composition and distribution of these two phases.

Segmental polyurethanes (PUs) contain two phases, which are the flexible soft-segment phase and the rigid hard-segment phase. The former is based on aliphatic polydiol and the latter is formed by aromatic diisocyanate and the chain extender that consists of low molecular weight

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Table I Notation and Molar Compositions of the PUs

Symbol	Molecular Weight of PTMO	Hard-segment Content (wt %)
110 series (MDI/PTMO/BD = 1/1/0)		
A1	250	56.80
B1	650	31.56
C1	1000	22.73
D1	2000	12.62
211 series (MDI/PTMO/BD = 2/1/1)		
A2	250	74.30
B2	650	50.33
C2	1000	39.25
D2	2000	24.10
615 series (MDI/PTMO/BD = 6/1/5)		
A6	250	90.20
B6	650	76.31
C6	1000	67.26
D6	2000	50.23
12111 series (MDI/PTMO/BD = 12/1/11)		
A12	250	94.90
B12	650	86.73
C12	1000	80.65
D12	2000	67.19
E12	2900	58.41

diol.^{10,11} The morphology of PUs is influenced by the molecular weight of the soft segment.^{12–16} The degree of phase separation is increased by using soft segment of high molecular weight.

In our previous study,¹⁷ the influence of the hard segment (fixed phase) was investigated. The results demonstrated that the content of the hard segment would decide whether the recovery of deformation was complete. To determine the influence of the soft segment, four series of specimens with different molecular weights of the soft segment (PTMO) were prepared. The thermal and dynamic mechanical properties of the specimens were measured using DSC and DMA. The morphologies of the PUs were also observed by TEM with a stained technique. Finally, the relationship between the shape-memory behavior and the morphology that depends on the molecular weight of PTMO was investigated.

EXPERIMENTAL

Materials

Reagent-grade poly(tetramethylene oxide) glycol (PTMO, MW = 2900, 2000, 1000, 650, and 250, Aldrich Chemical Co., Wisconsin, USA) and 1,4-butanediol (BD, Aldrich Chemical Co.) were dehydrated under a vacuum at 65°C before using. Reagent-grade 4,4'-diphenylmethane diisocyanate (MDI, Tokyo Chemical Inc., Tokyo, Japan) was melted at 45°C and used after removing the white precipitates in the melts. Reagent-grade *N,N'*-dimethylformamide (DMF, Aldrich Chemical Co.) was dehydrated with molecular sieves of 4 Å and used as a solvent.

Polymer Synthesis

Four series of PUs were synthesized with MDI and PTMO and the chain extender BD. The com-

Table II DSC Data of the Pure Soft Segment and Pure Hard Segment

Sample	Glass Transition T_g (°C)	Crystallization		Crystal Melting	
		T_c (°C)	ΔH (J/g)	T_m (°C)	ΔH (J/g)
Pure soft segment					
PTMO250	-95.1	-46.4	67.4	-7.9	74.4
PTMO650	— ^a	—	—	20.2	94.0
PTMO1000	—	—	—	23.6	96.8
PTMO2000	—	—	—	27.7	99.3
PTMO2900	—	—	—	45.8	131.6
Pure hard segment					
HS	100.1	150.4	33.3	192.8, 214.9, 231.6	40.9

^a “—” indicates that the thermal behavior was not observed.

Table III Characteristic Temperature of the PUs

Sample	Glass Transition T_g (°C)		Crystallization T_c (°C)		Crystal Melting T_m (°C)	
	Soft-segment-rich Phase	Hard-segment-rich Phase	Soft-segment-rich Phase	Hard-segment-rich Phase	Soft-segment-rich Phase	Hard-segment-rich Phase
110 series (MDI/PTMO/BD = 1/1/0)						
A1	22.9	— ^a	—	—	—	—
B1	-23.2	—	—	—	—	—
C1	-42.3	—	—	—	—	—
D1	-59.2	—	-10.9	—	24.8	—
211 series (MDI/PTMO/BD = 2/1/1)						
A2	29.4	—	86.3	—	127.1	—
B2	0.5	—	53.8	—	142.8	—
C2	-20.7	—	40.2	—	145.4	—
D2	-58.4	—	35.9	—	171.9	—
615 series (MDI/PTMO/BD = 6/1/5)						
A6	50.4	—	83.9	166.5	153.5	181.1, 201.6
B6	—	56.3	—	94.2	—	184.0, 203.5
C6	—	51.1	—	92.2	—	187.4, 204.6
D6	-66.1	79.2	-26.0	131.7	20.5	191.9, 209.3
12111 series (MDI/PTMO/BD = 12/1/11)						
A12	—	69.4	—	94.5	—	170.9, 189.4, 219.4
B12	—	65.8	—	113.9	—	185.9, 206.5, 224.1
C12	—	75.2	—	118.8	—	185.5, 206.8, 222.1
D12	-69.7	88.3	-37.8	129.4	21.5	190.4, 210.2, 228.3
E12	-68.0	90.1	-37.0	133.3	25.1	193.7, 213.1, 235.7

^a “—” indicates that the thermal behavior was not observed.

positions of the materials and their notation are listed in Table I. A modified two-step polymerization was adopted.¹⁷ Then, the PU solution was cast onto a glass plate and kept at 65°C for 24 h, and the PU film was immersed in purified water overnight. Finally, the residual ingredients and other impurities were removed under a vacuum at 65°C for 24 h.

Polymer Characterization

Differential Scanning Calorimetry (DSC)

The thermal properties of PUs were measured by a DuPont 9900 thermal analyzer with a DSC module, purged with nitrogen gas, and quenched with liquid nitrogen. The specimens (10 mg) were

heated in sealed aluminum pans and scanned from -150 to 250°C using a heating rate of 10°C per min. The cell was calibrated using an indium standard.

Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties were measured in the tensile mode at a fixed frequency of 1 Hz and under nitrogen gas purging by a DuPont 983 DMA. To negate the DMA's dependence on the Poisson ratio, a length-to-thickness ratio that was larger than 10 was used. The measured rectangular specimens were heated from -150 to 200°C using a heating rate of 5°C/min. The data of the storage modulus and loss modulus were recorded.

Table IV Heat Change Data of the Peak of the PUs

Sample	Crystallization ΔH (J/g)		Crystal Melting ΔH (J/g)	
	Soft-segment-rich Phase	Hard-segment-rich Phase	Soft-segment-rich Phase	Hard-segment-rich Phase
110 series (MDI/PTMO/BD = 1/1/0)				
A1	— ^a	—	—	—
B1	—	—	—	—
C1	—	—	—	—
D1	35.08	—	36.29	—
211 series (MDI/PTMO/BD = 2/1/1)				
A2	12.42	—	12.17	—
B2	6.52	—	8.66	—
C2	6.28	—	10.97	—
D2	—	—	—	—
615 series (MDI/PTMO/BD = 6/1/5)				
A6	24.23	10.70	15.44	27.93
B6	—	17.19	—	19.41
C6	—	9.43	—	19.98
D6	11.86	7.40	14.51	7.62
12111 series (MDI/PTMO/BD = 12/1/11)				
A12	—	22.05	—	30.31
B12	—	24.76	—	29.84
C12	—	17.75	—	25.36
D12	8.53	17.32	11.71	18.33
E12	8.67	6.89	9.94	11.43

^a “—” indicates that the thermal behavior was not observed.

Transmission Electron Microscopy (TEM)

TEM images were observed on a TEM Hitachi H-600. The stained method was used as described in the previous report.¹⁷

Shape-memory Behavior

The shape-memory behavior was examined by a bending test¹⁸ as follows: The specimen was bent to an angle θ_i ($\sim 90^\circ$) at 80°C and kept the deformation. The deformed specimen was quenched to -20°C and then the external force was released. Finally, the deformed specimen was heated by a fixed heating rate and the relationship between the change of angle θ_f and the temperature was recorded. The ratio of the recovery was defined¹⁸ as $(\theta_i - \theta_f)/\theta_i$. This process is designated as the temperature series test hereafter.

RESULTS AND DISCUSSION

Morphology of the PUs (Tables II–IV)

Differential Scanning Calorimetry

Figure 1 shows the thermal behavior of PTMO with different molecular weights and the results indicated that PTMO2900, PTMO2000, PTMO1000, and PTMO650 only showed the crystal melting behavior. In Figure 2, the crystal behavior of PTMO as shown in Figure 1 interfered with the introduction of MDI; thus, the specimens only showed the amorphous state at low temperature. However, the amorphous D1 would recrystallize in the heating process; then, the crystal melted at a higher temperature. On the other hand, their T_g would shift to low temperature when the molecular weight of PTMO increased.

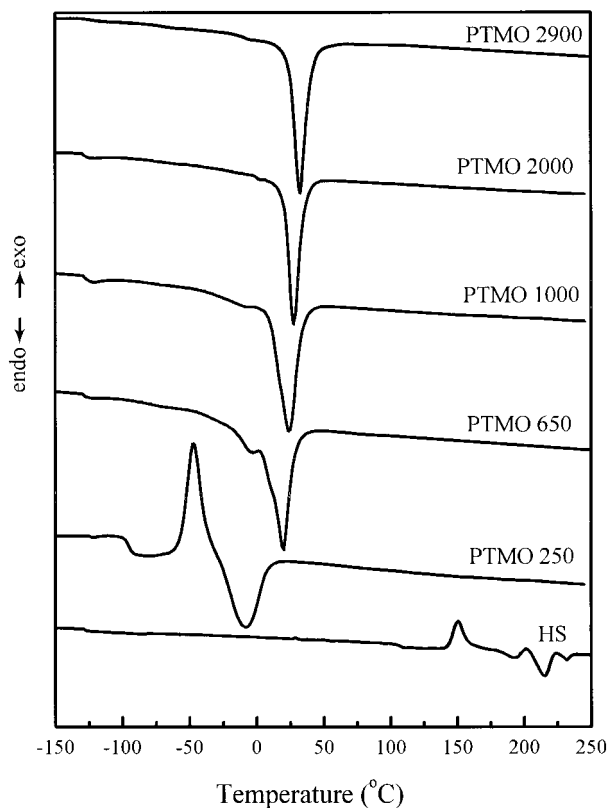


Figure 1 DSC scanning of pure soft segment and pure hard segment.

Figure 3 indicates that all the specimens had a similar thermal change, as follows: They were in a glassy state at the beginning and then recrystallized during the heating process.

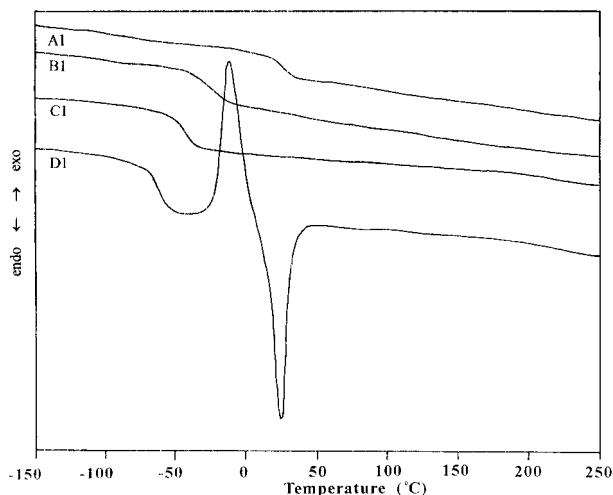


Figure 2 DSC scanning of the 110 series.

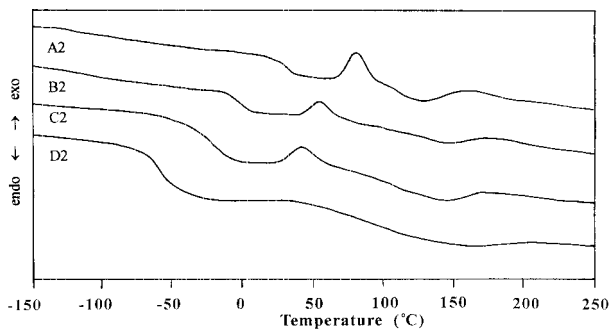


Figure 3 DSC scanning of the 211 series.

Finally, the crystals of A2, B2, C2, and D2 were melted by heating to a high temperature. However, the T_g 's and T_c 's of A2, B2, C2, and D2 shifted to low temperature and the behavior of the glass transition would be clearer when a higher molecular weight of PTMO was used, as shown in Figure 3, while their T_m 's were increased but the melting behavior became unclear gradually. These results implied that their hard segment would not mix with PTMO; thus, the T_m 's would shift to that of the pure hard segment (HS) gradually. Therefore, the phase morphology of the PUs would tend to separate when the high molecular weight PTMO was used.¹²

Figure 4 shows the DSC analysis for A6, B6, C6, and D6. The results indicate that the introduction of high molecular weight PTMO would lead to phase separation between the soft segment and the hard segment. A6 contained two phases, which were the soft-segment-rich phase

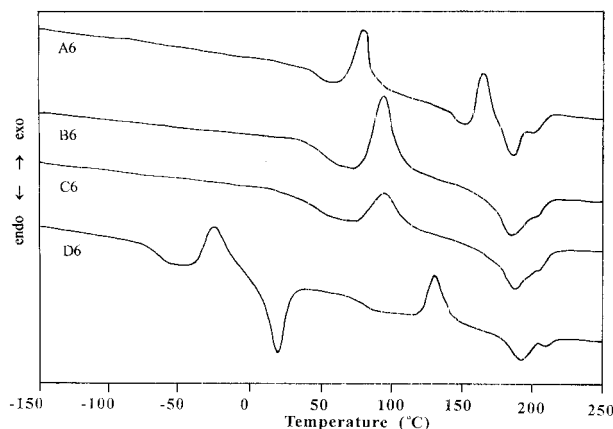


Figure 4 DSC scanning of the 615 series.

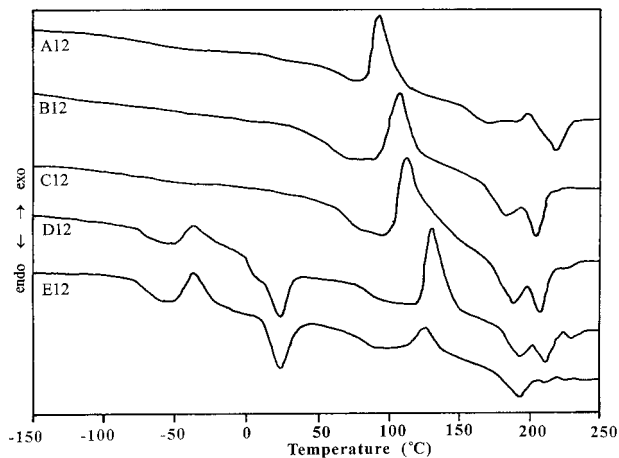


Figure 5 DSC scanning of the 12111 series.

and the hard-segment-rich phase. The soft-segment-rich phase was of PTMO mixed with the short hard segment.¹⁷ However, B6 and C6 did not display a similar soft-segment-rich phase to that of A6. Their melting temperatures would shift to those of the HS, that is, they displayed a similar thermal behavior as that of the HS. However, D6 showed the thermal behavior of the soft segment and the hard segment individually, indicating that the PTMO2000 of D6 would not mix with the short hard segment as the soft-segment-rich phase of A6, but behaved as that of D1. Hence, D6 would show obviously the phase-

separating behavior and similar results were also found for D12 and E12. Because the molecular weight of the soft segment was not large enough, B6 and C6 did not show the same thermal behavior as that of B1 or C1.

A12, B12, and C12 showed similar curves in the DSC analysis, and their T_c 's and T_m 's also gradually shifted to that of the HS in Figure 5. Consequently, the properties of the hard-segment-rich phase were more similar to that of the HS when the molecular weight of PTMO was increased. The crystal of the hard segment of C12, D12, or E12 was more perfect than that of A12 or B12. So, the T_g 's of their hard-segment-rich phase would gradually shift to that of the HS and their crystal structures were also similar to that of the HS. Consequently, if the soft segment possessed a large enough molecular weight (e.g., PTMO2900 and PTMO2000), phase separation between the hard and soft segments would be observed easily. On the other hand, phase inversion of the soft-segment phase of the PUs was found. When the molecular weight of the soft segment was low, it would mix with the short hard segment as that of A6. However, if the molecular weight of the soft segment was increased, it would demix from the short hard segment as that of D6.

Dynamic Mechanical Analysis (DMA)

The results of the DMA of the PUs, based on the same mol ratio and various molecular weights of

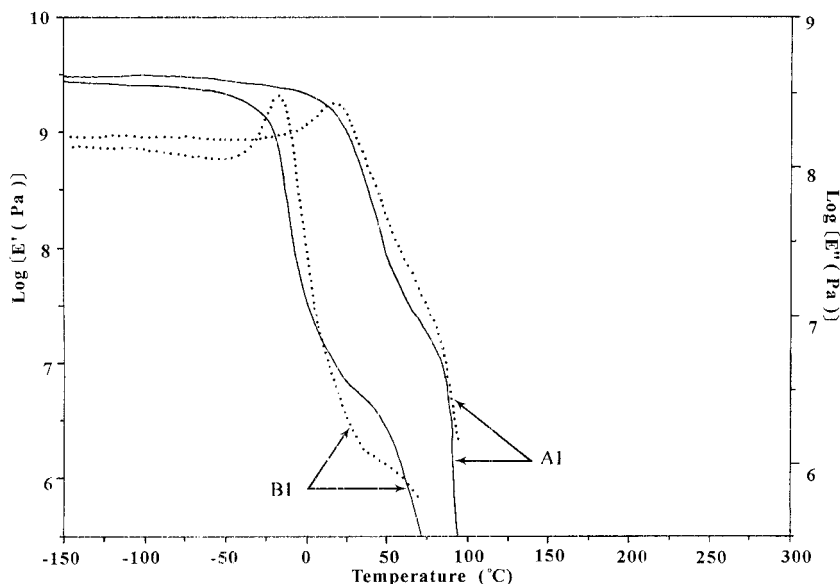


Figure 6 DMA analysis of the 110 series.

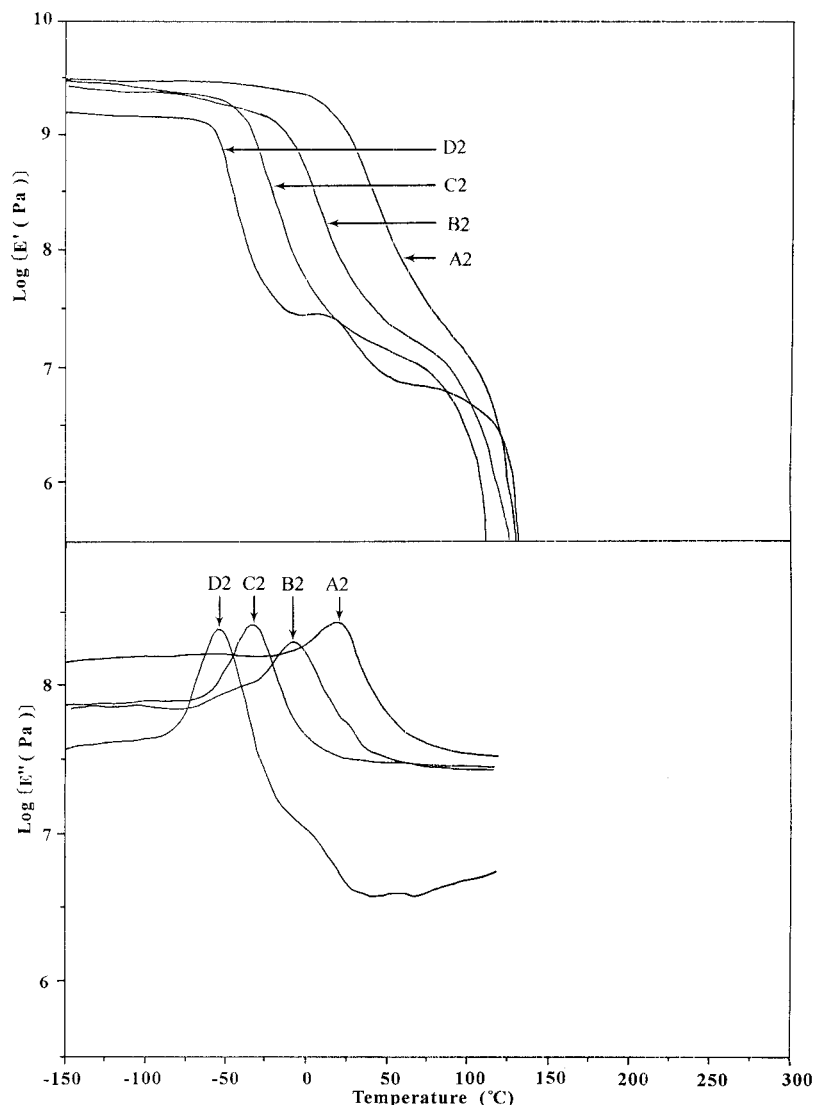


Figure 7 DMA analysis of the 211 series.

PTMO, are displayed in Figures 6–9 and listed in Table V. They show similar curves of E' and E'' with the same mol ratio of the monomers. The low glass transition temperature would shift to high temperature, when the low molecular weight of PTMO was introduced. The width of the peak of E'' would be reduced if we introduced a higher molecular weight of PTMO. However, this tendency would be unclear when more MDI and BD were used, as shown in Figures 8 and 9. The softened temperature of the hard-segment-rich phase would shift to high temperature when a low molecular weight of PTMO was used, as shown in Figures 6–8. However, the difference of the soft-

ened temperature between the 12111 series was small, as shown in Figure 9.

The modulus ratio that was defined as $E'_{T_g-20^\circ\text{C}}/E'_{T_g+20^\circ\text{C}}$ (ref. 8) would increase when a high molecular weight PTMO was introduced in the 110 series or the 211 series. However, the modulus ratio of the 615 series showed little difference. The same results were also found for the 12111 series.

Transmission Electron Microscopy (TEM)

Figure 10 shows TEM micrographs of RuO_4 -stained PUs. By comparing the micrograph of C12

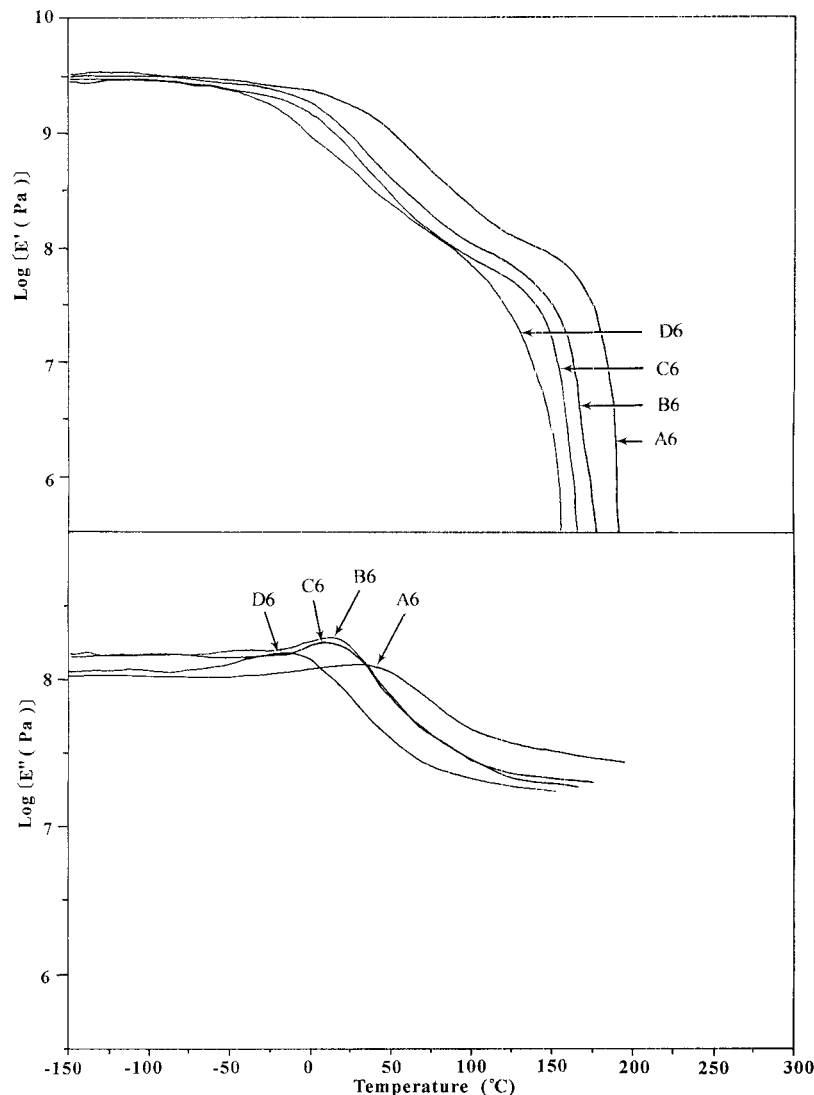


Figure 8 DMA analysis of the 615 series.

and D12 with that of A12, they displayed the same morphological distribution and the size of their dispersed phase showed little difference. For this reason, the PUs that contained the same mol ratio displayed the same morphology as the results of the DSC and DMA. However, the numbers of the dispersed phase of D12 was larger than those of C12.

Shape-memory Behavior

By the temperature series study, the shape-memory behavior of the PUs is as shown in Figures 11–13. The PUs that contained the same composi-

tion of monomers showed a similar recovering rate, but the temperature range of recovering of them was different. In the DSC and DMA studies, the soft-segment-rich phase of A2 and B2 were similar, but A2 showed a higher T_g than that of B2 by using a high molecular weight of PTMO. B2, with a low T_g , showed that almost all its deformation was recovered before heating to 0°C, as shown in Figure 11. B2 could not recover its original shape because it contained less hard segment. However, A2 would recover its original shape after heating to high temperature by containing a high content of the hard segment. In Figure 12, B6 and C6 could not recover completely and B6

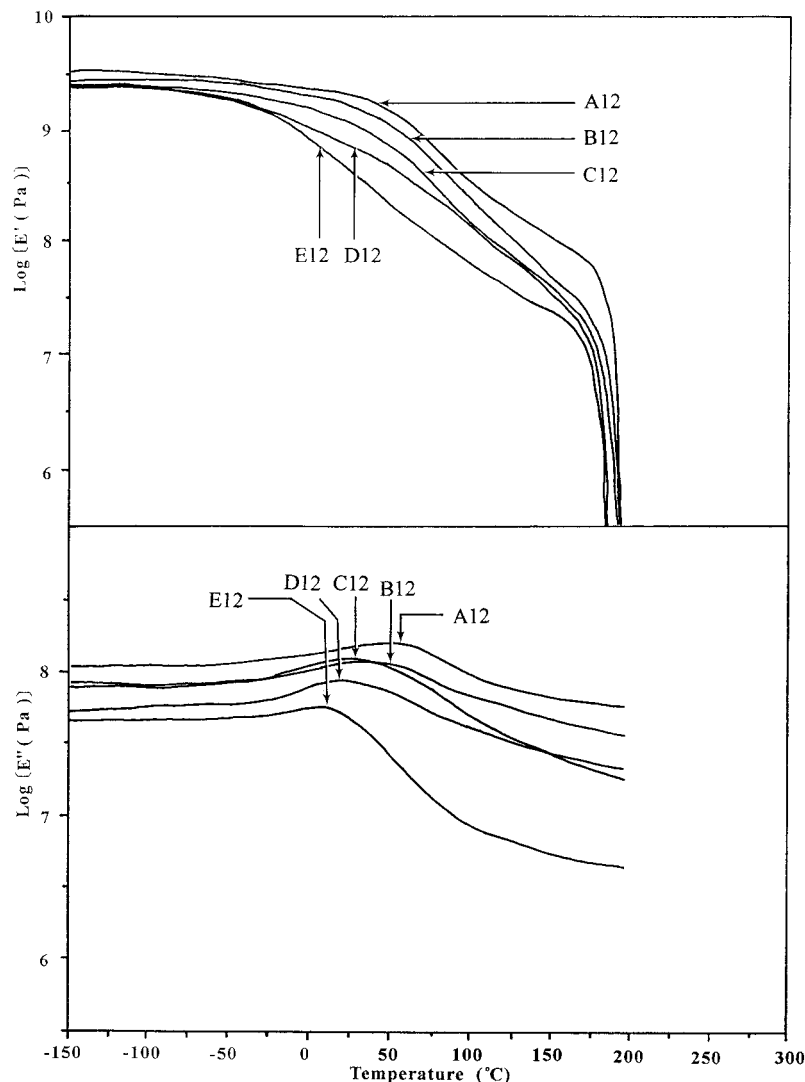


Figure 9 DMA analysis of the 12111 series.

showed a higher recoverable ratio than that of C6. Because the morphologies of the hard-segment-rich phase of B6 and C6 were different from that of A6 and the content of the hard segment was lower than that of A6, they would show different shape-memory behavior on the high-temperature zone of recovery as described above. At the initial temperature range (-20 to 0°C), A6 and B6 would fix the deformation and keep the ratio of recovery lower than 10%. However, the deformed C6 would not behave as would A6 or B6 at the same temperature range. In the DSC study, the soft-segment phase would demix with the short hard segment if a high molecular weight PTMO was used. For this reason, the soft-segment phase of C6 con-

tained less short hard segment. It caused the C6's T_g to shift to low temperature. Hence, the recovering temperature of deformed C6 was reduced and the strength of the reversible phase was not strong enough to resist the recovery of deformation that was performed by the fixed phase at the initial temperature range. In Figure 13, the deformed specimens would recover their original shape because the content of the hard segment was rich enough. However, the recoverable ratio curve of D12 showed the delaying behavior of recovery at about 80% because of the phase separation of the soft segment and the hard segment. On the other hand, the numbers of the dispersed phase of D12 was larger than those of C12

Table V DMA Data of the PUs

Sample	Glass Transition T_g (°C)	Storage Modulus Ratio ^a
110 series (MDI/PTMO/BD = 1/1/0)		
A1	16.1	34.26
B1	-13.4	139.64
211 series (MDI/PTMO/BD = 2/1/1)		
A2	17.1	14.74
B2	-8.1	18.41
C2	-36.4	24.64
D2	-56.0	32.06
615 series (MDI/PTMO/BD = 6/1/5)		
A6	26.6	4.00
B6	16.0	3.87
C6	8.9	4.02
D6	-18.4	4.04
12111 series (MDI/PTMO/BD = 12/1/11)		
A12	54.1	3.87
B12	38.4	3.87
C12	22.4	4.01
D12	17.3	4.05
E12	15.1	4.12

^a Storage modulus ratio was defined as $E'_{T_g-20^\circ\text{C}}/E'_{T_g+20^\circ\text{C}}$.⁸

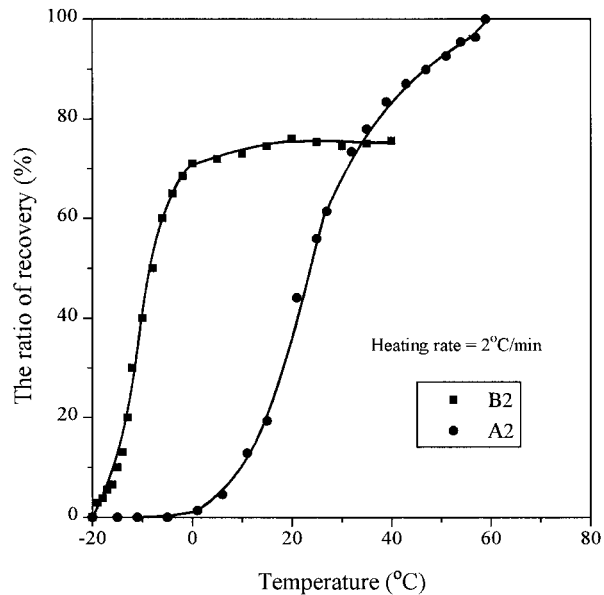


Figure 11 Shape-memory behavior of the 211 series in temperature series study.

through TEM observation. Hence, the numbers of the dispersed phase would influence the shape-memory behavior of the PUs.

As the studies above, the results demonstrated that the shape-memory behavior of PUs would be influenced by the morphology of the

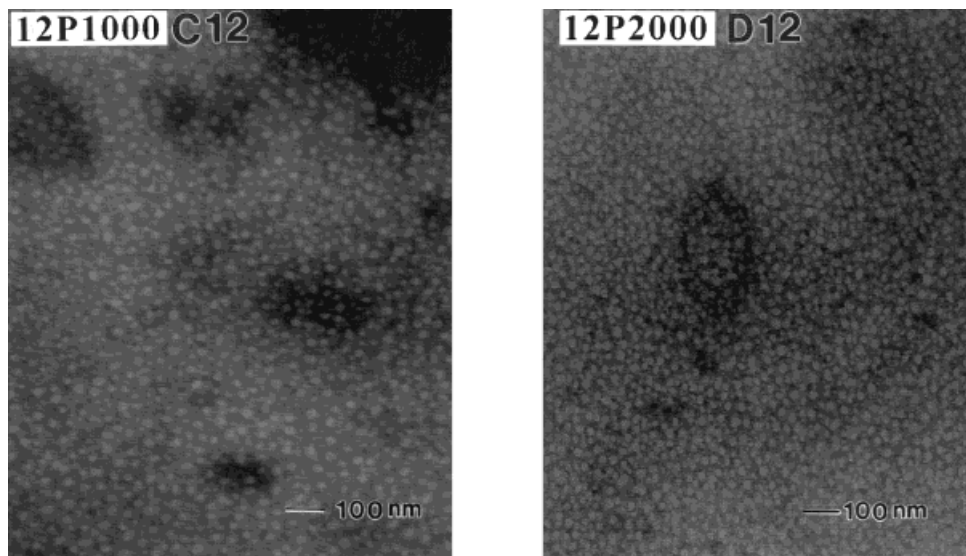


Figure 10 TEM micrographs of 12111 series: C12(12P100) and D12(12P2000) ($\times 60,000$).

soft-segment phase. The shape-memory PUs would be applied at different operating temperatures because of their different T_g 's. But they would show a similar shape-memory behavior. The PUs that contained the high molecular weight PTMO would tend to phase separate between the soft segment and the hard segment. In the shape-recovering process, the deformed specimens that contained the high molecular weight PTMO would recover some deformation on the initial zone, as demonstrated by the comparison of the 211 series and the 615 series. On the other hand, the content of the hard segment would be relatively reduced if high molecular weight PTMO was selected. The deformed PUs could not recover to their original shape. The recovering behavior would be delayed because of the phase separation and increasing the numbers of the dispersed phase.

CONCLUSION

The PUs would show the shape-memory behavior that depended on the morphology of the PUs. The morphology of the PUs and their T_g 's depended on the molecular weight of PTMO. The soft-segment phase would vary from the phase that was mixed with the short hard segment to

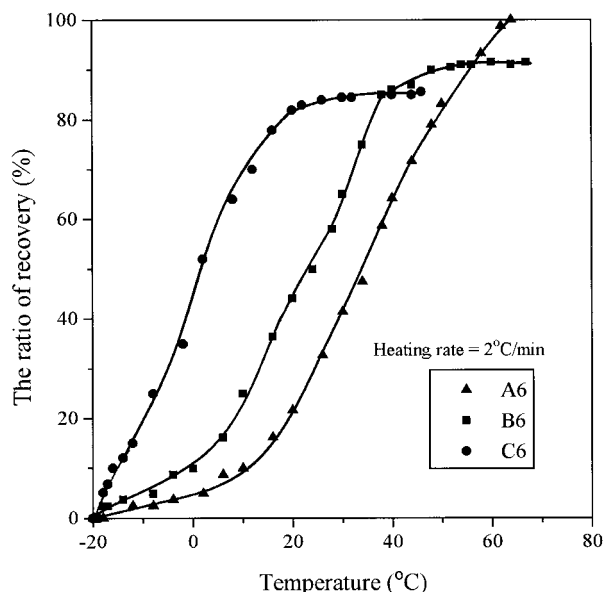


Figure 12 Shape-memory behavior of the 615 series in temperature series study.

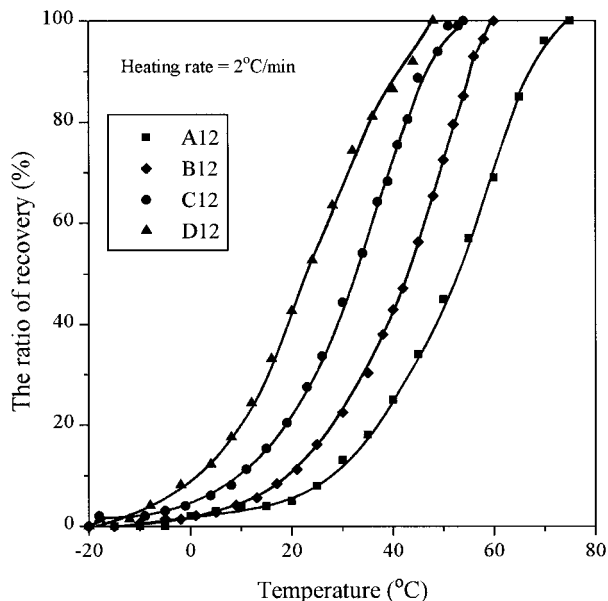


Figure 13 Shape-memory behavior of the 12111 series in temperature series study.

a different phase that was demixed from it when the molecular weight of PTMO was increased. The PUs, with the same composition, would show a similar shape-memory behavior in the investigation of shape-memory behavior. As for the influence of the soft segment (PTMO) on the shape-memory behavior, the results indicated that the deformed specimens would recover some deformation at the low-temperature range by using a high molecular weight of PTMO. The deformation of PUs would be completely recovered by introducing low molecular weight PTMO. Finally, increasing the numbers of the dispersed phase of PUs would reduce the recovery rate at the high-temperature zone.

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