

THERMALLY STIMULATED SHAPE MEMORY BEHAVIOR OF (ETHYLENE OXIDE-BUTYLENE TEREPHTHALATE) SEGMENTED COPOLYMER

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Abstract The thermally stimulated shape memory behavior of ethylene oxide-butylene terephthalate (EOBT) segmented copolymers with different soft segment molecular weight and hard segment content was investigated. The deformation recovery ratio R_f of the EOBT samples increases with the soft segment molecular weight and the hard segment weight content, while the average overall deformation recovery speed V_f increases with the hard segment content. The temperature of maximum deformation recovery speed (T_M) is determined by the melting temperature of the soft segment crystals and the stability of the crystallized hard segment domains.

Keywords Ethylene oxide-butylene terephthalate segmented copolymers, Shape memory, Crystallized hard segment

INTRODUCTION

It is well known that segmented copolymers (for example, polyurethane and polyether-ester) may exhibit a novel thermally stimulated shape memory behavior at a comparatively low temperature (that is about 60 °C)^[1-10]. Thermally stimulated shape memory behavior of the poly(ϵ -caprolactone) based polyurethane demonstrated 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 prerequisites for the shape memory behavior^[1-4]. The response temperature of the shape memory is dependent on the melting temperature of the soft segment crystals. The final recovery ratio and the recovery speed are mainly related to the stability of the hard segment domains under stretching and dependent on the hard segment content of the copolymer.

The ethylene oxide-ethylene terephthalate segmented copolymers (EOET) with different long soft segments and different hard segment contents also possess similar thermally stimulated shape memory properties to those of the poly(ϵ -caprolactone) based polyurethanes. The high crystallinity of the soft segment regions and the stable physical crosslinks around the melting temperature of the soft segment crystals are two necessary conditions for the shape memory behavior^[5, 6]. The extraction experiments and NMR analysis of the EOET segmented copolymers have shown that due to the different reaction possibility between the reaction fractions in the synthesis of EOET segmented copolymers the compositional heterogeneity inevitably occurs in the reaction products^[5, 6]. The experiments have also proved that the compositional heterogeneity of the EOET segmented copolymer is unfavorable for the shape memory behavior. Therefore, it is essential to control and guarantee the compositional homogeneity of the segmented copolymer for good shape memory behavior^[9].

It is known that in the poly(ϵ -caprolactone) based polyurethane the crystallization of the hard segments is difficult, but the hard segments can form hydrogen bonds with both hard segments and soft segments; in the EOET segmented copolymer the crystallization of the hard segments also is slow and not easy, but they can not

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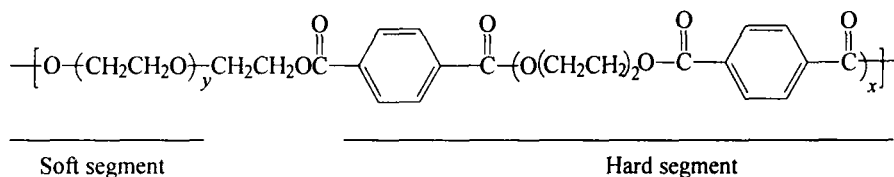
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form hydrogen bonds. For ethylene oxide-butylene terephthalate segmented copolymer (EOBT), the hard segments also can not form hydrogen bonds, but they crystallize easily and quickly, this feature should exert an important influence on the segmented copolymers' shape memory behavior. Therefore, the EOBT segmented copolymer should act as a model sample for studying the role of the crystallized physical crosslinks in the shape memory behavior of the segmented copolymers.

EXPERIMENTAL

Material Characterization

The EOBT segmented copolymers were formed by melt transesterification of 1,4-butanediol, dimethyl terephthalate and poly(ethylene oxide)^[8]. The number-average molecular weight of the soft segments used is 6,000 and 10,000, respectively. The structural unit of the copolymer can be expressed as the following:



The samples were designated by the soft segment molecular weight followed by the hard segment weight content, for example, EOBT6000-30.

Characteristic parameters of the segmented copolymers are summarized in Table 1. The hard segment weight content was calculated referring to the bands of $\delta = 8.25$ and 3.89 detected by a JEOL FX90Q NMR spectrometer. The intrinsic viscosity was measured at 30°C using 1,1,2,2-tetrachloroethane as the solvent. The melting and crystallization temperatures of the samples were obtained by DSC (Perkin-Elmer DSC-2C). All the samples were heated up to 530 K , then quenched to 210 K . The following reheating and cooling curves were recorded to determine the melting and crystallization temperatures of the samples. The scanning rate was 20 K/min .

Table 1. Characteristic parameters of EOBT segmented copolymers

Sample	$[\eta]$ (dL/g)	$\bar{L}_h^a$ (mol unit)	$T_c(^{\circ}\text{C})^b$ (soft)	$T_m(^{\circ}\text{C})^c$ (soft)	ΔH_{ms} (J/g)	$T_c(^{\circ}\text{C})^d$ (hard)	$T_m(^{\circ}\text{C})^e$ (hard)	ΔH_{mh} (J/g)
Pure PEO6000			26.7	62.9	143.2			
EOBT6000-30	1.27	12.4	27.5	50.3	80.6	150.9	198.2	26.9
EOBT6000-35	1.07	14.0	28.2	49.6	79.4	161.9	199.2	37.8
Pure PEO10000			29.5	65.5	147.0			
EOBT10000-25	1.07	13.6	28.1	3.7	91.1	155.0	206.8	24.8
EOBT10000-30	1.14	19.8	32.6	53.8	91.1	163.6	217.8	40.7

^a Average hard segment length

^b The crystallization temperature of the soft segments

^c The melting temperature of the soft segments

^d The crystallization temperature of the hard segments

^e The melting temperature of the hard segments

Sample Preparation

Films of the samples with a thickness of about 0.5 mm were cast from chloroform solution in a Teflon mold. Each strip sample of 50 mm length and 5 mm width was stretched slowly to a certain extension ratio (120%) under the temperature of 60°C .

Thermally Stimulated Deformation Recovery

In our laboratory, the deformation recovery at continuously increasing temperatures was observed directly on a hot stage controlled by a temperature regulator. The length of the stretched strip and the corresponding stretch temperature were recorded simultaneously. The heating rate was $1 \pm 0.2\text{ K/min}$.

RESULTS

Melting and Crystallization of the Soft and the Hard Segments

Figure 1 exhibits the DSC thermograms of the EOBT samples. Two endothermal or exothermal peaks occur on every melting or crystallization curve, respectively. The data of DSC results are listed in Table 1. It was pointed out in our previous work^[11, 12] that the peaks at low temperature belong to the melting or crystallization of the soft segments, while the peaks in the high temperature range belong to those of the hard segments. It is obvious that in EOBT segmented copolymers both the soft and the hard segments can crystallize although their crystallizability is lower than that of the corresponding homopolymers due to the influence of the soft and the hard segments on each other. As pointed out in our previous work^[12], the crystallizability of the soft segments decreases with the hard segment content when the soft segment molecular weight is low (< 6000). But, if the molecular weight of the soft segments is above 6,000, the flexibility of the soft segments is so good that the movement of the soft segments is slightly influenced by the hard segment content in a certain range, which results in the crystallizability of the soft segments having little change with the hard segment content.

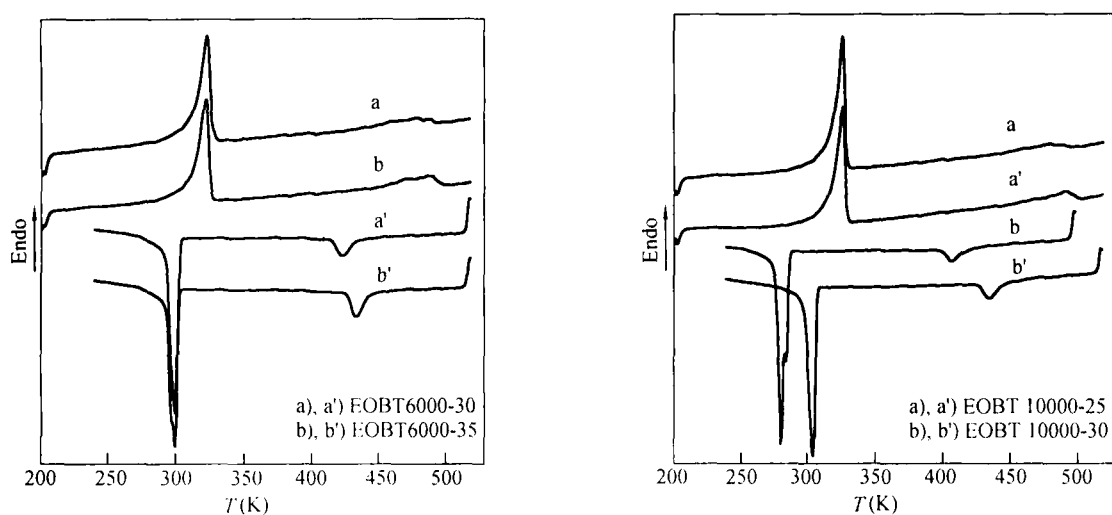


Fig. 1 DSC heating and cooling curves of EOBT segmented copolymers

The crystallization and melting temperatures of the hard segments are essentially monotonically dependent upon the hard segment length but not the hard segment weight content. It is clearly shown in Table 1 that the melting temperature of the hard segments increases with the hard segment average length. However, the corresponding melting enthalpy is also related to the soft segment molecular weight^[11, 12]. For samples with the same soft segment molecular weight, the melting enthalpy of the hard segments increases with the hard segment weight content.

Thermally Stimulated Shape Memory Behavior of EOBT Samples

Here three parameters can be used to characterize the shape memory effect of the EOBT samples as defined on the typical deformation recovery curve demonstrated in Fig. 2, and explained in our previous paper^[6].

The deformation recovery curves of EOBT samples are exhibited in Fig. 3 and Fig. 4. They are similar to the shape memory behavior of the segmented polyurethanes and EOET segmented copolymers^[1-6]. It is obvious that the deformation recovery ratio R_f of the EOBT samples increases with the soft segment molecular weight and the hard segment weight content. Comparatively, the R_f of EOBT samples (refer to Table 2) is higher than that of EOET samples^[5, 6]. The temperature of maximum deformation recovery speed (T_M) also increases dramatically with the soft segment molecular weight. However, for the average overall deformation recovery speed V_r , the hard segment content plays the major role, that is, increasing the hard segment weight content can raise the recovery speed. The V_r of EOBT6000-30 is relatively slow and the deformation recovery can be divided into two

steps. This unexpected phenomenon may be related to the sample’s severe compositional heterogeneity revealed in previous work^[8]. But it should be noted that T_M of EOBT segmented copolymers with the same soft segment molecular weight increases with the hard segment content, which is contrary to the results obtained for PU and EOET shape memory materials.

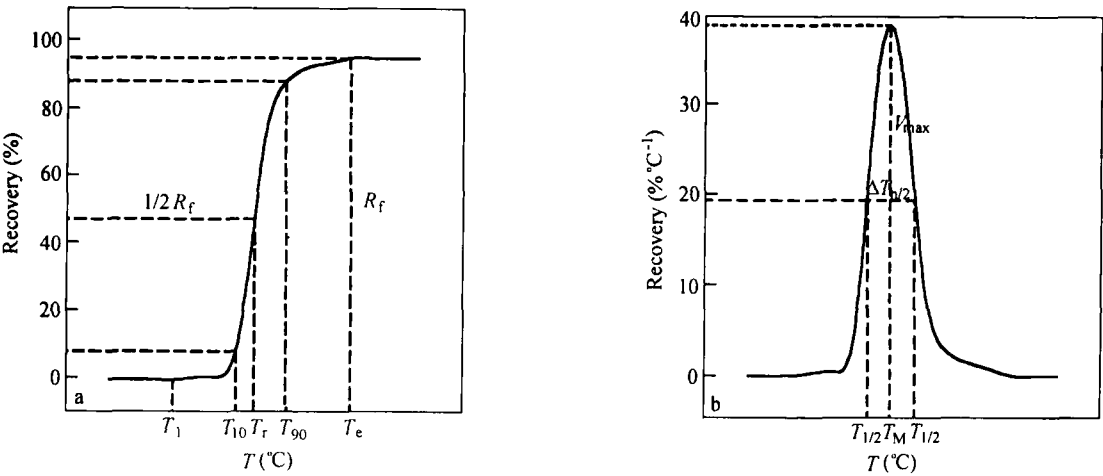


Fig.2 Thermally stimulated deformation recovery curve and its characteristics
Integral deformation recovery curve
Differential deformation recovery curve
 R_f (%): final deformation recovery ratio
 V_r (% min⁻¹): average overall deformation recovery speed $(0.8(T_{90}-T_{10})^{-1}dT/dt)$
 T_M (°C): temperature of the maximum deformation recovery speed

Table 2. Characteristics of deformation recovery of EOBT segmented copolymers

Sample	R_f (%)	T_M (°C)	V_r (% min ⁻¹)
EOBT6000-30	91	42.1	0.07
EOBT6000-35	94	45.8	0.13
EOBT10000-25	97	52.1	0.11
EOBT10000-30	95	59.9	0.16

DISCUSSION

Generally, the crystallizability of the soft segments and the stability of the physical crosslinks formed by the hard segments are considered to be the major influential factors for the thermally stimulated shape memory effect of segmented copolymers^[1, 2, 5, 6, 10]. In the EOET and PU systems, the temperature of maximum deformation recovery speed is mainly determined by the melting temperature of the soft segments, but slightly decreases with the hard segment content because with the same soft segment molecular weight, increasing the hard segment content will destroy the crystallization of the soft segments to a greater extent^[1-6]. In the EOBT samples investigated in this work, the soft segments have excellent crystallizability so that they crystallize quickly. The melting temperature and enthalpy of the soft segments are hardly affected by the hard segment content because the crystallization of the hard segments results in the phase separation to a greater extent^[12]. On the other hand, in contrast to the PU and EOET segmented copolymers, the hard segments in EOBT copolymers can form crystalline domains, which act as the physical crosslinks. Due to the hard segments confined in the crystal lattice, the stability and toughness of the physical crosslinks should be superior to those formed through polar interaction or hydrogen bonding of amorphous hard segments in PU and EOET segmented copolymers. During the stretching and recovering process of the samples, the physical crosslinks are not readily destroyed, leading to a high deformation recovery ratio. At the same time their movement, with every crystalline domain as a unit, will suffer considerable resistance when shifting in the soft segment matrix. Just for this reason, the EOBT

copolymers with high hard segment content need higher temperature for the deformation recovery. With the same soft segment molecular weight, the greater the hard segment content, the higher the crystallinity of the hard segments will be, and hence the higher the deformation recovery temperature. In conclusion it may be important to emphasize that the crystallization of the hard segments in segmented copolymers is an efficient factor for calibrating the thermally stimulated shape memory behavior of the segmented copolymer.

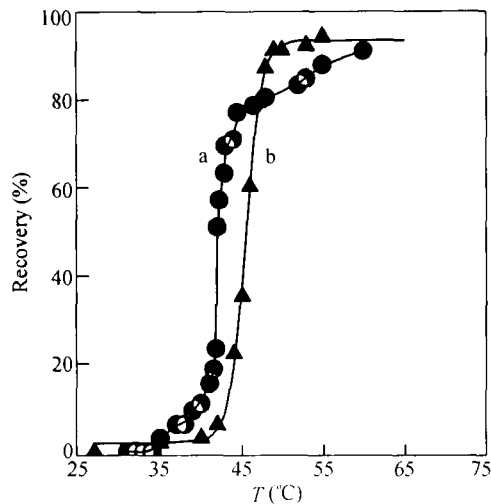


Fig. 3 Deformation recovery curves of EOBt samples (a) 6000-30 and (b) 6000-35

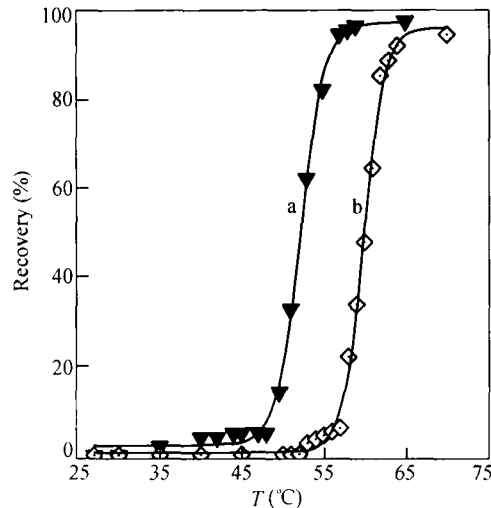


Fig. 4 Deformation recovery curves of EOBt samples (a) 10000-25 and (b) 10000-30

CONCLUSIONS

The thermally stimulated shape-memory effect of EOBt segmented copolymers in which both the soft and the hard segments can crystallize was investigated preliminarily in this paper. It was found that the physical crosslinks in the copolymers formed by the crystalline hard segments have a distinctive influence on the shape-memory effect of the materials. These crosslinks are different from those formed by the amorphous hard segments. In EOBt segmented copolymer the deformation recovery temperature is determined not only by the melting temperature of the soft segment crystals but also by the stability of the crystallized hard segment domains.

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