

PREPARATION OF LIQUID CRYSTALLINE COPOLYESTERS WITH SPACERS BASED ON BISPHENOL-A, BISPHENOL-S OR POLYSULFONE BY DIRECT POLYCONDENSATION

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ABSTRACT

Four series of copolyesters were synthesized by direct polycondensation reaction between aromatic dicarboxylic acids and bisphenols by using tosyl chloride and N, N-dimethylformamide (DMF) in pyridine under mild conditions. The electron-rich hydroxyl groups of bisphenols favoured the polycondensation reaction and the order of relative reactivities of bisphenols is as follows:

bisphenol-A > hydroquinone ~ bisphenol-S > chlorohydroquinone. The mesomorphic properties of copolyesters were examined by birefringence under polarizing microscope, melt transparency, DSC and X-ray diffraction. The minimum molar fraction of mesogenic units needed for the appearance of liquid crystallinity is not higher than 0.1 despite of the different varieties and lengths of the spacers studied.

INTRODUCTION

The direct polycondensation reaction between aromatic dicarboxylic acids and bisphenols by means of tosyl chloride and N, N-dimethylformamide (DMF) in pyridine (Py) can be operated under mild conditions to obtain the wholly aromatic copolyesters which have enough molecular weight for offering steady transition temperatures^[1, 2]. Higashi et al. have reported that the reaction was effective in polycondensation with a mixture of terephthalic and isophthalic acids, but when one of the acids was used alone, the product obtained has low molecular weight. In addition, the aliphatic 1, 4-cyclohexane diol is less reactive than aromatic diol toward the polycondensation with aromatic acids^[3]. The competitive reactivities of different bisphenols were investigated in this paper and liquid crystalline copolyesters containing spacers based on bisphenol-A, bisphenol-S or polysulfone oligomer (PSF) were synthesized.

EXPERIMENTAL

Preparation and purification of raw materials

Tosyl chloride (TsCl), isophthalic acid (IPA), bisphenol-A (BPA), 4, 4-

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Received July 10, 1987

dihydroxydiphenylsulfone (BPS) and benzoic acid were recrystallized from petroleum ether, ethanol, benzene, ethanol and water, respectively. DMF was refluxed over P_2O_5 and distilled in vacuum. Py was refluxed over KOH and distilled, p-chlorophenol (PCP) was distilled in vacuum. Chlorohydroquinone (CHQ)^[4], hydroquinone (HQ)^[4] and hydroxy terminated polysulfone oligomers (PSF)^[5] were prepared or purified according to the literature.

Polycondensation

A typical preparation procedure of polymer No. 420 was described as follows:

3 mmol DMF and 13 mmol TsCl were dissolved in 10 ml Py. The solution was maintained at room temperature for 10 min and then poured into a mixture of 2.5 mmol terephthalic acid (TPA) and 2.5 mmol IPA in 10 ml Py. White precipitates were formed during about 10 min at room temperature. The mixture changed into clear solution after heating at 120 °C for 10 min with stirring. The solution of 2.5 mmol HQ and 2.5 mmol BPA in 10 ml Py was added dropwise in 20 min. The reaction was continued at 120 °C for 5 h, 10 ~ 20 ml Py was introduced and then the reaction mixture was poured into methanol. The product was filtered, washed and dried.

Characterization of polymers

Inherent viscosities were determined in PCP/tetrachloroethane (TCE) mixed solvent at 30 °C; ^1H -NMR spectra were recorded on Varian a FT-80A NMR spectrometer using $CF_3COOD/CDCl_3$ (1:1, by volume) as solvent; thermoanalysis was performed on a DT-30 DSC instrument (Shimadzu) at a heating rate of 20 °C/min; X-ray diffraction pattern was obtained on a BD-74 diffractometer with $CuK\alpha$ as radiation source and polarizing photomicrographs were taken on melting point apparatus of type X6 (made in Beijing) with magnification of 100.

RESULTS AND DISCUSSION

1. Copolyesters and their solubility

In order to verify the effectiveness of the catalyst system the model condensation reaction of a mixture of benzoic acid and p-chlorophenol was carried out and p-chlorophenyl benzoate was obtained in a yield of 94.8% (94%, as reported in literature^[3]) with M. P. 85—6 °C and strong absorptions at 1725 cm^{-1} and 1160 cm^{-1} , characteristic bands of ester group in the IR spectrum.

The direct polycondensation of TPA and bisphenols gave the product insoluble in Py, the reaction proceeded only with limited success and gave rise to the formation of polyester of low molecular weight. In order to minimize the effect of polymer solubility on the molecular weight of the resulting polymer, the polycondensation of a mixture of TPA and IPA was chiefly examined, because the reaction proceeded in Py homogeneously. Four series of copolyesters based on TPA/IPA-HQ/BPA, TPA/IPA-HQ/BPS, TPA/IPA-CHQ/BPS and TPA/IPA-HQ/PSF were synthesized.

We examined the direct polycondensation of TPA /IPA and BPA /hexamethylenediol at first and obtained the product with η_{inh} only 0.12. This result is similar to the reaction between 1, 4-cyclohexane diol and TPA /IPA, which also gave the product with low molecular weight as reported by Higashi et al.^[3] and it indicated the low reactivity of the aliphatic diols toward the direct polycondensation.

Inherent viscosities of copolyesters based on HQ /BPA reached around 1.0 (Table 1), but if the BPS was used instead of BPA, the η_{inh} values were only below 0.6 and decreased with increasing the feed ratio of BPS /HQ. η_{inh} values of copolyesters based on PSF were in the middle of those based on BPS and BPA.

Table 1 Inherent viscosity and solubility of copolyesters

No. .	Feed molar ratio of monomers	η_{inh}	Solubility		
			in Py	in PCP /TCE (2 : 1 , by vol . .)	in CF ₃ COOH
TPA /IPA-HQ /BPA					
330	1 /1- 4 /1	0.77	-	+	-
416	1 /1-3 /2	0.86	+	+	+
420	1 /1-1 /1	0.98	+	+	+
422	1 /1-2 /3	1.13	+	+	+
504	1 /1-1 /4	0.90	+	+	+
107	1 /1-0 /2	0.84	+	+	+
329	3 /2-4 /1	-	-	*	-
TPA /IPA-HQ /BPS					
406	3 /2-4 /1	-	-	*	-
410	3 /2-3 /2	0.51	+	+	+
508	1 /1-1 /4	0.27	+	+	+
TPA /IPA-CHQ /BPS					
403	3 /2-4 /1	0.57	*	+	+
507	1 /1-1 /4	0.20	+	+	+
TPA /IPA-HQ /PSF					
414	3 /2-4 /1	0.82	+	+	+
424	3 /2-3 /2	0.42	+	+	+
511	3 /2-0 /5	0.43	+	+	+

*only suspended in the solvent

For the same copolyester series, the solubilities of copolyesters decrease with the increase of the fraction of mesogenic units based on TPA and HQ or CHQ in the chain. Since most of polycondensation products are soluble, the formation of polymer containing merely mesogenic units could be ruled out, for the latter is insoluble in the solvents.

2. Competitive reactivities of various bisphenols toward direct polycondensation

In order to understand the relative reactivity of various bisphenols were the chemical compositions of the polycondensation products determined. For TPA /IPA-HQ /BPA copolyesters the fraction of BPA moieties in the copolyester is higher than that in the feed ratio of bisphenols (Table 2). This shows that BPA is more reactive than HQ . The relative reactivities of HQ , BPS and CHQ were similar to each other , and the molar ratio of bisphenols in feed was quite close to that in copolyester . (Table 3)

Table 2 Compositions of copolyesters based on TPA /IPA-HQ /BPA

No .	Molar ratio in copolyester (HQ/BPA)	
	By feed ratio	By ¹ H-NMR *
420	0.50 : 0.50	0.46 : 0.54
422	0.40 : 0.60	0.29 : 0.71
504	0.20 : 0.80	0.07 : 0.93

* δ_{CH_3} - (in BPA) = 1.71 ppm ; $\delta_{\text{C}_6\text{H}_4}$ - (in bisphenols) = 7.13 - 7.48 ppm

Table 3 Compositions of copolyesters based on TPA /IPA-HQ (or CHQ) /BPS

Copolyester based on	No .	Composition of copolyester		HQ (or CHQ) : BPS (in mol)	
		S-content (wt - %)	Cl-content (wt - %)	In feed	In copolyester
HQ /BPS	406	2.32	8.16	0.80 : 0.20	0.79 : 0.21
	410	4.30		0.60 : 0.40	0.58 : 0.42
	508	7.08		0.20 : 0.80	0.21 : 0.79
CHQ /BPS	403	2.39	8.16	0.80 : 0.20	0.77 : 0.23 ^a 0.74 : 0.26 ^b
	507	7.26		0.20 : 0.80	0.18 : 0.82

a) according to S-content ; b) according to Cl-content

The electron-rich hydroxyl groups of BPA are favourable to the attack on carboxyl groups (about the detailed mechanism of direct polycondensation, see literature [3]). Although the electron density of hydroxyl group in HQ or CHQ is higher than that in BPS , once one hydroxyl group of HQ or CHQ molecule is esterified, the electron density of another hydroxyl group of the molecule will decrease . This will lead to the similarity of the reactivity of the three bisphenols, among which CHQ seems less reactive than the two others. This may be due to the presence of electron-withdrawing Cl atom . Thus the order of the relative reactivities of bisphenols may be expressed as follows :



3. Liquid crystallinity and transition temperature of copolyesters

The mesomorphic properties of copolyesters were examined by melt transparency

and birefringence under polarizing microscope. The copolyesters based on HQ/BPA, HQ/BPS or CHQ/BPS showed melt anisotropy within a broad extent of molar fractions of mesogenic units (Table 4). For example melts of copolyesters based on HQ/BPA, in the range of 10 mol-% to 40 mol-% of mesogenic unit fraction in feed, show apparent birefringence in the polarizing photomicrograph. While the fraction was higher than 40 mol-%, the solubility of the product was poor, and the η_{inh} could not be detected. Whereas the fraction was lower than 10 mol-% the product fused into extinctive melt.

Table 4 Bulk properties of copolyesters

No.	Composition of copolyesters in feed		η_{inh}	T_g	T_f	T_i	Birefrin- gence	Transparency of melt
	Molar ratio	Mesogenic unit fraction *						
	TPA/PA -HQ/BPA							
330	1/1-4/1	0.40	0.77	170	330	> 350	+	opaque
416	1/1-3/2	0.30	0.86	205	285	330	+	opaque
420	1/1-1/1	0.25	0.98	197	280	320	+	opaque
422	1/1-2/3	0.20	1.13	190	300	330	+	opaque
504	1/1-1/4	0.10	0.90	205	290	330	+	transpa.
107	1/1-0/2	—	0.84	—	270	—	—	transpa.
329	3/2-4/1	0.48	—	—	330	> 350	+	opaque
	TPA/PA -HQ/BPS							
406	3/2-4/1	0.48	0.58	—	320	> 350	+	opaque
410	3/2-3/2	0.36	0.51	195	270	300	+	opaque
508	1/1-1/4	0.10	0.27	185	210	240	+	transpa.
	TPA/PA -CHQ/BPS							
403	3/2-4/1	0.48	0.57	180	280	340	+	opaque.
507	1/1-1/4	0.10	0.20	—	185 ^Δ	225 ^Δ	+	transpa.
	TPA/PA -HQ/PSF							
414	3/2-4/1	0.48 (0.125) **	0.82	195	280	330	+	opaque
424	3/2-3/2	0.36 (0.071) **	0.42	200	230	—	—	transpa.
511	3/2-0/5	0 (0) **	0.43	202	230	—	—	transpa.

* feed molar fraction of HQ or CHQ based upon total moles of all bisphenols; ** calculation was based on BPA or BPS instead of PSF moieties; ^Δ determined by DSC.

It is interesting to point out that copolyester No. 422 which contained the mesogenic unit fraction only 14.5 mol-% as determined by ¹H-NMR (calculated from data

of Table 2) showed evident liquid crystallinity both by melt transparency and birefringence under cross polarizers (Fig. 1a). For copolyester No. 504 with mesogenic unit fraction only 3.5%, the anisotropy was still observed under polarizing microscope (Fig. 1b), but this could not be confirmed by the melt transparency detected by naked eye.

The low fraction of mesogenic units needed for copolyesters prepared may be explained by the contribution to the formation of liquid crystallinity made by the rigid structural units of triad ($-C_6H_4OOC C_6H_4COO C_6H_4-$) with three phenyl nuclei in spacers, as we have pointed out in our previous work^[4], besides mesogenic units.

In regard to copolyesters based on HQ/BPS or CHQ/BPS the minimum fraction of mesogenic units needed for the formation of melt anisotropy is also low (around 10 mol-%) (Fig. 1c and 1d).

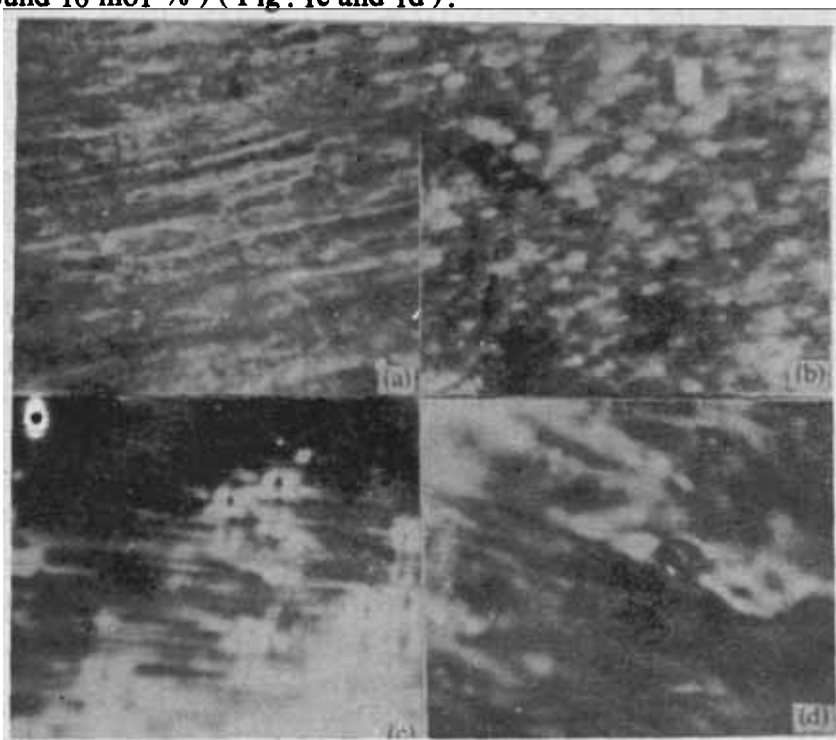


Fig. 1 Photomicrographs of melts (magnification $\times 100$) (a) copolyester No. 422, at 310° , sheared; (b) No. 504, at 305° ; (c) No. 507, at 210° , sheared; (d) No. 410, at 284° , sheared

In order to understand the effect of chain length of the spacer on liquid crystallinity of the products, we prepared polyesters based on HQ and hydroxyl terminated PSF terechelic oligomers of molecular weight 2.5×10^3 . The melts of copolyesters with feed molar fractions of mesogenic units higher than 0.48 were anisotropic ones (Table 4). If we calculated the molar fraction of mesogenic units on the base of BPA or BPS instead of PSF moieties, we can see that the minimum molar fraction needed for the liquid crystallinity is not higher than 0.125.

For all the four series of copolyesters we studied, the values of T_i and T_f were observed under polarizing microscope except that the T_i of copolyester No. 507 and T_m values of three copolyesters (as shown in Table 4) were detected by DSC. Melting points of most polyesters could not be observed by DSC and this may be due to their

poor crystallinity, as verified by the powder X-ray diffraction analysis. For example, sample No. 416 showed only diffuse haloes in the scanning range ($2\theta = 10-30^\circ$) (Fig. 2). In addition, since the fact of non-crystalline polyesters fused into optically anisotropic melts may infer the possibility that the existence of crystalline wholly aromatic polyesters in the birefringent melts could be ruled out. Thus the anisotropy could only characterize the mesomorphic behaviour of polyesters.

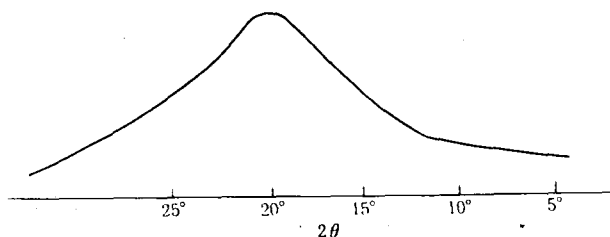


Fig. 2 X-ray diffraction pattern of copolyester No. 416.

Acknowledgement The authors are indebted to the National Natural Science Foundation of China for financial support of this work and also grateful to Zhang Zhibin and Lu Yingxian for their help in the preparation of PSF and DSC measurement, respectively.

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