Studies on Thermally Stimulated Shape Memory Effect of Segmented Polyurethanes

FENGKUI LI,[1] XIAN ZHANG,[1] JIANAN HOU,[1] MAO XU,[1] XIAOLIE LUO,[2] DEZHU MA,[2] BYUNG KYU KIM[3]

[1] Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica, Beijing 100080, China

[2] Department of Materials Science, Chinese University of Science and Technology, Hefei 230026, China

[3] Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

ABSTRACT: The shape memory behavior of a series of polycaprolactone/methane diisocyanate/butanediol (PCL/MDI/BDO) segmented polyurethanes of different composition was studied. The molecular weight of PCL diols was in the range of 1600–7000, and the hard segment content varied from 7.8 to 27% by weight. Film specimens for shape memory measurements were prepared by drawing at temperatures above the melting temperature of the soft segment crystals and subsequent quick cooling to room temperature under constrained conditions. The shape memory process was observed and recorded in a heating process. Parameters describing the recovery temperature, ability, and speed were used to study the influence of structure and processing conditions on the shape memory behavior of the sample. It was found that the high crystallinity of the soft segment regions at room temperature and the formation of stable hard segment domains acting as physical crosslinks in the temperature range above the melting temperature of the soft segment crystals are the two necessary conditions for a segmented copolymer with shape memory behavior. The response temperature of shape memory is dependent on the melting temperature of the soft segment crystals. The final recovery rate and the recovery speed are mainly related to the stability of the hard segment domains under stretching and are dependent on the hard segment content of the copolymers. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1511–1516, 1997

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INTRODUCTION

Shape memory polymers are materials that may "remember" their original shape when they are deformed. It means that they are able to take the original shape almost completely at appropriate conditions. Because the shape memory effect usually occurs under heating, they are thermally stimulated shape memory materials. Thermal shrinkage is a well known and very common phenomenon for deformed plastic samples. It also shows some extent of deformation recovery. However, the recovery rate, the percentage of the recovered strain in total strain, is usually very low, about 5–30%, in the case of thermal shrinkage. The shape memory effect of polymers is characterized by a large value of recoverable strain, usually more than 100%, and high recovery rate, not less than 80–90%, and is unique for polymer samples of special structure and morphology.

As compared with its metallic counterpart, the advantages of the polymeric shape memory material are low cost and excellent processability. The first shape memory polymer product of commercial importance was made of polyethylene cross-

Table I   Parameters and DSC Results for Segmented Polyurethanes

Sample	Mole Ratio PCL/MDI/BD	M_n of PCL Prepolymer	Hard Segment (wt %)	$[\eta]$ (dL/g)	T_c (°C)	ΔH_c (J/kg Soft)	Crystallinity (%)	T_m (°C)
M-132-1.6	1/3/2	1600	36.8	0.20	—	.000	0	—
M-132-4.0	1/3/2	4000	19.0	0.36	−0.8	.041	30.5	47.8
M-121-5.0	1/2/1	5000	10.6	0.60	11.9	.053	39.3	50.3
M-132-5.0	1/3/2	5000	15.7	1.04	−0.8	.041	30.2	48.0
M-143-5.0	1/4/3	5000	20.3	0.95	−4.0	.027	20.0	44.9
M-121-7.0	1/2/1	7000	7.8	1.11	15.3	.054	40.1	50.7
M-132-7.0	1/3/2	7000	11.7	0.77	12.9	.053	39.2	50.7
M-143-7.0	1/4/3	7000	15.4	0.97	7.3	.046	34.0	50.7
M-154-7.0	1/5/4	7000	18.7	0.98	8.4	.042	30.8	49.5

linked by reaction with ionizing radiation.[1] Much work has been done in industry laboratories for developing new materials with shape memory and their applications.[2,3] However, very few contributions were found in the open literature. Tobushi et al.[4] studied the mechanical properties, including the cyclic tensile test, of two polyurethane samples with shape memory features, but no data about their structure and composition were given. Recently we reported our results in studies of some segmented polyurethane samples that may exhibit excellent thermally stimulated shape memory effect with a large value of recoverable deformation and high recovery rate.[5,6] The advantage of using segmented copolymers is the possibility of controlling the critical recovery temperature to meet the needs of different applications. Besides, their thermoplastic nature makes them quite convenient in processing. A model has been proposed to explain the mechanism of shape memory effect of segmented copolymers.[5,6] In this work a series of polycaprolactone (PCL) based polyurethanes with different soft segment length and composition were prepared and the relationship between the shape memory effect and the structure and morphology of the polyurethane samples and also the processing conditions were investigated.

EXPERIMENTAL

Segmented polyurethanes were obtained by a two-step method involving end capping the hydroxyterminated PCL with 4,4′-diphenylmethane diisocyanate (MDI) followed by reaction in solution with the chain extender 1,4-butanediol (BDO). Samples of different soft and hard segment lengths were used. Table I gives the composition, soft segment molecular weight, and intrinsic viscosity of the polyurethane samples. The intrinsic viscosity was measured in N,N'-dimethylformamide (DMF) at 30°C.

The melting and crystallization behavior was studied by using a Perkin–Elmer DSC-4 apparatus in heating and a cooling processes, respectively. The melting and crystallization temperatures (T_m and T_c) of the samples are given in Table I. The crystallinity was calculated from the enthalpy data ΔH_c of the crystallization peak by using the 0.14 J/kg enthalpy value for fusion of 100% crystalline PCL given by Crescenzi et al.[7]

Film specimens with thickness about 0.5 mm were prepared by casting of polyurethane solutions in DMF. The concentration of the solutions was about 10%. The cast films were first slowly dried at 40–50°C, then vacuum dried at 80°C for 100 h. The dried specimens were kept in a desiccator at room temperature before use.

Specimens for shape memory studies were prepared by stretching the solution cast film to different draw ratios at a draw temperature (T_D) above the melting temperature of the PCL segment crystals and subsequent quick cooling to a temperature (T_s) under constrained conditions with constant length. Rectangular specimens about 30 mm in length and 5 mm in width were used in this work. If not specially noted, the specimens were kept at 80°C for 1 min before stretching, the T_s was the room temperature 16°C, and the time period of setting under constraint at T_s was 2 min. The deformation recovery effect of the above prepared specimens under heating was directly measured under an Olympus BHSP polarizing microscope equipped with a hot stage. The heating rate used was 2.7°C/min.
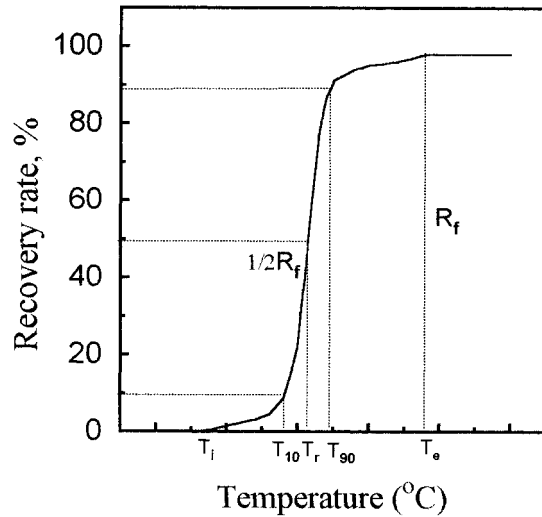
The experimental results of recovery measure-

Figure 1 The thermal recovery curve and characteristics of the recovery behavior.

Figure 2 The thermal recovery curves of polyurethanes with PCL molecular weight 1600 and 4000.

ments are presented in terms of thermal recovery curves (Fig. 1), which describe the change of recovery rate, the ratio of recovered strain to the total strain of the specimen as a function of temperature in a heating process of constant heating rate. It is an S-shaped curve. In the low temperature region the size of the specimen does not change with temperature. The recovery process begins at an initial temperature (T_i). The recovery rate changes slowly at the initial stage and then increases abruptly in a narrow temperature range. It may approach a final value of recovery rate (R_f), and the recovery process finishes at an end temperature (T_e). Several parameters can be obtained from the recovery curve for describing the characteristic features of the shape memory behavior of the specimens. The final recovery rate characterizes the recovery ability of the specimen. The temperature corresponding to a recovery rate value $\frac{1}{2}R_f$ on the thermal recovery curve, T_r, is called the response temperature or the average response temperature of the shape memory polymer specimen. A parameter V_r is proposed to characterize the speed of the recovery process, which is defined as

$$V_r = \frac{0.8 \cdot R_f \cdot \varepsilon_1}{T_{90} - T_{10}} \times \frac{dT}{dt}$$

where ε_1 is the total strain of the specimen before the thermal recovery test; T_{10} and T_{90} are the temperatures corresponding to the recovery rate of $0.1R_f$ and $0.9R_f$ on the recovery curve, respec-
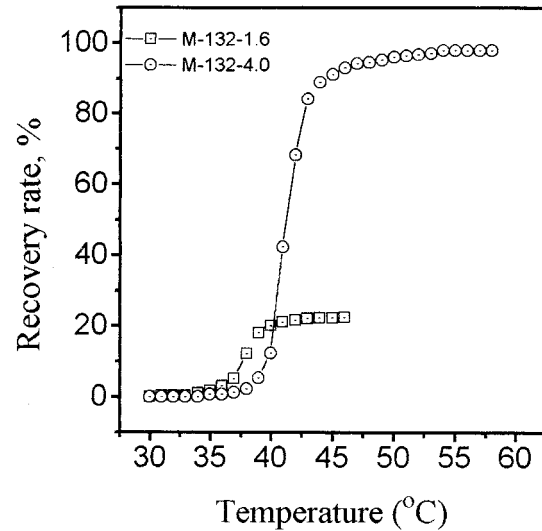
tively; and dT/dt is the average heating rate of the recovery measurement. V_r is the average recovery speed of the specimen at temperature T_r.

RESULTS AND DISCUSSION

The recovery curves for polyurethane specimens with different soft segment lengths are given in Figures 2–4, respectively. The draw ratio used in specimen preparation was around 1.8 for all the specimens. Data from these recovery curves are
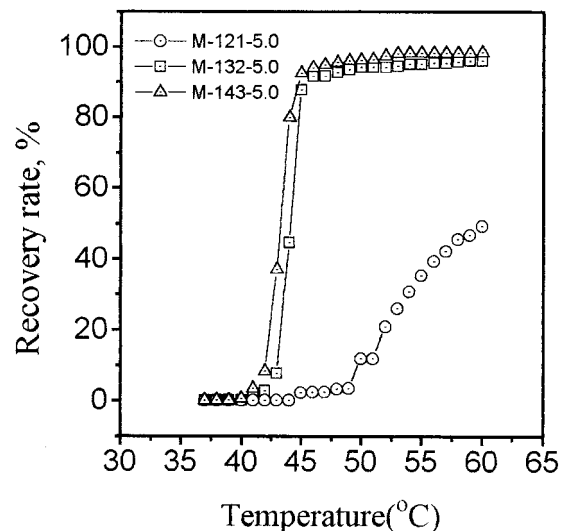

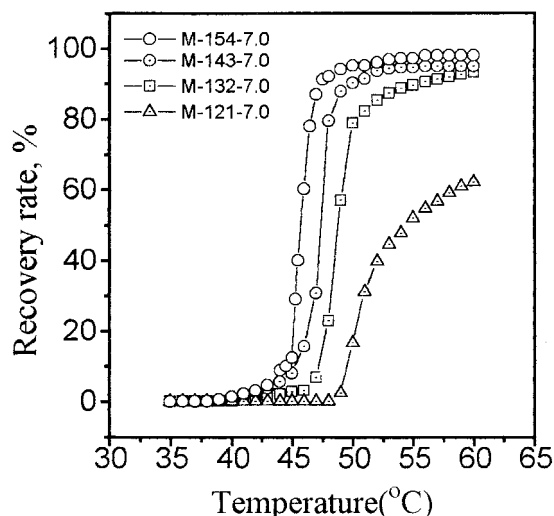**Figure 3** The thermal recovery curves of polyurethanes with PCL molecular weight 5000.

Figure 4 The thermal recovery curves of polyurethanes with PCL molecular weight 7000.

summarized in Table II. The influence of molecular structure on the shape memory effect of segmented polyurethanes is obvious. Specimens of polyurethanes with short soft segment length and number average molecular weight (M_n) of 1600 exhibit very small deformation recovery effect, while specimens of polyurethanes with low hard segment content only show moderate recovery rate, less than 50–60%. Only specimens of polyurethanes with longer soft segment length and higher hard segment content are excellent shape memory polymers, having a high final recovery rate up to 93–98%. Their response temperature was in the range of 43.0–48.6°C, and the average recovery speed varied from about 0.5 to 1.4 min^{-1}. It seems that the response temperature is dependent on the melting temperature of soft segment crystals of the polyurethanes samples, while the final recovery rate and the recovery speed are mainly related to the hard segment content of the polyurethanes.

According to the mechanism of shape memory effect for segmented copolymers proposed in previous studies,[5,6] the high crystallinity of the PCL soft segment regions and the formation of stable hard segment domains in the temperature range above the melting temperature of soft segment crystals are the two necessary conditions for a segmented copolymer with shape memory features. For PCL-based polyurethanes[8] it was recently found that the crystallinity of PCL was depressed in segmented polyurethanes, and a lower limit of PCL molecular weight (around 2000–3000) was found, below which the PCL segments

were not able to crystallize at the usual processing conditions. Besides, our results[8] also show that the formation of stable hard segment domains becomes very difficult in segmented polyurethanes having low hard segment content, and there was a lower limit of hard segment content, about 10% by weight. Only above that limit the samples may have enough hard segment domains acting as physical crosslinks at temperatures above the melting temperature of the PCL crystals. This means that the shape memory behavior of polyurethanes of different composition and chain structure given above are quite reasonable and are good examples for elucidating the mechanism of the memory effect for segmented copolymers.

In addition to the chemical structure and composition of the polymer molecules, the shape recovery behavior of the specimens should be influenced by the processing conditions during their preparation. Studies on these problems are important not only for understanding the mechanism of shape memory effect, but also for controlling the properties of these samples in practical applications. Results for sample M-154-7.0 are given below. The effect of T_D, the draw ratio, and the time period t_D at T_D after drawing were examined. Figure 5 shows that the shape memory behavior of the specimens remained almost unchanged when they were drawn at temperatures 10–30°C above the T_m of the soft segment crystals. Specimens prepared at 50°C, almost the T_m of the soft segment crystals, exhibit lower response temperature and speed and slightly less final recovery rate. Figure 6 shows the results of specimens with different draw ratios. The final recovery rate decreases with increasing draw ratio. After a draw ratio of about 3 the final recovery

Table II   Shape Recovery Results for Polyurethanes with Different Length of Soft Segments

Samples	Draw Ratio	T_r (°C)	R_f (%)	V_r (min^{-1})
M-132-1.6	1.73	38.0	22.2	0.02
M-132-4.0	1.81	43.0	97.7	0.44
M-121-5.0	1.77	54.3	50.1	0.11
M-132-5.0	1.76	43.7	96.0	0.99
M-143-5.0	1.80	43.0	98.4	1.13
M-121-7.0	1.79	51.8	60.0	0.15
M-132-7.0	1.76	48.6	93.3	0.38
M-143-7.0	1.78	47.3	94.9	0.47
M-154-7.0	1.81	45.7	97.9	0.61

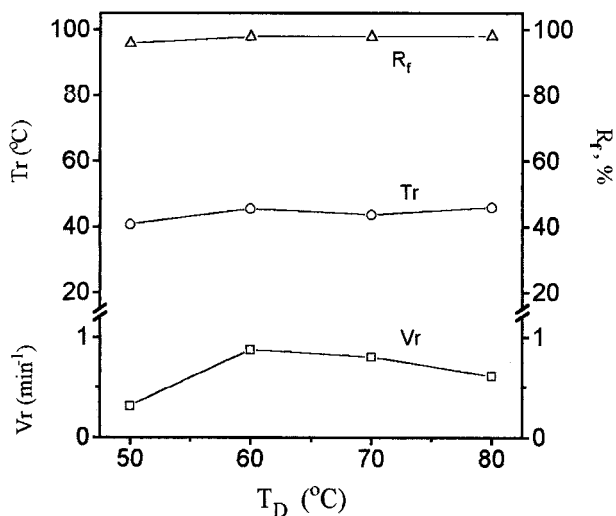**Figure 5** The influence of T_D on the shape memory behavior of polyurethanes.

Figure 7 The influence of t_D on the shape memory behavior of polyurethanes.

rate becomes less than 90%. The recovery speed also decreases with draw ratio, while the response temperature was only slightly lowered. The time period t_D also exhibits obvious influence on the final recovery rate and the recovery speed of the specimens (Fig. 7), but the response temperature was not very sensitive to the variation of t_D. The influence of the setting temperature after drawing and time period of keeping the constrained specimens at the setting temperature was also studied. It was found that these parameters do not produce a significant effect on the shape memory behavior of the segmented polyurethane samples.
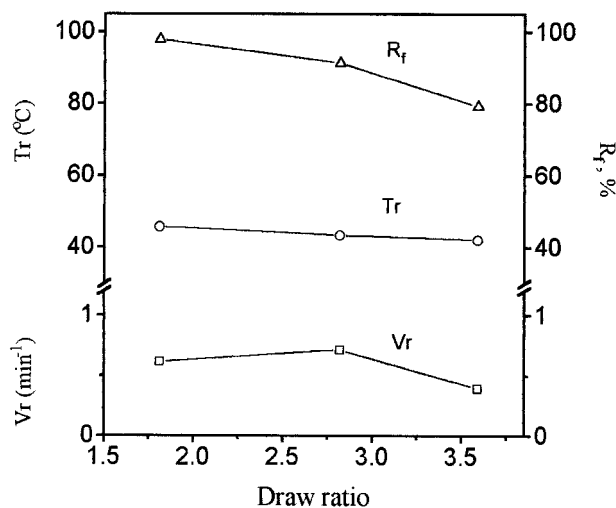
High values of the final recovery rate resulted

from the existence of an ideal elastic network in the specimens under stretching at temperatures above the melting temperature of the soft segment crystals. The decrease of R_f values from unity shown above implies that the specimens cannot be considered as ideal elastic networks under drawing, meaning that the hard segment domains, acting as physical crosslinks in segmented polyurethane samples, are not very stable and are sensitive to the conditions of specimens preparation, like the draw ratio and the time period of keeping the constrained specimens at draw temperature. These results give us an idea of the conditions of using our polyurethane samples as
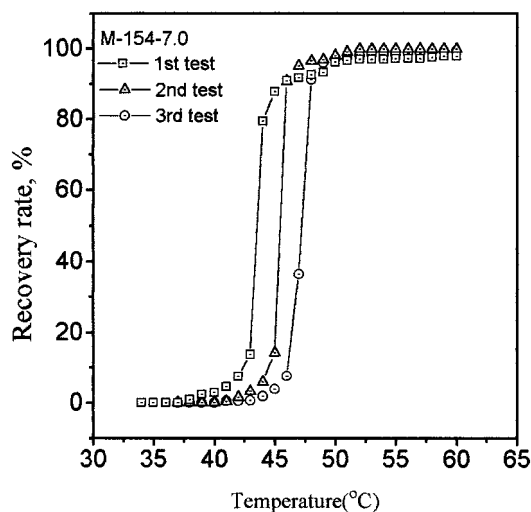

Figure 6 The influence of the draw ratio on the shape memory behavior of polyurethanes.

Figure 8 The thermal recovery curves of sample MDI-154-7.0 in repeat test.

Table III Shape Recovery Data of Sample M-154-7.0 in Repeat Tests

Cyclic Times	Draw Ratio	T_r (°C)	R_f (%)	V_r (min^{-1})
First	1.95	43.5	97.8	.80
Second	1.89	45.9	99.1	.73
Third	1.93	47.0	99.1	1.00

shape memory materials and also indicate the importance of improving the stability of the hard segment domains in developing polymers of excellent shape memory properties.

The behavior of specimens of M-154-7.0 in repeated or cyclic testing was also studied. The draw ratio and the final recovery rate were all calculated with respect to the actual length of the specimen before each cycle, but not the original length before testing. The recovery curves of the repeated tests are shown in Figure 8, and data from these curves are given in Table III. The response temperature rises with repeating cycles from 43.5 to 47°C, and the final recovery rate increases and approaches unity. This implies that after the destroy of some "weak" crosslinks in the repeating test, the specimens may become a dynamically ideal elastic network, the deformation of which is almost completely reversible.

CONCLUSIONS

The high crystallinity of the soft segment regions at room temperature and the formation of stable hard segment domains acting as physical crosslinks in the temperature range above the melting temperature of the soft segment crystals are the two necessary conditions for a segmented copolymer with shape memory behavior. The response temperature of shape memory is dependent on the melting temperature of the soft segment crystals. The final recovery rate and the recovery speed are mainly related to the stability of the hard segment domains under stretching and are dependent on the hard segment content of the copolymers.

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