

SYNTHESIS AND CHARACTERIZATION OF THERMOTROPIC COPOLYESTERS AND COPOLY(ESTER-AMIDE)S CONTAINING OXYETHYLENE-ETHER AS THE SPACER^{*}

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ABSTRACT

Flexible oxyethylene-ether was introduced into the aromatic copolyesters and copoly(ester-amide)s to reduce the melting point of resulting polymers. The melting point was greatly reduced to 200°C or even lower in some cases, and the molecular weight was satisfactorily high as reflected by inherent viscosity. The polymers exhibited high thermal stability and good mechanical properties as determined by TGA and mechanical tests. The copolyester showed better crystallinity and liquid crystallinity than corresponding copoly(ester-amide)s with similar monomer composition as reflected by POM observation and WAXD study. The melting points for both copolyesters and copoly(ester-amide)s showed great dependence on the p-acetoxybenzoic acid (PAB) content in monomer composition and reached the lowest value when PAB was 29 mol%.

INTRODUCTION

Thermotropic liquid crystal behavior of polymeric systems had been

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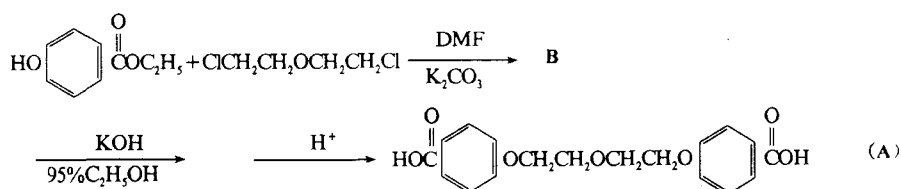
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intensively investigated in recent years^[1-3]. In order to obtain melt processibility of liquid crystal polymers ($T_m < 350^\circ\text{C}$), various approaches were tried to disrupt the chain packing. The most common modification was to incorporate flexible links consisting of short aliphatic chains (flexible spacer). If the flexible spacers were introduced into polymer backbone by ester bonds, it might be difficult to obtain high molecular weight products because of the ease of decomposition of aliphatic-aromatic ester bond under the ester exchange catalyst which was often used to improve the reaction rate. Recently, while the di-alkoxy spacers were used to improve the heat stability and molecular weight as described by several patents^[4,5], the melting points of the products were still closing to 300°C .

The objective of our work was to prepare materials which may be used as a reinforcing agent in the so-called "in-situ composite" for conventional thermoplastics, e. g. PS, PP, etc. Thus the melting point of the liquid crystalline polymer should not exceed the "processing window" of the matrix, and the structure should govern the properties of the resulting polymer, e. g. with respect to molecular weight, thermal and oxidative stability. In this work, the effect of using a flexible unit containing oxyethylene-ether in aromatic copolyesters and copoly (ester-amide)s was investigated, in which p-acetoxybenzoic acid (PAB) was used as a comonomer up to 60 mol% to modify the molecular weight and melting point of the resulting polymers.

EXPERIMENTAL

Preparation of bis[2-(4'-carboxylphenyloxy)ethyl]ether (A)



A was obtained by alkaline hydrolysis of bis [2-(4'-ethoxycarbonylphenyloxy)ethyl]ether (**B**) which was prepared by the method described by Griffin and Haven^[6]. In a 500 ml three-necked flask, ethyl 4-hydroxybenzoate (33.24g/0.20 mol) was dissolved in 25 ml of DMF, then anhydrous potassium

carbonate (26.5g/0.25 mol) and 0.10 mol bis (2-chloroethyl)ether was added to the reaction flask, followed by the addition of 25 ml of DMF. The mixture was refluxed with continuous stirring, allowed to cool, and then poured into 2 liters of cold water. The solution containing the precipitated solid was kept overnight in a refrigerator, then filtered, washed well with water, and allowed to dry in air. Thereafter, it was recrystallized from 95% ethanol and finally dried under vacuum at 50°C for 48h. The yield of **B** was 27.3g (68%). **B** (20.1g/0.05 mol) was added to 500 ml of a 10% (w/v) solution of potassium hydroxide in 95% ethanol. The resulting suspension was stirred under reflux for 4h. It was then diluted with 2L water to dissolve the potassium salt of **A**. Concentrated hydrochloric acid was added to the solution until it showed acidic to the pH test paper. The deposit crude **A** was filtered, washed with water and dried. It was purified by recrystallization from DMF-95% ethanol. Yield, 14.2g (82%), mp, 310°C (lit ^[7] 309–313°C).

Acetylation of p-aminophenol, hydroquinone, and p-hydroxybenzoic acid

p-Aminophenol (15g) was acetylated with 50 ml of acetic anhydride and 45 ml of pyridine for 10h with stirring at room temperature and raised to 80°C to complete the reaction for 1h. The crude product was recrystallized in acetic acid, yield: 23.5g (89%), mp: 140°C. Diacetylated hydroquinone and p-acetoxybenzoic acid were obtained by reaction of hydroquinone and p-hydroxybenzoic acid with excess amount of anhydride^[1,8].

Polymerization

p-Acetoxybenzoic acid and diacetylated p-aminophenol or diacetylated hydroquinone were polymerized using 10 mg $\text{Sb}_2\text{O}_3/\text{Zn}(\text{CH}_3\text{CO}_2)_2$ as catalyst in a stream of dried nitrogen. A general polymerization procedure was used for all the experiments: The monomer mixture was heated to 225°C for 40 mins in a cylindrical glass polymerization tube, then raised to 275°C over a period of 40 mins. The polymerization was continued at 280°C for 1h under the stream of nitrogen until most of the acetic acid (90%) was evolved. There after, vacuum was employed from 10 mmHg to 0.5 mmHg over a period of 1h. The polymer thus obtained was grounded.

RESULTS AND DISCUSSION

The basic physical properties of copolymers

The polymerization data and thermal properties of two series of polymers were summarized in Tables 1 and 2.

Table 1 Polymerization data and thermal properties of the thermotropic copolyesters

Polymer A	Molar ratio			Total monomer (g)	$T_m^{b)}$ (°C)	$T_i^{c)}$ (°C)	Yield (%)	$\eta_{inh}^{d)}$ (dl · g ⁻¹)
	I	II	III					
APAB-O ^a)	100	100	0	5.40	227	292	81	0.42
APAB-17	100	100	40	6.01	200	330	83	0.27
APAB-23	100	100	60	6.32	194	385	91	0.64
APAB-29	100	100	80	6.62	174	410	87	0.31
APAB-33	100	100	100	6.93	192	/	93	0.86
APAB-50	100	100	200	8.46	240	/	92	0.69
APAB-60	100	100	300	5.00	262	/	88	0.67

a) Refer to molar percent of PAB in the monomer mixture. b) By DSC.

c) By polarizing microscopy. d) Determined in mixed solution of p-chlorophenol and tetra-chloroethane (by 40/60 weight ratio) with concentration of 0.5g/dl at 30 °C

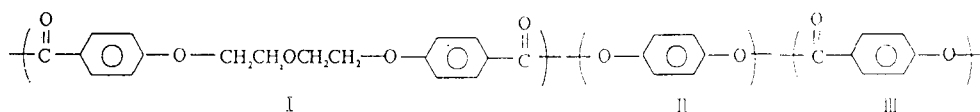
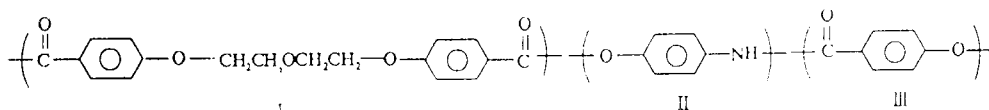


Table 2 Polymerization data and thermal properties of thermotropic copoly(ester-amide)s

Polymer B	Molar ratio			Total monomer (g)	$T_m^{b)}$ (°C)	$T_i^{c)}$ (°C)	Yield (%)	$\eta_{inh}^{d)}$ (dl · g ⁻¹)
	I	II	III					
BPAB-0 ^a	100	100	0	5.40	246	300	89	0.51
BPAB-17	100	100	40	6.01	232	370	92	0.63
BPAB-23	100	100	60	6.32	200	/	96	1.06
BPAB-29	100	100	80	6.62	180	/	88	0.59
BPAB-33	100	100	100	6.93	203	/	91	0.71
BPAB-50	100	100	200	8.46	240	/	90	0.83
BPAB-60	100	100	300	5.00	269	/	90	0.78



The inherent viscosities of these polymers were quite high, especially for the copolyester containing 33 mol% PAB(APAB-33) and the copoly (ester-amide) containing 23mol% PAB(BPAB-23). Generally, the molecular weight of the

polyester was controlled by several factors: 1. the monomers which control the main properties of products; 2. the way of polymerization, e. g. solution or melt polymerization; 3. the polymerization conditions which modify the molecular structure. The most common method used for the synthesis of main-chain thermotropic liquid crystal polymer (TLCP) was melt condensation followed by solid phase polymerization to obtain polymer material with high molecular weight. As summarized in Tables 1 and 2, it was seen that the copoly (ester-amide)s had melting temperature somewhat higher than those of the corresponding copolyesters, which might be due to hydrogen bonding in copoly (ester-amide)s. Coincidentally, the lowest melting compositions for both the series were the samples with 29%mol PAB. This effect was well illustrated in Fig. 1.

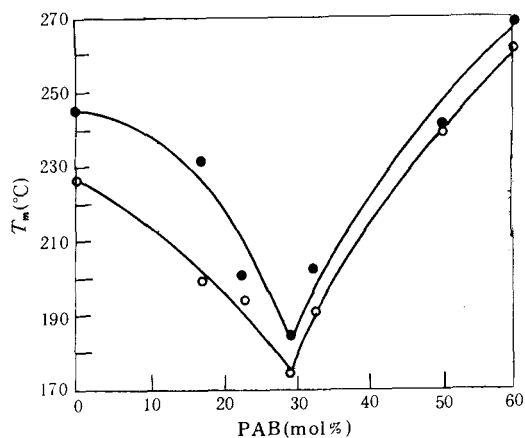


Fig. 1 The dependence of melting temperature on the content of PAB unit in polymer (○) APAB and (●) BPAB

The melting point was first reduced by adding PAB comonomer to the minimum at 29mol% PAB and then increased. It is well known that copolymerization is an effective way to reduce the melting point of polymers. As a matter of fact, this strategy has been widely used in synthesis of commercial TLCP materials^[9]. The chain structure was disrupted by copolymerization with PAB, resulting in the decrease of

melting point. Meanwhile, the longer colinear chain segments of PAB moiety might also increase the melting point of the resulting polymer if the content of PAB units was too high.

Being a structure material, an important question is whether the materials are thermally stable under the conditions which they show mesophase behavior. Therefore, the thermal stability was investigated by TGA. No significant weight loss in air was recorded below 330°C which was well above the melting points for the polymers. The thermal stability is somewhat reduced after introduction of amino groups.

Crystallinity and liquid crystallinity

All these polymers show typical nematic schlieren texture observed on a hot stage of a polarizing microscope. It was noticed that the copolymer containing higher amount of PAB comonomer displayed brighter color at the temperature range of mesophase (ΔT) than the copolymer containing less content of PAB. This difference in color became weaker and weaker, and finally disappeared for the polymers containing more than 29mol% PAB. The nematic phase of the copolymers was also identified by WAXD studies.

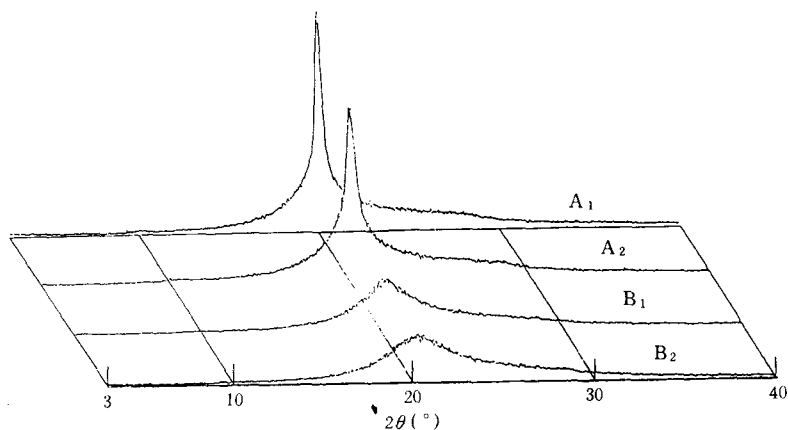


Fig. 2 WAXD diffraction patterns of APAB-33(A_1, A_2) and BPAB-33(B_1, B_2).

A_1, B_1 : crystallized at room temperature; A_2, B_2 : quenched with ice-water

Fig. 2 showed the WAXD spectra of APAB-33 and BPAB-33. The WAXD peaks for the quenched samples appeared at $2\theta = 20.3^\circ$ (corresponding to nematic phase, $d = 0.437\text{nm}$) were sharper and more intensive for the copolyester than that of copoly(ester-amide). This might be ascribed to the higher liquid crystallinity for the former. Although there was only one peak in WAXD patterns for both the crystallized samples of APAB-33 and BPAB-33, the crystallinity could be improved systematically with annealing, especially for the copoly(ester-amide) as reflected from both WAXD spectra (Fig. 3) and DSC thermograms (Fig. 4).

After annealed at 170°C for about 30 minutes, another diffraction peak at $2\theta = 21.8^\circ$ could be clearly seen, suggesting that the chain packing in the solid state became more perfect after annealing. The enthalpy change (ΔH_m) was also

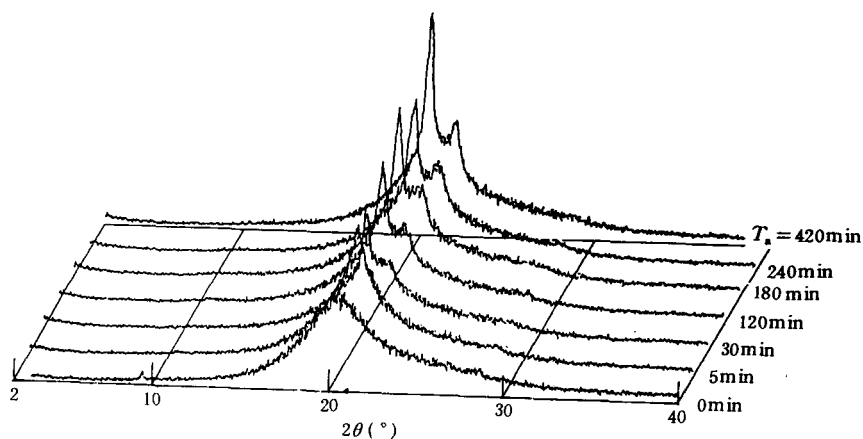


Fig. 3 WAXD diffraction patterns of BPAB-33 after annealed at 170°C for different time (T_a)

increased gradually with annealing (Fig. 5), indicating that the degree of crystallinity was improved. However, this kind of solid state could not be reached again immediately after it melted. Comparatively, the copolyester crystallized much more quick than copoly(ester-amide), and annealing did not affect much the solid structure of copolyester except that the degree of crystallinity was increased as reflected by the increasing of diffraction peak. These results demonstrated that the melting and crystallization behavior of copoly(ester-amide)s

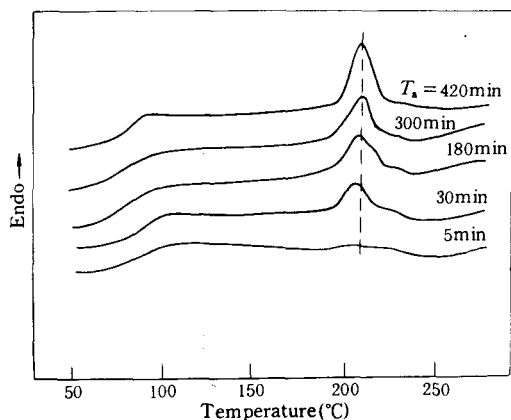


Fig. 4 DSC heating curves of BPAB-33 after-annealed for different time (T_a)

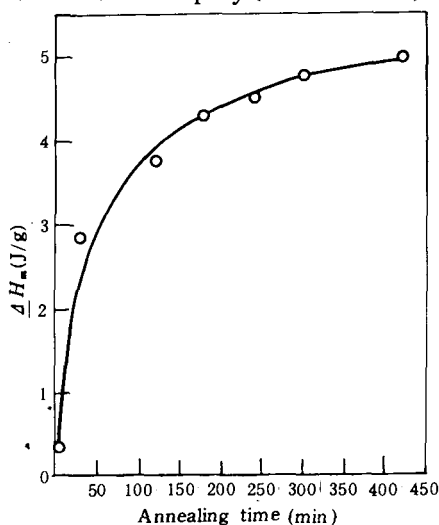


Fig. 5 ΔH_m versus annealing time for BPAB-33

showed greater thermal history dependence than that of copolyesters. These differences may be ascribed to the higher melt viscosity of copoly(ester-amide)s resulted from hydrogen bonds, so that thermodynamic effect played a significant role on the crystallization behavior of copoly(ester-amide)s.

Mechanical Properties

In order to study the mechanical properties, the polymer APAB-23 and BPAB-23 were synthesized on a scale of 100g for one reaction. The resulting polymers were injection molded at 230 °C. The mechanical properties were listed in Table 3.

Table 3 Mechanical properties of the polymers

Polymer	Tensile		Flexural		Elongation at break(%)
	Strength (MP _a)	Modulus (GP _a)	Strength (MP _a)	Modulus (GP _a)	
APAB-23	97.1	3.67	110.59	5.01	7.3
BPAB-23	121.0	4.88	132.76	5.89	5.6

It can be seen that the strength and modulus were satisfactorily high. As the characteristic of LCP, the strength and modulus showed great dependence on drawing, which was due to the development of orientation in fibers.

Keywords:

Synthesis and comparison; Liquid crystalline polymer; Copolyester; Copoly(ester-amide)

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