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Block copolyetheresters

7. Block copolyetheresters with poly(pentamethylene *p,p′*-bibenzoate) segments

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SUMMARY

Block copolyetheresters with hard segments of poly(pentamethylene *p,p'*-bibenzoate) and soft segments of poly(tetramethylene ether) have been prepared by melt polycondensation of dimethyl *p,p'*-bibenzoate, 1,5-pentanediol and poly(tetramethylene ether) glycol(PTMEG) with molecular weights of 650, 1000 and 2000. The polymer composition is governed by the charge molar ratio(x) of PTMEG to dimethyl *p,p'*-bibenzoate. The block copolyetheresters with x=0.05, 0.1 and 0.2 display a monotropic smectic phase due to the poly(pentamethylene *p,p'*-bibenzoate) segments. But the block copolyetheresters with x=0.3 exhibit no liquid crystalline behavior. The molecular weight of the PTMEG used has significant effect on the glass transition temperature and crystallizability of the polyether segments. It can be seen from the glass transition temperature results that the miscibility between amorphous parts of the polyether segments and those of the polyester segments is also dependent on the molecular weight of the PTMEG used.

INTRODUCTION

The concept of block copolymer can be used to design thermoplastic elastomers(1,2). A typical commercial example is the block copolyetheresters(1-6). The hard segments of the block copolyetheresters described in the literature are often semi-crystalline 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 exhibit thermotropic liquid crystalline behavior(7-10). Thus some of our previously prepared block copolyetheresters with hard segments of poly(alkylene *p,p'*-bibenzoate) and soft segments of poly(tetramethylene ether) were found to show liquid crystallinity which originates from the poly(alkylene *p,p'*-bibenzoate) segments(11). However, little is known about the effects of the sequence length of poly(tetramethylene ether) and the polymer composition on their properties.

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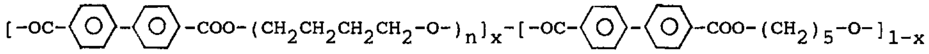
In this paper, the synthesis and properties of a series of block copolyetheresters with hard segments of poly(pentamethylene p,p'-bibenzoate) and soft segments of poly(tetramethylene ether) of different sequence length are described. These block copolyetheresters have the general formula:



where n is the degree of polymerization of the poly(tetramethylene ether)glycol(PTMEG) used in the synthesis and x is the molar fraction of the PTMEG in the diol units.

EXPERIMENTAL

The block copolyetheresters were prepared by melt polycondensation of dimethyl *p,p'*-bibenzoate(BB), 1,5-pentanediol (PDO) and PTMEG similar to a method described previously(11).

The intrinsic viscosity of the block copolyetheresters in phenol/*syn*-tetrachloroethane (60/40 wt/wt) was determined by an Ubbelohde viscometer at 30°C. The thermal properties from 40 to 250°C were determined by a Perkin Elmer DSC7 at a heating rate or cooling rate of 20°C/min under nitrogen. The low temperature thermal properties from -100 to 60°C were determined by a Du Pont 910 DSC at a heating rate of 20°C/min under nitrogen. The texture was investigated by a Leitz Polarizing Microscope equipped with a heating stage. The X-ray diffraction patterns were recorded on a Mac Science Diffractometer equipped with a Laue camera.

The IR spectra were measured by a Perkin Elmer 1600 series FTIR. The characteristic peaks of the block copolyetheresters are at 2796-3043 cm^{-1}(C-H stretching), 1714 cm^{-1} (C=O stretching of the ester groups), 1608, 1559 and 1469 cm^{-1}(aromatic absorptions), and 1113 cm^{-1}(ether groups). The proton NMR spectra of the block copolyetheresters in trifluoroacetic acid were determined by a Bruker AM 400 NMR. Peak assignments: H1(aromatic protons): 7.7 and 8.2 ppm; H2(methylene protons of Ar-COO-CH_2- of PDO and PTMEG units): 4.6 ppm; H3(methylene protons of PTMEG unit other than H2): 3.8-4.2 ppm; H4(methylene protons of PDO and PTMEG units other than H2 and H3: 1.8-2.1 ppm.

RESULTS AND DISCUSSION

Synthesis and Spectroscopic Analysis

In the preparation of the block copolyetheresters, the charge molar ratio of 1,5-pentanediol(PDO) to dimethyl *p,p'*-bibenzoate(BB) was held at 1.4:1.0 and that of PTMEG to BB was x:1.0. It should be noted that poly(tetramethylene ether) glycol(PTMEG) would not be distilled off during synthesis significantly due to its high boiling point. The excess 1,5-pentanediol would be distilled off. Thus, the composition of the block copolyetheresters is dependent mainly on the charge molar ratio of PTMEG to BB.

The polymer composition can be determined by proton NMR similar to those described by a previous paper(12). Consider BB5-PE650(0.1), the charge molar ratio of PTMEG650 to BB was 0.1:1.0, and that of PDO to BB was 1.4:1.0. The measured molar ratio of BB:PDO:PTMEG650 in polymer is 1.0:0.89:0.10. It shows that PTMEG650 was not distilled off significantly, but most of the excess 1,5-pentanediol was distilled off during synthesis. Clearly, the molar ratio of PTMEG to BB determines the composition of a given block copolyetheresters. Thus, the block copolymers are denoted as BB5-PEm(x), where BB5 means the poly(pentamethylene *p,p'*-bibenzoate) hard segment, m is the molecular weight of the PTMEG used, and x is the charge molar ratio of the PTMEG to BB.

Thermal Transition of the Polyester Segments

Since only the polyester hard segments may form a liquid crystalline phase, a poly(pentamethylene *p,p'*-bibenzoate), BB5, is used here for comparison. In the range of 40 to 250°C, the second run DSC heating curve and the cooling curve of BB5 exhibit two peaks. BB5 exhibits two endotherms at 177°C(T_I) and 214°C(T_{II}) upon heating and two exotherms at 191°C(T_a) and 81°C(T_b) upon cooling. After cooling from 240°C to about 180°C, BB5 displays a fan-like texture when observed on the polarized microscope. The X-ray diffraction pattern of BB5 exhibits a sharp inner ring at d=1.58 nm. The layered spacing is slightly shorter than the fully extended length of the repeat unit of the poly(pentamethylene-*p,p'*-bibenzoate) segment indicating the possible existence of a smectic phase. Thus BB5 exhibit a smectic phase and is enantiotropic.

Typical second run DSC heating and cooling curves of the block copolyetheresters are shown in Figure 1. In the temperature range of 50 to 250°C, the second run DSC heating curves of all block copolyetheresters show a main endothermic peak(denoted as T_h). The cooling curves of some block copolyetheresters exhibit two exotherms(denoted as T_a and T_b) and those of other polymers exhibit only one exotherm(denoted as T_b). The transition temperature(s) and the corresponding transition heat(s) are summarized in Table 1. These data indicate that the thermal properties of the block copolyetheresters are different from those of BB5, and dependent on their composition. The thermal properties of the block copolyetheresters are affected mainly by the polyester segments. Thus the difference in thermal properties would be due to the sequence length and the content of the polyester segments.

From the DSC heating curves, the smectic transition of the block copolyetheresters cannot be distinguished. However, the DSC cooling curves of some block copolyetheresters exhibits two obvious exotherms indicating the appearance of smectic transition. The DSC cooling curves of the block copolyetheresters with x=0.05, 0.1 and 0.2 show two obvious exotherms, T_a and T_b. In combination with the presence of a

Table 1. Thermal transitions of the polyester segments.

Sample	T_h (°C)	ΔH_h (J/g)	T_a (°C)	ΔH_a (J/g)	T_b (°C)	ΔH_b (J/g)
BB5-PE650(0.05)	181	24.1	157	6.2	85	13.4
BB5-PE650(0.1)	177	19.2	141	3.6	89	12.7
BB5-PE650(0.2)	161	11.1	121	1.6	83	6.9
BB5-PE650(0.3)	135	8.4	---	---	88	8.9
BB5-PE1000(0.05)	182	22.5	155	5.2	92	11.8
BB5-PE1000(0.1)	174	15.6	142	3.5	82	8.9
BB5-PE1000(0.2)	149	9.6	117	1.3	77	7.0
BB5-PE1000(0.3)	131	4.5	---	---	80	6.5
BB5-PE2000(0.05)	182	21.3	157	4.9	89	9.1
BB5-PE2000(0.1)	180	12.0	156	3.6	81	7.6
BB5-PE2000(0.2)	177	5.5	150	1.2	81	4.0
BB5-PE2000(0.3)	114	2.1	---	---	78	3.2

sharp inner ring of the X-ray diffraction pattern and the display of birefringent texture observed by the polarized microscope, it can be seen that a smectic phase is formed between T_a and T_b. Thus T_a is an isotropic-smectic transition, and T_b a smectic-crystalline transition. Comparing the smectic order, the isotropic-smectic transition heat, of BB5(16.6 J/g) with that of the block copolyetheresters(<7J/g), the presence of the poly(tetramethylene ether) segments seems to depress the smectic order significantly. As x increases, the sequence length of the polyester segments of the block copolyetheresters, and the transition temperature and the transition heat of the isotropic-smectic transition decreases. It is not surprising that as the sequence length of the polyester segments is further shorter as in the case of x=0.3, the isotropic-crystalline transition disappears, and only an isotropic-crystalline transition is displayed upon cooling. In other words, the block copolyetheresters with x=0.3 exhibit no smectic phase.

Thermal Transition of the Polyether Segments

The low temperature DSC heating curves(-100 to 60°C) of the three PTMEGs exhibit a step inflection and a very large endotherm. 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) for the PTMEGs. The T_g, T_m and the heat of fusion of the PTMEGs are listed in Table 2. The T_g of the three PTMEGs is about -74°C. The T_m increases as the molecular weight of the PTMEG increases. Their heat of fusion is around 65-90 J/g indicating they have high tendency to crystallize after cooling.

Typical low temperature DSC heating curves of the block copolyetheresters are shown in Figure 2. The thermal transitions within this temperature range are contributed to the polyether segments. The low temperature transitions of the

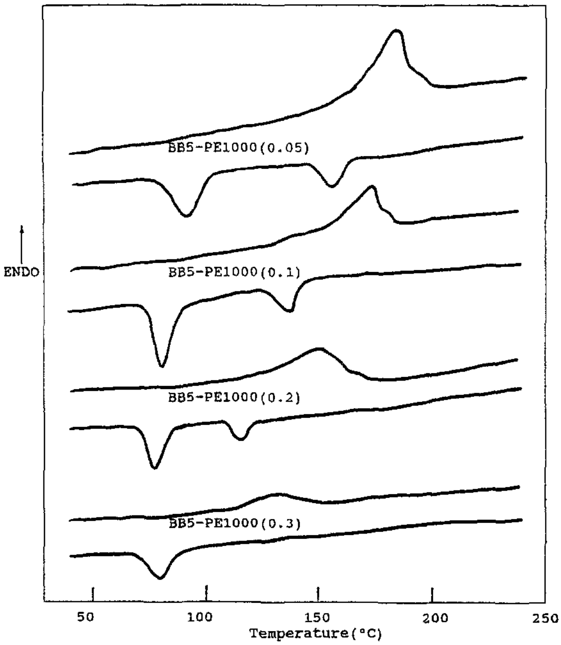


Figure 1. Second run DSC heating curves and cooling curves of BB5-PE1000(x)s.

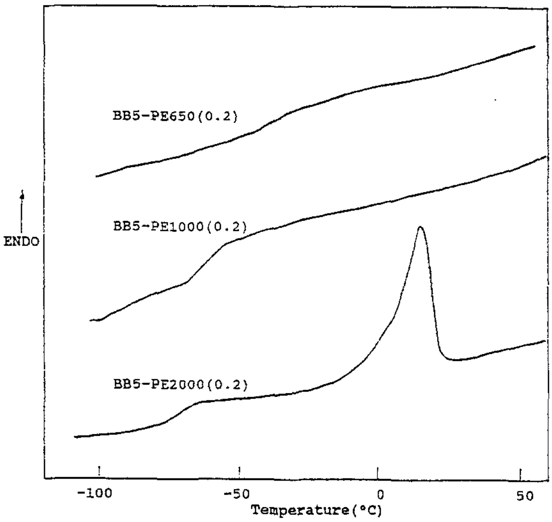


Figure 2. Low temperature DSC heating curves of the block copolyetheresters.

polyether segments are listed in Table 2. It can be seen that the low temperature thermal properties of the polyether segments are significantly different from those of the PTMEGs, especially the crystalline properties.

It can be seen from Table 2 that the T_g of the polyether segments depends mainly on the molecular weight of PTMEG used. The T_g of BB5-650(x) series is around -39 to 45°C. The T_g of BB5-PE1000(x) series is about -64°C and that of BB5-PE2000(x) series is about -68°C. This is considerably different from the case of some commercial block copolyetheresters such as the block copolyetheresters with soft segments of poly(tetramethylene ether) and hard segments of poly(butylene terephthalate)(6).

The T_g of each series of BB5-PE1000(x) and BB5-PE2000(x) is almost independent of their composition and rather close to that of the corresponding PTMEG(-74°C). Thus, the amorphous parts of the poly(tetramethylene ether) segments in these two series of block copolyetheresters would be immiscible with the amorphous parts of the poly(pentamethylene *p,p'*-bibenzoate) segments possibly due to the presence of the more rigid *p,p'*-bibenzoate unit. However, the T_g of the polyether segments is slightly(5-10°C) higher than that of the PTMEGs. This may be due to the presence of the polyester segments which restrict the motion of the polyether segments.

The T_g of the polyether segments in BB5-PE650(x)s is significantly(20 to 30°C) higher than that of other two series and PTMEGs. The T_g is rather independent of the composition. Thus the amorphous parts of the polyether segments in BB5-PE650(x)s would be partially miscible with the amorphous parts of the poly(pentamethylene *p,p'*-bibenzoate) segments.

Table 2. Low temperature thermal transition temperatures of the polyether segments.

Sample	T_g(°C)	T_m(°C)	ΔH_m(J/g)
PTMEG650	-74	18	65.2
BB5-PE650(0.05)	-43	---	---
BB5-PE650(0.1)	-39	---	---
BB5-PE650(0.2)	-40	---	---
BB5-PE650(0.3)	-45	---	---
PTMEG1000	-74	24	87.2
BB5-PE1000(0.05)	-62	---	---
BB5-PE1000(0.1)	-66	---	---
BB5-PE1000(0.2)	-65	---	---
BB5-PE1000(0.3)	-64	---	---
PTMEG2000	-74	31	89.2
BB5-PE2000(0.05)	-66	17	7.7
BB5-PE2000(0.1)	-68	19	14.4
BB5-PE2000(0.2)	-69	16	21.5
BB5-PE2000(0.3)	-70	19	28.5

The block copolyetheresters BB5-PE2000(x)s show different melting peaks from that of the PTMEG2000. The T_m and the heat of fusion of the polyether segments the block copolyetheresters are lower than those of the PTMEG2000. Thus the crystallizability of the polyether soft segments of the block copolyetheresters is affected by the presence of the polyester hard segments significantly.

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