

SYNTHESIS AND CHARACTERIZATION OF AROMATIC LIQUID CRYSTALLINE COPOLYESTERS WITH REGULAR SEQUENCE STRUCTURE

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ABSTRACT

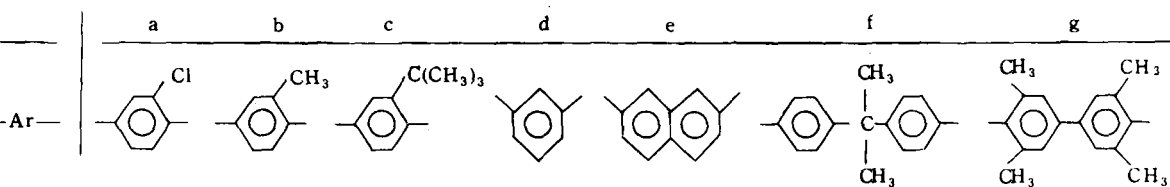
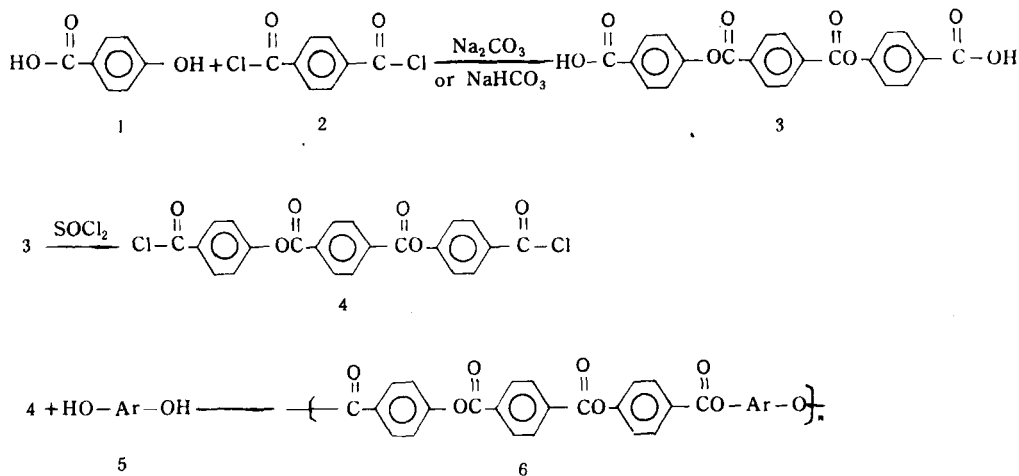
Several novel aromatic liquid crystalline copolyesters with regular sequence structure were prepared by melt Schotten-Baumann polycondensation via complex monomer. Polarizing microscope with hot stage, thermal analysis and X-ray diffraction were used to investigate the structure and properties of the copolyesters. The effects of structural units, such as flexible spacer, noncolinear meta-linked phenylene unit, crankshaft unit, kink with flexible bridging unit and various substituted benzene rings on melting temperature of aromatic copolyesters were studied and discussed on the basis of crystalline structure of the polymers.

INTRODUCTION

In recent years, thermotropic, main-chain polyesters have received considerable attention owing to the possibility of producing high performance fibers and self-reinforced plastics from their liquid crystalline melts. The two representative aromatic, para-linked polyesters, poly(p-hydroxybenzoic acid) and poly(p-phenylene terephthalate), however, have too high melting temperature for melt processing. Various approaches have been proposed to reduce melting temperature of polyesters in order to make them tractable, i.e. incorporation of noncolinear meta-linked phenylene units, kinks with flexible bridging units, crankshaft unit and flexible spacers into polymer backbone, substitution on benzene ring and copolymerization^[1,2]. Wholly aromatic random copolyesters and regular copolyesters with rigid mesogens and flexible spacers have been extensively studied. Several authors^[3-7] have investigated the effects of substituents on aromatic ring and central bridging units of kinks on melting temperature of copolyesters. Nevertheless, there have been few reports on the effects of different structural units mentioned above on properties of aromatic liquid crystalline copolyesters. Probably due to the fact that not all the copolyesters containing those structural units exhibit mesogenic behaviors.

In this paper, a para-linked, highly rigid moiety, oxybenzoyl, was used to enhance the mesophase formation ability of copolyesters through preparation of complex monomer from p-hydroxybenzoic acid and terephthaloyl dichloride. Copolyesters with regular sequence structure were synthesized from the complex monomer and various diphenols by melt Schotten-Baumann polycondensation. In this way sequence structures of the copolyesters were brought under control and the disturbance of different sequence structure which is common in random copolymerization was eliminated. The

resulting copolyesters were characterized and effects of different structural units on melting temperature were studied. Synthesis scheme of the copolyesters is shown as follows :



EXPERIMENTAL

Materials

3, 3', 5, 5'-tetramethyl-4, 4'-biphenol was prepared by carbon-carbon coupling of 2, 6-dimethylphenol followed by reduction with a $\text{Na}_2\text{S}_2\text{O}_4$ and NaOH solution. The reaction mixture was recrystallized three times from acetic acid, m.p. $232.5 - 233^\circ\text{C}$.

$$\text{C}_{16}\text{H}_{18}\text{O}_2 \text{ (242.3)}$$

Calcd; C 79.31, H 7.49

Found: C 79.08, H 7.42

Complex monomer 4, 4'-(terephthaloyldioxy) dibenzoyl dichloride (**4**) was synthesized by a modified two-step procedure. After an attempt to prepare 4, 4'-(terephthaloyldioxy) dibenzoic acid (**3**) under the condition described by Bilibin et al.^[8] failed, Na₂CO₃ or NaHCO₃ was used in the interfacial condensation reaction instead of NaOH.

Other monomers were purchased and purified by conventional methods.

Synthesis of copolyesters

Stoichiometric amount of complex monomer **4** and the appropriate diphenol (**5**) were charged into a polymerization tube which was purged with N₂ three times. The mixture was initially heated to a temperature ca. 20 °C above the m. p. of the diphenol. Polycondensation was carried out for 10 min. under a slow stream of N₂.

Then the temperature was increased as indicated : 250 °C for 2 hr., 320 °C for 1 hr., 320 °C under reduced pressure (<0.5 mmHg) for 30 min.. The product was ground, extracted with acetone overnight, washed with acetone and dried in vac. at 80 °C for 4–8 hr.. Shown in Table 1 are the initial polymerization temperature and inherent viscosity of the copolyesters. For comparison, a copolyester (**6h**) containing methylene flexible spacer was also synthesized from 4,4'-(hexandioyldioxy)dibenzoyl dichloride and 3,3',5,5'-tetramethyl-4,4'-biphenol.

Characterization

Inherent viscosity was determined at 30 ± 0.1 °C (0.5 g/dl) by using phenol / p-chlorophenol/1,1',2,2'-tetrachloroethane as solvent.

Thermal properties of the copolyesters were studied by means of Dupont 9900 differential scanning calorimetry and Dupont 951 thermogravimetric analyser with a heating rate of 20 °C/min.. Textures of mesophase were studied with a Leitz Ortholux polarizing microscope equipped with a hot stage. Photographs were taken from quenched samples.

Wide angle X-ray diffractograms (WAXD) of virgin samples were obtained on Rigaku D/max III B diffractometer with nickel-filtered CuK α radiation. The scanning rate was 8 °/min.. Wide angle X-ray diffractograms of mesophase were obtained by heating the sample to a temperature ca. 30 °C above melting temperature on Rigaku D/max III B Theta-Theta diffractometer with a high temperature accessory. Small angle X-ray diffractograms (SAXD) of mesophase were obtained on samples prepared by quenching copolyester melts with liquid nitrogen.

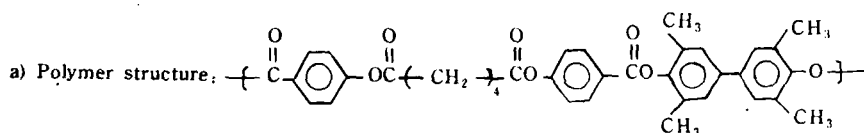
RESULTS AND DISCUSSION

General properties

The results of polycondensations are summarized in Table 1.

Table 1 Conditions and results of polycondensation

Polymer	Initial polycondensation temperature in °C	Yield in weight – %	Inherent viscosity in dl/g
6a	130	97	–
6b	160	98	–
6c	160	75	–
6d	130	97	–
6e	200	95	–
6f	180	91	1.22
6g	250	95	–
6h a)	b)	–	–



b) Polycondensation condition : 160 °C / 1 hr., 250 °C / 50 min., 300 °C / 30 min., 300 °C vac. / 30 min.

Although the reaction between acid chloride and hydroxy group in the synthesis of liquid crystalline copolyesters by using complex monomer **4** is a very rapid one, the polycondensation reactions were still carried out for a long time in order to obtain polymers with higher molecular weight. The stepwise polymerization procedure and

application of vacuum to the polymerization system at the last stage also served this purpose. The molecular weights of the resulting copolyesters are expected to be reasonably high as indicated by the measured inherent viscosity of copolyester (6f) ($I. V. = 1.22 \text{ dl/g}$). Among the copolyesters listed in Table 1, copolyesters (6c), (6d), (6f) and (6h) are slightly soluble in mixed solvents such as p-chlorophenol/1, 1', 2, 2'-tetrachloroethane, phenol/p-chlorophenol/1, 1', 2, 2'-tetrachloroethane, trifluoroacetic acid/dichloromethane. The other copolyesters (6a), (6b), (6e) and (6g), however, are insoluble in the above mentioned mixed solvents and other solvents, such as 1, 1', 2, 2'-tetrachloroethane, phenol/p-chlorophenol and phenol/1, 1', 2, 2'-tetrachloroethane. Hence measurement of molecular weights of the copolyesters is very difficult, even impossible for some copolyesters.

All the copolyester melts are turbid and exhibit strong stir-opalescence, indicating the character of liquid crystallinity. When viewed through a cross polarizing microscope, they display threaded-schlieren texture which is typical of nematic mesophase. Fig.1 shows typical textures of mesophase of the copolyesters.



Fig.1 Textures of regular copolyester mesophase
a) 6d quenched from 340 °C ; b) 6b quenched from 410 °C $\times 320$

X-ray diffractograms of the mesophase of copolyester 6e can be seen in Fig.2. The wide angle X-ray diffractogram at 400 °C (Fig. 2) shows a diffuse peak centered at 2θ of ca. 20 °, similar to that of monomeric nematogen. The small angle X-ray diffractogram does not display any peak in the 2θ range from 0.15 ° to 5 °, which excludes the possibility of smectogen, thus confirming nematic nature of the copolyesters.

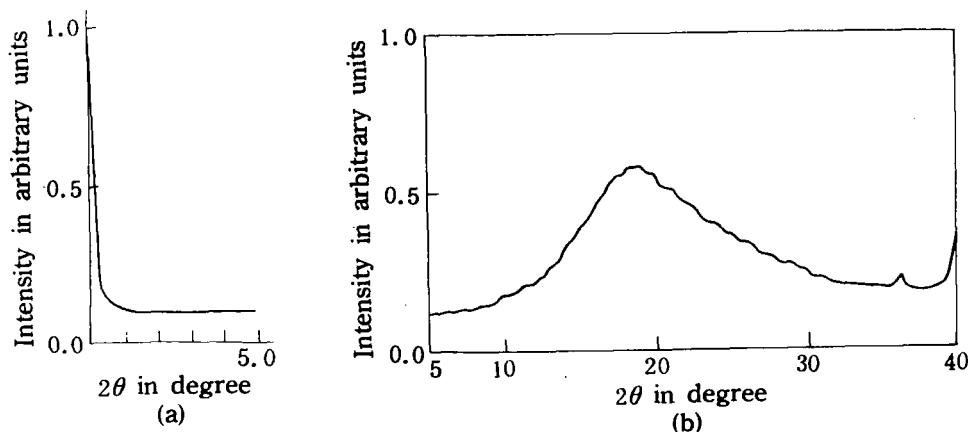


Fig.2 X-ray diffractogram of regular copolyester mesophase, sample : 6e
a) SAXD sample quenched from 400 °C ; b) WAXD at 400 °C

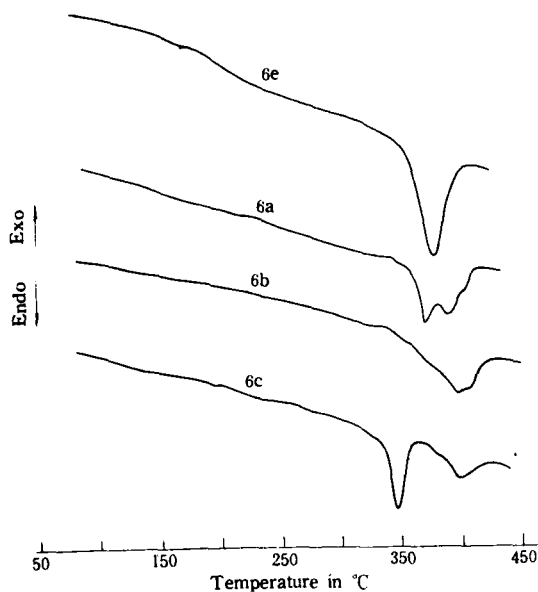


Fig.3 DSC traces of virgin samples of aromatic copolyesters, heating rate 20 °C/min.

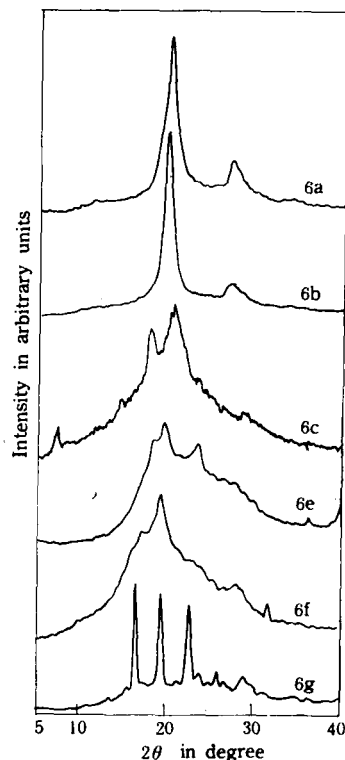


Fig.4 Wide angle X-ray diffractograms of virgin samples of copolyesters

Properties of the regular copolyesters, along with the diameters of the diphenol units, are listed in Table 2. Glass transitions could not be positioned in the DSC heating traces of the virgin samples, except copolyester 6e and 6f. Fig. 3 shows some DSC traces of the copolyesters. The heating trace of copolyester 6e displays a prominent glass transition at 156 °C, however, that of copolyester 6f exhibits a weak glass transition at 133 °C.

Table 2 Properties of regular copolyesters

Polymer	D in Å ^{a)}	T_{kk} in °C ^{b)}	T_m in °C ^{c)}	ΔH_m in kJ/mol ^{d)}	T_d in °C ^{e)}	X_c in % ^{f)}
6a	7.82	365	386	10.0	—	39
6b	7.89	—	395	11.8	—	43
6c	9.06	—	344	6.7	395 ^{g)}	30
6d	7.36	—	322	0.82	—	—
6e	7.36	—	370	9.4	451	18
6f	8.40	—	323	1.7	466	25
6g	9.07	203	409	24.0	450	63
6h	9.07	185	255	6.3	—	—

a) Diameter of the diphenol unit, calculated from structural data of the unit

b) Crystal-crystal transition temperature

c) Melting temperature

d) Enthalpy change on melting transition

e) Decomposition temperature, taken at the onset of significant weight loss

f) Degree of crystallinity, measured according to the method described in ref. 9

g) Isotropization temperature

Thermal stability of the regular copolyesters was studied by thermogravimetry. The onset of significant weight loss was taken as decomposition temperature (T_d). For copolyester **6c**, isotropization temperature (T_i) is used instead of T_d for evaluation of mesophase stability. The data in the sixth column of Tab. 2 indicate that the decomposition temperatures of the regular copolyesters measured are roughly the same. It is suggested that mesophase stability, which is determined by the difference of T_m and T_d (or T_i), depends mainly on melting temperature with an exception of copolyester **6c**.

Effects of structural units on melting temperature

All the virgin samples show melting endotherms in their DSC thermograms. Virgin samples of copolyesters **6a**, **6g**, and **6h** also exhibit crystal-crystal transition prior to melting in heating runs. The crystal-crystal transition temperatures are listed in Table 2.

The copolyesters in this study have definite sequence structure i. e. the p-oxybenzoyl moiety is distributed alternatively in polymer backbone. Hence, it is expected that any differences in melting temperature should be attributed to structural unit effect, assuming that molecular weight differences of the copolyesters, if any, are not important. The melting temperatures of the regular copolyesters in the present investigation range from 255 °C to 409 °C, depending on the structural units used. Copolyester **6g** which contains symmetrically substituted biphenyl moiety has the highest melting temperature, while copolyester **6h** which is incorporated with methylene spacer has the lowest melting temperature. The melting temperature of copolyester **6h** decreases by 154 °C compared with the wholly aromatic counterpart **6g**. It is shown that incorporation of flexible spacer is the most effective way to reduce melting temperature. Copolyesters **6d** and **6e** both contain noncolinear structural units but the former possesses lower stiffness than the latter, leading to a 48 °C decrease in melting temperature.

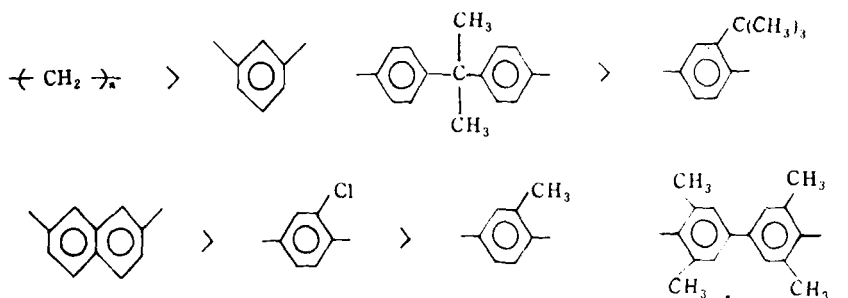
The three monosubstituted hydroquinone units in copolyesters **6a**, **6b** and **6c** are different in size and polarity of the substituents. Copolyesters **6a** and **6b** are not much different in the size of the substituents, as shown by the diameters in Table 2. Their melting temperatures are almost the same. On the contrary, copolyesters **6b** and **6c** are not much different in the polarity of the substituents, but the diameter of the monosubstituted hydroquinone unit in copolyester **6c** is 1.17 Å larger than that in copolyester **6b**, resulting in a depression of melting temperature by 51 °C. Based on these results, it is believed that the depression of melting temperature of wholly aromatic copolyester through substitution on benzene ring arises mainly from steric effect of the substituents, with very little contribution by polar effect. That is consistent with the conclusion drawn from the investigation on polymers incorporated with flexible spacers 10.

Fig. 4 shows powder wide X-ray diffractograms of virgin samples of the copolyesters. Certain diffraction peaks can be seen in each diffractogram, indicating semicrystalline nature of the copolyesters. As expected from the diphenol units the crystalline structures vary from polymer to polymer, as shown by differences in the number and shape of the diffraction peaks. Copolyesters **6c**, **6e** and **6f**, which have lower melting temperatures, show larger amorphous peak. Their crystalline diffraction peaks are ill-defined. The degree of crystallinity is relatively low compared with the

other three copolyesters (see the seventh column in Table 2). It is believed that the disruption of perfect regularity of simple, para-linked aromatic chains by incorporation of irregular structural units results in the decrease of chain packing efficiency, hence the crystal perfectness of the polymers. Therefore, it seems reasonable to conclude that the depression of melting temperature of aromatic polyesters arises mainly from the disruption of crystalline structure of the polymers, in morphological point of view. Investigations on random copolyesters based on p-hydroxybenzoic acid, terephthalic acid and 2, 7-dihydroxynaphthalene support the conclusion.

CONCLUSION

Aromatic liquid crystalline copolyesters with regular sequence structure have been synthesized and characterized for the effects of structural units on liquid crystalline properties. The regular copolyesters prepared have been identified as thermotropic nematogens. The structural units in the aromatic copolyesters with definite chain structure strongly influence melting temperature and thermal stability of mesophase. Incorporation of flexible spacer into polymer main chain is the most effective way to reduce melting temperature. Monosubstitution on benzene ring to depress melting temperature results in predominant steric effect, rather than polar effect. According to the data in Table 2, it appears that the effectiveness of reducing melting temperature by incorporation of irregular structural units is in the following order:



One possible reason for the depression of melting temperature of aromatic copolyesters by irregular structural units is the disruption of crystalline structure of the polymers.

Keywords :

Aromatic copolyester ; Thermotropic liquid crystal ; Melting temperature; Structural unit

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