

STUDIES ON THERMOTROPIC LIQUID CRYSTALLINE COPOLYESTERS: POLY (ARYLENE TEREPHTHALATE-CO-HEXAMETHYLENE TEREPHTHALATE)

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ABSTRACT

A series of copolyesters based on terephthaloyl chloride, hexamethylene glycol and hydroquinone or chlorohydroquinone were prepared. The copolymers showed composition-dependent liquid crystalline properties as verified by visual observation of stir-opalescence, polarizing microscope and DSC. The copolyesters with aromatic diol contents over a certain extent ($x \geq 0.2$) were thermotropic with wide liquid crystalline temperature ranges. Comparing with the copolyesters based on butylene glycol or ethylene glycol, the minimum fraction of aromatic diol (x value) used to get the liquid crystallinity for all these copolyesters is around 0.2 regardless of the chain lengths of aliphatic glycols. $^1\text{H-NMP}$ studies revealed that copolyesters have microstructure of block sequence distribution and the mesogenic segments shorter than triad with three phenyl nuclei will not provide the liquid crystallinity.

Liquid crystalline polymeric materials have been one of the most attractive fields in polymer chemistry. The thermotropic aromatic copolyesters have such desirable properties as ease of processability and superior mechanical properties, which offer important utility, and therefore a lot of products have been commercialized e.g. under the trade names Xydar, Ekonol, Vectra and Unitika^[1]. The effect of mesogenic unit content and the length of spacers in copolyesters on the formation of thermotropic liquid crystallinity, however, still remained unclear. The previous work^[2] from our laboratory described the liquid crystal behaviour of poly (arylene terephthalate-co-tetramethylene terephthalate) and estimated the minimum amount of mesogenic units necessary for obtaining liquid crystalline copolymers. In this paper a series of thermotropic copolyesters was prepared from hexamethylene diol (HD), terephthaloyl chloride (TC) and hydroquinone (HQ) or chlorohydroquinone (CHQ). The effect of chain length of aliphatic glycol and the necessary amount of aromatic diol on the formation of liquid crystallinity of the products were studied and the chain microstructure parameters were estimated.

EXPERIMENTAL

Materials

TC, HQ, CHQ, HD and other raw materials were prepared or purified by methods already described^[2,3].

Preparation of copolyesters. A typical polycondensation procedure for copolyester HCQ_{0.3} could be described as follows: 10 mmol TC, 3 mmol CHQ and 7 mmol HD were introduced into a round-bottom flask. The temperature of the oil bath was gradually increased to 200°C, and the

reaction was continued at this temperature for 8 h with stirring. The product was dissolved in 1,1,2,2-tetrachloroethane (TCE), and precipitated with acetone. The product was washed with acetone, water and then acetone again, and dried in vacuum at 56°C. Pale-gray powder was obtained.

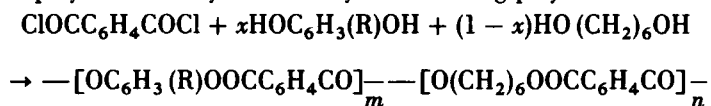
Characterization of polymers

The inherent viscosity (η_{inh}) and the intrinsic viscosity ($[\eta]$) were determined in *p*-chlorophenol/TCE (60/40 by volume) mixed solution at 25°C; $^1\text{H-NMR}$ spectrum were recorded on a Varian FT-80A NMR spectrometer using $\text{CF}_3\text{COOD}/\text{CDCl}_3$ (5/5 by volume) as solvent; polarizing photomicrographs were taken from polarizing microscope of type X6 (made in Beijing); melting points were determined with a CDR-1 DSC instrument (made in Shanghai) at a heating rate of 10°C/min or observed under microscope.

RESULTS AND DISCUSSION

1. Preparation of copolyesters and their solubility

A series of copolyesters was synthesized by the following polycondensation reaction:



In this paper where $\text{R} = \text{H}$ or Cl we will use HHQ_x or HCQ_x to represent a certain copolyester, where the first capital H denotes the hexamethylene diol, HQ or CQ denotes hydroquinone or chlorohydroquinone, respectively, and x is the molar fraction of aromatic diol used in feed.

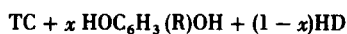
The solubility of copolymers becomes poor as the fraction of the aromatic diol fed increased. For a given x value, the solubility of HCQ polyesters is better than that of HHQ ones (Table 1)

Table 1 Solubility of copolyesters (+ soluble; - insoluble)

Copolymer	TCE	TCE / $\text{ClC}_6\text{H}_4\text{OH}$ (4:6)*	CF_3COOH	$\text{CF}_3\text{COOH} / \text{CHCl}_3$ (1:1)*
PBT**	+	+	+	+
$\text{HHQ}_{0.1}$	+	+	+	+
$\text{HHQ}_{0.2}$	+	+	+	+
$\text{HHQ}_{0.3}$	-	+	-	+
$\text{HHQ}_{0.4}$	-	+	-	+
$\text{HHQ}_{0.5}$	-	-	-	-
$\text{HHQ}_{1.0}$	-	-	-	-
$\text{HCQ}_{0.1}$	+	+	+	+
$\text{HCQ}_{0.2}$	+	+	+	+
$\text{HCQ}_{0.3}$	+	+	+	+
$\text{HCQ}_{0.5}$	-	+	-	+
$\text{HCQ}_{1.0}$	-	-	-	-

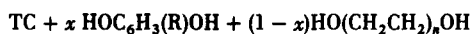
* by volume;

** poly (butylene terephthalate)

Table 2 Bulk properties of copolyesters

Copolymer		$T_m(^{\circ}\text{C})$		$T_i(^{\circ}\text{C})^*$	η_{inh}	$[\eta]$	Melt an- isotropy	Stir opa- lescence
R	x	DSC	microscope					
H	0.1	153	158	—	0.48	0.48	no	none
H	0.2	157	160	210	0.39	0.39	yes	strong
H	0.3	165	170	290	0.68	0.69	yes	strong
H	0.4	—**	180—190	> 350	0.47	0.48	yes	middle
H	0.5	—**	210—220	> 350			yes	weak
Cl	0.1		130	—			no	none
Cl	0.2	130	130	138	0.30	0.30	yes	middle
Cl	0.3	147.6	145	> 350	0.47	0.48	yes	strong
Cl	0.5	—**	130—140	> 350	0.35	0.35	yes	strong

* Isotropic temperature; ** cannot be detected.

Table 3 Liquid crystal properties of copolyesters.

Copolymer			$T_m(^{\circ}\text{C})$		$T_i(^{\circ}\text{C})$
R	n	x	DSC	Microscope	
H	2	0.11			—
H	2	0.18	193		230
H	2	0.33	202		> 350
H	3	0.10	153	158	—
H	3	0.20	157	160	210
H	3	0.30	165	170	290
H	3	0.40		180—190	> 350
H	3	0.50		210—220	> 350
Cl	2	0.11	201		—
Cl	2	0.18	197		220
Cl	2	0.33	187		> 350
Cl	2	0.54		220—230	> 350
Cl	3	0.10		130	—
Cl	3	0.20	130	130	138
Cl	3	0.30	147	145	250
Cl	3	0.50		130—140	> 350

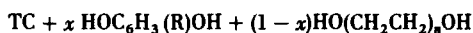
2. Liquid crystalline properties of copolyesters

The anisotropy of the melts was studied under the polarizing microscope (Table 2). When $x=0.1$ the copolyesters of both HHQ and HCQ series fused into extinctive melts; while $x=0.2$, the melts were anisotropic with obvious stir-opalescence. The bright area decreased at 210–220°C for HHQ_{0.2} and at 138°C for HCQ_{0.2} and became extinctive gradually at higher temperatures, but the transition (T_i) could not be observed in DSC. As the x value increased further, the liquid crystal temperature range (ΔT) broadened. With the same x value HHQ copolyester has a wider range of ΔT and higher T_m than those of HCQ one. When the sample cover-slide was squeezed along a certain direction, macroscopic orientation of different degrees could be observed (Fig.1).

3. Effect of the chain length of aliphatic glycol and feed amount of aromatic diol on the formation of liquid crystalline copolyesters

Markova et al.^[4] have studied the copolyesters based on TC, HQ and aliphatic glycol with different length of hydrocarbon chains and showed obvious liquid crystallinity for the copolyesters of butylene glycol (BG) as $x=0.25$ –0.125 within a temperature range around 150°C. These results were in accordance with those described in the previous paper^[2] from our laboratory. But if the HD was used instead of BG, they obtained copolymers decomposed before fusing as $x > 0.25$, and for $x=0.25$, ΔT value was only close to 11°C. Thus, they concluded that the chain length of aliphatic glycol and the amount of aromatic diol essentially influence on the formation of liquid crystallinity of the products.

Table 4 Composition and microstructure parameters of copolyesters



Copolyester				Triad fraction			Mean seq. length		B
n	R	x	m	P _{BTB}	P _{BTA}	P _{ATA}	L _{BT}	L _{AT}	
3	H	0.20	0.17	0.70	0.24	0.06	6.7	1.5	0.84
3	H	0.30	0.34	0.49	0.34	0.17	3.9	2.0	0.76
3	Cl	0.20	0.14	0.76	0.15	0.06	11.3	1.8	0.66
3	Cl	0.30	0.34	0.47	0.37	0.16	3.6	1.9	0.81
2*	H	0.18	0.19	0.69	0.24	0.07	6.8	1.6	0.78
2*	H	0.33	0.33	0.55	0.25	0.20	5.4	2.6	0.57
2*	Cl	0.11	0.14	0.76	0.19	0.05	9.0	1.5	0.77
2*	Cl	0.18	0.24	0.64	0.24	0.12	6.3	2.0	0.65
2*	Cl	0.33	0.32	0.54	0.29	0.17	4.7	2.2	0.67

* From lit.[2], where the parameters were expressed based upon the moieties of monomers, but here we recalculated upon the structural units, i.e. B, T and A.

However, we prepared the copolyesters based on TC, HD and HQ or CHQ, the melts of which showed clearly anisotropic behaviour within $x = 0.2$ — 0.5 without decomposition (Table 3).

In addition, it is interesting to note that the minimum x value of polyesters of both HHQ and HCQ series for obtaining liquid crystallinity is around 0.2 . The minimum x value for copolymers using BG in stead of HD is 0.18 (Table 3) and for copolymers based on ethylene glycol (EG) is $0.15^{[5,3]}$. Therefore we concluded that the minimum x value for obtaining the liquid crystallinity is around 0.2 regardless of the copolyesters based on whether BG, HD or EG.

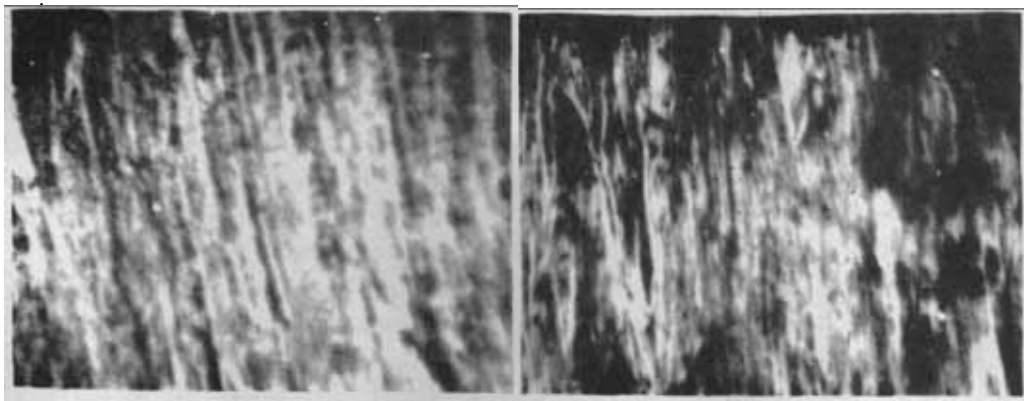


Fig.1 Polarizing microscopic photographs of melts (sheared, magnification $\times 100$)

(a) HCQ_{0.3} at 181°C; (b) HHQ_{0.3} at 217°C

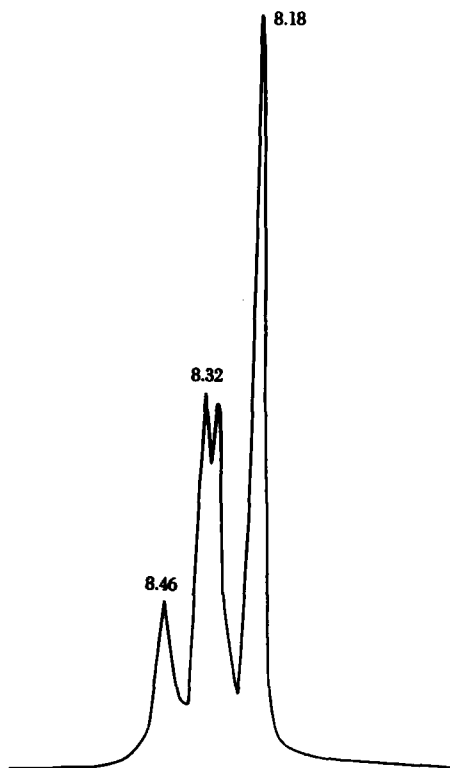


Fig.2 ^1H -NMR spectrum of HHQ_{0.4}

For a given value of n being 2 or 3, by increasing the feed amount of HQ or CHQ the T_i and ΔT increased. For a given x value of HQ (or CHQ), T_m and T_i decreased as the chain length of aliphatic glycols increased.

4. Sequence distribution of copolyester chains

The composition and microstructure parameters of chains can be estimated by the triad integral areas according to the following peaks in $^1\text{H-NMR}$ spectrum^[2].

—O(HD)OCC ₆ H ₄ COO(HD)—	(BTB)	$\delta = 8.18$ ppm
—O(HD)OCC ₆ H ₄ COO(Ar)—	(BTA)	$\delta = 8.32$ ppm
—O(Ar)OCC ₆ H ₄ COO(Ar)—	(ATA)	$\delta = 8.46$ ppm

The data in Table 3 show that the degree of randomness (B) of four series of copolyesters are between 0 and 1, that is to say that liquid crystalline copolyesters have microstructure of block sequence distribution indicating the formation of a certain length of the mesogenic segments. by increasing the x value the mean sequence length of mesogenic units L_{AT} increased. Regardless of the copolyesters based on HQ or CHQ and BG or HD, the copolyesters fused only into isotropic melts as the L_{AT} less than 1.5. This means that in copolymers the mesogenic segments shorter than triad with three phenyl nuclei could not provide the liquid crystallinity. These results are in correspondence with those by Galli et al.,^[6] who have pointed out that the mesogenic units of triad could offer the liquid crystallinity only with shorter spacers.

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Keywords:

Liquid crystalline copolyesters; Poly(arylene terephthalate-co-hexamethylene terephthalate); Minimum mesogenic fraction; Sequence distribution; Microstructure parameters/

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