

# Compositional Heterogeneity, Thermostable, and Shape Memory Properties of Ethylene Oxide-Ethylene Terephthalate Segmented Copolymer with Long Soft Segment

DEZHU MA, MINGTAI WANG, MOZHEN WANG, XIAOYUN ZHANG, XIAOLIE LUO

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

Received 13 August 1997; accepted 26 November 1997

**ABSTRACT:** Ethylene oxide-ethylene terephthalate segmented copolymers (EOET) with long PEO segment or high PET content have showed an obvious compositional heterogeneity. The EOET copolymers with compositional heterogeneity could be separated into soluble and insoluble fractions by extraction with chloroform.  $^1\text{H-NMR}$  measurements showed that the former contains much lower PET content than the average content value, and the latter is in reverse. DSC results revealed that PET segments in the latter would crystallize more easily, but in the former PEO segments exhibits more intensive melting peak. The thermogravimetric behaviors of EOET copolymers were between PEO and PET homopolymers. The EOET copolymers with serious compositional heterogeneity showed two stages of weight loss. TGA was sensitive to indicate the compositional heterogeneity in EOET copolymers. The compositional heterogeneity could impart a great influence on the shape memory behavior of EOET copolymers. The recovery curve of EOET copolymers with serious compositional heterogeneity also can exhibit two stages of deformation recovery. Generally, the component with worse memory behavior in EOET copolymer is an unfavorable factor, and the addition of EOET copolymer with better memory behavior into the blend is a favorable factor for the blend system. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 947–955, 1998

**Key words:** poly(ethylene oxide); poly(ethylene terephthalate); shape memory; segmented copolymer; compositional heterogeneity

## INTRODUCTION

Ethylene oxide-ethylene terephthalate (EOET) segmented copolymers of poly(ethylene oxide) (PEO) and poly(ethylene terephthalate) (PET) were first described by Coleman<sup>1</sup> in 1945 in the attempt to reduce the crystallinity of PET and increase the hydrophilicity to improve the dyeability with hydrophilic dyes. Reed<sup>2</sup> and Reed and Gilding<sup>3</sup> revealed that the copolymers might be degraded in the physiological environment, and

have also described the degradation mechanism when it was used as a possible candidate for “biodegradable elastomers.” Recently, M. Nagta et al.<sup>4</sup> also reported EOET and PEO-poly(butylene terephthalate) (PBT) families of the copolymers which could be used as biodegradable polymers. Investigation on the hardness and thermal properties of EOET-containing segments of different molecular weight has been published elsewhere.<sup>5</sup> Dynamic mechanical analyses (DMA) of EOET copolymers have been carried out in our lab<sup>6</sup> over a large temperature range ( $-150$ – $50^\circ\text{C}$ ).

In previous work<sup>7,8</sup> we have shown that EOET copolymer may exhibit thermally stimulated shape memory behavior. Our work<sup>6</sup> has

Correspondence to: D. Ma.

*Journal of Applied Polymer Science*, Vol. 69, 947–955 (1998)  
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/050947-09

revealed the relationship between the shape memory effect and the dynamic mechanical behavior in EOET segmented copolymers. The basic features of the shape-memory behavior of the segmented copolymers are that the crystallinity of soft segments of the segmented copolymers determined the recovery temperature and both final recovery of deformation and recovery speed depend on the crystallizability of PEO segments and stability of physical crosslinks formed by the hard segments.

Any copolymer could have a certain composition distribution due to different reaction probability between components. In segmented copolymers, maybe, the attention should be paid to the composition distribution and the compositional heterogeneity between macromolecules, especially. It has been found in the case of polybutadiene/2,4-TDI or 2,6-TDI-based polyurethanes that because of the heterogeneity of the reaction system the macromolecules of the segmented copolymers can vary greatly in their chemical composition and average hard segment length.<sup>9,10</sup>

Undoubtedly, the compositional heterogeneity necessarily leads to the change of the molecular segregation in the segmented copolymers which will simultaneously influence the morphology of the samples. The influence of molecular segregation on crystal morphology has been reported for a polyester-polyether segmented copolymer.<sup>11</sup> These phenomena are related to the molecular heterogeneity in chemical composition and average hard segment length.

In our laboratory again the compositional heterogeneity has been revealed in the EOET segmented copolymers. Moreover, the compositional heterogeneity becomes very evident when the soft segment length increases greatly. It is evident that the compositional heterogeneity of segmented copolymers can affect both the crystallinity of the soft segments and the stability of physical crosslinks formed by the hard segments. Therefore, the compositional heterogeneity of EOET segmented copolymers necessarily influence the shape memory effects of EOET segmented copolymers strongly, which is a main part of this work.

Thermogravimetric analyses of the EOET segmented copolymers was carried out. We found that the thermogravimetric behavior of EOET segmented copolymer is closely related to the composition and the compositional heterogeneity of EOET segmented copolymers.

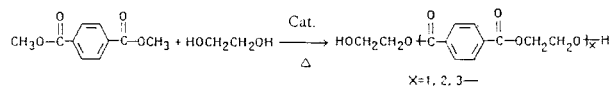
## EXPERIMENTAL

### Preparation and Characterization of EOET Copolymers

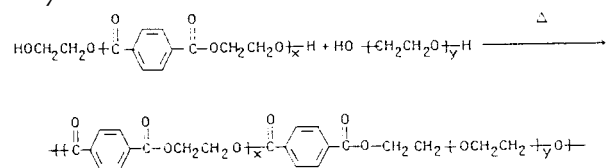
#### Synthesis

The synthesis of EOET segmented copolymers is divided into two steps:

#### Transesterification



#### Polycondensation



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

#### Intrinsic Viscosity

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

### Measurements of EOET Copolymers and Their Fractions

#### Proton Spectra

The compositions of EOET segmented copolymers were obtained using a JEOL FX-90Q spectrometer. The bands at 8.25 and 3.89 ppm were used for the compositional calculation. The solvent was  $\text{CF}_3\text{COOH}$ , in which all segmented copolymers, including the fractions insoluble in chloroform, and several EOET segmented copolymers with evident compositional heterogeneity can be dissolved.

#### DSC Measurement

DSC curves were measured under high pure nitrogen by a Perkin-Elmer DSC-2C apparatus equipped with a TADS microcomputer and an intracooler II. The DSC was calibrated with ultra-pure indium. Each sample was heated to 550 K,

**Table I Characteristic Parameters of Segmented EOET Copolymers**

Sample	$M_w$ of PEO	$W_h\%$ <sup>a</sup>		$L_{n,h}$ <sup>b</sup>		$[\eta]$ (dL/g)	Solubility in CHCl <sub>3</sub>
		Theory	By NMR	Theory	By NMR		
EOET2000-25	2000	25	26.9	3.5	3.9	0.58	s <sup>c</sup>
EOET2000-30	2000	30	31.0	4.5	4.7	0.60	s
EOET2000-35	2000	35	35.3	5.6	5.7	0.67	s
EOET2000-40	2000	40	42.0	6.9	7.5	0.73	s
EOET2000-45	2000	45	47.0	8.5	9.2	0.62	s
EOET4000-25	4000	25	27.6	6.9	7.9	0.81	s
EOET4000-30	4000	30	32.0	8.9	9.8	0.76	s
EOET6000-20	6000	20	21.2	7.8	8.3	0.91	s
EOET6000-25	6000	25	25.7	10.5	11.0	0.69	s
EOET6000-30	6000	30	31.5	13.4	14.4	0.70	ps <sup>d</sup>
EOET6000-35	6000	35	37.0	16.8	18.4	0.60	ps
EOET10000-15	10000	15	16.5	9.2	10.3	0.87	s
EOET10000-20	10000	20	21.8	13.0	14.7	0.85	s
EOET10000-25	10000	25	27.0	17.4	19.3	0.57	ps
EOET20000-25	20000	25	27.8	34.7	39.9	0.95	ps

<sup>a</sup>  $W_h\%$ , hard content in weight.<sup>b</sup>  $L_{n,h}$ , average length of hard segment.<sup>c</sup> s, soluble in CHCl<sub>3</sub>.<sup>d</sup> ps, partly soluble in CHCl<sub>3</sub>.

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.

#### Thermogravimetric Analysis (TGA)

Thermogravimetric analysis curves were measured using a WRT-3 model TG-DTG analyzer (made in Shanghai Balance Plant, PRC). The measure temperature range was 40–500°C. The heating rate was 10°C/min. The weight of the sample was ~ 8 mg. The measurement was carried out in a dry air atmosphere.

#### Measurement of Thermally Stimulated Shape Memory of Samples

##### 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 10 mm and a width of 4 mm was stretched at 50°C by a universal testing machine (DSC-5000) with a thermostatically controlled oven made in Japan (Shimadzu Co.). The stretching temperature was ~ 50°C. The constant strain rate was 5 mm/min, and the extension ratio was ~ 200%. The strip samples for EOET segmented

**Table II <sup>1</sup>H-NMR Analytic Results for Soluble and Insoluble Fractions in Segmented EOET Copolymers Extracted by Chloroform**

Sample	Residue after Extraction (wt %)	Insoluble Fraction		Soluble Fraction		Original Sample	
		$W_h\%$ <sup>a</sup>	$L_{n,h}$ <sup>b</sup>	$W_h\%$	$L_{n,h}$	$W_h\%$	$L_{n,h}$
EOET6000-30	39.2	37.8	19.2	27.1	11.6	31.5	14.4
EOET6000-35	48.3	51.6	33.3	29.8	13.3	37.0	18.4
EOET10000-25	34.4	33.9	26.8	22.1	14.8	27.0	19.3
EOET20000-25	29.0	57.8	142.7	13.7	16.5	27.8	39.9

<sup>a</sup>  $W_h\%$ , hard content in weight.<sup>b</sup>  $L_{n,h}$ , average length of hard segment.

copolymers insoluble in chloroform were prepared in a CS 183 Mini Max molder and molded at 240°C within a minute.

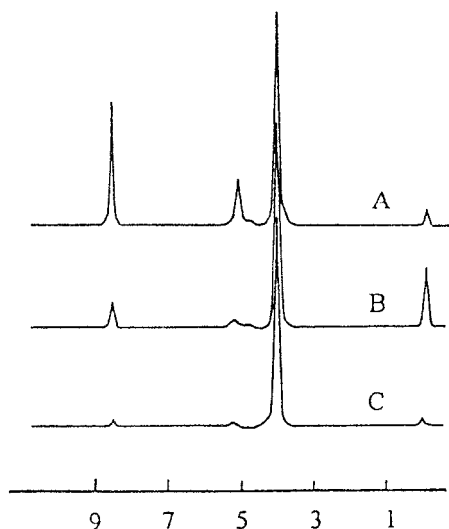
### Thermally Stimulated Deformation Recovery

A hot stage with a glass cover was controlled by a YCC-1612APIP temperature regulator made in the Xiamen 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 increase of temperature was directly observed by a magnifying glass on the hot stage. The heating rate of the recovery measurement was 1°C/min.

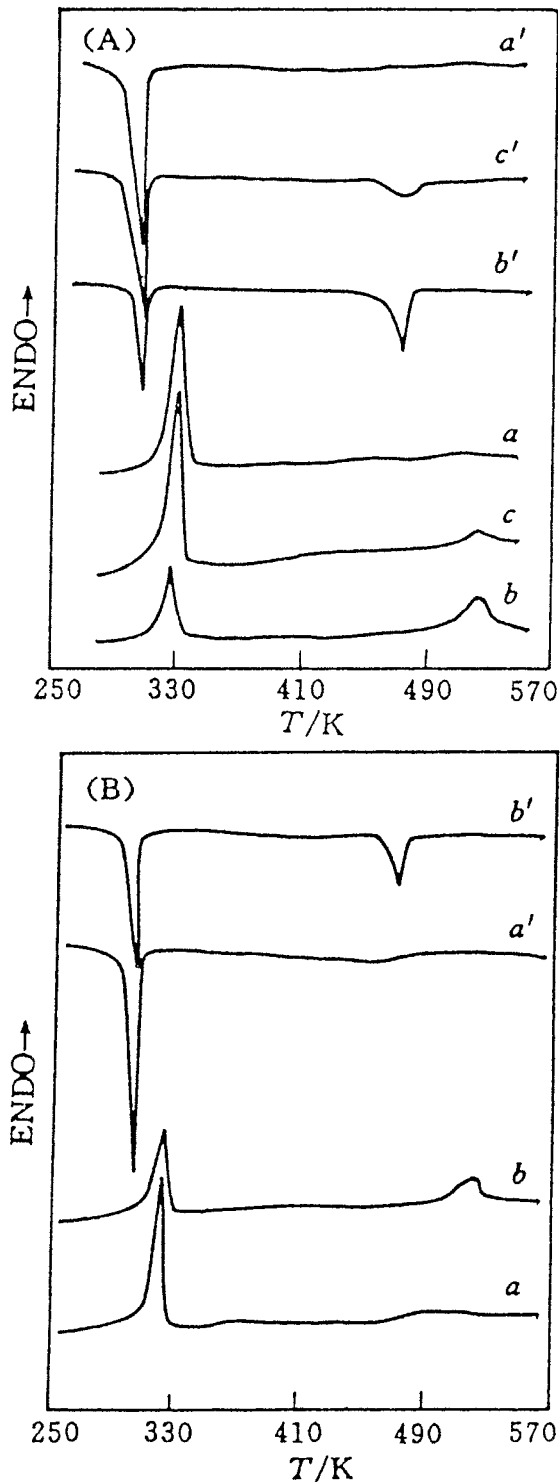
## RESULTS AND DISCUSSION

### Characterization of Compositional Heterogeneity

From data listed in Table I it can be seen that four EOET segmented copolymers (EOET 6000-30 and 35, EOET10000-25, EOET20000-25) are not completely soluble in chloroform. These samples were extracted by chloroform. The soluble and insoluble fractions of these samples were measured by proton NMR, respectively. Their hard segment content and length are listed in Table II. It is obvious that EOET6000-35 segmented copolymer contained insoluble fraction with hard segment content of 51.6% in weight, which is much higher than that in corresponding soluble fraction. The compositional heterogeneity has be-



**Figure 1**  $^1\text{H-NMR}$  spectra of EOET20000-25 segmented copolymers. (A) insoluble fraction in  $\text{CHCl}_3$ ; (B) original sample; (C) soluble fraction in  $\text{CHCl}_3$ .



**Figure 2** DSC melting and thermal crystallization spectra of EOET20000-25 (A) and EOET6000-35 (B) segmented copolymers. (a, a') soluble fraction in  $\text{CHCl}_3$ , (b, b') insoluble fraction in  $\text{CHCl}_3$ ; (c, c') original sample.

come very strong in EOET20000-25, in which the hard segment content in insoluble fraction is 4.2 times of the hard segment content in soluble frac-

**Table III** Data from DSC Heating and Cooling Curves of EOET Segmented Copolymers

Sample	Soft Segment					Hard Segment				
	$T_m$ (K)	$\Delta H_m$ (cal/g)	$X_c$ (%)	$T_c$ (K)	$\Delta H_c$ (cal/g)	$T_m$ (K)	$\Delta H_m$ (cal/g)	$X_c$ (%)	$T_c$ (K)	$\Delta H_c$ (cal/g)
EOET6000-30s <sup>a</sup>	324.1	12.9	38.1	299.8	14.3	483.7	1.6	20.6	457.2	1.7
EOET6000-30i <sup>b</sup>	322.5	10.8	37.4	297.9	10.9	514.1	3.5	32.3	477.1	3.1
EOET6000-35s	325.2	15.2	46.7	304.0	15.2	487.4	2.0	23.4	449.8	2.5
EOET6000-35i	324.8	8.7	38.7	302.2	9.9	518.7	5.1	34.4	469.7	4.3
EOET10000-25s	329.5	19.4	53.7	297.0	18.7	/	/	/	—	—
EOET10000-25i	336.3	15.2	49.6	300.9	13.9	531.4	4.4	45.2	468.5	3.6
EOET20000-25s	332.6	18.3	45.7	307.9	18.3	428.1	2.3	58.5	—	—
EOET20000-25i	331.6	9.2	47.0	310.5	7.4	525.0	10.3	62	477.1	6.2

<sup>a</sup> s, soluble in CHCl<sub>3</sub>.

<sup>b</sup> i, insoluble in CHCl<sub>3</sub>.

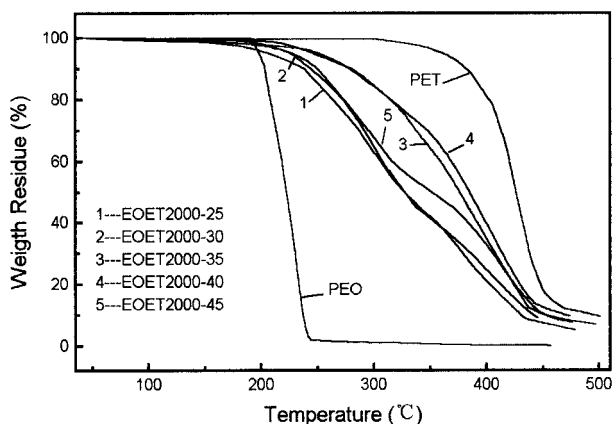
tion. Proton spectra of insoluble and soluble fractions in chloroform for EOET20000-25 are shown in Figure 1. The compositional heterogeneity has been exhibited very clearly.

NMR results show that the EOET segmented copolymers with compositional heterogeneity consist of two parts: high hard segment content part and low hard segment content part. Such compositional heterogeneity could influence the properties of segmented copolymer, as described below.

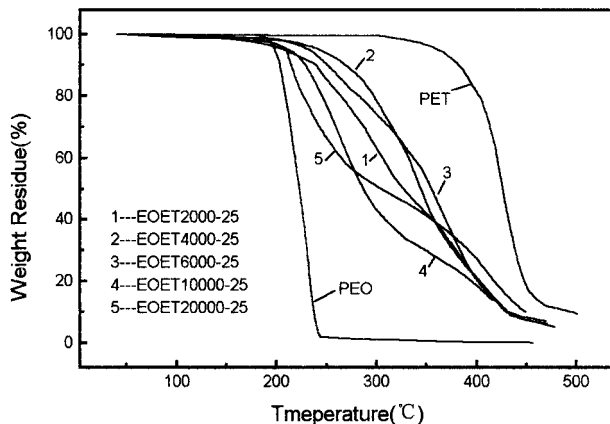
### Compositional Heterogeneity and Crystallization Behavior

DSC heating and cooling curves for soluble, insoluble fractions in chloroform and the original sample of EOET20000-25 and EOET6000-35 segmented copolymers are shown in Figure 2. The corresponding data from DSC heating curves and

cooling curves for four EOET segmented copolymers with compositional heterogeneity are summarized in Table III. Obviously, high temperature melting peak and crystallization peak belong to the hard segments in segmented copolymers, and low temperature melting peak and crystallization peak should be associated with soft segments in segmented copolymers. The curves in Figure 2 show that hard segments in insoluble fractions in chloroform could crystallize easily and their melting peaks are much stronger. In contrast, the melting peak and crystallization peak of soft segments in the insoluble fractions are weaker than those in the soluble fractions for the same EOET segmented copolymers. Generally, the longer the PEO soft segment and the higher the hard segment content, the stronger the compositional heterogeneity of the segmented copolymer and the



**Figure 3** Thermogravimetric analysis curves for EOET2000 segmented copolymers with different hard segment content (from 25% to 45%).



**Figure 4** Thermogravimetric analysis curves for EOET25 segmented copolymers with different soft segment length (from 2000 to 20,000).

**Table IV** TGA Data for EOET Segmented Copolymers

Sample	$T_i$ (°C) <sup>a</sup>	$T_{10}$ (°C) <sup>b</sup>	$T_{1/2}$ (°C) <sup>c</sup>	$T_{max}$ (°C) <sup>d</sup>
PEO	187.5	203.8	223.1	234.4
PET	328.2	381.6	427.1	423.9
EOET2000-25	199.8	239.2	327.2	299.0
EOET2000-30	196.4	244.3	328.4	296.5
EOET2000-35	196.5	277.8	374.2	392.2
EOET2000-40	213.9	280.3	385.5	397.7
EOET2000-45	199.7	250.1	351.8	425.4
EOET4000-25	215.9	270.0	344.9	345.8
EOET6000-20	190.9	216.5	344.8	338.3
EOET6000-25	207.1	263.4	353.1	354.6
EOET6000-30	200.5	254.0	349.6	339.2
EOET6000-35	198.0	257.3	330.8	305.0
EOET10000-25	186.6	231.4	285.7	268.8
EOET20000-25	186.0	210.9	305.8	333.5

<sup>a</sup>  $T_i$ , initial decomposition temperature.

<sup>b</sup>  $T_{10}$ , temperature for 10% weight loss.

<sup>c</sup>  $T_{1/2}$ , temperature for sample with 50% residual weight fraction.

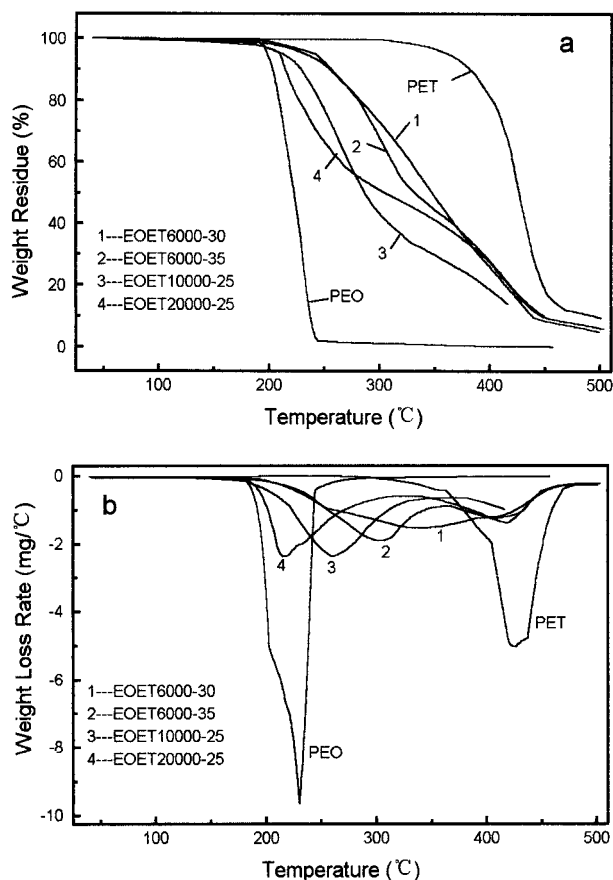
<sup>d</sup>  $T_{max}$ , temperature for maximum rate of decomposition.

bigger the difference of the crystallization behavior between insoluble and soluble fractions.

### Compositional Heterogeneity and Thermogravimetric Behavior

The thermogravimetric analysis curves for EOET2000 segmented copolymers with different hard segment content and EOET25 segmented copolymers with different soft segment length are shown in Figures 3 and 4. The corresponding data about different thermal decomposition temperature are listed in Table IV. From Figures 3 and 4 and data in Table IV it can be seen that the pure PET is much more thermostable than pure PEO, and EOET segmented copolymers possess the middle thermostability.

When the molecular weight of soft segment in EOET segmented copolymer is constant, the thermostability of EOET segmented copolymers becomes better with increasing hard segment content generally, as shown by Figure 3. But, the EOET2000-45 segmented copolymer behaves differently; it seems to be compositionally heterogeneous. In this sample two stages of weight loss exist; maybe the component with lower hard segment content underwent decomposition at lower temperature. It is interesting that the EOET2000-45 segmented copolymer as a whole can dissolve in chloroform; this solvent cannot separate the component with high hard segment content from the component with low hard segment content in the EOET 2000-45 segmented copolymer. It could



**Figure 5** Integral (a) and differential (b) thermogravimetric analysis curves for EOET6000-30 and 6000-35, EOET10000-25 and EOET20000-25 segmented copolymers.

be that the thermogravimetric analysis is a sensitive method to distinguish the components with different hard segmented copolymer in EOET segmented copolymers.

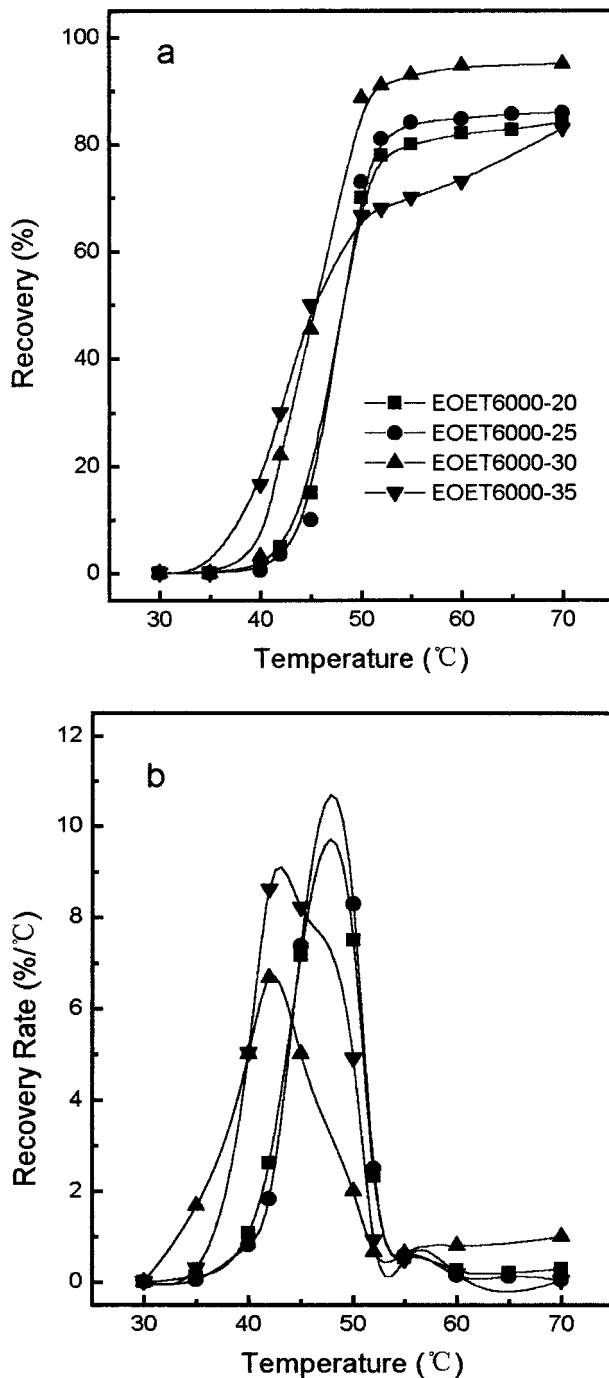
Figure 4 shows that when the hard segment content is 25% and the molecular weight of soft segment is <6000, the thermostability of EOET segmented copolymers increases with increasing molecular weight of the soft segment. However, EOET10000-25 and EOET20000-25 segmented copolymers appeared to be quite different; in these two segmented copolymers the change of the weight residue with temperature again exhibits the evident two stages, which seems to be the result of strong compositional heterogeneity in these segmented copolymers.

The four EOET segmented copolymers with evident compositional heterogeneity exhibit a common thermogravimetric behavior, as shown in Figure 5. It can be found that the differential curves more clearly demonstrate the effect of the compositional heterogeneity on the thermogravimetric behavior in these four EOET segmented copolymers. Also, it can be seen that the thermogravimetric analysis curves of EOET10000-25 and EOET20000-25 segmented copolymers exhibited such compositional heterogeneity, which is consistent with the results from proton NMR spectra.

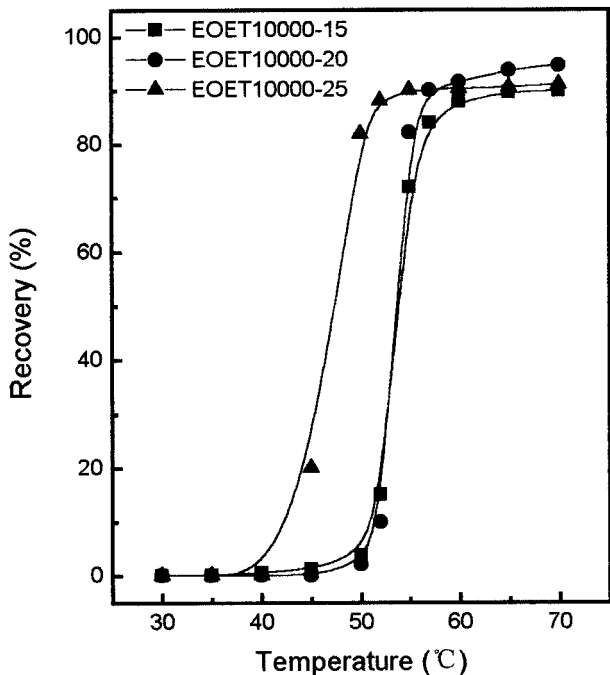
#### Compositional Heterogeneity and Shape Memory Behavior

Figure 6 shows that when the molecular weight of soft segment is 6000 and the hard segment content is not more than 30%, the shape memory behavior becomes better with increasing hard segment content. As shown above, the EOET6000-30 segmented copolymer has compositional heterogeneity, but it is not serious; therefore it did not give the evident influence on the shape memory behavior of this segmented copolymer. However, the compositional heterogeneity of EOET6000-35 segmented copolymer has already become very strong, therefore the shape memory curve of this segmented copolymer has exhibited much worse memory behavior and the deformation recovery seems to be divided into two stages. It is evident that in the EOET6000-35 both the maximum recovery and recovery temperature are lower than those in others, and the recovery temperature range is also wider as well. Again, the differential shape memory curve more effectively exhibited the influence of the compositional heterogeneity on the shape memory behavior.

From the shape memory curves of EOET10000 segmented copolymers with different hard segment length in Figure 7, it can be found that the EOET10000-25 segmented copolymer shows worse shape memory behavior than the other EOET 10000 segmented copolymers. Such phenomena should be related to the compositional

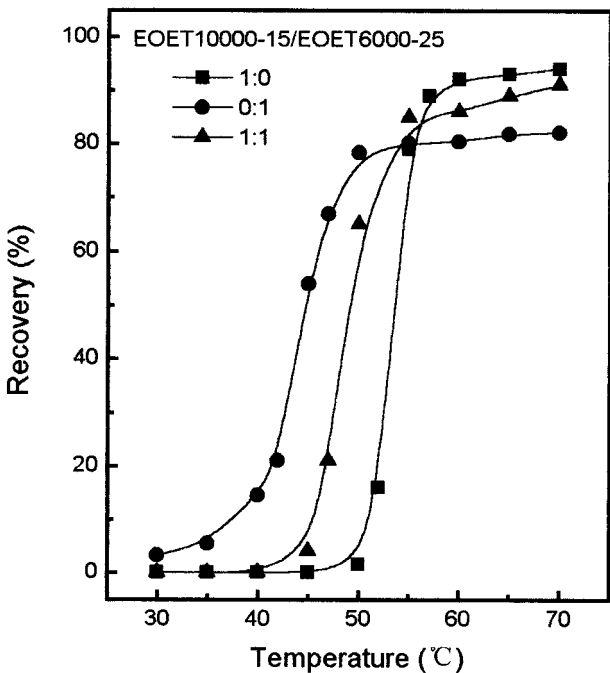


**Figure 6** Integral (a) and differential (b) shape memory curves for EOET6000 segmented copolymers with different hard segment content.



**Figure 7** Shape memory behavior of EOET10000 segmented copolymers with different hard segment content.

heterogeneity in EOET10000-25 segmented copolymer in which a part of soft segments in the segmented copolymer crystallize badly and a part of

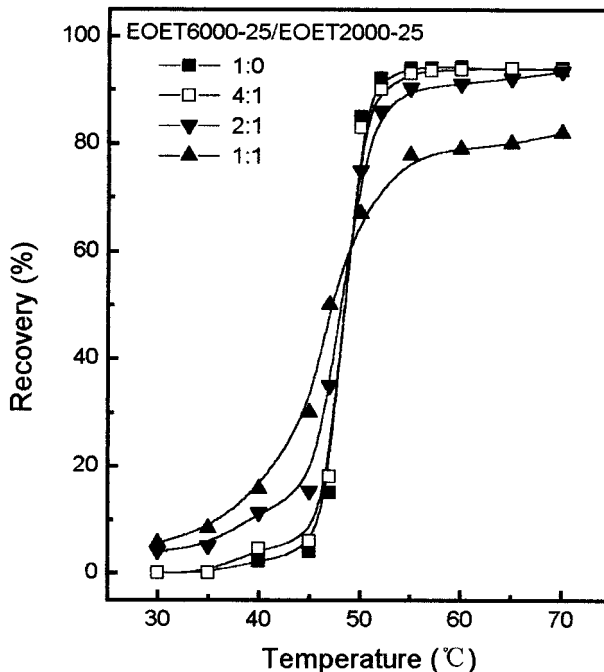


**Figure 8** Shape memory behavior of blend of EOET segmented copolymers with different hard segment content and different soft segment length.

the physical crosslinking points are not so stable. In fact, the bad crystallization of soft segments in fractions with high hard segment content may lead to the deformation recovery at lower temperature, and not well-developed physical crosslinking points (which consist of hard segments) in the fractions with low hard segment content may lead to lower maximum deformation recovery.

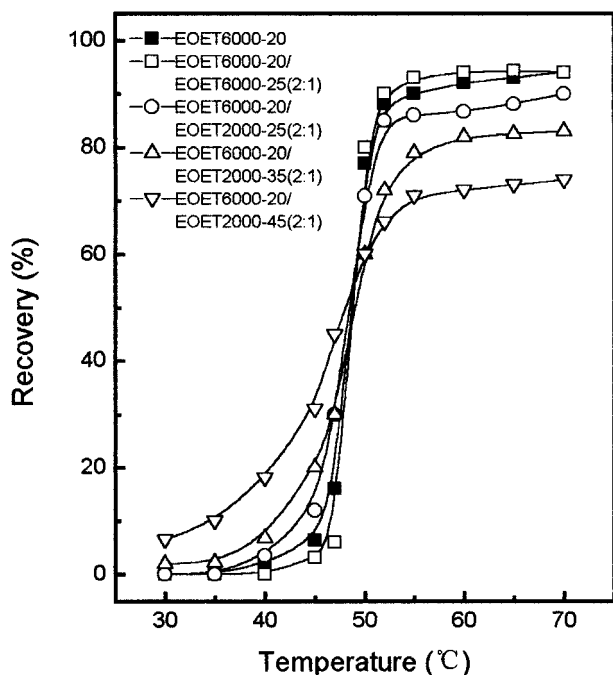
The shape memory curves in Figure 8 show that the addition of the EOET6000-25 segmented copolymer into the EOET10000-15 segmented copolymer may make the shape memory function of the blend worse than that of EOET10000-15 segmented copolymer. Although the shape memory function of the blend is still better than that of EOET6000-25 segmented copolymer, it is more closed to shape memory behavior of EOET6000-25 segmented copolymer.

Figure 9 shows that the addition of EOET2000-25 segmented copolymer into EOET6000-25 segmented copolymer only gives rise to the decrease of the shape memory function of EOET6000-25 segmented copolymer, for which the reason should lie in that EOET2000-25 segmented copolymer almost does not possess the shape memory function. Figure 10 shows that the addition of EOET6000-25 segmented copolymer into EOET6000-20 segmented copolymer can improve



**Figure 9** Shape memory behavior of blends of EOET segmented copolymers with same hard segment content and different soft segment length in different proportion of two components.





**Figure 10** Shape memory behavior of blends of EOET segmented copolymers with same soft segment length and different hard segment content and with different soft segment length and different hard segment content in the same proportion of two components.

the shape memory function of EOET6000-20 segmented copolymer. The change in shape memory function is due to that the shape memory function of EOET6000-25 segmented copolymer is better than that of EOET6000-20 segmented copolymer. However, the addition of any EOET2000 segmented copolymer into EOET6000-20 segmented copolymer can only make shape memory function of EOET6000-20 segmented copolymer worse, even when EOET2000 segmented copolymer contains the 45% hard segment content.

## CONCLUSION

Long PEO segment and high PET content in the EOET copolymers may result in a serious compositional heterogeneity, which can impose lots of influences on the properties of the copolymers.

The influence of the compositional heterogeneity on the crystallization behaviors of the soft and

hard segments in EOET copolymer is complicated. The trend that the temperature range of melting process for soft segment crystals becomes wider and shifts to lower temperature is an unfavorable factor for the shape memory effect of EOET copolymer.

The compositional heterogeneity in EOET copolymers can give the evident influence on their thermogravimetric behavior, and the thermogravimetric property is very sensitive to the compositional heterogeneity in EOET copolymers.

On the whole, the compositional heterogeneity in EOET copolymers makes their shape memory behavior worse. The EOET copolymers with a better shape memory effect may improve the worse one in their blends. Therefore, blending EOET segmented copolymers with different shape memory behavior may be used as a method of creating a necessary shape memory EOET copolymer.

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. D. Coleman, *J. Polym. Sci.*, **14**, 15 (1954).
2. A. M. Reed, Ph.D. Thesis, University of Liverpool, 1979.
3. A. M. Reed and D. K. Gilding, *Polymer*, **22**, 499 (1981).
4. M. Nagta et al., *Polymer Int.*, **39**, 83 (1996).
5. J. Slonecki, *Polymer*, **31**(8), 1464 (1990).
6. Mingtai Wang, Xiaolie Luo, and Dezhu Ma, *Eur. Polym. J.*, to appear.
7. Xiaolie Luo, Xiaoyun Zhang, Mingtai Wang, Dezhu Ma, Mao Xu, and Fengkui Li, *Journal of China University of Science and Technology*, **27**, 103 (1997).
8. Xiaolie Luo, Xiaoyun Zhang, Mingtai Wang, Dezhu Ma, Mao Xu, and Fengkui Li, *J. Appl. Polym. Sci.*, **64**, 2433 (1997).
9. M. Xu, W. J. Macknight, C. H. Y. Chen, and E. L. Thomas, *Polymer*, **24**, 1327 (1983).
10. C. H. Y. Chen, R. M. Briber, E. L. Thomas, M. Xu, and W. J. Macknight, *Polymer*, **24**, 1333 (1983).
11. M. Xu, S. R. Hu, M. Y. Wu, C. F. Chen, and Y. Z. Jin, *Polym. Commun. (China)*, **1**, 27 (1982).