

SYNTHESIS AND CHARACTERIZATION OF MAIN CHAIN AROMATIC LIQUID CRYSTAL COPOLYESTERS WITH X-SHAPED AND ROD-SHAPED MESOGENIC UNITS*

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Abstract A series of main chain liquid crystal aromatic copolyesters with X-shaped and rod-shaped mesogenic units were synthesized via solution condensation polymerizations of 4,4'-(α,ω -octanedioxy)-dibenzoyl dichlorides with 2,5-bis(p-octanoxo benzoyloxy)-hydroquinone and diphenol. All of the copolyesters showed thermotropic liquid crystalline behaviors through observations using DSC, polarized microscopy and X-ray diffraction. The melting point (T_m) and the isotropization temperature (T_i) change regularly with varying the content of diphenol unit in the copolymers.

Keywords Liquid crystal polymer; X-shaped and rod-shaped mesogenic units; Aromatic copolyester; Synthesis and characterization

INTRODUCTION

The phase transition temperatures of liquid crystal polymers are commonly modified by introducing substituent groups, flexible segments, twisting components and a different rigid mesogenic component to the main chain^[1-7]. The present paper represents the synthesis of liquid crystal polymers by introducing to the main chain two kinds of the mesogenic units, one with an X-shape and the other a rod-shape. All of the copolymers showed thermotropic liquid crystalline behaviors. Their transition temperatures can be well adjusted by altering the ratio of the two kinds of mesogenic units.

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EXPERIMENTAL

Characterization

The monomers and polymers were characterized by the following techniques and conditions:

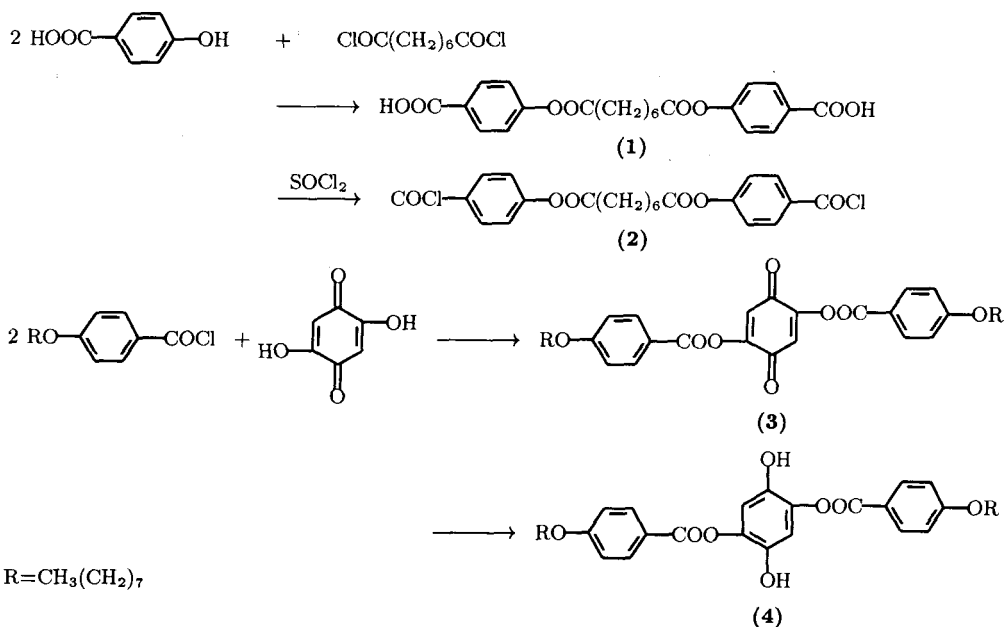
Melting point measuring: WRS-1 apparatus, Shanghai Physical and Optical Instrument Factory. Heating rate: 1°C/min. Elemental analysis: MOD1106 (Italy), ¹H NMR: ARX400, with CDCl₃ or CF₃COOD as solvent based on TMS., MS: VG-ZAB-HS, EI source. IR: SHIMADZU-435 with KBr tablets, DSC: SHIMADZU-50, with heating rate of 10°C/min., TG: RIGAKU with heating rate of 20°C/min under N₂, WAXD: RIGAKU D/MAX-3B with Cu target, voltage: 35 KV; electric current: 30 mA; scanning rate: 5°/min; scanning scope: 5—35°, GPC: Waters 201, polystyrene standard.

Specific viscosity determination was carried out using an Ubbelohde dilution viscometer in a mixed solvent of phenol/tetrachloroethane/p-chlorophenol (25/35/45 in volume) at 40°C with polymer concentration of 0.5 g/dl.

Liquid crystalline texture study: a Leitz polarizing microscope with a heating stage.

Monomer synthesis

The monomers were synthesized through the following reaction route:



Preparation of compounds **1** and **2** The preparations of compounds **1** and **2** were carried out according to the procedures in literature [8]. The characterization results are listed in Table 1.

Table 1 Characterization of compounds **1**, **2**, **3** and **4**

Compound	1	2	3	4
Yield (%)	82.7	88.0	72.0	97.0
Melting point (°C)	255.8—256.7	113.5—114.6	115.9—116.9	177.4—178.6
Clearing point (°C)	> 300°*	—	166.0	182.0
Elemental analysis				
C% (Calc.)	63.37 (63.76)	58.41 (58.55)	71.56 (71.50)	71.31 (71.26)
H% (Calc.)	5.27 (5.25)	4.37 (4.47)	7.41 (7.33)	7.71 (7.46)
Cl% (Calc.)	—	15.63 (15.71)	—	—
IR (KBr, cm ⁻¹)	3300—2400 (COOH) 1687, 1757 (C=O) 1205(COC)	1756, 1780 (C=O) 1205(COC) 878(1, 4-Ar)	1730 (C=O, ester) 1685 (C=O, quinone) 1310 (COC=C) 1255 (COC)	3345 (OH) 1710 (C=O) 1328 (COC=C) 1260 (COC)
¹ H NMR (DMSO- <i>d</i> ₆ , CDCl ₃ or CF ₃ COOD, ppm)	1.50—1.69 (8H, m, (CH ₂) ₄) 2.47—2.73 (4H, t, OCH ₂) 7.21—8.06 (8H, m, Ar-H)	1.50—1.90 (8H, m, (CH ₂) ₄) 2.55—2.70 (4H, t, OCH ₂) 7.19—8.20 (8H, m, Ar-H)	0.90—0.93 (6H, t, CH ₃) 1.35—1.49 (24H, m, (CH ₂) ₆) 6.35 (2H, s, quinone) 7.08—8.17 (8H, m, Ar-H)	0.91—0.94 (6H, t, CH ₃) 1.36—1.95 (24H, m, (CH ₂) ₆) 4.04—4.30 (4H, q, OCH ₂) 7.10—8.26 (10H, m, Ar-H)
MS (m/z)				
M ⁺ (%)	—	461.0 (4.0)	—	606.0 (3.0)
base		121 (100.0)		233.0 (100.0)

* with decomposition

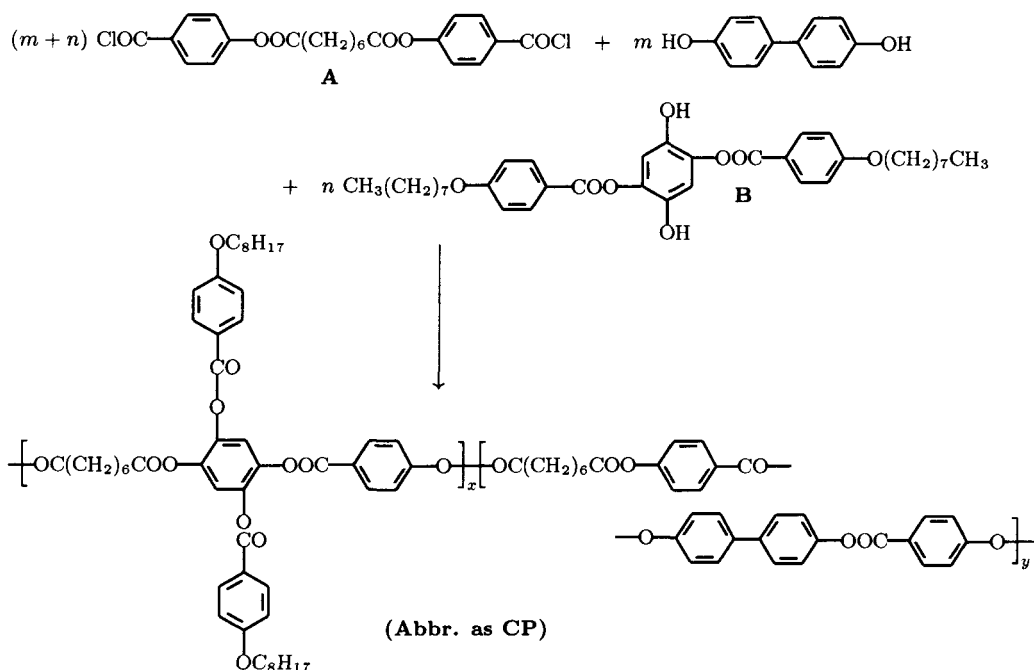
Preparation of compound **3** p-Octanoxo-benzoyl chloride (12.1 g, 45 mmol) was dissolved in a mixed solvent composed of 20 ml dry THF and 3.2 ml pyridine, cooled with ice-water. A THF solution of 2.8 g (20 mmol) of 2,5-dihydroxy quinone was dropped into above solution under sufficient stirring. When finished dropping, the reaction solution was further stirred for two hours and then filtrated. THF in

the filtrate was evaporated. The residue was washed with acetone. After recrystallization from 1,4-dioxane, the product was isolated as yellow needle-like crystals and was proved as compound **3** (Table 1).

Preparation of compound 4 Compound **3** (2.0 g, 3.6 mmol) was dissolved in 30 ml of THF at room temperature. Into which were added 44 ml water solution saturated with NH_4Cl containing 9.4 g of $\text{Na}_2\text{S}_2\text{O}_4$. After stirring for 10 min., THF in the reaction mixture was evaporated. The product was isolated as a white solid by filtration, washing with water and drying in vacuo. Its characterization results are listed in Table 1.

Polymer synthesis^[9]

The polymers were synthesized by the following reactions:



With the protection of nitrogen the monomer **B**, 2,5-bis(p-octanoxyl benzoyloxy)-hydroquinone, and diphenol in different weight ratio were dissolved in 1,4-dioxane in the presence of proper amount of pyridine. An equimolar of monomer **A**, 4,4'-(α,ω -octanedioxyloxy)-dibenzoyl dichlorides, was added. The mixture was allowed to react under reflux for 12 h. The polymers were isolated by precipitation from methanol as white powders, filtrated, sequentially washed with water and methanol, and then dried in vacuo.

RESULTS AND DISCUSSION

All of the low molar mass compounds **1**, **2**, **3** and **4** were proved as their structure shown above by using elemental analysis, ^1H NMR, IR and MS. All of them but compound **2** showed liquid crystalline behaviors on a polarizing microscope with a heating stage. Upon heating, the compounds **1**, **3** and **4** melted to form a liquid crystal phase showing typical thread or schlieren textures. The transition temperatures observed from polarizing microscope were in good agreement with those determined from DSC.

All of the copolymer samples are white powders and insoluble at room temperature in THF except for samples CP7, CP8 and CP9. Their transition temperatures taken from DSC and TG, and their molecular weights measured by GPC or specific viscosity parameters determined in a mixed solvent, are shown in Table 2.

Table 2 Thermal properties and molecular parameters of the copolymers

Copolymers	Weight ratio ^{a)}	Phase transition temperature (°C)	ΔT (°C)	$[\eta]^{\text{b)}}$ (dl/g)	$\overline{M}_n$	$\overline{M}_w$	T_d (°) ^{c)}
CP-1	0/100	K168N267I	99	0.32			363
CP-2	10/90	K165N260I	95	0.25			360
CP-3	20/80	K163N255I	92	0.24			354
CP-4	40/60	K159N250I	91	0.30			349
CP-5	50/50	K158N240I	82	0.27			346
CP-6	60/40	K150N238I	88	0.28			338
CP-7	80/20	K139N237I	98	0.24	5500	14000	329
CP-8	90/10	K126N225I	99	0.21	5000	12000	334
CP-9	100/0	K110N182I	72	0.25	6600	15000	331

a) The ratio between monomer B and 4,4'-biphenol

b) Intrinsic viscosity number

c) Temperature of decomposition (5% weight loss in N_2).

Phase transition temperature determined by DSC.

It can be seen from Table 2 that the polymer CP1 having no structural unit from monomer **B** showed the highest melting and isotropization temperatures among the present series of polymers. This is because that the polymer CP1 is composed of only the rod-shaped mesogenic units without substituent groups and that it has the most regular structure and a better symmetry. The transition temperatures of the copolyesters lowered along with the increase of the structural unit from monomer **B**. This is resulted from the bulkier substituents in the X-shaped mesogenic units. As

the increase of the number of the structural units from monomer **B**, the regularity of the macromolecules is lowered, which would also lower the packing efficiency of the macromolecules in crystal lattice.

The specific viscosity of the polymers is ranging from 0.21 to 0.32, which indicates that the polymers have relatively lower molecular weights. Molecular weight measurement of the THF soluble samples of CP7, CP8 and CP9 showed a more clear illustration, which gave number average molecular weights ranging from 5500 to 6600. The decomposition temperature (T_d) of the polymers is ranging from 329 to 363°C and tends to be lowering with the increase of the structural component from monomer **B**.

The observations using DSC and polarizing microscope illustrated that all of the polymers showed the thermotropic liquid crystalline behavior. From their DSC curves in Fig.1, it can be found that all showed two endothermal peaks in the process of heating. The first ones illustrated the melting of the polymers from solid phase to mesomorphic phase, and the second ones are the transition of the polymers from the mesomorphic phase to the isotropic liquid phase.

The results obtained from polarizing microscope with a heating stage were in a good agreement with those from DSC. The powder samples of the polymers showed a weak birefringence at room temperature indicating that the polymers have crystallinity of some extent. Heating the polymer samples to above their melting temperature, the polymers went into

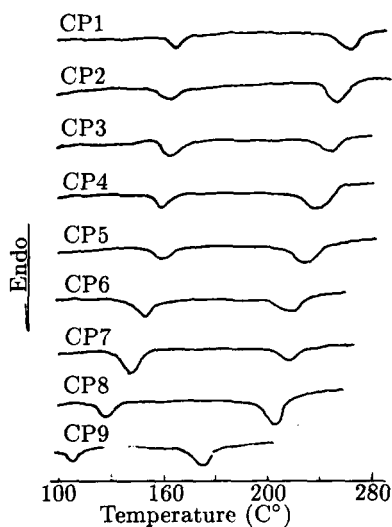


Fig.1 DSC thermograms (first heating scan) of copolymers

crystal phase. In the liquid crystal phase, polymer CP1 had the poorest mobility. The melt mobility of the polymers became better and better along with increasing the content of the X-shaped mesogenic units in the polymer composition. Clear thread or schlieren textures were observed for all polymers studied, which illustrated that the polymers are nematic liquid crystals. As examples, the liquid crystalline textures of polymers CP2 and CP8 were given in Fig.2. The banded texture was also observed for all samples except for CP8 and CP9 in their liquid crystal phase

when subjected with a shear force as shown in Fig.3. It indicated that the polymers

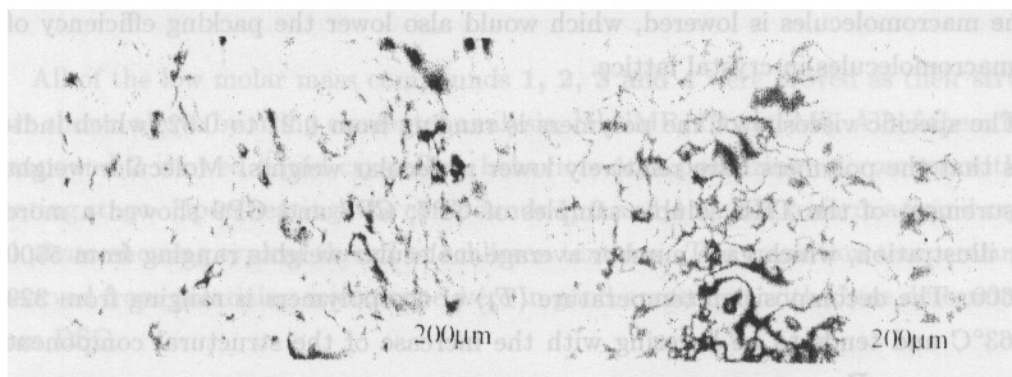


Fig.2 Texture of copolymers, (a) CP2 taken at 250°C; (b) CP8 taken at 195°C

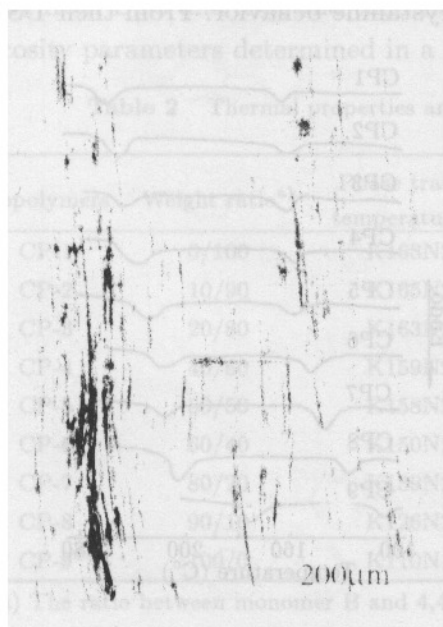


Fig.3 Banded texture of copolymer CP2 taken at 210°C. The arrow indicates the shearing direction

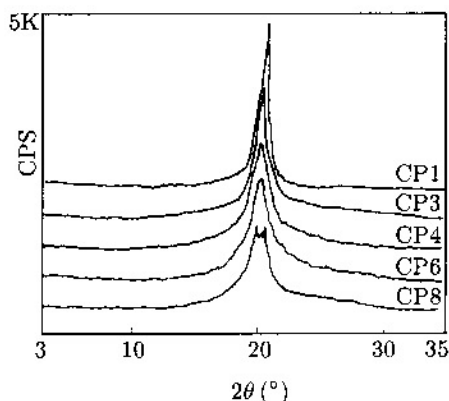


Fig.4 WAXD powder patterns of copolymers CP1, CP3, CP4, CP6 and CP8

have rather rigid chains. The birefringence disappeared with further heating. The polymers transformed from liquid crystal phase to isotropic liquid phase. Cooling from the isotropic liquid phase, the birefringence appeared again.

The WAXD study illustrated that the polymers with different composition showed different crystallinity. Diffraction peaks with different strength can be found at 2θ near 20° on the WAXD curves of polymers CP1, CP3, CP4, CP6 and CP8 (Fig.4).

CP1 gave the strongest diffraction peak, which showed the polymer has the highest crystallinity. The strength of the diffraction peaks was weakened and broadened along with the increase of the content of the X-shaped mesogenic units in the polymer composition, indicating a decreased regularity of molecular packing.

If the samples of CP2, CP4, CP6 and CP8 were heated to above their corresponding T_m , kept for 10 min., and then quenched with ice water, only a diffused peak at 2θ near 20° appeared on their WAXD curves. This is typical for a quenched nematic liquid crystal polymer.

In conclusion, all the polymers studied are liquid crystalline with a nematic phase. The phase transition temperatures, both T_m and T_i , decrease with increasing the content of the X-shaped mesogenic units in polymer chains. To the least, a temperature range of 72 degrees was observed for the mesophase of the polymers.

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