

Thermally Stimulated Shape-Memory Behavior of Ethylene Oxide–Ethylene Terephthalate Segmented Copolymer

XIAOLIE LUO,¹ XIAOYUN ZHANG,¹ MINGTAI WANG,¹ DEZHU MA,¹ MAO XU,² FENGKUI LI²

¹ Department of Material Science and Engineering, University of Science and Technology of China, Hefei, Anhui, 230026, People's Republic of China

² Beijing Institute of Chemistry, Chinese Academy of Science, Beijing, 100080, People's Republic of China

Received 5 June 1996; accepted 2 December 1996

ABSTRACT: A series of ethylene oxide–ethylene terephthalate segmented copolymers (EOET) with different long soft segments and different hard-segment contents were synthesized. The thermally stimulated shape-memory behavior of EOET segmented copolymer is characterized by the maximum recovery (R_f), the recovery temperature (T_r), and the recovery speed (V_r) or the temperature (T_M) of the maximum deformation recovery rate against temperature and the maximum recovery speed (V_M). These parameters show that the features of thermally stimulated shape-memory effects of EOET segmented copolymers are following: The crystallinity of soft segments determines the temperature T_r and T_M , and the parameters R_f , V_r , and V_M depend on the stability of the physical crosslinks formed by the hard segments, which at the same time are influenced by the length of soft segment. R_f , V_r , and V_M decrease with prolongation of the keeping time (t_k) and increasing stretching ratio. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 2433–2440, 1997

Key words: ethylene oxide–ethylene terephthalate copolymer; shape memory; long soft segment

INTRODUCTION

Crosslinked polyethylene is a commercial thermally stimulated shape-memory material.¹ A rectangular specimen is stretched at the melting point of the crystallizable crosslinked polyethylene and the deformation of the specimen is frozen by quenching; then, the specimen is reheated and the frozen deformation is recovered. The recovery speed increases abruptly at a certain temperature and the specimen may approach a final value of

the recovery in the end. The entropy of the system decreases in the stretching process and increases in the recovery process. The increasing of the entropy is the driving force of the recovery for the frozen deformed specimen.

The segmented polyurethane with a long soft segment can also exhibit the shape-memory effect. Such a poly(ϵ -caprolactone) ($M_n > 5000$)-based polyurethane with a hard-segment content (15%) may show 95% of the recovery.^{2–5} The segmented polyurethane, as a thermally stimulated shape-memory material, has its own feature: Its crosslink is not chemical, i.e., the hard segments in the polyurethane aggregate and form the physical crosslinking points through polar interaction, hydrogen bond, and crystallization. Generally, such physical crosslinking points cannot be broken below 120°C, but the used segmented polyurethane will begin to flow above 240°C. Just the

Correspondence to: D. Ma.

Contract grant sponsor: National Nature Science Foundation of China.

Contract grant sponsor: The National Key Projects for Fundamental Research "Macromolecular Condensed State," The State Science and Technology Commission of China.

© 1997 John Wiley & Sons, Inc. CCC 0021-8995/97/122433-08

thermoplastic nature makes them quite convenient in processing and it is possible to control the critical recovery temperature to meet the needs of different applications.

The ethylene oxide–ethylene terephthalate segmented copolymers were first synthesized by Coleman.^{6,7} This family of copolymers was studied in an attempt simultaneously to reduce the crystallinity of PET and to increase the hydrophilicity to improve dyeability with hydrophilic dyes. In our laboratory, the EOET segmented copolymers were synthesized and used as the matrix of the new electrolyte adulterated with LiClO₄. It has exhibited good ionic conductivity.⁸ At the same time, the transesterification and polycondensation of hydroxy-terminated poly(ethylene oxide) and ethylene glycol with dimethyl terephthalate and sodium dimethyl isophthalate sulfonate can lead to the formation of an ethylene oxide (ethylene terephthalate-*co*-sodium ethylene isophthalate sulfonate) segmented copolymer (EOET–SO₃Na). This segmented copolymer is a new single cationic conductor.⁹

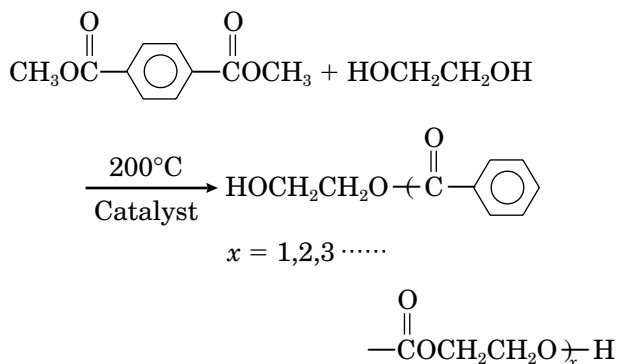
In the present work, a series of ethylene oxide–ethylene terephthalate segmented copolymers with long soft segments were synthesized. The thermally stimulated shape-memory behavior of EOET segmented copolymers was studied. The length of the soft segment, the hard-segment content, and the processing conditions all can have an important influence on the shape-memory effects.

EXPERIMENTAL

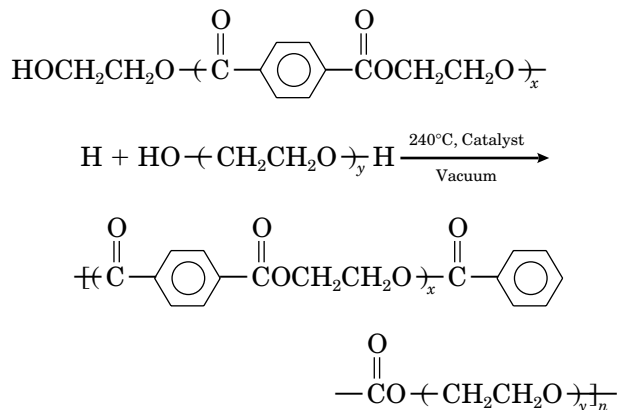
Synthesis of Sample

The synthesis of the ethylene oxide–ethylene terephthalate segmented copolymer is divided into two steps:

Transesterification



Polycondensation



The parameters of EOET segmented copolymers with different long soft segments [poly(ethylene oxide)] and different hard-segment [poly(ethylene terephthalate)] contents are shown in Table I.

Characterization of Samples

Intrinsic Viscosity

Ethane tetrachloride in which all EOET segmented copolymers can be dissolved is used as the solvent for the viscosity measurement. The measure temperature is 30°C.

Proton Spectra

The compositions of EOET segmented copolymers were obtained using a JEOL FX-90Q spectrometer. A series of typical proton spectra of EOET6000 segmented copolymers is shown in Figure 1. The bands of 8.25 and 3.89 ppm were used for the compositional calculation.

DSC Measurement

DSC curves were measured by a Perkin-Elmer DSC-2C apparatus equipped with a TADS microcomputer and an intracooler II. The DSC was calibrated with ultrapure indium. Each sample was heated up to 550 K, then quenched to 210 K. The melting point is obtained from the reheating curve, and the crystallization temperature, from the cooling curve. Both heating rate and cooling rate are 20 K/min.

Spherulite Morphology

Both the soft segments and the hard segments in EOET segmented copolymer can grow spheru-

Table I Parameters of EOET Segmented Copolymers

Sample	M_w PEO	Hard-Segment Content		$[\eta]$ (dL/g)	T_m (K) (PEO)	T_c (K) (PEO)
		Theoretical	Experimental			
EOET4000-25	4000	25	27.6	0.81	328	293
EOET4000-30	4000	30	32.0	0.76	325	293
EOET6000-20	6000	20	21.2	0.91	330	297
EOET6000-25	6000	25	25.7	0.69	330	295
EOET10000-15	10,000	15	16.5	0.87	335	304
EOET10000-20	10,000	20	21.8	0.85	333	300

lites. The spherulite morphology was observed by a polarizing microscope.

Thermally Stimulated Shape-memory Measurement

Preparation of Sample

The films with a thickness of 0.2 mm were cast from the chloroform solution in a rectangular polytetrafluoroethylene mold. Each strip sample with a length of 60 mm and a width of 4 mm was stretched by a universal testing machine (DCS-5000) with a thermostatically controlled oven made in Japan (Shimadzu Co.). The stretching temperature was about 50°C. The constant strain rate was 5 mm/min. The extension ratio was about 220%.

Thermally Stimulated Deformation Recovery

In our laboratory, a hot stage with a glass cover was controlled by a YCC-1612APIP temperature regulator made in the Xiamei Yuguang electronic plant. The hot stage was equipped with a stainless scale with an accuracy of 0.5 mm. The deformation recovery with the continuous increasing of temperature was directly observed by a magnifying glass on the hot stage. The heating rate of the recovery measurement was 1°C/min.

RESULTS AND DISCUSSION

Melting and Crystallization of Soft and Hard Segments in EOET Segmented Copolymer

The basic parameters are listed in Table I. All samples can be dissolved in chloroform, which suggests that the composition in these segmented copolymers is more or less homogeneous. The data about the melting temperature and the thermal

crystallization temperature for the cast films of the segmented copolymers show that the higher the molecular weight of the soft segment the easier is the crystallization. The corresponding supercooling for the crystallization is lower and the corresponding melting temperature is higher. Simultaneously, if the hard-segment content is higher, the crystallization of the soft segments becomes more or less difficult, the corresponding supercooling for the crystallization is higher, and the corresponding melting temperature is lower. For all cast films of EOET segmented copolymers, the crystallization of the hard segments is not obvious in the DSC measurement. Such an experimental fact implies that in the cast films of the EOET segmented copolymer the polar interaction rather than the crystallization of the hard segments mainly determines the formation of the physical crosslink.

In fact, the hard segments of the EOET segmented copolymers not only can be crystallized but also can grow spherulites as shown in Figure 2. It is evident that after annealing at 120 and 35°C both soft and hard segments have obviously crystallized. The photopicture measured at 70°C shows that the hard segments in the EOET 6000-25 segmented copolymer have grown spherulites with a distinguishable extinction cross. Observed by DSC, the crystallization of the hard segments is considerably weak, even in such a case.

Characterization Parameters of the Thermally Stimulated Shape-memory Behavior of EOET Segmented Copolymer

With a continuous increase of temperature, the stretched strip undergoes deformation recovery, which reflects the memory effect of EOET segmented copolymer. The recovery percentage of the

deformation is plotted against temperature. The plot of the experimental data gives an S-shape curve (integral deformation recovery curve or integral curve of the memory effect) as shown in Figure 3. In the low-temperature region, the length of the stretched strip changes weakly with the temperature and the deformation recovers slowly, but when the temperature reaches the range of 45–55°C, the deformation recovery changes abruptly. In a narrow region of the temperature, most of the deformation recovery can be completed. Further heating will lead to the final deformation recovery. For such an S-shape deformation recovery curve, we introduce the following parameters:

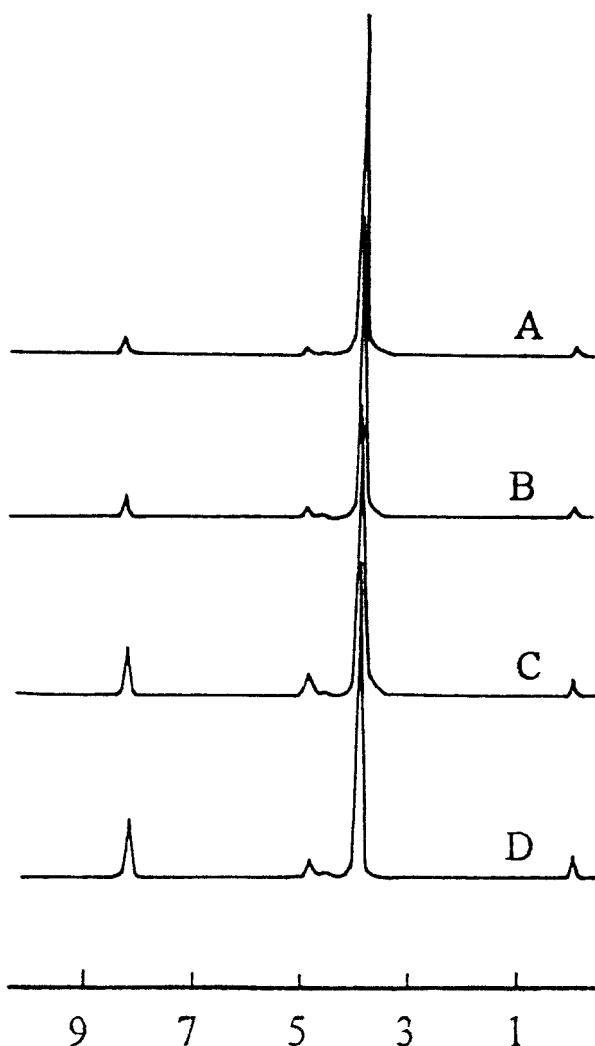


Figure 1 Proton spectra of EOET segmented copolymers: (A) EOET6000-20; (B) EOET6000-25; (C) EOET6000-30; (D) EOET6000-35.

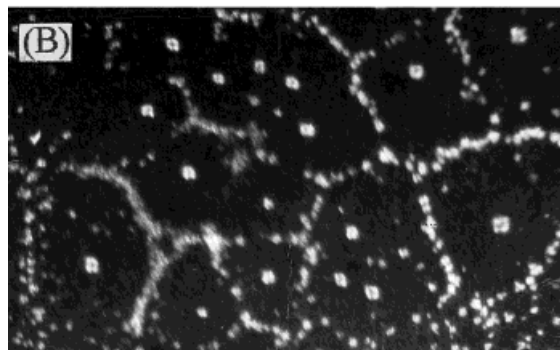
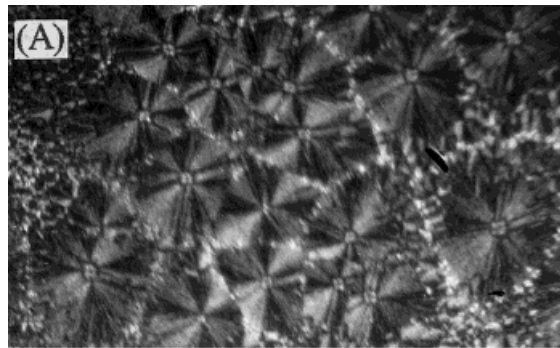


Figure 2 Spherulite morphology of hard segments observed by a polarizing microscope after crystallization at 120°C for 6 h and at 35°C for 12 h: (A) EOET6000-25 measured at room temperature; (B) EOET6000-25 measured at 70°C.

T_i temperature of initial deformation recovery
 T_{10} temperature of 10% deformation recovery
 T_r temperature of 50% deformation recovery
 T_{90} temperature of 90% deformation recovery
 T_e temperature of final deformation recovery
 R_f final deformation recovery.

From the corresponding differential deformation recovery curve, a new parameter can be derived:

T_M temperature which corresponds maximum deformation recovery rate against temperature.

The deformation recovery speed can be characterized as the following:

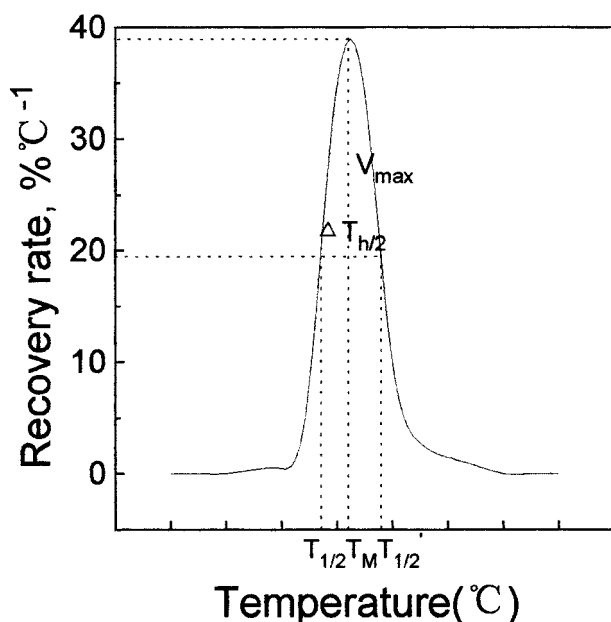
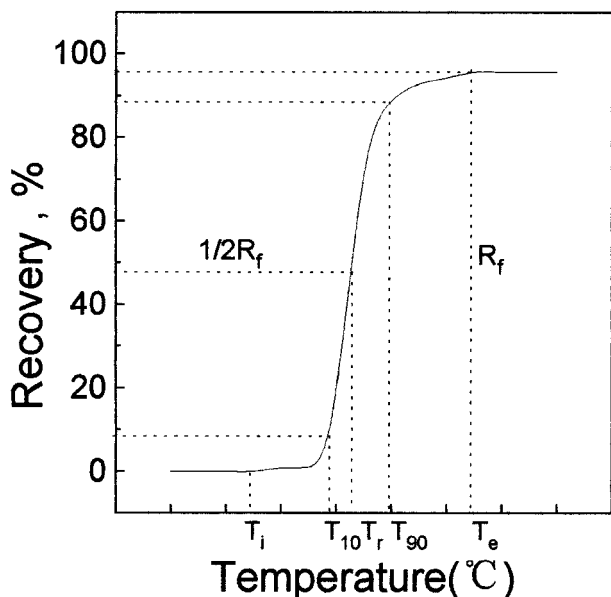


Figure 3 Thermally stimulated deformation recovery curve and its characteristics: (A) integral deformation recovery curve; (B) differential deformation recovery curve.

$$V_r = 0.8 (T_{90} - T_{10})^{-1} \cdot dT/dt$$

for the integral curve of the memory effect

$$V_M = 0.5 (\Delta T_{h/2})^{-1} \cdot dT/dt$$

for the differential curve of the memory effect

Here, the latter representation may be more ob-

jective for the characterization of the deformation recovery behavior (i.e., the shape-memory effect). For each sample, the parameters R_f , T_r , and V_r or R_f , T_M , and V_M can be used in the characterization, respectively.

Thermally Stimulated Shape-memory Behavior of EOET Segmented Copolymers with Different Soft-segment Length and Different Hard-segment Content

The deformation recovery of the six EOET segmented copolymer strips were observed and the corresponding deformation recovery curves are shown in Figures 4–8. From these curves, the calculated values of the parameters R_f , T_r , V_r , T_M , and V_M were determined and are listed in Table II.

The analysis of the deformation recovery curves and their corresponding characteristic parameters has shown the following laws: When the hard-segment contents in EOET segmented copolymers are same, the higher the molecular weight of the soft segments the easier is the crystallization of the soft segments. Therefore, the melting temperature of the soft-segment crystal is higher and the corresponding temperature T_r and T_M is also higher. Simultaneously, when the molecular weight of the soft segments in EOET segmented

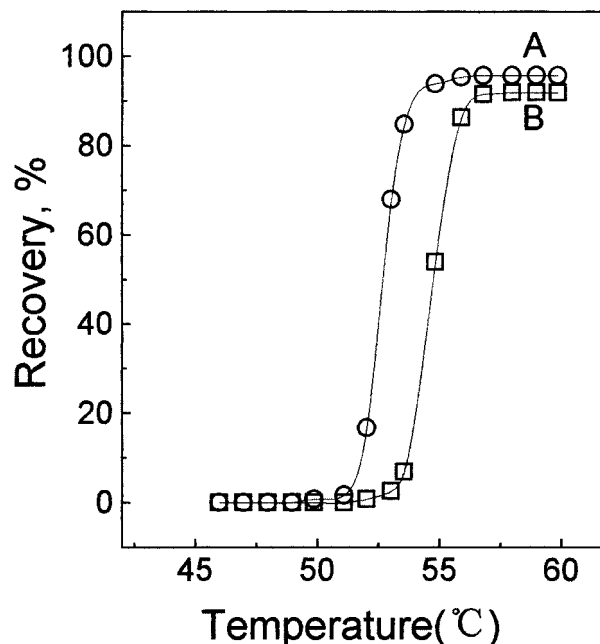


Figure 4 Deformation recovery curves of (A) EOET10000-20 and (B) EOET10000-15 segmented copolymer.

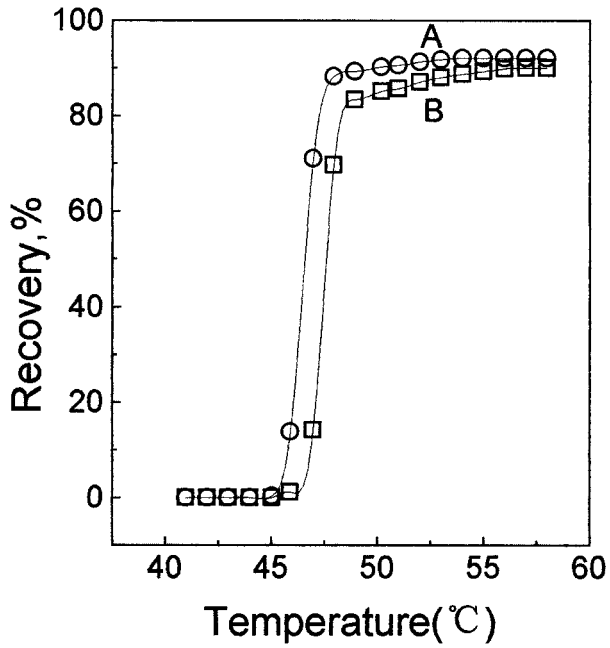


Figure 5 Deformation recovery curves of (A) EOET6000-25 and (B) EOET6000-20 segmented copolymer.

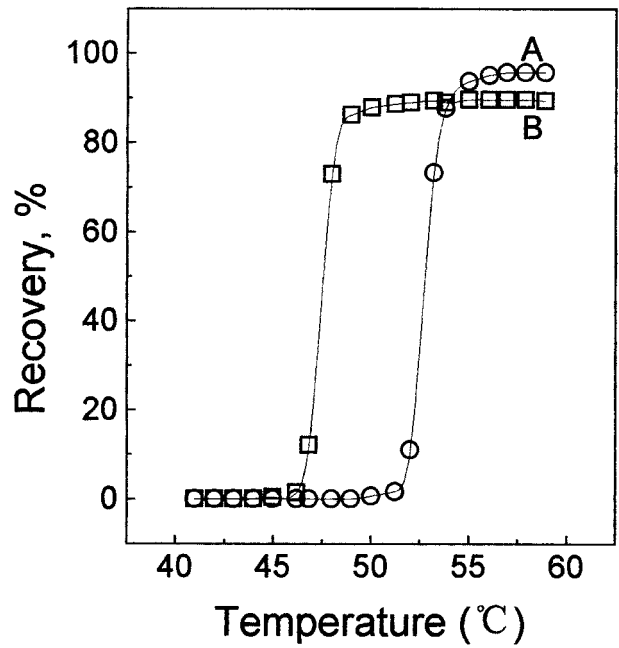


Figure 7 Deformation recovery curves of (A) EOET10000-20 and (B) EOET6000-20 segmented copolymer.

copolymers is the same, the higher the hard-segment content the more difficult is the crystallization of the soft segments. Furthermore, the melt-

ing temperature of the soft-segment crystal is lower and the corresponding temperature T_c and T_m is also lower. All these show that the situation

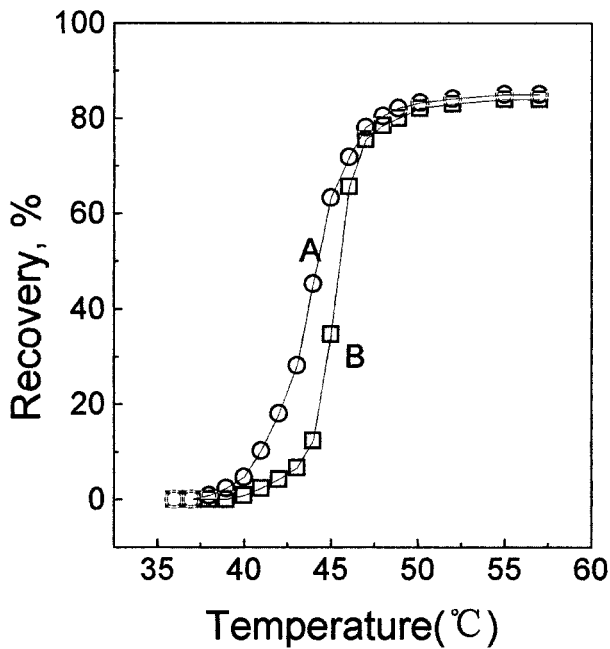


Figure 6 Deformation recovery curves of (A) EOET4000-30 and (B) EOET4000-25 segmented copolymer.

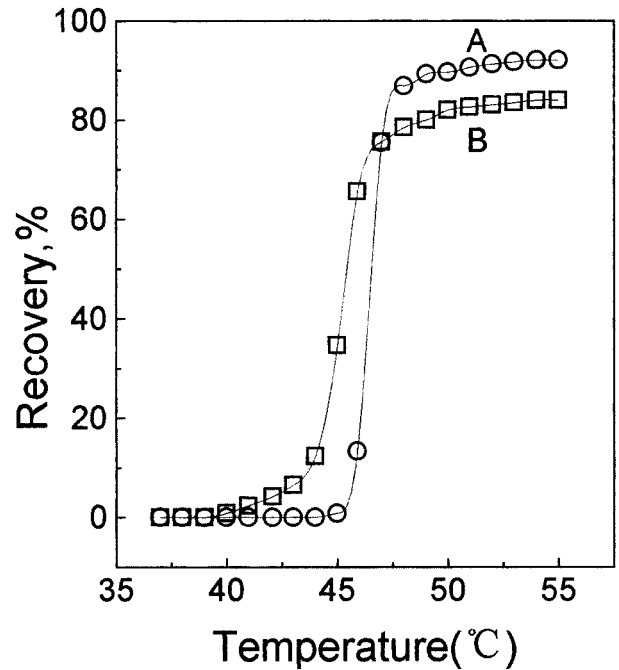


Figure 8 Deformation recovery curves of (A) EOET6000-25 and (B) EOET4000-25 segmented copolymer.

Table II Characteristic Parameters of Shape Recovery of EOET Segmented Copolymers

Sample	EOET 4000-25	EOET 4000-30	EOET 6000-20	EOET 6000-25	EOET 10000-15	EOET 10000-20
R_f (%)	84	85	90	92	93	95
T_r (°C)	45	44	48	46	55	53
V_r (min ⁻¹)	0.23	0.14	0.50	0.53	0.38	0.44
V_M (min ⁻¹)	0.19	0.21	0.25	0.26	0.20	0.23
V_{max} (min ⁻¹)	0.26	0.18	0.40	0.42	0.35	0.42
T_M (°C)	45.2	43.9	47.3	46.5	54.5	52.7

of the soft-segment crystallization determines the thermally stimulated deformation recovery temperature T_r and T_M .

The thermally stimulated deformation recovery R_f certainly also depends on the hard-segment content and the molecular weight of the soft segments in the EOET segmented copolymers. It can be imagined that if the physical crosslinking points, which are formed by the hard segments, are very well aggregated and are not destroyed in the stretching, the thermally stimulated deformation recovery should be complete. This is an ideal situation of the memory effect. In fact, it is not so, but making the hard segments aggregated as well as possible is feasible. To properly select the kinds of hard segments and the hard-segment contents just is a more convenient and effective way. Here, the experimental results have shown that if the hard-segment contents in EOET segmented copolymers with the same soft segment length are higher, they aggregate relatively better and the corresponding deformation recovery is higher. Therefore, the order and stability of the physical crosslinks which are formed by hard segments are the first factor, which determines the thermally stimulated deformation recovery; however, the influence of the soft-segment length still should not be neglected. The increasing of the entropy in the deformation recovery process is the driving force. The higher the molecular weight of the soft segment, the higher is the increase of the entropy in the deformation recovery process. Naturally, for these EOET segmented copolymers which have the longer soft segment, the corresponding final deformation recovery R_f is higher.

The thermally stimulated recovery speed of the EOET segmented copolymer may be influenced by many factors. From the experimental data about the deformation recovery speed V_r and V_m , it can be found that two-expression methods have a similar effect. When the soft-segment

length is same, the higher the hard segment content the higher is the deformation recovery speed. The influence of the soft-segment length on the deformation recovery speed is more complex, so it is difficult to give a clear conclusion about it at present.

Influence of Some Conditions on Thermally Stimulated Deformation Recovery of the EOET Segmented Copolymer

As shown in Figure 9, the change of the stretching temperature (T_s) in the used region does not have an obvious influence on the final deformation recovery R_f of the EOET6000-20 segmented copolymer. However, Figures 10–12 exhibit the following features: The final deformation recovery R_f , the deformation recovery speed V_r , and the V_M of the EOET10000-15 segmented copolymer decrease with increasing stretching ratio; at the

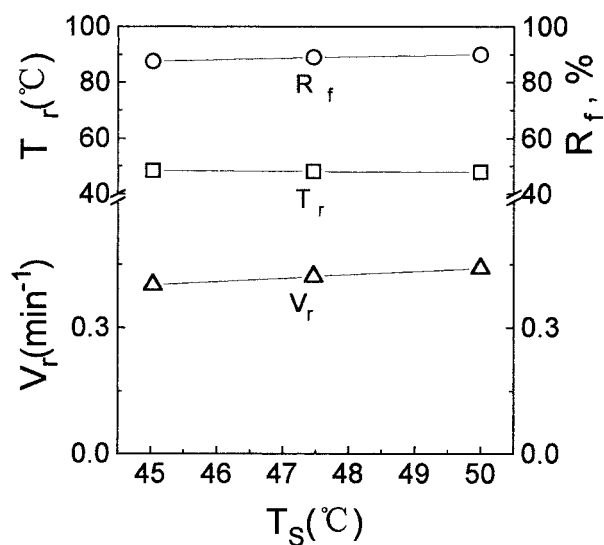


Figure 9 The influence of T_s on the shape-memory behavior of EOET6000-20.

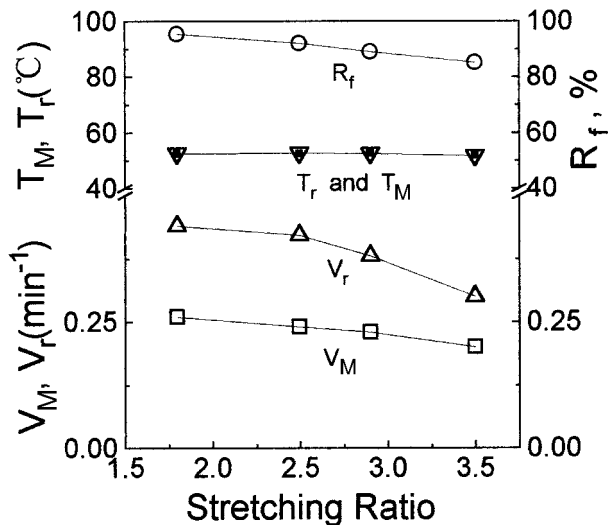


Figure 10 The influence of the stretching ratio on the shape-memory behavior of EOET10000-15.

same time, they decrease obviously with prolongation of the keeping time (t_k) at a constant stretching ratio and a given temperature. The last exper-

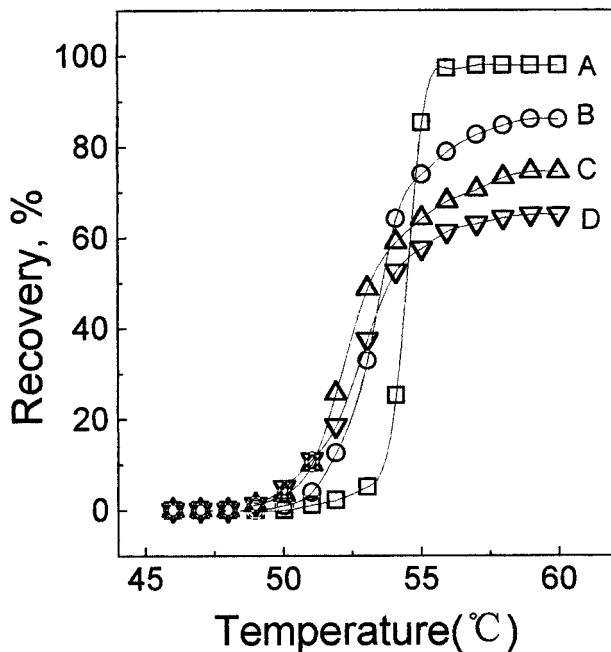


Figure 11 Deformation recovery curves of EOET10000-15 segmented copolymers with the different t_k at the stretching ratio 180% at 55°C: (A) 0 min; (B) 3 min; (C) 6 min; (D) 10 min.

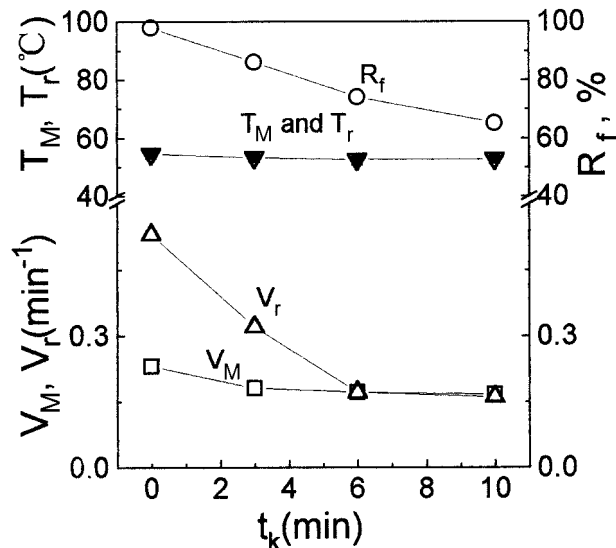


Figure 12 The influence of t_k on the shape-memory behavior of EOET10000-15.

imental result exhibits that when the keeping time t_k at a constant stretching ratio is prolonged the physical crosslinking point is destroyed. The hard segments in the crosslink may undergo a certain displacement.

We are grateful to the National Nature Science Foundation of China and "The National Key Projects for Fundamental Research 'Macromolecular Condensed State,' The State Science and Technology Commission of China" for supporting this work.

REFERENCES

1. S. Ota, *Radiat. Phys. Chem.*, **18**, 81 (1981).
2. J. Hou, X. Ma, X. Luo, D. Ma, X. Zhang, W. Zhu, and M. Xu, in *Proceedings of the International Symposium on Polymer Alloys and Composites*, in Hong Kong 1994, p. 211.
3. J. Hou, X. Ma, X. Zhang, W. Zhu, M. Xu, X. Luo, and D. Ma, *Vysokomol. Soedin. A*, **37**, 1377 (1995).
4. F. Li, J. Hou, W. Zhu, X. Zhang, M. Xu, X. Luo, D. Ma, and B. K. Kim, to appear.
5. F. Li, J. Hou, W. Zhu, X. Zhang, M. Xu, X. Luo, D. Ma, and B. K. Kim, to appear.
6. D. Coleman, Br. Pat. 682,866 (1952) (to ICI Ltd.).
7. D. Coleman, *J. Polym. Sci.*, **14**, 15 (1954).
8. X. Luo, C. Wang, and D. Ma, *Chin. J. Polym. Sci.*, **12**, 210 (1994).
9. J. Ma, X. Luo, X. Wang, W. Liu, and D. Ma, *Chem. J. Chin. Univ.*, **16**, 1645 (1995).