

Preparation and thermotropic properties of copoly(4,4'-biphenylene sebacate-co-eicosanedioate)s

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SUMMARY

A series of thermotropic copoly(4,4'-biphenylene sebacate-co-eicosanedioate)s were prepared by melt polycondensation of 4,4'-biphenylene diacetate, sebacic acid and eicosanedioic acid. Their thermal transitions and liquid crystalline properties were investigated by DSC and polarized microscope. The copolyesters were found to exhibit a smectic phase, but no nematic phase was observed upon cooling. The smectic-isotropic transition temperature decreased as the content of eicosanedioate unit increased, and the corresponding transition heat did not change to a great extent. However, the crystalline-smectic transition temperature showed an eutectic behavior, and the crystalline-smectic transition heat was depressed considerably after copolymerization. The X-ray diffraction data of the copolyesters after thermal treatment were measured and compared with the thermal properties measured by DSC.

INTRODUCTION

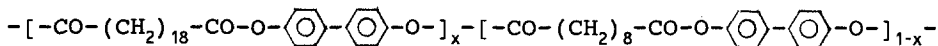
Mesogenic groups can be incorporated into polymers as side chains or main chains and side chain or main chain liquid crystalline polymers may be obtained. The liquid crystalline behavior is influenced by the structure of mesogenic groups and the presence of polymer backbone. In the case of side chain liquid crystalline polymers, particularly the mesogenic group is attached by a flexible spacer, the molecular conformation is not altered by the formation of the mesophase. Thus, the polymeric and mesogenic effects are often uncoupled, and the mesogenic effects are often predicted from those of low molecular weight mesogen. In the case of main chain liquid crystalline polymers, the mesogenic group forms part of the main chain. The polymer molecule must adopt a packing conformation which is compatible with the structure of the mesophase. The mesogenic and polymeric effects are closely coupled in this case[1]. Thus, the liquid crystalline behavior of the main chain liquid crystalline polymers will be significantly modified by copolymerization.

The homopolyesters of 4,4'-biphenol and some aliphatic diacids have been found to exhibit liquid crystalline

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behavior[1-3]. The homopolyesters with a spacer of odd carbon number were found to exhibit a nematic phase and those with a spacer of even carbon number exhibited a highly ordered smectic S_H phase. The influence of the carbon number of the spacer on their transition temperatures was also found to show an odd-even effect. Copolymerization has been found to have significant effects on the liquid crystalline behavior of their copolyesters[4-7]. The effects of different non-mesogenic rigid comonomers on the liquid crystalline behavior of their copolyesters were considerably different depending on the structure of the nonmesogenic units[4,5]. The copolyesters of 4,4'-biphenol with two different aliphatic diacids have been prepared by Watanabe and Krigbaum[6,7]. For the copolyesters of 4,4'-biphenol with azelaic acid and (+)-3-methyl adipic acid, the incorporation of a chiral (+)-3-methyl adipate unit rendered a cholesteric phase to be formed[6]. For the copolyesters of 4,4'-biphenol with two different linear aliphatic diacids, the effect of copolymerization on the liquid crystalline behavior was found to be dependent on various factors such as composition and the nature of the original homopolyesters[7]. The copolyesters of two nematic polyesters showed a nematic phase, and those of a nematic and a smectic polyester might showed both nematic and smectic phases. Some of the copolyesters of two smectic polyesters exhibited a smectic phase. Some of the copolyesters of two smectic polyesters exhibited a smectic phase upon heating but exhibited a nematic phase additionally and a smectic phase upon cooling. However, little study has been involved in the copolyesters containing a long aliphatic dicarboxylate unit such as eicosanedioate unit.

In this paper, a series of thermotropic copolyesters were prepared, their general formula is shown below:



where x is the molar fraction of eicosanedioic acid based on the diacid monomers. The effect of this long chain diacid comonomer on their properties was studied.

EXPERIMENTAL

Eicosanedioic acid was obtained from Okamura Oil Mill, Ltd.(Japan). Sebacic acid was Merck reagent grade and 4,4'-biphenol was supplied by Tokyo Chemical Industry Co., Ltd. 4,4'-Biphenylene diacetate was obtained by reacting 4,4'-biphenol with acetic anhydride followed by recrystallizing twice from acetone solution. The homopolyesters and copolyesters were prepared by reacting aliphatic diacids(sebacic acid and eicosanedioic acid) with equal moles of 4,4'-biphenylene diacetate. Typical procedure was described as in a previous paper[5].

The intrinsic viscosity(IV) of the polyesters in phenol/TCE(syn-tetrachloroethane) at 30°C was determined by an Ubbelohde Viscometer. The polyesters were heated in a Perkin-

Elmer DSC-2 under nitrogen to 300°C and then cooled to room temperature at a cooling rate of 20°C/min. Their second run thermal properties were then determined at a heating rate of 20°C/min. The liquid crystalline texture was investigated by a Leitz Polarizing Microscope equipped with a heating stage. The polyester samples were heated in the heating stage to above their isotropization temperature and then cooled to room temperature at a cooling rate of about 20°C/min. The thermal history after this treatment would be similar to that of the second run thermal properties measured by DSC. The X-ray diffraction patterns of the above treated copolyesters were determined by a Scintag PAD V Diffraction system using Cu K α radiation (wave length= 0.154 nm).

RESULTS AND DISCUSSION

Two homopolyesters, poly(4,4'-biphenylene sebacate) (PB8) and poly(4,4'-biphenylene eicosanedioate) (PB18), and nine copolyesters were prepared. Their intrinsic viscosity values are listed in Table I. Each copolyester is denoted as the mole% of eicosanedioic acid based on aliphatic diacid monomers, thus, IA50 indicates that the content of eicosanedioic acid is 50 mole% (x=0.5).

The second run DSC heating curves of the two homopolyesters and some copolyesters are shown in Figures 1, 2 and 3. PB8 showed two transitions at 212 and 283°C corresponding to a crystalline-smectic transition (T_m) and a smectic-isotropic transition (T_i) respectively as described previously[5]. PB18 showed two overlapped peaks at 164 and 172°C and a sharp peak at 195°C (Figure 3). When PB18 was cooled from 220°C to a temperature at about 190°C, a highly ordered smectic texture similar to that of PB8 was observed on the cross polarized microscope. The transition at 195°C would be a smectic-isotropic transition. The transition at 172°C would be a crystalline-smectic transition and that at 164°C would be a crystalline-crystalline transition.

Table I. Intrinsic viscosity (IV), T_m , ΔH_m , T_i , ΔH_i of the copolyesters.

	IV (dL/g)	T_m (°C)	ΔH_m (cal/g)	T_i (°C)	ΔH_i (cal/g)
PB8	0.61	212	9.6	283	13.2
IA10	0.89	172	4.6	264	10.4
IA20	0.72	140	1.9	250	12.2
IA30	0.80	110	1.6	230	11.3
IA40	0.77	94	1.0	220	11.5
IA50	0.70	100	1.5	206	11.4
IA60	0.54	112	2.7	203	12.1
IA70	0.26	129	3.1	202	12.9
IA80	0.14	152	6.3	197	12.1
IA90	0.37	170	9.1	195	11.0
PB18	0.39	172	11.2	195	9.6

Based on the second run thermal properties (Figures 1-3) and the texture observed on the polarized microscope, all the copolyesters exhibited a smectic phase. The transition temperatures (T_m and T_i) and the corresponding transition heats are listed in Table I. The smectic-isotropic transition temperature of the copolyesters decreased as the content of eicosanedioate unit increased. The smectic-isotropic transition ranged from 9.6 to 13.2 cal/g and did not vary considerably when the composition was changed. The effect of composition on the crystalline-smectic transition of the copolyesters was considerably different from that on the smectic-isotropic transition. The crystalline-smectic transition temperature (T_m) showed an eutectic behavior with a minimum at a content of eicosanedioate unit of about 40 mole%. The crystalline-smectic transition heat was also decreased considerably after copolymerization. At a content of eicosanedioate unit of 40 mole%, the crystalline-smectic transition heat reached a minimum and was as low as 1.0 cal/g which was an order lower than that of the homopolyesters (about 10 cal/g). The effect of copolymerization on the heating run thermal transitions of these copolyesters was similar to the cases described in the literature [7].

A typical DSC cooling curve (IA60) is shown in Figure 2. Upon cooling, two main exotherms were observed. All the copolyesters showed a rather sharp exotherm at a higher temperature corresponding to an isotropic-smectic transition. When observed on the cross polarized microscope, no nematic texture was found upon slow cooling. Thus, no nematic phase was developed upon cooling for these copolyesters. In the literature [7], the copolymers of PB10 (the number denotes the methylene carbon number of the polyester) and PB12, and those of PB8 and PB12 exhibited only a smectic phase upon cooling. However, the copolymers of PB6 and PB12 exhibited both a nematic phase and a smectic phase upon cooling. Those data might indicate that the greater difference in the length of spacers favored the formation of an additional nematic phase for those copolymers upon cooling. The difference in the length of spacers was even greater for our copolyesters, but no nematic phase was observed upon cooling. Thus, it is possible that no obvious trend could be predicted for the formation of an additional nematic phase of the copolyesters of two smectic polyesters upon cooling.

The X-ray diffraction patterns of some polyesters after thermal treatment (slow cooling) are shown in Figure 4. PB8 and the copolyesters with a content of eicosanedioate unit up to 80 mole% exhibited a sharp diffraction peak at $d=0.425$ nm ($2\theta=20.86^\circ$). There was no significant difference in diffraction pattern within this composition range. However, PB18 and IA90 showed considerably different diffraction patterns. PB18 showed three diffraction peaks at $d=0.44$, 0.40 and 0.375 nm. Thus, different crystallites might exist for PB18. The second run DSC heating curve of PB18 showed two overlapped peaks at 164 and 172°C which might be due to the melting of different crystallites. Thus, the peak at 164°C would be a

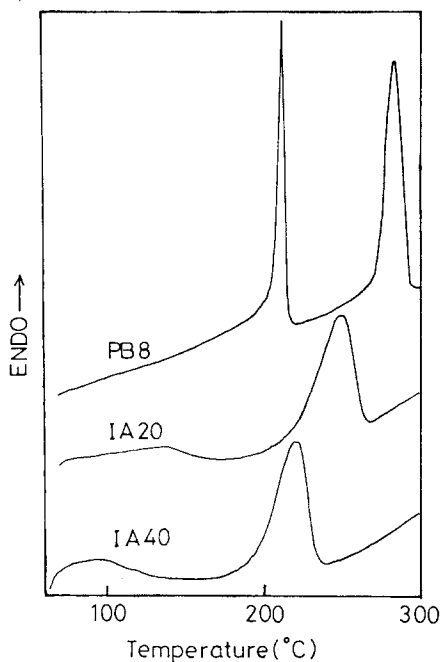


Figure 1. Second run DSC heating curves of PB8, IA20 and IA40.

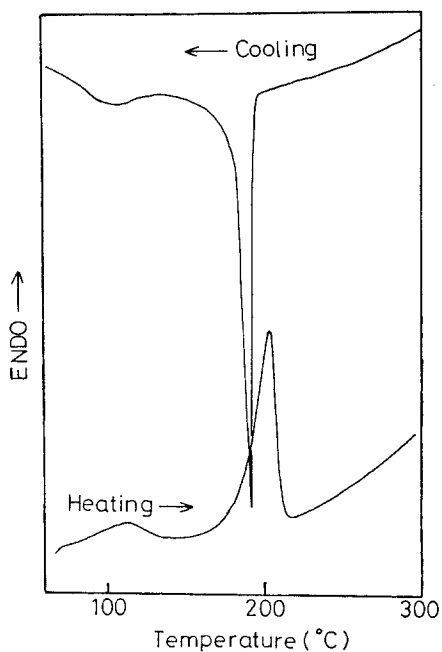


Figure 2. DSC cooling curve and second run DSC heating curve of IA60.

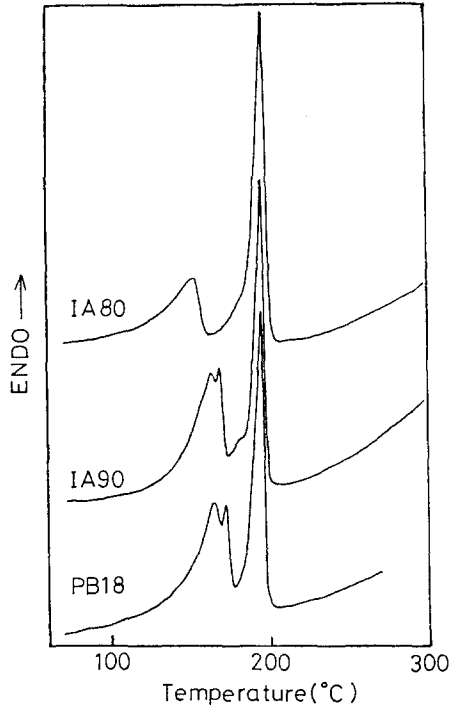


Figure 3. Second run DSC heating curves of IA80, IA90 and PB18.

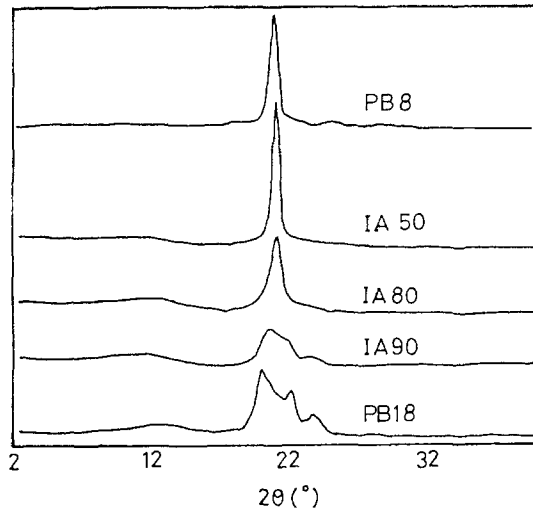


Figure 4. X-ray diffraction patterns of some polyesters.

crystalline-crystalline transition and that at 172°C would be a crystalline-smectic transition. IA90 showed a large and broad diffraction peak at about $d=0.43$ nm and a small and broad diffraction peak at about $d=0.38$ nm. Thus, different crystallites might also exist for IA90. Its second run DSC heating curve also showed two overlapped crystalline peaks corresponding to a crystalline-crystalline transition at 173°C and a crystalline-smectic transition at 170°C respectively. However, the diffraction peaks of IA90 were broader than those of PB18 and significant shifts in diffraction peaks were observed possibly due to copolymerization. For the copolyesters with a higher content of sebacate unit such as IA80, only a sharp diffraction peak at $d=0.425$ nm was observed and their second run DSC heating curves exhibited a crystalline peak corresponding to a crystalline-smectic transition and a smectic-isotropic transition. The X-ray diffraction data correlated qualitatively with their second run thermal properties, however, they could not distinguish the crystalline transition heat quantitatively for these copolyesters.

In conclusion, the copolyesters of 4,4'-biphenol, sebacic acid and eicosanedioic acid showed a smectic phase, and no nematic phase was observed upon cooling. As the content of eicosanedioate unit increased, the smectic-isotropic transition temperature decreased, but the corresponding transition heat did not change to a great extent. However, the crystalline-smectic transition temperature showed an eutectic behavior, and the crystalline-smectic transition heat was decreased considerably after copolymerization.

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