Block Copolyetheresters. V. Low-Temperature Properties of Thermotropic Block Copolyetheresters

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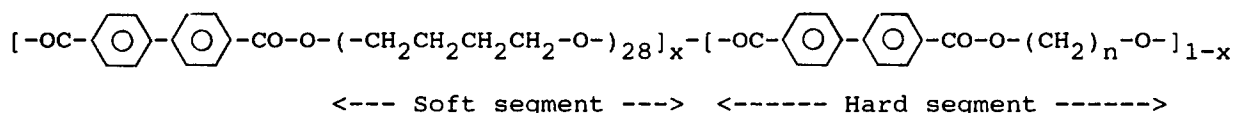
SYNOPSIS

The low-temperature properties of block copolyetheresters with hard segments of poly(alkylene p,p'-bibenzoate) and soft segments of poly(tetramethylene ether) were investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). In the temperature range of -100 to $60°C$, two transition temperatures, a glass transition temperature (T_g) and a melting temperature (T_m), were found by DSC and are attributed to the polyether segments. The T_g monitored by DSC of the polyether segments of the block copolyetheresters is around $-68°C$ and independent of the composition and the type of polyester segment. Thus, the amorphous parts of the polyether segments should be immiscible with the amorphous parts of the polyester segments. The polyether segments of the block copolyetheresters exhibit a lower T_m and a lower crystallinity than those of the poly(tetramethylene ether)glycol due to the presence of the polyester segments. The crystallizability of the polyether segments is dependent on the composition to some extent. The DMA data show that the dynamic modulus drops more abruptly around -10 to $15°C$, indicating that the mechanical properties may change significantly due to the melting of the polyether segments. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Most hard segments of block copolyetheresters described in the literature are semicrystalline polyesters.[1-6] It will be very interesting if the hard segment exhibits liquid crystalline behavior. The presence of the liquid crystalline phase may influence the rheological properties, crystalline properties, molecular orientation after processing, and physical properties. Various poly(alkylene p,p'-bibenzoate)s have been found to show thermotropic liquid crystalline behavior.[7-10] We designed these thermotropic polyesters as the hard segments of block copolyetheresters. The block copolyetheresters with hard segments of poly(alkylene p,p'-bibenzoate) and soft segments of poly(tetramethylene ether) were prepared by melt polycondensation of dimethyl p,p'-bibenzoate, a poly(tetramethylene ether)glycol with a molecular weight of 2000 g/mol, and an alkylene glycol described in detail previously.[11] These block copolyetheresters have the general formula as follows:

$$[-OC-\langle O \rangle-\langle O \rangle-CO-O-(-CH_2CH_2CH_2CH_2-O-)_{28}]_x-[-OC-\langle O \rangle-\langle O \rangle-CO-O-(CH_2)_n-O-]_{1-x}$$

<--- Soft segment ---> <------ Hard segment ------>

where x is the molar fraction of poly(tetramethylene ether) unit of the diol units in the polymers and n is the number of methylene units, which is from 2 to 10, and each block copolyetherester is denoted as BBn-PE(x).

The newly prepared block copolyetheresters were characterized by DSC and a polarized microscope, and some polymers were found to exhibit thermo-

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tropic liquid crystallinity. The glass transition temperature (T_g) and crystalline properties of the polyether soft segments will affect the low-temperature performance. In this article, the thermal properties and dynamic mechanical properties at low temperatures are investigated by differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), respectively.

EXPERIMENTAL

Materials

The block copolyetheresters with hard segments of poly(alkylene p,p'-bibenzoate) and soft segments of poly(tetramethylene ether) were prepared by melt polycondensation as described previously.[11] The polymers used in this study and their intrinsic viscosity values are listed in Table I.

Measurements

The X-ray diffraction patterns were recorded by a Mac Science diffractometer equipped with a Laue camera. The texture was investigated by a Leitz polarizing microscope equipped with a heating stage. The DSC measurements were carried out on a DuPont 910 DSC under nitrogen, and the samples were encapsulated in aluminum pans and scanned against an empty reference pan at a heating rate of 20°C/min. The scanned temperature range was from −100 to 60°C. The dynamic mechanical properties from −100 to 100°C were determined at a frequency

of 1 Hz and a heating rate of 5°C/min by a Perkin-Elmer DMA 7 with a three-point bending mode.

RESULTS AND DISCUSSION

X-ray Diffraction

Some of the block copolyetheresters have been found to exhibit a smectic phase as investigated by the DSC and polarized microscope.[11] This can be further proven by the X-ray diffraction study.

The X-ray diffraction patterns of BB5-PE(0.1) and BB7-PE(0.1) are shown in Figures 1 and 2, respectively. There is a sharp inner ring at Bragg spacing d = 1.58 and 1.73 nm, respectively, for BB5-PE(0.1) and BB7-PE(0.1). The observed layered spacing of the inner ring is slightly shorter than is the fully extended length of the repeat unit of the polyester segments, indicating possible existence of a smectic phase.[9] Except for BB2-PE(0.1), other BBn-PE(0.1)s exhibit an inner ring at d greater than 1 nm. Thus, the BBn-PE(0.1) series of block copolyetheresters with n = 3–10 may exhibit a smectic phase.

The polyether segments of the block copolyetheresters are amorphous above 25°C; thus, the X-ray diffraction peaks measured at room temperature contribute to the polyester segments. BB7-PE(0.1) exhibits five diffraction rings in the range of d = 0.3–0.6 nm as shown in Figure 1. All the BBn-PE(0.1)s except BB5-PE(0.1) exhibit some X-ray diffraction rings at d below 0.7 nm. However BB5-PE(0.1) shows a diffuse ring at d = 0.44 nm as shown in Figure 2, which indicates that the polyester seg-

Table I   The Intrinsic Viscosity (IV), T_g, T_m, ΔH_m and $\Delta H'_m$ Values for the Block Copolyetheresters

	IV (dL/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	$\Delta H'_m$ (J/g)
PTMEG 2000	—	−74	29	75.2	75.2
BB2-PE(0.1)	0.18	−67	22	15.7	36.3
BB2-PE(0.3)	0.99	−67	19	28.8	40.8
BB3-PE(0.1)	0.47	−67	20	16.0	38.0
BB3-PE(0.3)	0.98	−67	21	30.0	43.0
BB4-PE(0.1)	0.41	−68	18	15.2	37.0
BB4-PE(0.3)	1.46	−68	19	26.6	38.6
BB5-PE(0.1)	1.00	−67	21	14.1	35.3
BB6-PE(0.1)	0.99	−69	17	8.9	22.8
BB6-PE(0.2)	1.02	−69	15	14.9	26.1
BB6-PE(0.3)	1.50	−66	14	20.2	29.9
BB7-PE(0.1)	0.84	−69	22	5.8	15.2
BB8-PE(0.1)	0.88	−69	11	7.6	20.4
BB9-PE(0.1)	0.99	−69	11	6.6	18.1
BB10-PE(0.1)	1.03	−69	10	6.3	17.7

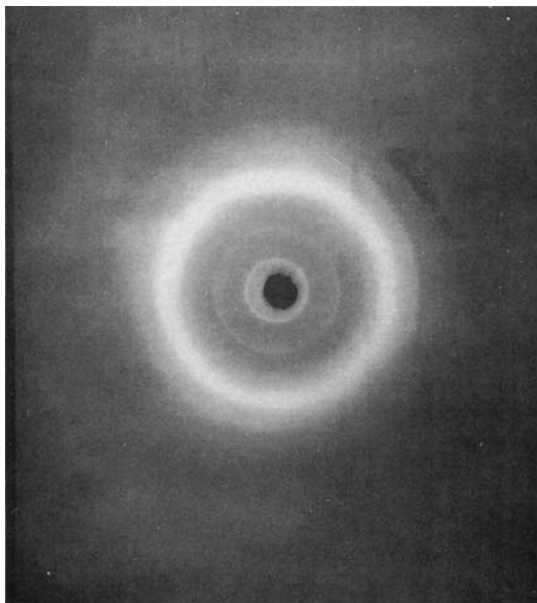**Figure 1** Photograph of X-ray diffraction pattern of BB5-PE(0.1).

Figure 2 Photograph of X-ray diffraction pattern of BB7-PE(0.1).

ments of BB5-PE(0.1) may be less crystalline in nature.

Low-temperature Crystalline Properties

Figure 3 shows the DSC heating curve of a PTMEG 2000 which was used to prepare the block copolyetheresters. The midpoint of the step inflection of the DSC heating curve is taken as the glass transition temperature (T_g) and the peak temperature of the endotherm is taken at the melting temperature (T_m). The PTMEG 2000 shows a T_g at $-74°C$ and a T_m at 29°C. The heat of fusion (ΔH_m) is 75.2 J/g. Thus, the PTMEG 2000 shows a high tendency to crystallize after cooling.

Typical low-temperature DSC heating curves of the block copolyetheresters are shown in Figure 4. The block copolyetheresters show a different melting peak from that of the PTMEG 2000. Two abbreviations of the heat of fusion concerning the melting of the polyether segments are used here. ΔH_m denotes the heat of fusion in J per g of polymer, and $\Delta H'_m$ denotes the heat of fusion in J per g of the polyether segments. The $\Delta H'_m$ value is obtained by dividing the ΔH_m value by the polyether content in the polymer. The values are listed in Table I. The T_m and the $\Delta H'_m$ of the polyether segments are lower than those of the PTMEG 2000. Thus, the crystallizability of the polyether soft segments is affected
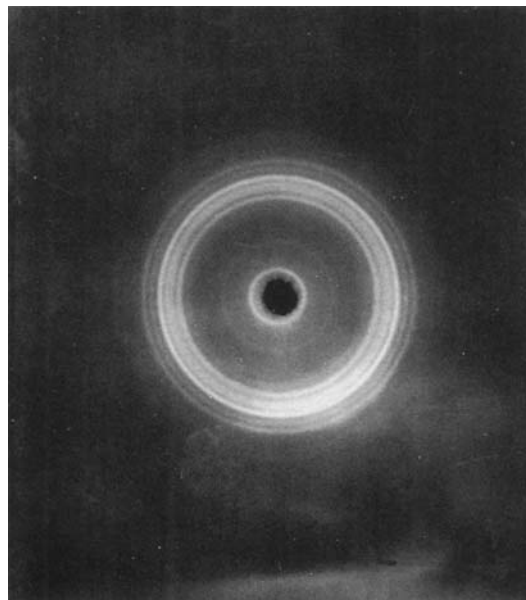
by the presence of the polyester hard segments significantly.

The $\Delta H'_m$ value of the first six polymers [BB2-PE(x)s, BB3-PE(x)s, and BB4-PE(x)s, where x = 0.1 and 0.3] are in the range of 36–43 J/g and they are about half of the ΔH_m of PTMEG 2000. The $\Delta H'_m$ values of BB6-PE(0.1) to BB10-PE(0.1) (in the range of 15.2–22.8 J/g) is significantly lower than that of the above six polymers. The $\Delta H'_m$ of BB5-PE(0.1) is 35.3 J/g and close to that of the first six polymers. The results indicate that the presence of different polyester segments influence the crystallizability of the polyether segments to a different extent even though the polyether content is similar. The $\Delta H'_m$ of three BB6-PE(x)s shows an
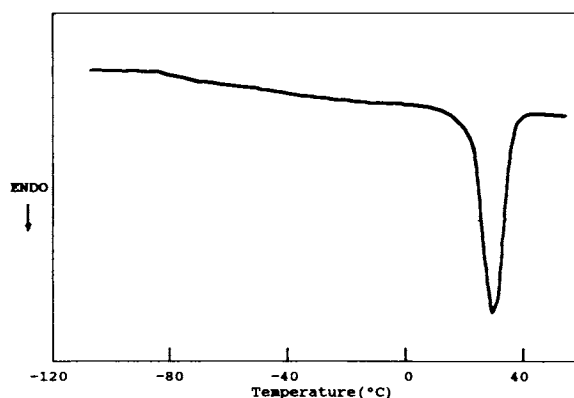

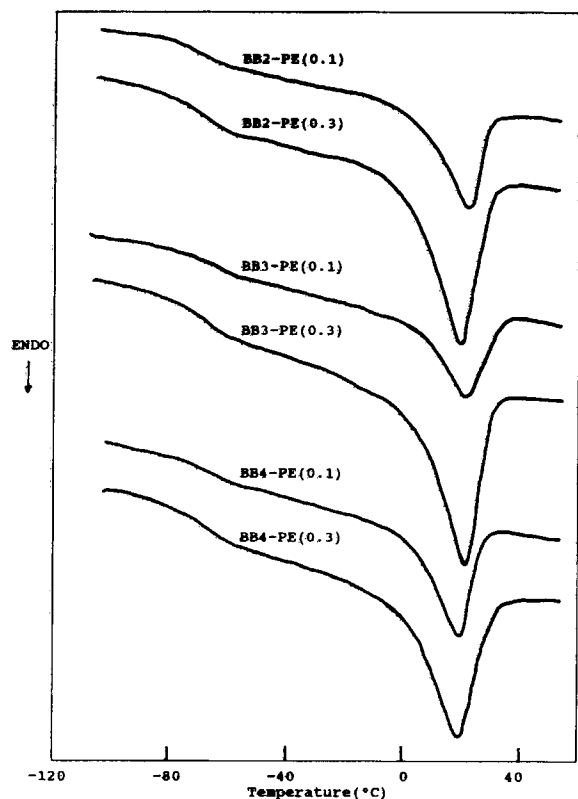**Figure 3** DSC heating curve of the PTMEG 2000.

Figure 4 DSC heating curves of BB2-PE(0.1), BB2-PE(0.3), BB3-PE(0.1), BB3-PE(0.3), BB4-PE(0.1), and BB4-PE(0.3).

increasing trend as the polyether content increases. This means that the presence of the polyester segments also affect the crystallizability of the polyether segments to a different extent in the BB6-PE(x)s.

There may be two factors affecting the crystallizability of the polyether segments for these block copolyetheresters: the molecular weight of the polymers and the crystallinity of the polyester segments. When the molecular weight of a block copolyetherester is relatively low as in the case of BB2-PE(0.1), BB3-PE(0.1), and BB4-PE(0.1), the restriction to the motion of the polyether segment may be lower and the polyether segments tend to crystallize more easily. Thus, these three polymers show a higher value of $\Delta H'_m$. When the crystallinity of the polyester segments is relatively low as in the case of BB2-PE(0.3), BB3-PE(0.3), BB4-PE(0.3), and BB5-PE(0.1), the polymer chain is more flexible and restricts the motion of polyether segments to a lesser extent, and it is easier for the polyether segment to crystallize and they show a higher value of $\Delta H'_m$. For BB6-PE(0.1) to BB10-PE(0.1), the higher crystallinity of the polyester segments in combination with the higher molecular weight of the

polymer restrict the motion of the polyether segments to a greater extent; thus, it is more difficult for the polyether segments to crystallize and they show a lower value of $\Delta H'_m$. Consider the three BB6-PE(x)s: When the polyether content of BB6-PE(x) increases, the crystallinity of polyesters segments decreases and the $\Delta H'_m$ increases.

Low-temperature Glass Transition Temperature

The midpoint of the step inflection of the DSC heating curve is taken as the glass transition temperature (T_g). The T_g data of PTMEG 2000 and the block copolyetheresters are listed in Table I. All the block copolyetheresters exhibit a T_g corresponding to the motion of polyether soft segment at $-68 \pm 2°C$ as shown in Table I. The T_g of the block copolyetheresters is only about 5°C higher than that of the PTMEG 2000. However, the T_g is independent of the composition and the type of alkanediol used in the preparing of the block copolyetheresters. This is considerably different from the case of some commercial block copolyetheresters such as the block copolyetheresters with hard segments of poly(butylene terephthalate) and soft segments of poly(tetramethylene ether).[6] In this study, the amorphous parts of the poly(tetramethylene ether) segments of the block copolyetheresters would be immiscible with the amorphous parts of the poly(alkylene p,p'-bibenzoate) segments due to the presence of the more rigid p,p'-bibenzoate unit.
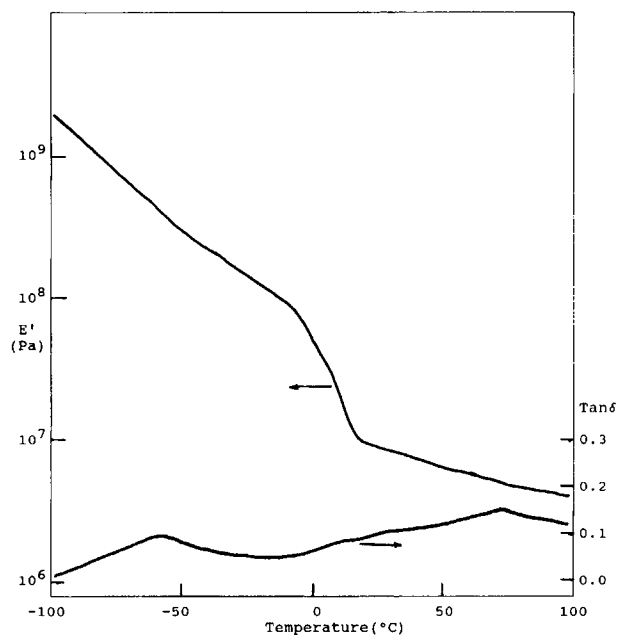

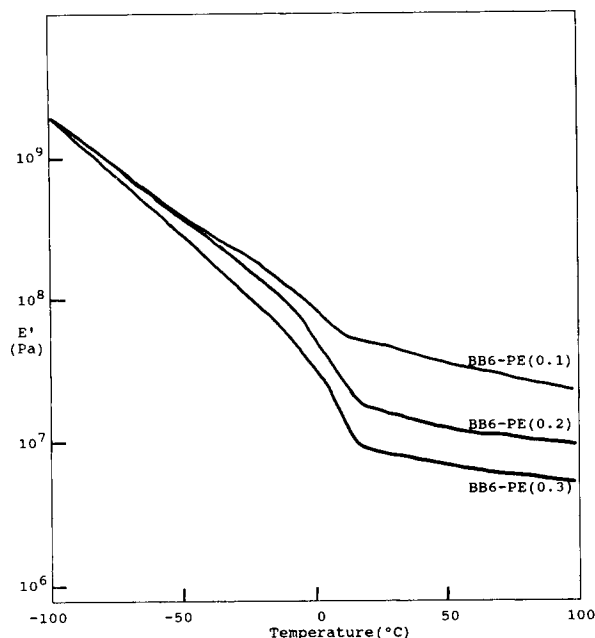**Figure 5** Dynamic mechanical curves of BB4-PE(0.3).

Figure 6 E' vs. temperature curves of BB6-PE(0.1), BB6-PE(0.2), and BB6-PE(0.3).

Thus, our block copolyetheresters show a similar T_g at about $-68°C$, close to that of the PTMEG 2000.

Dynamic Mechanical Properties

Figure 5 shows the typical dynamic mechanical curves of BB4-PE(0.3). The tan δ vs. temperature curve of BB4-PE(0.3) exhibits two transition peaks at -60 and $72°C$, respectively. The peak at $-60°C$ corresponds to the glass transition of the polyether segments and that at $72°C$ may be attributed to the polyester segments. The glass transition peak is also around $-60°C$ for other block copolyetheresters. From -100 to $-20°C$, the real part of the dynamic modulus, E', decreases gradually as the temperature is increased for BB4-PE(0.3). Then, E' decreases drastically with the increase of temperature in the temperature range of -10 to $15°C$; this may be associated with the melting of the polyether segments. Above $20°C$, the E' vs. temperature curves display a plateaulike behavior. The E' vs. temperature curves are affected significantly by the content of the polyether segments as shown in Figure 6. E' of the block copolyetheresters above $-30°C$ decreases as the content of the polyether segments increases, as expected and as shown in Figure 8 for BB6-PE(x)s. The abrupt drop in E' in the temperature range of -10 to $15°C$, possibly due to the melting of the polyether segments, indicates that the crystalline properties of the polyether segments affect

the mechanical properties of the block copolyetheresters.

CONCLUSION

The T_g of the polyether segments of the block copolyetheresters monitored by the DSC is around $-68°C$ and independent of the composition and the type of polyester segments. Thus, the amorphous parts of the polyether segments should be immiscible with the amorphous parts of the polyester segments. The polyether segments of the block copolyetheresters exhibit a lower T_m and a lower crystallinity than does the poly(tetramethylene ether)glycol due to the presence of the polyester segments. The tan δ vs. temperature curves display a transition peak at about $-60°C$, which may correlate with the T_g of the polyether segments. The E' of block copolyetheresters is dependent on the composition to some extent.

REFERENCES

1. N. R. Legge, G. Holder, and H. E. Schroeder, Eds., *Thermoplastic Elastomers: A Comprehensive Review*, Hanser, New York, 1987.
2. A. K. Bhowmick and H. L. Stephens, Eds., *Handbook of Elastomers: New Developments and Technology*, Marcel Dekker, New York, 1988.
3. J. C. Shivers and W. Chester, U.S. Pat. 3,023,192 (1962).
4. W. K. Witsiepe, U.S. Pat. 3,651,014 (1972).
5. G. K. Hoeschele, U.S. Pat. 3,801,547 (1974).
6. H. Schroeder and R. J. Cella, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., H. F. Mark, N. M. Bikales, C. G. Overberger, G. Menges, and J. I. Kroschwits, Eds., Wiley, New York, 1988, Vol. 12, pp. 75–117.
7. W. R. Krigbaum, J. Arsar, H. Toriumi, A. Ciferri, and J. Preston, *J. Polym. Sci. Polym. Lett. Ed.*, **20**, 109 (1982).
8. W. R. Krigbaum and J. Watanabe, *Polymer*, **24**, 1299 (1983).
9. J. Watanabe and M. Hayashi, *Macromolecules*, **21**, 278 (1988).
10. J. Watanabe and M. Hayashi, *Macromolecules*, **22**, 4083 (1989).
11. H. B. Tsai, C. Lee, and N. S. Chang, *Polym. J.*, **24**, 157 (1992).