

## COMPOSITIONAL HETEROGENEITY OF ETHYLENE OXIDE-BUTYLENE TEREPHTHALATE SEGMENTED COPOLYMER\*

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**Abstract** A series of ethylene oxide-butylene terephthalate (EOBT) segmented copolymers with different soft segment length and hard segment content were synthesized. The compositional heterogeneity was studied by solvent extraction. The results show that the compositional heterogeneity increases when soft segment length and hard segment content increase. The compositional heterogeneity is also reflected in the crystallization behavior and morphology of soft and hard segment in EOBT segmented copolymer. The more compositional heterogeneous the EOBT segmented copolymer is, the more different the morphology and the crystallization behavior between separated fractions. Compared with ethylene oxide-ethylene terephthalate (EOET) segmented copolymer, compositional heterogeneity in EOBT segmented copolymer is weaker. But the compositional heterogeneity in EOBT segmented copolymer with long soft segment and high hard segment content is still obvious.

**Keywords** Ethylene oxide-butylene terephthalate, Segmented copolymer, Compositional heterogeneity, Crystallizability, Morphology

### INTRODUCTION

Synthesis and characterization of poly(ether ester) containing both soft and hard segment along the chain backbone have been studied in several fields in recent years. Ethylene oxide-ethylene terephthalate (EOET) segmented copolymer, poly(tetramethylene oxide)-poly(tetramethylene terephthalate), poly(ethylene terephthalate)-poly(ethylene oxide-propene oxide), poly(ethylene terephthalate)-poly(tetramethylene oxide) were synthesized and studied by Coleman<sup>[1,2]</sup>, Nishimura<sup>[3]</sup>, Kobayashi<sup>[4]</sup> and Sumoto<sup>[5]</sup>, respectively. They exhibit good mechanical and thermal property plus the advantage of biodegradability<sup>[6]</sup>, shape memory effect<sup>[7]</sup>, thermoplastic elasticity<sup>[8]</sup>, and so on.

In fact, compositional heterogeneity is inseparably linked with the existence of segmented copolymer. Those methods that have been used to study heterogeneous sample with respect to the composition of the individual macromolecules are chromatography (thin-layer chromatography<sup>[9]</sup>, gel permeation chromatography<sup>[10]</sup>, etc.) fractionation (cross-fractionation<sup>[11]</sup>, solvent extraction<sup>[12-15]</sup>, etc.) and dynamic light scattering<sup>[16]</sup>.

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By solvent extraction, our previous works revealed that ethylene oxide-ethylene terephthalate segmented copolymers exhibit compositional heterogeneity<sup>[12, 17]</sup>. EOET segmented copolymers with long soft segment and high hard segment content have shown an obvious compositional heterogeneity.

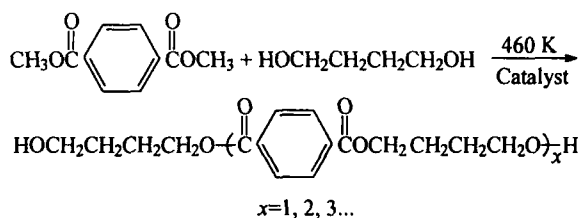
The hard segment content of EOET segmented copolymer studied<sup>[7, 12, 16-19]</sup> was limited in a low range because of the relative low reactivity of ethylene terephthalate prepolymer with hydroxyl terminated poly(ethylene oxide). To study the relationship between heterogeneity and composition further, ethylene terephthalate segment is substituted with butylene terephthalate segment. Up to now, ethylene oxide-butylene terephthalate (EOBT) segmented copolymer has seldom been studied. It was first synthesized by Wolfe<sup>[20]</sup>. Jerzy<sup>[21]</sup> investigated its hardness and thermal properties, and found that the hard segment content of polyester-polyether varied over a wide range. In this research, a series of EOBT segmented copolymer with different soft segment length and hard segment content were synthesized too. Using the segmented copolymer with a wide hard segment content range, we studied the relation of the compositional heterogeneity with both soft segment length and hard segment content. The effect of compositional heterogeneity on crystallization and morphology are discussed. The results presented here, together with the data about EOET copolymers, enable us to understand the compositional heterogeneity in EOBT copolymer more deeply. Our goal in this work is to elucidate the compositional heterogeneity of EOBT segmented copolymer and the influences of the compositional heterogeneity on the crystallization behavior and morphology of the segmented copolymer.

## EXPERIMENTAL

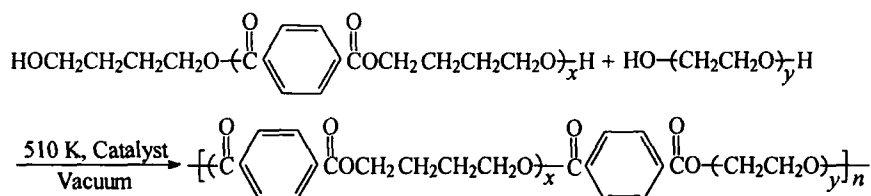
### Synthesis

EOBT segmented copolymers were synthesized via two steps. The first involved the ester exchange between dimethyl terephthalate and butylene glycol. The second was polycondensation of PBT prepolymer and hydroxyl terminated PEO.

Transesterification:



Polycondensation:



During the synthesis process, all the materials were proportionally added according to a certain mixture ratio. Thus, the hard segment content can be adjusted by changing the  $x/y$  ratio.

The characterization of the synthesized samples is summarized in Table 1. Samples are signified by the weight percent of hard segment and molecular weight of the soft segment, e.g. EOBT 4000-35 represents that the copolymer contains 35% hard segment and the molecular weight of soft segment is 4000.

**Table 1.** Parameters of EOBT segmented copolymers

| Sample        | $W_h(\%)$ |        | $L_{n,h}$ | $[\eta](\text{dL}\cdot\text{g}^{-1})$ | Solubility in $\text{CHCl}_3$ * |
|---------------|-----------|--------|-----------|---------------------------------------|---------------------------------|
|               | Theory    | By NMR |           |                                       |                                 |
| EOBT 2000-25  | 25        | 23.8   | 2.84      | 1.05                                  | S                               |
| EOBT 2000-30  | 30        | 30.4   | 3.97      | 1.08                                  | S                               |
| EOBT 2000-35  | 35        | 35.7   | 5.05      | 0.97                                  | S                               |
| EOBT 2000-40  | 40        | 40.1   | 6.09      | 1.52                                  | S                               |
| EOBT 2000-45  | 45        | 44.3   | 7.23      | 1.18                                  | S                               |
| EOBT 2000-60  | 60        | 60.2   | 13.75     | 0.99                                  | PS                              |
| EOBT 2000-70  | 70        | 67.3   | 18.71     | 0.64                                  | PS                              |
| EOBT 4000-30  | 30        | 30.2   | 7.87      | 1.36                                  | S                               |
| EOBT 4000-35  | 35        | 32.1   | 8.60      | 0.95                                  | S                               |
| EOBT 4000-40  | 40        | 40.5   | 12.38     | 0.94                                  | S                               |
| EOBT 4000-45  | 45        | 47.1   | 16.19     | 0.83                                  | PS                              |
| EOBT 6000-25  | 25        | 25.4   | 9.29      | 1.40                                  | S                               |
| EOBT 6000-30  | 30        | 31.3   | 12.39     | 1.27                                  | S                               |
| EOBT 6000-35  | 35        | 33.9   | 13.99     | 1.07                                  | S                               |
| EOBT 6000-40  | 40        | 39.2   | 17.58     | 1.22                                  | PS                              |
| EOBT 6000-45  | 45        | 45.3   | 22.59     | 1.55                                  | PS                              |
| EOBT 10000-25 | 25        | 23     | 13.58     | 1.07                                  | S                               |
| EOBT 10000-30 | 30        | 30.3   | 19.76     | 1.14                                  | S                               |
| EOBT 10000-35 | 35        | 33.65  | 23.05     | 1.14                                  | S                               |
| EOBT 10000-40 | 40        | 40.8   | 31.33     | 1.44                                  | PS                              |
| EOBT 10000-45 | 45        | 43.3   | 34.71     | 1.30                                  | PS                              |
| EOBT 10000-50 | 50        | 50.0   | 45.45     | 0.59                                  | PS                              |

\*S: soluble in  $\text{CHCl}_3$ , PS: partly soluble in  $\text{CHCl}_3$

$W_h$ : weight percent of hard segment content,  $L_{n,h}$ : average length of hard segment

### Solvent Extraction

All EOBT segmented copolymers were extracted with tetrahydrofuran (THF). Each sample was separated into a soluble fraction and an insoluble fraction. Fractions were cast on a glass plate, then dried in a vacuum oven.

### Measurement

#### Intrinsic viscosity

The EOBT segmented copolymers were measured at 30°C in phenol and tetrachloroethane mixed solvent (1:1 V/V).

#### Proton spectra

All samples and fractions were measured by JEOL FX-90Q spectrometer. Tetramethylsilane was used as the standard. The solvent was trifluoroacetic acid.

#### DSC measurements

DSC curves were measured under the protection of ultra-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 first scanned from 300 K to 530 K at a rate of 40 K/min and maintained at 530 K for 1 min to eliminate the influence of thermal history. Then it was quenched to 200 K. The sample was reheated to 520 K to get melting curves, and cooled to 200 K to get thermal crystallization curves. The melting temperature ( $T_m$ ) was recorded at the maximum of the corresponding endotherm peak in the reheating curve. The crystallization temperature ( $T_c$ ) was obtained from the cooling curve. Both heating rate and cooling rate were 20 K/min.

### Spherulite Morphology

Films sandwiched between clean microscope cover glasses were used. Before observation they were first heated to a treating temperature, 503 K, then cooled down to 413 K. After the isothermal crystallization of PBT segments at 413 K for 10 h, the PEO segments were isothermally

crystallized at 308 K for 20 h. By using a polarizing light microscope equipped with a hot stage, whose temperature was automatically controlled, the morphological observation of samples was carried out at room temperature and 343 K, respectively.

## RESULTS AND DISCUSSIONS

### *Compositional Heterogeneity of EOBT Segmented Copolymer*

Figure 1 shows the  $^1\text{H}$ -NMR spectra of the EOBT segmented copolymer with different hard segment content. Each spectrum has four obvious bands. As we can see, with increasing hard segment content, the intensity of bands changes regularly, so we can easily assign the peaks in the spectra for the hard segment and the soft segment. The assignment of the bands is listed in Table 2. The hard segment content ( $W_h\%$ ) can be calculated from the integration of band b and d by the following equation:

$$W_h\% = \frac{I_a \times 220 + (I_d - I_a) \times 148}{I_b \times 44 + I_a \times 220 + (I_d - I_a) \times 148} \times 100\%$$

Table 2. Assignment of chemical shift band in proton spectra

| Number | Chemical Shift | Assignment                                                             |
|--------|----------------|------------------------------------------------------------------------|
| A      | 2.2            | $-\text{OCH}_2\overset{*}{\text{CH}}_2\text{CH}_2\text{CH}_2\text{O}-$ |
| B      | 3.9            | $-\text{OCH}_2\overset{*}{\text{CH}}_2\overset{*}{\text{O}}-$          |
| C      | 4.6            | $-\text{ArCOOCH}_2\overset{*}-$                                        |
| D      | 8.2            | $\text{ArH}^*$                                                         |

The real hard segment content of samples calculated from the NMR curves are listed in Table 1. In order to study the compositional heterogeneity of EOBT segmented copolymers, we examine their solubility in chloroform at room temperature. From Table 1, it is found that the minimum hard segment content of copolymer that is partly soluble in chloroform decreases with an increase in soft segment length. The longer the soft segment, the greater the difficulty with which the polymer dissolves. Simultaneously, the greater the hard segment content, the greater the difficulty with which the polymer dissolves. This suggests that EOBT segmented copolymers with long soft segment or high hard segment content may somehow be more compositionally heterogeneous.

Because chloroform can dissolve most of the samples and THF is a relatively weak solvent for the polyester-polyether, the ethylene oxide segment dissolves in THF readily while butylene terephthalate segment cannot dissolve in THF. Therefore, THF is chosen to extract the EOBT segmented copolymer according to the large difference in solubility between the hard segment and the soft segment.

Figure 2 shows the NMR spectra of original sample and separated fractions of EOBT 10000-30 segmented copolymer. Bands of hard segment are evidently stronger for the insoluble fraction than that for the soluble fraction. It implies that the soluble fraction is relatively rich in soft segment and the insoluble fraction is rich in hard segment. The compositional heterogeneity is exhibited very clearly. A similar situation has also been found in other samples.

The relative amounts and composition of these fractions are listed in Table 3. The second column is the relative amounts of insoluble fraction after solvent extraction. If EOBT segmented copolymers contain more hard segment, the amount of residue after extraction was large. This agrees well with the conclusion from the solubility in chloroform. However, the amount of residue after extraction with soft segment length in EOBT segmented copolymer was unexpected. The residue of EOBT 6000 is more than that of EOBT 4000, as we expected. But the amount of corresponding EOBT 10000 drops greatly. This may be attributed to the strong interaction between

solvent and EOBT segmented copolymer with long soft segment.

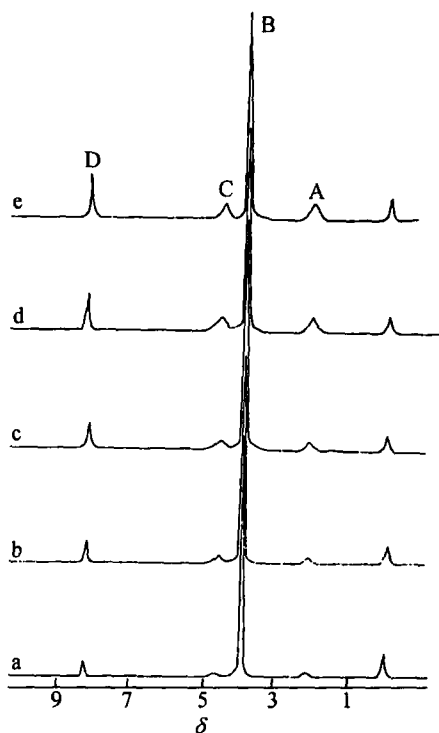


Fig. 1  $^1\text{H}$ -NMR spectra of samples containing 6000 PEO

a) EOBT 6000-25, b) EOBT 6000-30, c) EOBT 6000-35, d) EOBT 6000-40, e) EOBT 6000-45

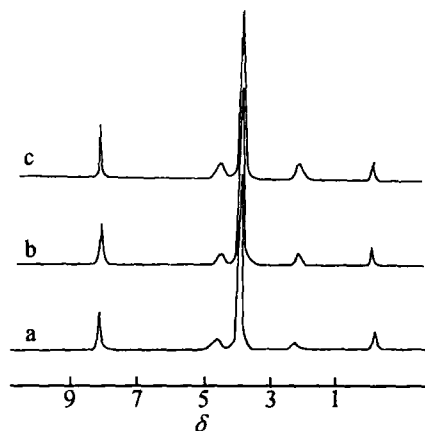


Fig. 2  $^1\text{H}$ -NMR spectra of EOBT 10000-35

a) Soluble fraction, b) Original fraction, c) Insoluble fraction

Table 3.  $^1\text{H}$ -NMR analytical results for original samples and separated fractions of EOBT segmented copolymer extracted with THF

| Sample       | Residue after extraction (%) | Insoluble fraction |          | Original Sample |          | Soluble fraction |          |
|--------------|------------------------------|--------------------|----------|-----------------|----------|------------------|----------|
|              |                              | $W_h(\%)$          | $L_{nh}$ | $W_h(\%)$       | $L_{nh}$ | $W_h(\%)$        | $L_{nh}$ |
| EOBT4000-30  | 40.8                         | 33.7               | 9.58     | 30.2            | 8.83     | 28.7             | 7.59     |
| EOBT4000-35  | 61.3                         | 36.8               | 10.98    | 32.5            | 9.08     | 28.8             | 7.63     |
| EOBT6000-30  | 59.9                         | 37.3               | 16.62    | 31.3            | 12.73    | 23.8             | 8.73     |
| EOBT6000-35  | 74.8                         | 36.5               | 16.06    | 34.0            | 14.40    | 27.5             | 10.6     |
| EOBT6000-40  | 76.7                         | 42.2               | 20.40    | 39.2            | 18.02    | 31.2             | 12.67    |
| EOBT10000-25 | 30.2                         | 27.8               | 17.76    | 23              | 13.78    | 20.8             | 12.11    |
| EOBT10000-30 | 39.2                         | 42.7               | 34.37    | 30.3            | 20.05    | 22.5             | 13.39    |
| EOBT10000-35 | 43.2                         | 54.8               | 55.92    | 33.7            | 23.45    | 16.7             | 9.25     |

Compositional heterogeneity is severe in EOBT segmented copolymer with high hard segment content. This can be confirmed further from the change of hard segment content and average hard segment length in fractions. In EOBT segmented copolymer with low hard segment content, the hard segment content of separated fractions are close. In those with high hard segment content, the values are different greatly. The change of average length of hard segment in fractions illustrates the conclusion more evidently. The tendency of hard segment content and average hard segment length in separated fractions with the change of soft segment length is also very clear. Compositional heterogeneity is more obvious in EOBT segmented copolymer with longer soft segment.

### Crystallization Behavior of EOBT Segmented Copolymer

The compositional heterogeneity will inevitably affect the crystallization behavior in EOBT segmented copolymers. Figures 3 and 4 show the melting and thermal crystallization curves of the original sample, and the separated fractions of EOBT 10000-35 and EOBT 4000-30 respectively. The melting peak and crystallization peak at high temperature should belong to the hard segment; while the peaks at low temperature should belong to the soft segment. Compared with insoluble fraction, the melting temperature and the crystallization temperature of soft segment in soluble fraction shift to high temperature, the melting peak and the crystallization peak become stronger. While the melting temperature and crystallization temperature of hard segment in soluble fraction shift to low temperature, the melting peak and crystallization peak become weaker or even disappear.

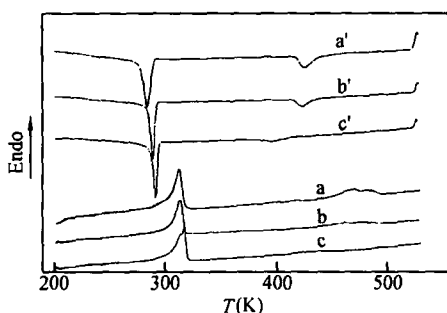


**Fig. 3** DSC melting and thermal crystallization spectra of EOBT 4000-35

a), a') Insoluble fraction; b), b') Original sample, c), c') Soluble fraction

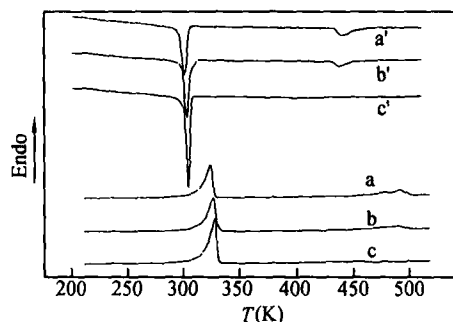


**Fig. 4** DSC melting and thermal crystallization spectra of EOBT 10000-30

a), a') Insoluble fraction; b), b') Original sample, c), c') Soluble fraction

The intrinsic viscosity of original samples and separated fractions of EOBT 10000 is listed in Table 4. There is little difference in intrinsic viscosity between the soluble fraction and insoluble fraction. So extraction with THF does not separate the segmented copolymers according to their molecular weight, but to their chemical composition. Therefore, the difference in crystallization behavior between the separated fractions does not correspond to the molecular weight but to chemical composition.

**Table 4.** Intrinsic viscosity of original samples and separated fractions of EOBT segmented copolymers

| Sample        | Intrinsic viscosity (dL/g) |                 |                    |
|---------------|----------------------------|-----------------|--------------------|
|               | Soluble fraction           | Original sample | Insoluble fraction |
| EOBT 10000-25 | 1.07                       | 1.07            | 1.16               |
| EOBT 10000-30 | 1.11                       | 1.14            | 1.19               |
| EOBT 10000-35 | 1.13                       | 1.14            | 1.15               |

All the corresponding data of DSC measurement for EOBT segmented copolymer with compositional heterogeneity are summarized in Table 5. The crystallizability demonstrates the compositional heterogeneity in EOBT segmented copolymers. The melting temperature and the crystallization temperature of soft segment in soluble fraction are higher than those in insoluble fraction. The corresponding enthalpy in soluble fraction is higher, too. This is attributed to the low hard segment content in soluble fraction. The lower the hard segment content, the less the hard segment affects the crystallization of soft segment. On the other hand, the higher the soft segment content, the more the soft segment affects the crystallization of hard segment. So the melting temperature and the crystallization temperature of hard segment in soluble fraction are lower than those in insoluble fraction. The corresponding enthalpy in soluble fraction is lower, too.

**Table 5.** Data from DSC curves of original samples and separated fractions of EOBT segmented copolymer

| Sample        | Soft segment |                                      |              |                                      | Hard segment |                                      |              |                                      |
|---------------|--------------|--------------------------------------|--------------|--------------------------------------|--------------|--------------------------------------|--------------|--------------------------------------|
|               | $T_m$<br>(K) | $\Delta H_m$<br>(J·g <sup>-1</sup> ) | $T_c$<br>(K) | $\Delta H_c$<br>(J·g <sup>-1</sup> ) | $T_m$<br>(K) | $\Delta H_m$<br>(J·g <sup>-1</sup> ) | $T_c$<br>(K) | $\Delta H_c$<br>(J·g <sup>-1</sup> ) |
| EOBT4000-30s  | 311.6        | 49.41                                | 287.1        | 47.44                                | 439.4        | 5.19                                 | 397.9        | 12.08                                |
| EOBT4000-30o  | 313.7        | 38.92                                | 285.9        | 39.84                                | 460.0        | 6.98                                 | 398.3        | 12.29                                |
| EOBT4000-30I  | 311.8        | 40.63                                | 288.5        | 44.14                                | 460.2        | 9.41                                 | 411.1        | 12.41                                |
| EOBT4000-35s  | 316.8        | 55.01                                | 292.2        | 51.75                                | 429.6        | 5.81                                 | 397.8        | 7.52                                 |
| EOBT4000-35o  | 313.5        | 43.68                                | 298.5        | 47.07                                | 459.6        | 12.12                                | 424.5        | 11.08                                |
| EOBT4000-35I  | 312.5        | 34.40                                | 285.2        | 39.12                                | 469.1        | 14.38                                | 426.5        | 14.88                                |
| EOBT6000-30s  | 323.6        | 63.58                                | 300.6        | 66.29                                |              |                                      |              |                                      |
| EOBT6000-30o  | 323.6        | 54.80                                | 295.4        | 55.05                                | 480.3        | 8.19                                 | 422.9        | 10.07                                |
| EOBT6000-30I  | 321.0        | 44.22                                | 294.5        | 46.27                                | 471.2        | 9.78                                 | 429.3        | 12.83                                |
| EOBT6000-35s  | 326.2        | 60.20                                | 299.1        | 55.89                                |              |                                      |              |                                      |
| EOBT6000-35o  | 325.2        | 50.33                                | 296.3        | 49.32                                | 489.0        | 13.42                                | 434.6        | 12.50                                |
| EOBT6000-35I  | 319.8        | 41.26                                | 297.1        | 35.78                                | 489.1        | 14.12                                | 442.9        | 17.81                                |
| EOBT6000-40s  | 322.8        | 55.38                                | 303.5        | 67.51                                |              |                                      |              |                                      |
| EOBT6000-40o  | 323.3        | 46.02                                | 304.4        | 41.17                                | 494.2        | 8.61                                 | 450.4        | 12.41                                |
| EOBT6000-40I  | 323.3        | 27.17                                | 302.0        | 28.2                                 | 495.1        | 9.15                                 | 452.1        | 11.62                                |
| EOBT10000-25s | 328.5        | 79.80                                | 300.0        | 76.41                                |              |                                      |              |                                      |
| EOBT10000-25o | 325.7        | 48.91                                | 302.9        | 48.28                                | 495.7        | 7.15                                 | 449.0        | 14.30                                |
| EOBT10000-25I | 324.7        | 55.26                                | 301.5        | 52.00                                | 481.4        | 9.66                                 | 439.7        | 17.81                                |
| EOBT10000-30s | 328.1        | 80.76                                | 305.2        | 77.87                                | 439.6        | 3.47                                 |              |                                      |
| EOBT10000-30o | 317.9        | 67.93                                | 309.0        | 65.25                                | 478.0        | 11.62                                | 450.3        | 11.58                                |
| EOBT10000-30I | 315.7        | 52.75                                | 306.1        | 52.12                                | 479.2        | 17.64                                | 455.2        | 19.27                                |
| EOBT10000-35s | 329.2        | 83.56                                | 302.9        | 83.31                                |              |                                      |              |                                      |
| EOBT10000-35o | 319.1        | 62.63                                | 309.4        | 62.20                                | 487.3        | 14.23                                | 446.7        | 12.71                                |
| EOBT10000-35I | 315.8        | 41.09                                | 306.8        | 37.33                                | 486.7        | 23.57                                | 458.8        | 24.37                                |

s: soluble fraction, o: original sample i: insoluble fraction

If EOBT segmented copolymers contain more hard segment, the crystallization behavior of separated fractions differs more pronouncedly. Simultaneously, with the increasing soft segment length, the larger disparity of crystallization behavior between separated fractions suggests greater heterogeneity in original sample. Crystallization behavior reflects the compositional heterogeneity. The difference of crystallizability in separated fractions becomes larger if the EOBT segmented copolymer is more compositionally heterogeneous.

### Morphology of EOBT Segmented Copolymer

To further understand the crystallization behavior of soft and hard segments, we studied the morphology of EOBT copolymer with PLM. Micrograph photos of fractions and samples of EOBT 10000-25 and EOBT 6000-30 are illustrated in Figs. 5 and 6, respectively. They also exhibit the compositional heterogeneity of EOBT segmented copolymer.

Both hard segment and soft segment can crystallize simultaneously in EOBT segmented copolymers from the treatment described above. Soft segments crystallize much more easily than hard segments. Thus at room temperature, only soft segment spherulites can be observed. Minute hard segment spherulites are hidden or superimposed by huge soft segment spherulites. When the soft segment spherulites melt at 70°C, the hard segment spherulites emerge in the field and can only be observed at higher magnification.

Spherulites of soft segment in EOBT segmented copolymers are large and perfect. Compared with those in original sample, the character and perfection of the soft segment spherulites in separated fractions remain essentially unaltered. At the same time, the size of soft segment spherulites in insoluble fraction decreases greatly, while that in soluble fraction increases. This is caused by the influence of the hard segment on the crystallizability of the soft segment. The soft

segment and hard segment are on the same molecular chain, so they will necessarily affect the crystallization behavior of each other. The insoluble fraction contains more hard segment, so the spherulites of soft segment are smaller.

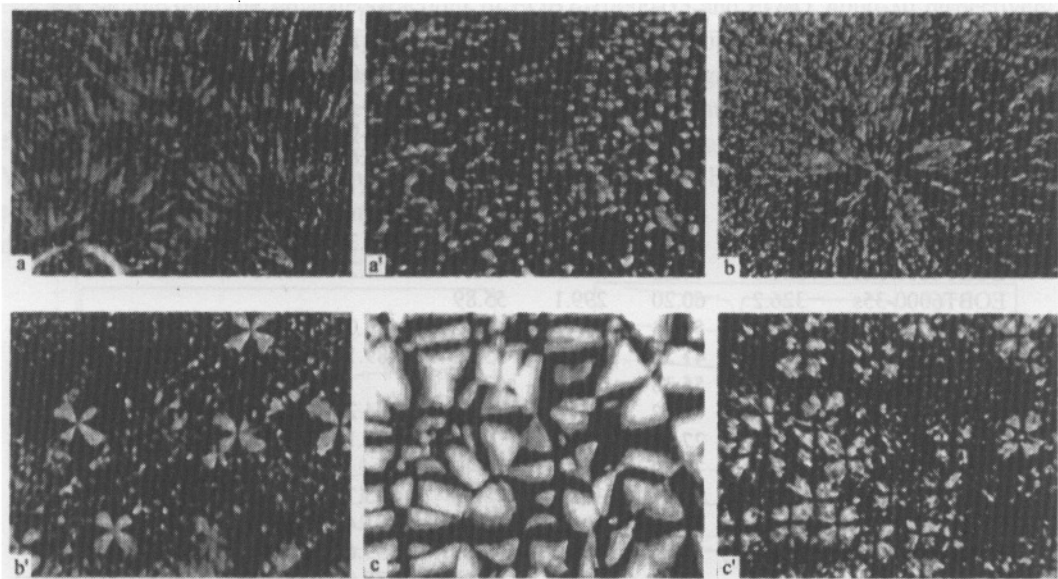


**Fig. 5** Polarizing light micrographs for EOBT 10000-25

a), a') Soluble fraction; b), b') Original sample; c), c') Soluble fraction

a), b), c) Taken at room temperature,  $\times 40$ ; a'), b'), c') Taken at  $70^{\circ}\text{C}$ ,  $\times 160$

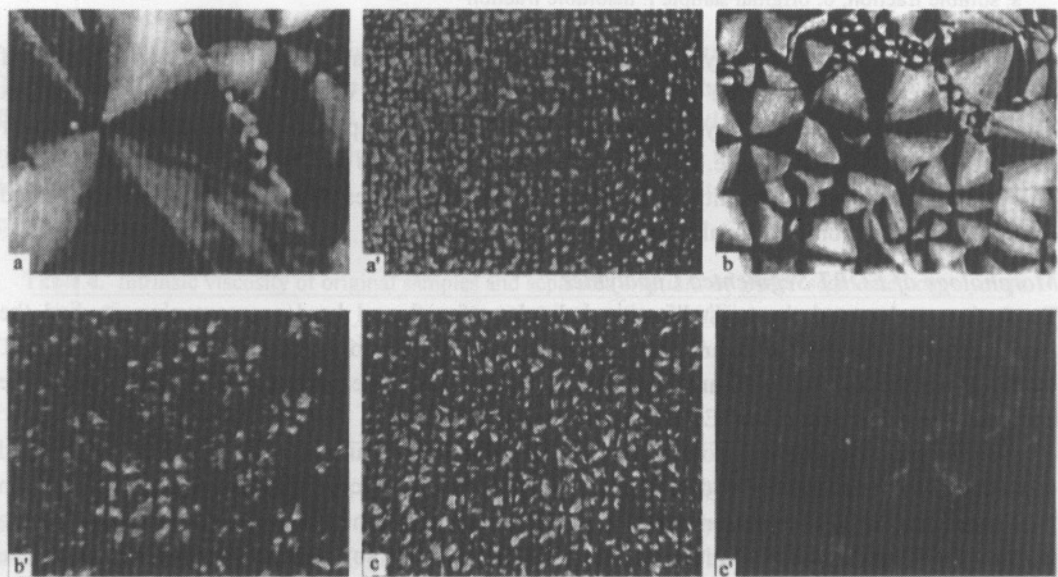


**Fig.6** Polarizing light micrographs for EOBT 6000-30

a), a') Soluble fraction; b), b') Original sample; c), c') Soluble fraction

a), b), c) Taken at room temperature,  $\times 40$ ; a'), b'), c') Taken at  $70^{\circ}\text{C}$ ,  $\times 160$

Compared with the hard segment spherulites in the original sample, in insoluble fraction the size and the amount of hard segment spherulites increase. However, The spherulites of hard segment disappear in soluble fraction. Because after extraction the soluble fraction is devoid of segmented copolymer with long hard segment, which can agglomerate to form spherulites. So the

hard segments in soluble fraction cannot form spherulites. EOBT segmented copolymers with long hard segment length exist in insoluble fraction. Thus much bigger spherulites of hard segments would be observed in the insoluble fractions.

The morphology of both hard segment and soft segment in EOBT segmented copolymer confirm the existence of compositional heterogeneity observed from DSC and NMR experiments.

### **Comparison of Compositional Heterogeneity in EOBT and EOET Segmented Copolymer**

In our previous work, we found that EOET segmented copolymers with high hard segment content and long soft segment length showed compositional heterogeneity. EOBT segmented copolymer is analogous to EOET segmented copolymer. It is interesting to compare the compositional heterogeneity between EOBT and EOET segmented copolymers.

The results of extraction of EOET segmented copolymer are listed in Table 6. Hard segment content in insoluble fraction is about 1.33 times as that in soluble fraction for EOBT 6000-35. For EOET 6000-35, hard segment content in insoluble fraction is about 1.73 times as that in soluble fraction. This value even exceeds the corresponding value (1.35 times) in EOBT 6000-40. If the average length of hard segment is used in comparison, the difference of compositional heterogeneity between EOET and EOBT segmented copolymer is more obvious. The average length of the hard segment in insoluble fraction is about 1.52 times of that in soluble fraction for EOBT 6000-35. For EOET 6000-35, the average length of hard segment in insoluble fraction is about 2.50 times of that in soluble fraction. This value also exceeds the corresponding value (1.61 times) of EOBT 6000-40. EOBT 10000-25 and EOET 10000-25 are other typical examples. The average length of hard segment in insoluble fraction is 1.47 times of that in soluble fraction for EOBT 10000-25. Average length of hard segment in insoluble fraction is about 1.81 times of that in soluble fraction for EOET 10000-25. This value is larger than that of EOBT 10000-25, but smaller than that (2.57 times) of EOBT 10000-30.

**Table 6.** <sup>1</sup>H-NMR analytical results for soluble and insoluble fractions of EOET segmented copolymer extracted by chloroform

| Sample       | Residue after extraction (%) | Insoluble fraction |           | Original sample |           | Soluble fraction |           |
|--------------|------------------------------|--------------------|-----------|-----------------|-----------|------------------|-----------|
|              |                              | $W_h$ (%)          | $L_{n,h}$ | $W_h$ (%)       | $L_{n,h}$ | $W_h$ (%)        | $L_{n,h}$ |
| EOET6000-30  | 39.2                         | 37.8               | 19.2      | 31.5            | 14.4      | 27.1             | 11.6      |
| EOET6000-35  | 48.3                         | 51.6               | 33.3      | 37.0            | 18.4      | 29.8             | 13.3      |
| EOET10000-25 | 34.4                         | 33.9               | 26.8      | 27.0            | 19.3      | 22.1             | 14.8      |
| EOET20000-25 | 29.0                         | 57.8               | 142.7     | 27.8            | 39.9      | 13.7             | 16.5      |

It seems that EOET segmented copolymer is more heterogeneous than EOBT segmented copolymer. However, the compositional heterogeneity in EOBT segmented copolymer with long soft segment and high hard segment content is still obvious.

The difference of compositional heterogeneity between EOET and EOBT segmented copolymer may be attributed to the different reaction activity of PET prepolymer and PBT prepolymer with hydroxyl terminated PEO macromolecules. When the molecular weight of the soft segment is 10000, EOBT 10000-45 could be synthesized successfully. If BT segment is substituted by ET segment, more homopolymer can be produced in the synthesis of EOET 10000-30. The hard segment content of EOBT segmented copolymer becomes higher than that of EOET segmented copolymer. The difference between reaction activity of PET and PBT prepolymer may be attributed to the following factors. First, PBT macromolecules are more flexible than PET macromolecules. Second, PBT prepolymer is more compatible with polyether. In the poly(butylene terephthalate)-poly(tetramethylene oxide)<sup>[21]</sup>, the hard segment can even increase up to 87%. Undoubtedly, the causes that lead to compositional heterogeneity in EOET and EOBT segmented copolymer should be further studied.

## CONCLUSION

EOBT segmented copolymers with long soft segment and high hard segment content are heterogeneous compositionally. They can be separated into soluble and insoluble fractions by extraction with tetrahydrofuran. The EOBT copolymers exhibit more compositional heterogeneity when the soft segment is longer or the hard segment content is higher. With increasing hard segment content or molecular weight of PEO segment, the difference between the average hard segment length of the separated fractions of EOBT segmented copolymers becomes larger. Different crystallization behavior and morphology of insoluble and soluble fractions also reflect the compositional heterogeneity in EOBT segmented copolymers. Compared with EOET segmented copolymers, the compositional heterogeneity in EOBT segmented copolymers is somehow weaker, but that in EOBT segmented copolymers with long soft segment and high hard segment content is still obvious.

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