

STUDIES ON THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTERS—POLY(ARYLENE TEREPHTHALATE-CO-BUTYLENE TEREPHTHALATE)

ZHANG Hongzhi (张鸿志) and NING Xin (宁新)

(Department of Chemistry, Peking University, Beijing)

ABSTRACT

A series of copolyesters based on bis(4-hydroxybutyl) terephthalate, terephthaloyl chloride and various aromatic diols (i.e. hydroquinone, chlorohydroquinone, bromohydroquinone or dihydroxybiphenyl) was prepared. ^1H -NMR studies revealed that the monomer units had microstructures close to random distribution in the chains. The copolymers showed composition-dependent liquid crystalline properties as verified by visual observation of stir opalescence, polarizing microscope, DSC and X-ray diffraction. The copolyesters with aromatic diol contents over a certain extent (for chlorohydroquinone $m \geq 0.33$) were thermotropic with wide liquid crystalline temperature ranges. The introduction of chlorohydroquinone into the copolyesters could gradually destroy the crystallinity of the polymers but retain the liquid crystalline characteristics.

INTRODUCTION

In recent years the research and application of liquid crystalline polymeric materials have been one of the most attractive fields in polymer science^[1,2]. A lot of papers has appeared on aromatic polyesters as thermotropic liquid crystalline materials. Jackson Jr. and coworkers prepared a sort of liquid crystalline copolymers by introducing into the polyethylene terephthalate backbone a rigid $\text{O}-\text{C}_6\text{H}_4-\text{CO}$ structure via transesterification and thus greatly enhanced the properties of the products^[3]. Similar attempts on the structure-like polybutylene terephthalate was unsuccessful because of the homo-polymerization of the *p*-acetoxybenzoic acid^[4]. In this paper a series of thermotropic liquid crystalline polymers were prepared from bis(4-hydroxybutyl) terephthalate, terephthaloyl chloride and various aromatic diols. Some of the properties of these polymers were characterized and studied.

EXPERIMENTAL

Purification and preparation of raw materials

1,1,2,2-Tetrachloroethane (TCE) was dried by molecular sieves and distilled. Pyridine

(Py) was refluxed over potassium hydroxide for two hours and then distilled. Terephthaloyl chloride (TC), hydroquinone (HQ), and 4,4'-dihydroxybiphenyl (DBP) were recrystallized^[5]. Chlorohydroquinone (CHQ)^[6], bromohydroquinone (BHQ)^[6] and bis(4-hydroxybutyl) terephthalate (BHBT)^[7] were prepared according to the literature. Melting points and boiling points of the monomers were in accordance with those in the literature.

Preparation of polymers

The polycondensation was carried out at room temperature. A typical preparation procedure of polymer CHQ_{0.5} could be described as follows: 0.01 mole BHBT was dissolved in 100 ml TCE/Py (80/20) solution, then 0.02 mole TC dissolved in 20 ml TCE was introduced with stirring. Two hours later 0.01 mole CHQ solution (in 20 ml TCE, 10 ml Py) was added. The reaction continued for another 22 hours before this solution was poured into excess 95% ethanol. The precipitate was filtered out and washed by water and ethanol for several times until Cl⁻ could not be detected in the filtrate. The product was dried in vacuum at 60°C and the final product was a white or pale-yellow fragile solid.

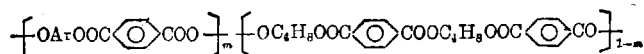
Characterization of the polymers

Intrinsic viscosity was determined in phenol/TCE (60/40 by weight) mixed solvent at 35°C; ¹H-NMR spectrum was recorded on a varian FT-80A NMR spectrometer using CF₃COOD:CDCl₃(1:1) as the solvent; thermoanalysis was carried out on a DuPont 1090 DSC instrument at a heating (cooling) rate of 10°C/min; polarizing photomicrographs were taken at a polarizing microscope equipped with hot-stage; X-ray diffraction pattern was obtained on a BD-74 diffractometer with CuKα as radiation source.

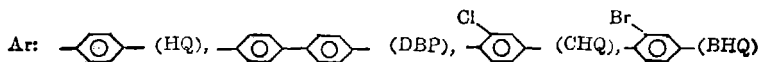
RESULTS AND DISCUSSION

Polymers and their basic properties

A series of copolyesters was synthesized. Their general constitutional formula can be expressed as follows:



where



In this paper we will use Ar_m to represent a certain copolymer, where Ar is the corresponding aromatic diol and *m* is the chain compositional fraction according to monomer feed ratio.

The solubility of the copolymers changes with the aromatic diols used. Within the same copolymer series, the solubility becomes poor as the amount of the aromatic diol in chain constitution increases. The wholly aromatic polyester of CHQ and HQ cannot be dissolved

in all the solvents tested (Table 1).

Table 1 Solubility of copolymers
(+ soluble, - insoluble)

Copolymer \ Solvent				
	$C_2H_2Cl_4$	$C_2H_2Cl_4 / C_6H_5OH$	CF_3COOH	$CF_3COOH / CHCl_3$
PBT*	+	+	+	+
BHQ _{0.5}	-	+	-	+
DBP _{0.6}	-	-	-	+
CHQ _{0.1}	+	+	+	+
CHQ _{0.3}	+	+	+	+
CHQ _{0.5}	+	+	+	+
CHQ _{0.7}	-	+	+	+
CHQ _{0.8}	-	-	-	+
HQ _{0.1}	+	+	+	+
HQ _{0.3}	+	+	+	+
HQ _{0.5}	-	-	-	+
CHQ _{0.5} ^Δ	+	+	+	+
PCT*	-	-	-	-
PHT*	-	-	-	-

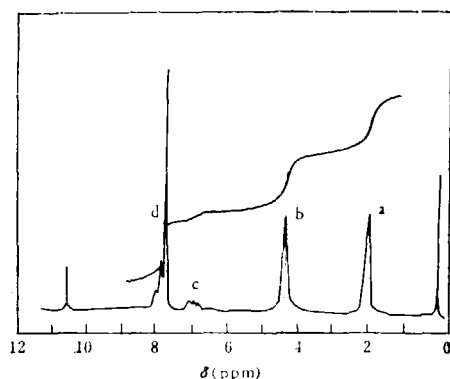
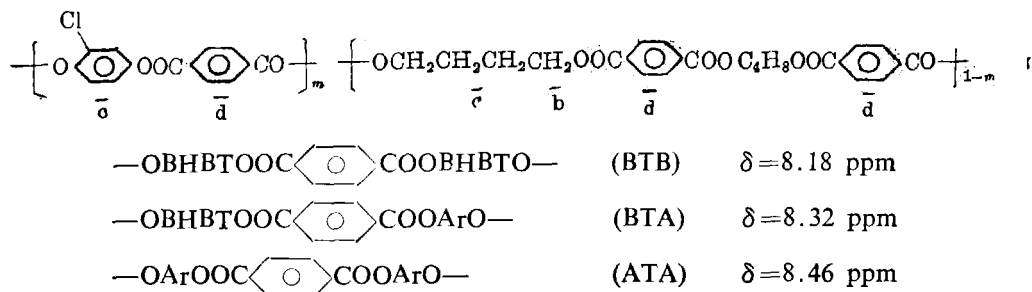
* PBT, PHT, PCT was the polymer of TC with BHBT, HQ, or CHQ respectively.

^Δ No Py was added to the system, the polycondensation was maintained at 145°C, HCl generated was taken away by flowing N₂.

IR spectra of the polymers also clearly show the influence of copolymer composition upon the absorbance strength. In the copolymer series of chlorohydroquinone, the absorbance of several peaks characterizing the phenyl ester formation (1486, 1238, 1170, 1060 cm⁻¹) increases as the aromatic diol fraction (*m*) in the chain increases.

NMR analyses

The ¹H-NMR spectrum of sample CHQ_{0.3} is given in Figure 1. In the range of 8.2–8.5 ppm the proton resonances of the terephthaloyl moiety give out three peaks at the testing resolution with chemical shifts at 8.18, 8.32, and 8.46 ppm. These peaks correspond to the different chemical circumstances of the terephthaloyl moiety in the copolymer chain as indicated by Korshak and coworkers^[8]. In this paper, they correspond to the following three kinds of triad:

Fig. 1 ^1H -NMR spectrum of $\text{CHQ}_{0.3}$ 

Spectrum of the PBT sample prepared by the same method shows, as expected, only a single peak at $\delta = 8.18$ ppm (BTB). According to the statistic theory of chain structure, we can determine from the triad integral areas (P_{BTB} , P_{BTA} , P_{ATA}) the microstructure parameters of the chain, and the composition parameter m of the copolymer as well^[9]. Because the statistics we deal with is about the sequence distribution of the monomer units, the proton contribution of the terephthaloyl moiety in the BHBT monomer at $\delta = 8.18$ ppm must be deleted in light of the resonance of its aliphatic protons (at $\delta = 2.1$ and 4.6 ppm) so that the integral areas can really represent the linking probabilities of TC with BHBT or aromatic diols.

Probability of unit AT proceeds to unit BT:

$$P_{\text{AB}} = P_{\text{ATB}} / (2P_{\text{ATA}} + P_{\text{ATB}})$$

Probability of unit BT proceeds to unit AT:

$$P_{\text{BA}} = P_{\text{ATB}} / (2P_{\text{BTB}} + P_{\text{ATB}})$$

Degree of randomness:

$$B = P_{\text{AB}} + P_{\text{BA}}$$

Mean sequence length:

$$\bar{L}_{\text{AT}} = 1/P_{\text{AB}}, \quad \bar{L}_{\text{BT}} = 1/P_{\text{BA}}$$

Composition parameter of the copolymer:

$$m = \bar{L}_{\text{AT}} / (\bar{L}_{\text{AT}} + \bar{L}_{\text{BT}})$$

It can be seen from Table 2 that the degree of randomness (B) of the copolymers is somewhat

between 0.8 and 0.9. That is to say that the distribution of the monomer units in the chain is close to a random distribution ($B=1$) and changes in m do not have a prominent influence on the value of B . From the viewpoint of monomer feeding procedures, the copolymer obtained should have had a chain microstructure somewhat dominated by an alternative distribution

Table 2 Composition and microstructure parameters of the copolyesters

Parameter Copolymer	m		Triad fraction			Mean seq. length		B
	Feed	Measured	P_{ATA}	P_{ATB}	P_{BTB}	$\bar{L}_{AT}$	$\bar{L}_{BT}$	
BHQ _{0.5}	0.50	0.45	0.28	0.34	0.38	2.6	3.2	0.69
DBP _{0.5}	0.50	0.42	0.20	0.44	0.36	1.9	2.6	0.90
CHQ _{0.2}	0.20	0.24	0.08	0.32	0.60	1.5	4.8	0.89
CHQ _{0.3}	0.33	0.38	0.19	0.39	0.42	2.0	3.2	0.82
CHQ _{0.5}	0.50	0.45	0.24	0.42	0.34	2.2	2.6	0.84
CHQ _{0.7}	0.67	0.64	0.43	0.42	0.15	3.0	1.7	0.91
CHQ* _{0.8}	0.80	0.84	—	—	—	—	—	—
HQ _{0.3}	0.33	0.30	0.11	0.37	0.51	1.6	3.8	0.90
HQ _{0.5}	0.50	0.52	0.31	0.41	0.28	2.6	2.4	0.81
CHQ _{0.5} ^Δ	0.50	0.60	0.38	0.43	0.19	2.8	1.9	0.89

* Because of the poor solubility, NMR spectrum had a low resolution (S/N), we could not get three peaks in the area.

Δ See the footnote in Table 1.

($B=2$) if the reaction between BHBT and TC had been totally fulfilled. But now the NMR analyses show that the reaction between terephthaloyl and aliphatic alcohols cannot be fulfilled under the conditions described above. That means there still existed a great number of alcoholic groups after reaction of two hours with the excess of terephthaloyl chloride. A copolymer microstructure of random distribution develops when the aromatic diol was then added. (Korshak reported that the reactivity of phenolic groups with acyl chloride was about ten times greater than that of alcoholic groups^[10].)

Thermoanalyses

The fusion endotherm of the polymers was much smaller than that of ordinary crystalline polymers, and usually with broad melting range. In the CHQ copolyester series, the melting peak weakens as the m value increases. When m reaches 0.67, neither melting nor crystallizing peaks could be found, thus it can be regarded as a noncrystalline materials. Most of the copolymers obtained decomposed at above 350°C, while BHQ_{0.5} decomposed at about 320°C. The transitions from the liquid crystalline state to the isotropic state (T_i) could not be observed.

Optical properties of the polymer melts

In Table 3 some of the bulk properties of the copolymers are listed. The anisotropy of the melts could be observed through polarizing microscope. In regard to CHQ copolymer series, $\text{CHQ}_{0.2}$ fused into an extinctive melt; the $\text{CHQ}_{0.3}$ melt was anisotropic with stir opalescence, the bright area decreased and became extinctive gradually at temperature above 220°C , but the transition could not be seen in the DSC scanning range. When m reached 0.5, clear stir opalescence and schlieren-like texture were observed and the melt did not extinct at above 300°C . The temperature range of liquid crystallinity was rather broad. Because of

Table 3 Bulk properties of the copolymers

Copolymer	Intrinsic viscosity	Melt point ($^{\circ}\text{C}$)	T_i transition ($^{\circ}\text{C}$)	Melt anisotropy	Stir opalescence	Crystallinity*
$\text{BHQ}_{0.5}$	0.25	185	>320	yes	strong	crystalline
$\text{DBP}_{0.5}$	—	202	>350	yes	vague	crystalline
$\text{CHQ}_{0.2}$	0.23	201	—	no	no	crystalline
$\text{CHQ}_{0.3}$	0.20	197	~ 220	yes	weak	crystalline
$\text{CHQ}_{0.5}$	0.18	187	>350	yes	strong	crystalline
$\text{CHQ}_{0.7}$	0.34	220**	>350	yes	strong	non-cryst.
$\text{CHQ}_{0.8}$	—	230**	>350	yes	vague	non-cryst.
$\text{HQ}_{0.1}$	0.19	—	—	no	no	crystalline
$\text{HQ}_{0.3}$	0.19	193	~ 230	yes	weak	crystalline
$\text{HQ}_{0.5}$	—	202	>350	yes	strong	crystalline
$\text{CHQ}_{0.5}^{\Delta}$	0.30	214	>350	yes	strong	crystalline
PBT	0.50	215	—	no	no	crystalline

* Determined by X-ray diffraction.

** Softening point.

the non-crystallinity of the $\text{CHQ}_{0.7}$, $\text{CHQ}_{0.8}$ samples, we could only observe a softening point under the microscope, that is the temperature when the original sample grain can be squeezed between slides. Above this temperature the $\text{CHQ}_{0.7}$ could flow easily with a strong stir opalescence while $\text{CHQ}_{0.8}$ could hardly flow and no clear stir opalescence could be observed. The HQ copolymer series have a similar trend to that of CHQ series (Table 3). Photomicrographs taken at the melts also clearly show the anisotropy of the melts. When the sample cover-slide was squeezed along a certain direction, macroscopic orientation of different degrees can be observed (Figure 2). For the non-crystalline samples like $\text{CHQ}_{0.7}$ we could get the same optical pattern after the sample was cooled to room temperature—the texture of the liquid crystals was retained.

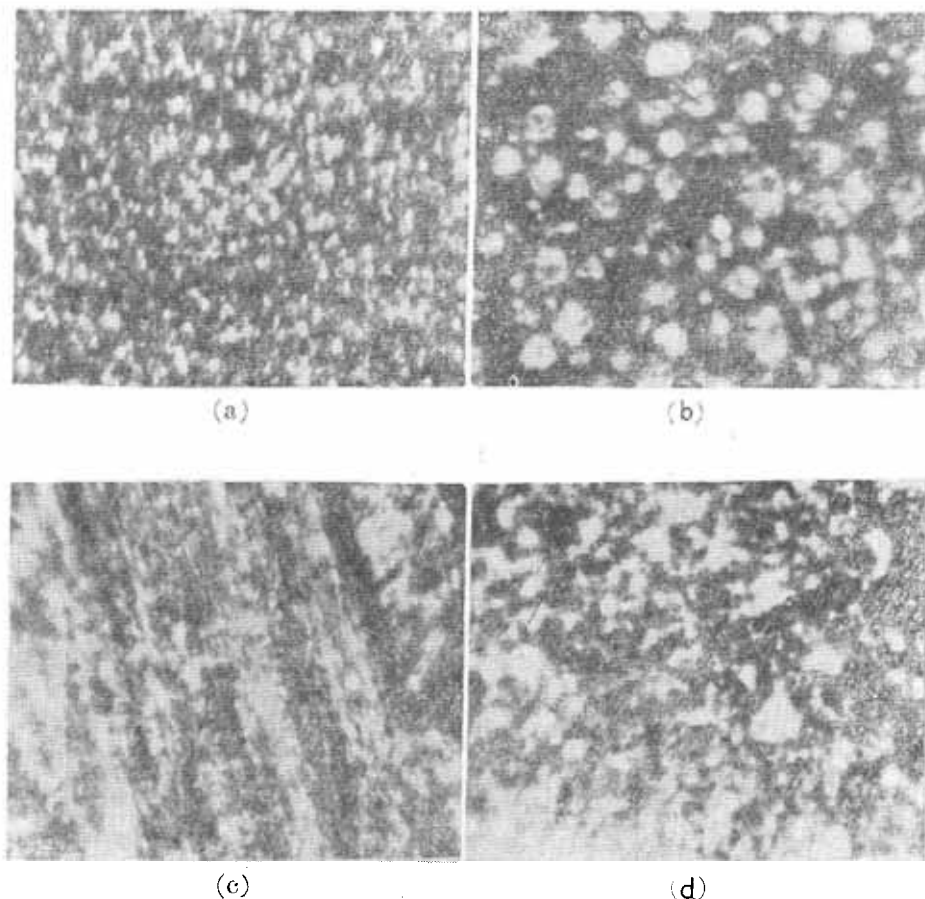


Fig. 2 Photomicrographs of the melts (magnification $100\times$)
 (a) $\text{CHQ}_{0.3}$ 200°C; (b) $\text{CHQ}_{0.5}$ 226°C; (c) $\text{CHQ}_{0.7}$ 238°C; (d) $\text{HQ}_{0.5}$ 283°C.

X-ray diffraction

Powder diffraction analyses of the samples were in accordance with the DSC analyses. PBT and PHT were highly crystalline while PCT was less ordered. Annealing treatment of the PCT would increase its crystalline peaks. In regard to the copolymers, HQ series all had strong crystalline peaks while CHQ series had comparatively weak crystalline peaks and correspondingly higher diffuse base. The diffraction patterns of $\text{CHQ}_{0.7}$ and $\text{CHQ}_{0.8}$ were non-crystalline characterized, showing that changes in the copolymer composition would change their crystallinity. When the melts were quenched, whether or not their morphology was maintained it depends on the relative values of their crystallizing rate and cooling rate. In our quenching treatment (250°C melts rapidly put into an ice bath), the PBT quenched sample still showed strong crystalline diffractions because of its very fast crystallizing rate; the quenched samples of $\text{HQ}_{0.3}$, $\text{HQ}_{0.5}$, $\text{CHQ}_{0.3}$, $\text{CHQ}_{0.5}$ also showed crystalline diffractions while the quenched samples of $\text{CHQ}_{0.5}^{\Delta}$, $\text{CHQ}_{0.7}$ showed only comparatively ordered diffuse haloes in the scanning range ($2\theta=3^{\circ}\text{--}35^{\circ}$) and no crystalline peaks could be observed. Therefore

the possibility of the existence of crystalline wholly aromatic polyesters in the melts could be ruled out. The optical anisotropy of the melts thus only characterizes their liquid crystalline behavior. Figure 3 shows the diffraction pattern of the $\text{CHQ}_{0.7}$ quenched sample. The central position of this diffuse halo located at $2\theta = 19.5^\circ$. The corresponding structural period according to Bragg equation is $4.55\text{\AA}$ which is in accordance with the lateral packing period of the nematic liquid crystalline chains^[11].

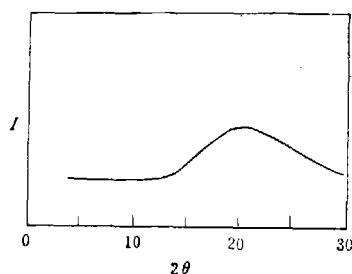


Fig. 3 X-ray diffraction pattern of the quenched sample of $\text{CHQ}_{0.7}$ melt

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