

PROPERTIES AND MICROSTRUCTURE OF AROMATIC LIQUID CRYSTALLINE COPOLYESTERS

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ABSTRACT

The properties and structures of thermotropic liquid crystalline copolyesters based on *p*-hydroxybenzoic acid (PHBA), terephthalic acid (TPA) and bisphenol A (BPA) were studied by DSC, WAXD, hot stage polarized microscopy and NMR. It was found that most of the copolyesters were soluble in many common organic solvents. The copolyesters had low T_m/T_f values and a broad range of liquid crystal phase, making the polymers readily melt-processable. The effects of annealing at different temperatures on the copolyester containing 33% PHBA were also discussed. It was noted that annealing at ca. 200°C (below $T_c - n$) could lead to the increasing of the crystallinity of the copolyester while the microstructure and sequence structure had not changed. Annealing at ca. 280°C (near $T_c - n$) could bring a change of crystal and sequence structure and simultaneously made the microdomains be ordered more perfectly.

INTRODUCTION

In recent years thermotropic liquid crystalline (LC) polyesters have received a great deal of attention^[1,2]. Among thermotropic copolyesters, those based on *p*-hydroxybenzoic acid (PHBA) are attractive especially. However, fundamental studies of such polymers are difficult because of their low solubility in most solvents which greatly limits the use of techniques aimed at relating microstructure to the properties. In this regard, we have synthesized wholly aromatic copolyesters from *p*-acetoxybenzoic acid (PABA), terephthalic acid (TPA) and acetoxybisphenol A (ABPA) in recent years. As these three kind of monomers are produced on a large scale, the copolyesters may have the potentiality to be developed into a new kind of high technique material, and its synthesis and characterization^[3,4] will have special meaning for future applications. On the other hand, the polyesters are soluble in many organic solvents, and therefore, their properties and molecular characteristics

can be investigated in solution. In this paper thermal properties and liquid crystallinity of the copolyesters were studied by use of differential scanning calorimetry (DSC), polarized microscopy, and X-ray analyses. The effect of annealing at different temperatures on thermal properties, crystallization and microstructure was also investigated.

EXPERIMENTAL

Synthesis and heat treatment of copolyesters

All the polyesters were prepared from equimolar amounts of terephthalic acid and acetoxymphenol A mixed with the required amount of p-acetoxymbenzoic acid. The preparation is similar to that of Zhang et al.^[5]. The mixture of monomers was placed in a bath preheated at 280°C and stirred at this temperature under a slow stream of nitrogen gas for 2 h. During this period acetic acid was liberated continuously. The temperature of the reaction mixture was raised to and maintained at 290°C for 1.5 h, then at 300°C for 1 h, and then 320°C for 2 h. Finally, the reaction system was evacuated and stirring was continued for about 1 h. The PHBA/BPA/TPA composition, transition temperatures, solubility and inherent viscosity are listed in Table 1.

Table 1 Properties of copoly (PHBA/BPA/TPA)

Sample No.	PHBA% (mol)	T_g (°C)	T_m (°C)	T_d (°C)	$[\eta]$ (dl/g)	Solubility	Opalescence
P ₀	0	187	384	480	0.601	PCP	No
P ₁	10	166	359	440	0.485	PCP, TFA	Yes
P ₂	20	180	285	428	0.603	PCP, TFA	Yes
P ₃	33	177	280	430	0.560	THF, PCP, TFA	Yes
P ₄	50	188	321	425	0.522	THF, PCP, TFA	Yes
P ₅	60	181	—	480	—		No

PCP: p-chlorophenol; TFA: trifluoroacetic acid; $[\eta]$ =inherent viscosity

Annealing was conducted in a vacuum oven preheated to a desired temperature under N₂ atmosphere. Afterward, the annealed samples were slowly cooled to room temperature (ca. 10°C/min) in the vacuum oven.

Physical characterization

All DSC traces were made using a Perkin Elmer DSC-2 Differential Scanning Calorimeter at a heating rate of 20°C/min. Inherent viscosities were measured with a Canon-Ubbelohde viscometer in p-chlorophenol (PCP) at 45°C. ¹³C NMR spectra were obtained on a Varian Unity 400 NMR spectrometer using CF₃COOD/CDCl₃ (vol. ratio 3:2) as solvent. The optical texture of the melts was examined on a hot

stage (Mettler FP-5) attached to a polarizing microscope (Leitz, Ortholux). Wide-angle X-ray Diffraction studies were carried out by a D/Max-rB diffractometer using $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

Table 1 shows some of the properties of the copoly (PHBA/BPA/TPA), Probably, most interesting property of these polymers is their good solubility in some organic solvents such as THF, PCP and CF_3COOH , which allow either inherent viscosity measurements or NMR sequence analyses to be performed. The solubility of copolyesters also showed that under our synthetic conditions the formation of polymers containing merely mesogenic (PHBA) units can be ruled out, because the homopolymer of 4-hydroxybenzoic acid is insoluble. When viewed through a cross polarizing microscope, they display threaded-schlieren texture which is typical of nematic mesophase. The nematic phase of each of the copolyesters persisted up to 400°C at which either no loss of stir opalescence or no "black" background was observed. When the PHB unit mole amount is from 10 to 50%, the melts of copolyesters show obvious birefringence in the polarizing photomicrograph.

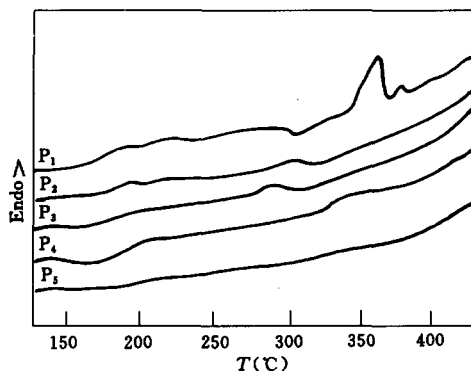


Fig. 1 DSC curves of virgin samples of copolyesters

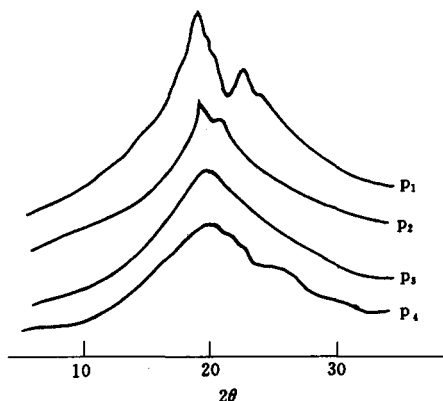


Fig. 2 WAXD of virgin samples of copolyesters

The DSC scans of the copolyesters are shown in Fig. 1. Generally, the transition peaks are very weak and broad, while glass temperatures for this series of copolyesters are high, ranging from 166 – 188°C . Thermal analysis shows that most of the as-polymerized samples possess little or no crystallinity, their crystalline nature can be further supported by X-ray diffractograms as shown in Fig. 2, some samples show weak crystalline or amorphous diffractions. DSC traces indicate that melting transition, if present, are extremely small or very broad. The DSC heating, cooling and reheating traces for sample P_3 shown in Fig. 3 are typical for this class

of polyesters. P_3 displays a weak broad endothermic transition (ca. 0.96 J/g) at 280°C (onset temperature) upon first heating. On cooling, no reversal of the initial phase transition, i.e., crystallization, could be detected. Upon reheating the same polymer sample, only a glass transition was observed. On cooling, P_3 remains in nematic phase until room temperature to form the "liquid crystalline glass state" which could be observed by optical microscopy. Structural irregularity caused by a random sequence of monomer units, together with the random existence of nonlinear structure, certainly would hinder crystallization.

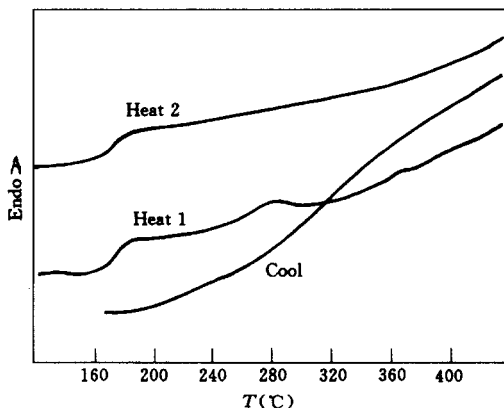


Fig. 3 Thermal behaviour of copoly (PHBA/BPA/TPA) for P_3

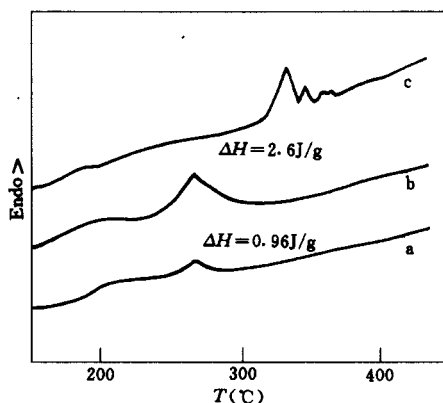


Fig. 4 DSC curves of copoly (PHBA/BPA/TPA) for P_3 (a) as-made sample (b) annealed, 18 h, 200°C (c) annealed, 8 h, 280°C

A sample of the P_3 copolyester was annealed at 200°C (below T_{c-n}) for 18 h and then examined by DSC, WAXD and ^{13}C NMR. In Fig. 4b, the DSC thermogram showed a sharp increase in transition enthalpy indicating an increase of crystallinity. The increase in the degree of crystallinity with annealing can also be observed from WAXD (Fig. 5b). However, it was observed that ^{13}C NMR spectra of the copolyester remain unchanged in triad ratios as shown in Fig. 6. The attribution of these resonance peaks was reported in earlier work^[6]. Symbols B, T and P in Fig. 6 were used to express BPA, TPA and PHBA, respectively. One can conclude from these results that the increased ordering in the DSC and WAXD was primarily the result of the slow chain diffusion, which provides a higher concentration of the crystalline ordering present prior to annealing. Under the present annealing condition, i.e., with the absence of catalyst and at a relatively low temperature, i.e., below T_m , the copolyester does not undergo any sequence randomization. On the other hand, a significant increase in $[\eta]$ was observed during annealing, i.e., from 0.56 to

0.65. Hence, some transesterification reactions were occurred in the solid state but limited to the end groups because of the greatly reduced mobility of end groups within the polycrystalline phase at 70–80°C below the T_{c-n} . It should be noted that although the copolyester is random, because of the rod-like nature of the chains there is a tendency for segregation of like sequences into poorly formed three dimensional crystallites.^[7] The fact that annealing results in an increase in the transition enthalpy but with no upward shift in temperature is an additional evidence along with the ^{13}C NMR triad analysis that the microstructure has not changed.

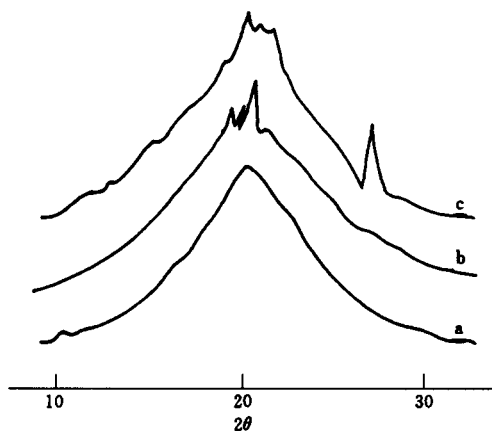


Fig. 5 WAXD of copoly (PHBA/BPA/TPA) for P_3 (a) as-made sample; (b) annealed, 18 h, 200°C; (c) annealed, 8 h, 280°C

A sample of P_3 copolyester was heated for 8 h at 280°C (near T_{c-n}). DSC analysis showed a completely altered spectrum with the peak at 280°C completely disappearing and being replaced by several new peaks near 335°C (see Fig. 4c). In addition, comparison of the two X-ray diffractograms shown in curves a and c of Fig. 5, a new offequatorial maximum is observed at $d = 0.32$ nm after annealing signifying the presence of some three-dimensional order. These two diffraction peaks at 2θ of about 20° and 27° appear to be reminiscence of PHBA crystal structure^[8,9]. It is known that X-ray diffraction patterns of a copolyester should be very sensitive to its sequence^[10,11]. So we may conclude that the sample's crystalline structure changes on annealing. Inherent viscosity $[\eta]$ increase from 0.56 to 0.78. ^{13}C NMR analysis showed that triad distribution of the copolyester was changed, indicating a sufficient degree of aggregation of the respective PPP, TPP and PPB units has occurred to a level of order comparable to that of the original material. These indicate that interchain transesterification has occurred in polycrystalline regions, to produce the more highly ordered structures. In fact these new endotherms near 335°C are typical of these sequence structures.

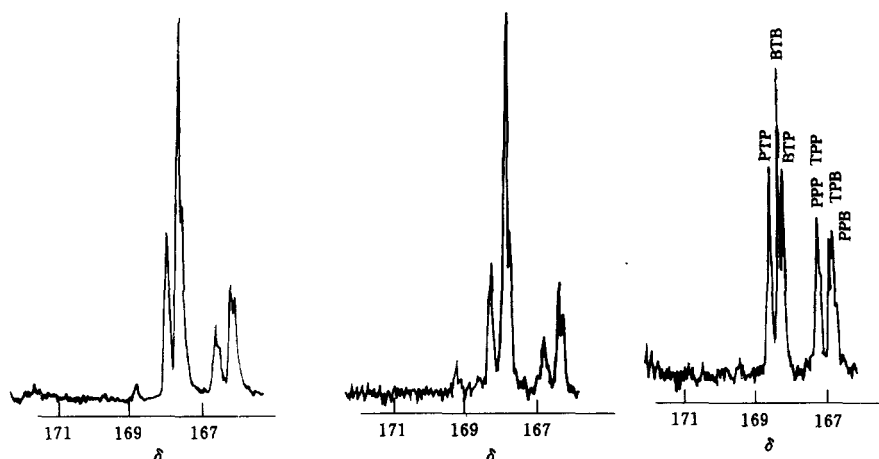


Fig. 6 ^{13}C NMR of copoly (PHBA/BPA/TPA) for P_3 (a) as-made sample; (b) annealed, 18 h, 200°C ; (c) annealed, 8 h, 280°C

It was concluded that annealing at $70\text{--}80^\circ\text{C}$ below T_{c-n} , physical diffusion processes dominate to yield an increasing of the crystallinity along with increased molecular weight, transesterification reactions are limited to the end groups and the microstructure has not changed. Annealing near T_{c-n} , chemical processes dominate and simultaneously make the microdomains be ordered more perfectly. Analysis by ^{13}C NMR proved that interchain transesterification had occurred.

Keywords:

Liquid crystalline copolyester; Characterization; Microstructure; NMR

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