

SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTAL POLYMERS WITH T-SHAPED TWO-DIMENSIONAL MESOGENIC UNITS (II)*

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ABSTRACT

A series of liquid crystalline polymers with T-shaped two-dimensional mesogenic units were synthesized via low temperature solution polycondensation of 2-(4'-alkoxy-phenyl) hydroquinone with various diacyl dichlorides. The polymers were found to be nematic and shown thermotropic liquid crystalline behaviors through observations using DSC, polarized microscopy and X-ray diffraction. The melting temperature T_m and the isotropization temperature T_i of the polymers change regularly with varying of the monomer structures.

INTRODUCTION

The synthesis of liquid crystal polymers containing two-dimensional mesogenic units from monomers having corresponding structure is a new research field in recent years^[1]. As previously reported, we have synthesized some series of such polymers with X-shaped mesogenic units^[2-4]. Later on we have reported a new series of liquid crystal polymers with T-shaped two-dimensional mesogenic units synthesized by low temperature solution condensation of N-2, 5-dihydroxybenzilidine aniline monomers with different diacyl dichlorides^[5-7]. In order to compare the mesogenic properties of liquid crystalline polymers with different structure, the present paper is concerned with another new series of such T-shaped liquid crystal polymers synthesized by condensation of 2-(4'-alkoxy-phenyl) hydroquinone with different diacyl dichlorides.

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EXPERIMENTAL

1. Characterization

The monomers and polymers were characterized by the following techniques:
Melting point measuring: WRS-1 apparatus, Shanghai Physical and Optical Instrument Factory. Heating rate: 1°C/min.

Elemental analysis: MOD 1106 (Italy).

¹H NMR: ARX 400, with CDCl₃ as solvent based on TMS.

MS: VG-ZAB-MS, EI source.

IR: SHIMADZU-435 with KBr tablets.

DSC: SHIMADZU-50, with heating rate of 20°C/min.

TG: RIGAKU with heating rate of 20°C/min under N₂.

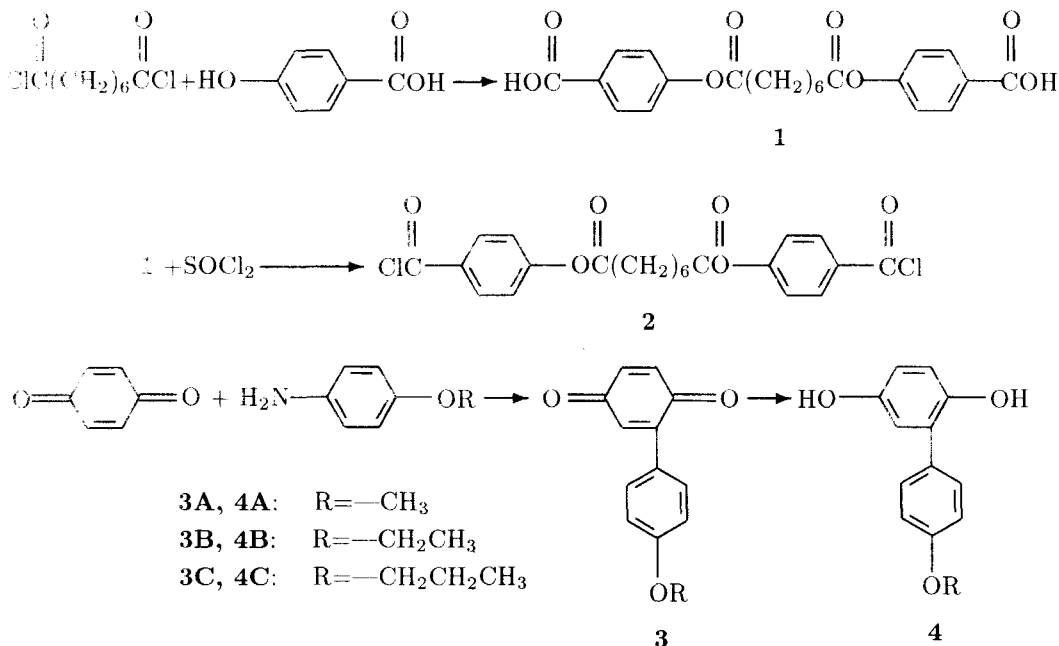
WAXD: RIGAKU D/MAX-3B with Cu target. Voltage: 40 kV; electric current: 30 mA; scanning rate: 5°/min; scanning scope: 5–35°.

GPC: Waters 201, polystyrene standard.

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

2. Monomer synthesis

The monomers were synthesized through the following reaction route:



(1) Preparation of compound 1

10.0 g (72 mmol) of p-hydroxy-benzoic acid was dissolved in a mixture solvent composed with 80 ml of THF and 8 ml of pyridine. 5.2 g (25 mmol) of suberoyl chloride was added dropwise within 1 h at 0°C under stirring. After reacting for further 3 h, about 2/3 part of solvent was removed under reduced pressure. The residue was cooled down by using an ice-water bath, filtrated and washed with water and methanol till the filtrate becoming clear. After dried and recrystallized from 1, 4-dioxane, 8.3 g of product was formed (81% yield). The product was proved as compound **1** through the following characterizations: melting point: 255.8—256.9°C; elemental analysis found (calc.): C 63.37 (63.76), H 5.35 (5.27)%; IR (KBr, cm^{-1}): 3300—2400 (COOH), 1760 (C=O), 1600 and 1500 (aromatic ring frame work), 880 (1, 4-Ar); ^1H NMR (δ , ppm, DMSO- d_6): 1.50—1.69 (8H, m, $-\text{[CH}_2\text{]}_4$), 2.47—2.73 (4H, t, $-\text{COCH}_2-$), 7.21—8.06 (8H, m, Ar—H).

(2) Preparation of compound **2**

5.0 g (12 mmol) of compound **1** was put into 30 ml of SOCl_2 , heated and dissolved and then refluxed for 3 h. The excess SOCl_2 was removed under reduced pressure and the residue was recrystallized from a mixed solvent of chloroform and hexane. After dried in vacuo, 4.7 g of product was formed (87% yield). The product was proved as compound **2** through the following characterizations: melting point: 113.5—114.6°C; elemental analysis found (calc.): C 58.43 (58.55), H 4.39 (4.47), Cl 15.79 (15.71)%; IR (KBr, cm^{-1}): 1782 (C=O), 1600 and 1500 (aromatic ring frame work), 880 (1, 4-Ar); ^1H NMR (δ , ppm, DMSO- d_6): 1.50—1.90 (8H, m, $-\text{[CH}_2\text{]}_4$), 2.55—2.70 (4H, s, $-\text{COCH}_2-$), 7.19—8.20 (8H, m, Ar—H); MS (m/e): 451 (M^+), 121.0 (100%).

(3) Preparation of compounds **3**

Taking **3B** as an example.

In a 500 ml beaker containing 27.4 g (200 mmol) of p-ethoxy-aniline, 100 g of crashed ice and 53 ml of concentrated hydrochloric acid, 75 ml water solution of 13.8 g of sodium nitrate was added dropwise under stirring. The mixture was allowed to react at a temperature of lower than -2°C . The reaction finished till testing by a Congo red test paper turned to light blue and a KI-starch test paper turned to gray-blue. The diazo salt solution was then added slowly into a separated 2000 ml beaker containing 21.6 g (200 mmol) of quinone and 67.0 g of NaHCO_3 with 50 g of crashed ice and 500 ml of cold water under stirring. During the addition, the reaction temperature was kept less than -10°C . Then, the reaction mixture was stirred for further 4 h. After filtrated, washed with water and dried in vacuo, the

product was recrystallized from n-butanol and proved as compound **3B**.

The other compounds of **3** were prepared in a similar manner, and their characterization results are collected in Table 1.

Table 1 The characterization results of compounds **3**

Compd.	Yield (%)	T_m (°)	Elemental analysis (%)		IR (KBr, cm^{-1})				
			C (Calc.)	H (Calc.)	C=O	Ar-Ring	1, 4-Ar OMe	C—O—C	
3A	76.7	120.1—120.9	72.83(72.89)	4.65(4.70)	1680	1600,1580	860	2830	1250
3B	75.4	112.0—112.6	73.62(73.67)	5.37(5.30)	1675	1600,1570	860		1248
3C	70.5	90.7—91.6	74.32(74.36)	5.87(5.82)	1678	1600,1576	862		1240

(4) Preparation of compounds **4**

Taking **4B** as an example.

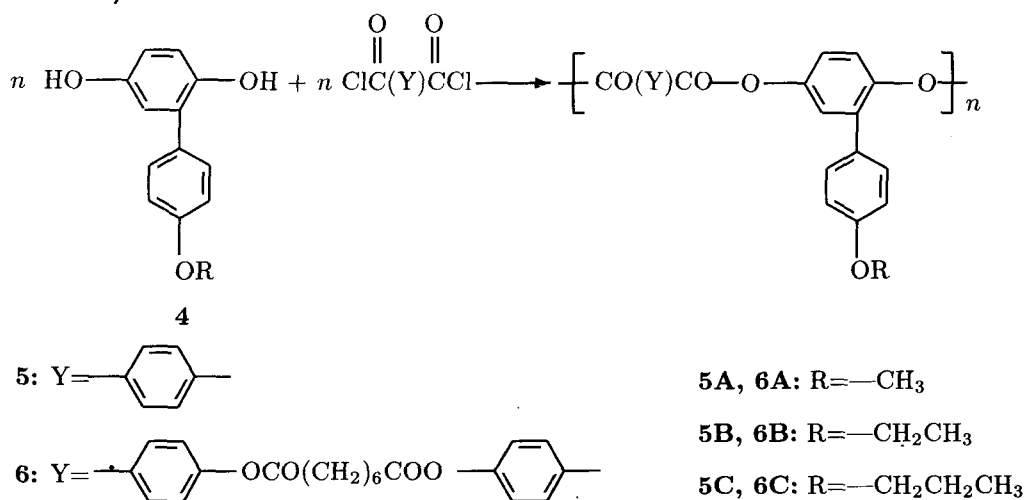
Table 2 The characterization results of compounds **4**

Compd.	4A	4B	4C
Yield (%)	83	82	75
T_m (°C)	75.8—76.2	95.5—96.6	70.0—70.4
Elemental analysis			
C% (Calc.)	72.15(72.21)	73.07(73.03)	73.72(73.75)
H% (Calc.)	5.54(5.59)	6.17(6.13)	6.66(6.60)
IR (KBr, cm^{-1})	3470(OH)	3480(OH)	3500(OH)
	2830(OMe)	1600,1566	1600,1570
	1600,1570	(aromatic ring	(aromatic ring
	(aromatic ring	frame work)	frame work)
	frame work)	1240(C—O—C)	1240(C—O—C)
	1250(C—O—C)	880,820,780	880,825,780
	880,820,780	(1,4-Ar and	(1, 4-Ar and
	(1, 4-Ar and	1, 2, 4-Ar)	1, 2, 4-Ar)
1, 2, 4-Ar)			
¹ H NMR	3.85 (3H, s, Me)	1.43—1.46(3H, t, Me)	1.04—1.07(3H, t, Me)
δ , ppm, CDCl_3)	6.70—7.38	4.05—4.11(2H, q, CH_2)	1.79—1.86(2H, m, $\text{CH}-2$)
	(7H, m, Ar-H)	6.71—7.37	3.94—3.98 (2H, t, OCH_2)
		(7H, m, Ar-H)	6.69—7.36 (7H, m, Ar-H)
MS (m/e)	216 (M^+ , 100%)	230 (M^+ , 100%)	244 (M^+ , 68%)

In a three-necked flask equipped with a mechanical stirrer, thermometer and N₂ inlet tube, 75 ml CHCl₃ solution containing 35.0 g (150 mmol) of **3B** was added into a saturated water solution of 250 mmol of Na₂S₂O₄. The mixture was stirred at room temperature for 30 min., then filtrated, washed with water and dried in vacuo. Crude product of **4B** was formed in 94.3% yield (30.5 g). The crude products of **4** were further purified by acetylation and then alcoholysis. 23.0 g (100 mmol) of the crude product of **4B** was dissolved in 30.6 g (300 mmol) of acetic anhydride, adding several drops of concentrated sulfuric acid. The reaction mixture was refluxed for 3 h under stirring, kept at room temperature over night, and then poured into 500 ml of cold water. After filtration, acetylated product of **4B** was formed through recrystallization from n-butanol and dried in vacuo. The acetylated products of **4A** and **4C** were prepared in a similar way, but the purification of them was performed through distillation and then recrystallization from n-butanol. The alcoholysis of the acetylated products of **4** was conducted by using absolute methanol, followed by routine procedures. The characterization results of products **4** are listed in Table 2.

3. Polymer synthesis

The polymers were synthesized by the following reactions:



For the synthesis of polymer **5A**, to a solution composed of 1 ml of pyridine and 5 ml of 1,1,2,2-tetrachloroethane containing 2.5 mmol of compound **4A**, equimolar amount of terephthaloyl chloride in 5 ml of 1,1,2,2-tetrachloroethane was slowly added dropwise at 0°C. The mixture was allowed to react at 0°C for 24 h and at room temperature for 72 h. Polymer was isolated by precipitation from methanol as

white powder, filtrated and dried in vacuo. Further purification was conducted by reprecipitation the THF solution of the crude polymer from methanol. The other polymers **5** and **6** were prepared in a similar way.

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, NMR, IR and MS etc., and all of them but compound **1** showed no liquid crystalline behavior through observations from a polarizing microscope with a heating stage. Upon heating, compound **1** melted and became liquid crystal phase, birefringence was observed obviously. Isotropization was not observed till above 300°C while slightly decomposition occurred at such a high temperature.

All the six polymer samples are white powders soluble in THF. Their transition temperatures takes from DSC, TG and polarized microscope with a heating stage and molecular weights measured by GPC are shown in Table 3.

Table 3 Properties of polymers

Polymer	$T_m(^{\circ}\text{C})$	$T_i(^{\circ}\text{C})$	$T_d(^{\circ}\text{C})$	$\overline{M}_n$	$\overline{M}_w$
5A	210	335	356	5300	11000
5B	200	327	345	5500	12000
5C	195	320	340	5200	10000
6A	108	165	190	6500	13000
6B	96	142	178	6000	11000
6C	78	125	150	6200	12000

The number average molecular weight of the polymers is ranging from 5200 to 6500 as can be seen from Table 3. Two possible reasons may cause the lower molecular weight. One might be the not exactly molar ratio of the charged two monomers, especially in case of using diacyl dichloride. The other one might be from the steric hindrance of the bulky substituent on the hydroquinone ring, especially in case of no flexible spacing segments. When flexible spacing segment was introduced to the main chain and getting longer, higher molecular weight polymer can be formed and the polymerization was also getting easier.

The mesogenic properties of a liquid crystal polymer can be greatly influenced by the molecular structure. In the present series of polymers, the size of the substituent groups given considerable influence to their mesogenic properties. As shown

in Table 3, larger substituent group normally gave lower T_m and T_i . As the increase of the size of the substituent group in the polymers, the intermolecular or inter-chain segment interactions would be weakened, which would also weaken the packing efficiency of the macromolecules in the crystal lattice. In the mean time, as the number of carbon atoms in the polymer side chain increased, the molecular internal rotation become more complicated, which would increase the molecular conformational entropy and then the T_m and T_i of the polymer would also be lowered. The chain rigidity of polymers **5** is higher than that of polymers **6**, so that the T_m and T_i of the former are much higher than those of the latter.

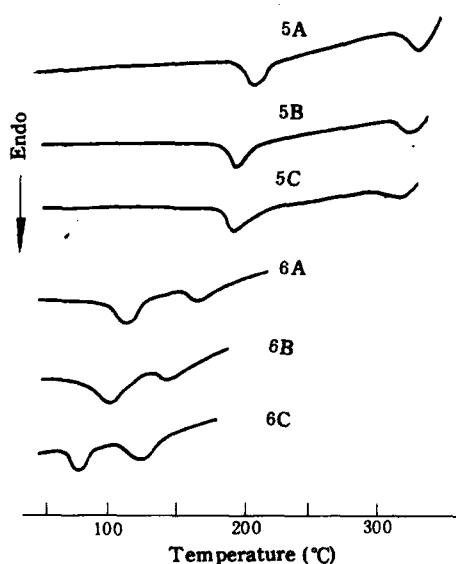


Fig. 1 DSC thermograms (first heating scan) of polymers **5** and **6**

Fig. 1 shows the DSC curves of the polymers. As it can be found that all of them showed two endothermic peaks in the process of heating. The first ones illustrate the melting of the polymers from solid phase to mesogenic phase, and the second ones are the transition of the polymers from mesogenic phase to isotropic liquid phase.

The transition temperatures of the polymers observed from polarizing microscope with a heating stage were the same as those obtained from DSC. Heating the polymer samples to above melting temperature, clear threaded

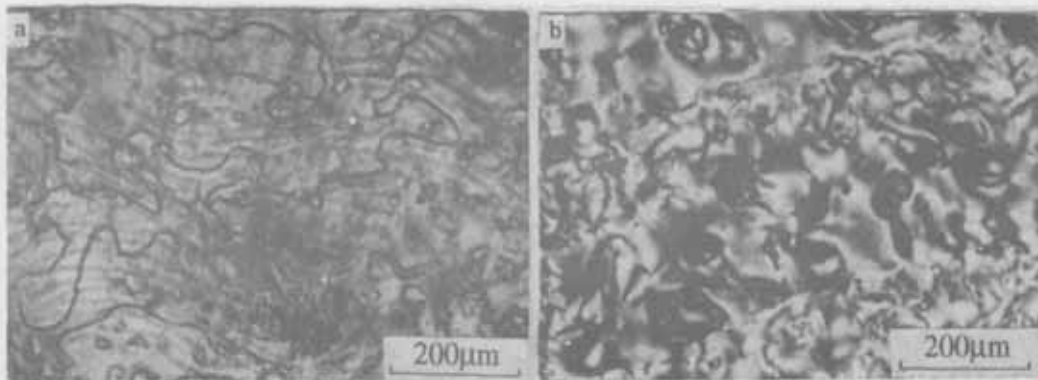


Fig. 2 Photomicrographs under crossed polarizers of polymers (a) **5B** taken at 248°C; (b) **6B** taken at 120°C

texture can be observed for all polymers studied, which illustrate that the polymers are nematic thermotropic liquid crystals. Fig. 2 shows the liquid crystalline textures of polymers **5B** and **6B**. The threaded texture of **5B** is typical in liquid crystal polymers, which is easier to be observed especially for the thick samples. Straight or bent tiny thread was the illustration of line directional disordering. For the sample was thick, the line directional disordering was only slightly affected by the sample surface. Only the two ends of the line might be fixed on the surface, the other part could be freely moved within the sample. As a fact of result, the projection of the line on the plane was not a black point but appeared as a black thread. If the two ends of the directional disordering line was not restrained by the surface, they can also be moved freely within the sample together with the molecular thermal movement, which would result in old thread disappearing and new thread formation during observation.

Diffraction peaks can be found on the WAXD curves of polymers **5** and **6** from Fig. 3, which showed the polymers have crystallinity in some extent. The molecular chain of polymers **5** is more regular than that of polymers **6**, which gave the polymers **5** better crystallinity than polymers **6**. Samples of **5A** and **6A** were heated to above their corresponding T_m and kept for 10 min., then quenched with ice water, dispersive peak at 2θ near 20° was appeared on their WAXD curves, which is a typical character for nematic liquid crystal polymers.

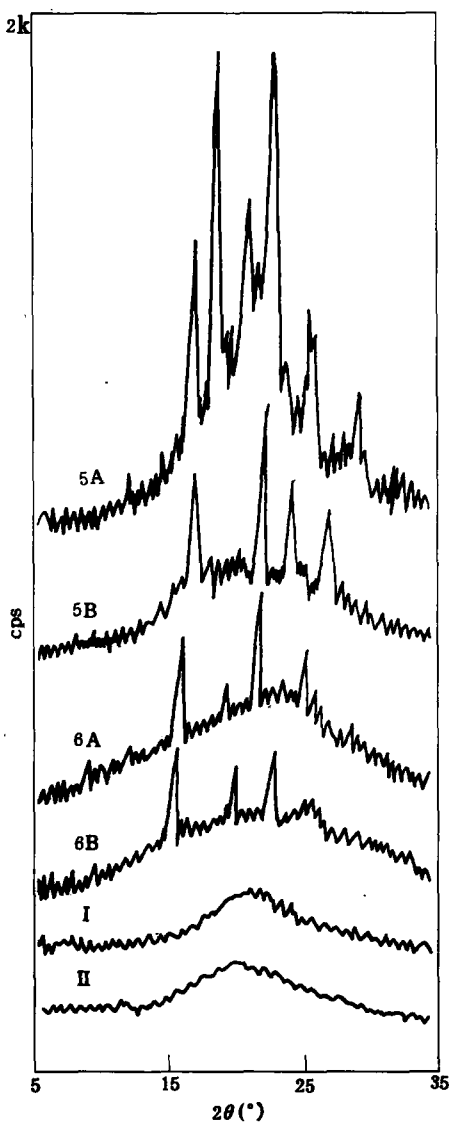


Fig. 3 WAXD curves of **5A**, **5B** and **6A**, **6B** of the polymers. I (**5A**), quenched from 240°C ; II (**6A**), quenched from 130°C

Keywords:

T-shaped two-dimensional mesogenic units; Liquid crystal polymer; Polymer synthesis.

REFERENCES

- [1] Zhou, Q.F., *Polym. Bull.*, **1991**, (3): 160.
- [2] Li, Z.F.; Zhou, Q.F.; Zhang, Z.Y., et al., *Acta Polym. Sinica* (in Chinese), **1990**, (1): 51.
- [3] Li, Z.F.; Zhou, Q.F. and Zhang, Z.Y., *Acta Polym. Sinica* (in Chinese), **1990**, (6): 694.
- [4] Li, Z.F.; Zhang, Z.Y.; Fu, X.Y., et al., *Acta Polym. Sinica* (in Chinese), **1992**, (5): 611.
- [5] Zhang, C.X.; Li, Z.F. and Zhou, Q.F., *Chinese J. Polym. Sci.*, **1993**, 11 (4): 348.
- [6] Li, Z.F.; Chen, Z.J.; Zhang, S.Y., et al., *Chem. J. Chinese Univ.*, **1994**, 15 (11): 1723.
- [7] Li, Z.F.; Chen, Z.J.; Zhang S.Y., et al., *Chinese J. Polym. Sci.*, **1996**, 14 (1): 71.