

SYNTHESIS OF MAIN CHAIN LIQUID CRYSTALLINE COPOLYESTERS WITH X-SHAPED TWO-DIMENSIONAL MESOGENIC UNIT AND CROWN ETHER CYCLE*

Jing-wu Wang^a, Shi-jun Zheng^a, Xiao-hui Xu^a, Xing-qi Zhu^b, Shu-yuan Zhang^b,
Tie-sheng Li^a and Zi-fa Li^{a**}

^aCollege of Materials and Engineering, ^bDepartment of Chemistry, Zhengzhou University,
Zhengzhou 450052, China

Qi-feng Zhou

Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering,
Peking University, Beijing 100871, China

Abstract A novel series of main chain liquid crystalline copolyesters with X-shaped two-dimensional mesogenic unit and crown ether cycle of *cis*-4,4'-bis(4-hydroxyphenylazo) dibenzo-18-crown-6 was prepared via solution condensation polymerization from 4,4'-(α,ω -hexanedioxyloxy) dibenzoyl dichloride (M_1), 2,5-bis(*p*-octyloxybenzoyloxy) hydro-quinone (M_2) and *cis*-4,4'-bis(4-hydroxyphenylazo) dibenzo-18-crown-6 (M_3). Monomer M_1 was synthesized by esterification and substitution of adipoyl chloride with *p*-hydroxybenzoic acid, monomer M_2 was synthesized by esterification and reduction reaction of 2,5-dihydroxybenzoquinone and *p*-octanoylbenzoyl chloride and monomer M_3 was synthesized by diazotization and coupling reaction of *cis*-diaminodibenzo-18-crown-6 with phenol. The molecular weights of copolyesters are not high, and the intrinsic viscosity $[\eta]$ of copolyesters ranges from 0.25–0.35. The monomers' structures were identified by using elemental analysis, IR, UV, ¹H-NMR, MS, etc. All the copolyesters are yellowish powders and insoluble in THF and CHCl₃ at room temperature except CP9. The properties of copolyesters were investigated by using GPC, $[\eta]$, DSC, TG, WAXD and POM. It was found that all the copolyesters entered into liquid crystal phase when they were heated to above their melting temperature (T_m). The typical smectic and nematic phase texture can be observed on POM. Their mesophase transition temperature and thermal stability change regularly with varying the content of *cis*-4,4'-bis(4-hydroxyphenylazo) dibenzo-18-crown-6 unit in the copolyesters.

Keywords: X-shaped two-dimensional mesogenic unit; Crown ether; Liquid crystalline copolyesters; Synthesis.

INTRODUCTION

The polymers containing two-dimensional mesogenic units were first synthesized by H. Ringsdorf *et al.*^[1] in 1986, but the concept of liquid crystal polymers with two-dimensional mesogenic units (LCPTDMU) was not proposed at that time. The relationship between structure and the properties of the polymers was not studied. The concept of LCPTDMU was formally proposed by Zhou^[2] in 1990. The basic consideration for designing and preparing such polymers is that the liquid crystalline polymers constructed in this way would be expected to show good mechanical properties both in the molecular chain direction and also in the lateral direction.

Inspired by the H. Ringsdorf and Zhou's work, Li *et al.* has synthesized many liquid crystalline polymers with two-dimensional mesogenic units and studied the relationship between structure and the properties of the

* This work was supported by the National Natural Science Foundation of China (No. 29974026) and the Natural Science Foundation of Henan Province.

** Corresponding author: Zi-fa Li (李自法), E-mail: lzf@zzu.edu.cn

Received October 21, 2004; Revised January 18, 2005; Accepted March 7, 2005

polymers^[3–7]. Xu's group^[8, 9] has also done some researches on the relationship between structures and the behaviors of the LCPTDMU. Although materials with high mechanical properties made by LCPTDMU have not been obtained, it is also very interesting to synthesize and study the relationship between the structures and behaviors of LCPTDMU.

Liquid crystalline polymers containing crown ether possess the properties of both liquid crystal and select the coordination ability of crown ether, therefore, liquid crystalline crown ether polymers can be used widely in ion recognizing, bionic membrane, signal and information transferring in molecular level due to their fine-order structure and functional group^[10–12]. The studies of liquid crystalline crown ether polymers were not reported since 1988, when Cowie *et al.*^[13] first reported their research on liquid crystalline crown ether in which crown ring was connected with polymer main chain directly. Until now, there are few papers of liquid crystalline polymers with crown ether presented^[14–16].

In order to create a new kind of functional polymers, a series of main chain liquid crystalline copolyesters with X-shaped two-dimensional mesogenic unit and crown ether ring were synthesized by reacting the monomer containing X-shaped two-dimensional mesogenic unit with non-liquid crystal comonomer containing benzo-18-crown-6. The relationship between the structures and their liquid crystalline properties was also investigated.

EXPERIMENTAL

Characterization

The monomers and copolyesters were characterized by the following techniques.

Ultraviolet-visible spectra were obtained on an UV-2401 PC spectrophotometer in DMF (100 mg/L). IR spectra were recorded on a Perkin-Elmer 1750 FT-IR spectrometer using KBr pellet. ¹H-NMR spectra were measured with a Bruker DPX 400 spectrometer with DMSO-d₆ or CDCl₃ or CF₃COOD as the solvent and tetramethylsilane as the standard. Mass spectra were recorded with a Finnigan-MAT ZAB-HS spectrometer in FAB. Elemental analysis was obtained with a Carlo Erba 1160 elemental analyzer. Melting points were measured on a WRS-1 melting point apparatus and the thermometer was uncorrected. The phase-transition temperatures were determined with a Netzch DSC-204 calorimeter equipped with a liquid-nitrogen cooling accessory. The heating and cooling rates were controlled at 10 K/min. The phase transition temperature reported in this paper is obtained from DSC traces. Thermogravimetric analysis (TGA) was performed on a NETZCH TG-204 thermal analysis instrument to determine the thermal decomposition temperature at a heating rate of 10 K/min under nitrogen atmosphere. Wide-angle X-ray diffraction (WAXD) was carried out on a Rigaku D/MAX-3B apparatus with a Ni-filtered Cu-K α radiation, 35 kV voltage, 30 mA electric current, and a scanning rate of 4°/min. The scanning range of 2 θ for copolymers was from 1.4° to 40°. Gel permeation chromatography (GPC) measurements were performed on a Waters 515-410-2010 apparatus, with polystyrene as a standard, and THF as an eluant at a flow rate of 1.0 mL/min. Intrinsic viscosity measurement were performed on an Ubbelodhe viscometer at (40 $\pm$ 0.05)°C using phenol/tetrachlorethane/4-chlorophenol mixed solvent (25/35/45 by volume) in concentration of 0.5 g/dL. Polarized optical microscopy (POM) observation was performed on a Nikon Ecliphase E600 polarizing microscope equipped with a hot stage.

Materials

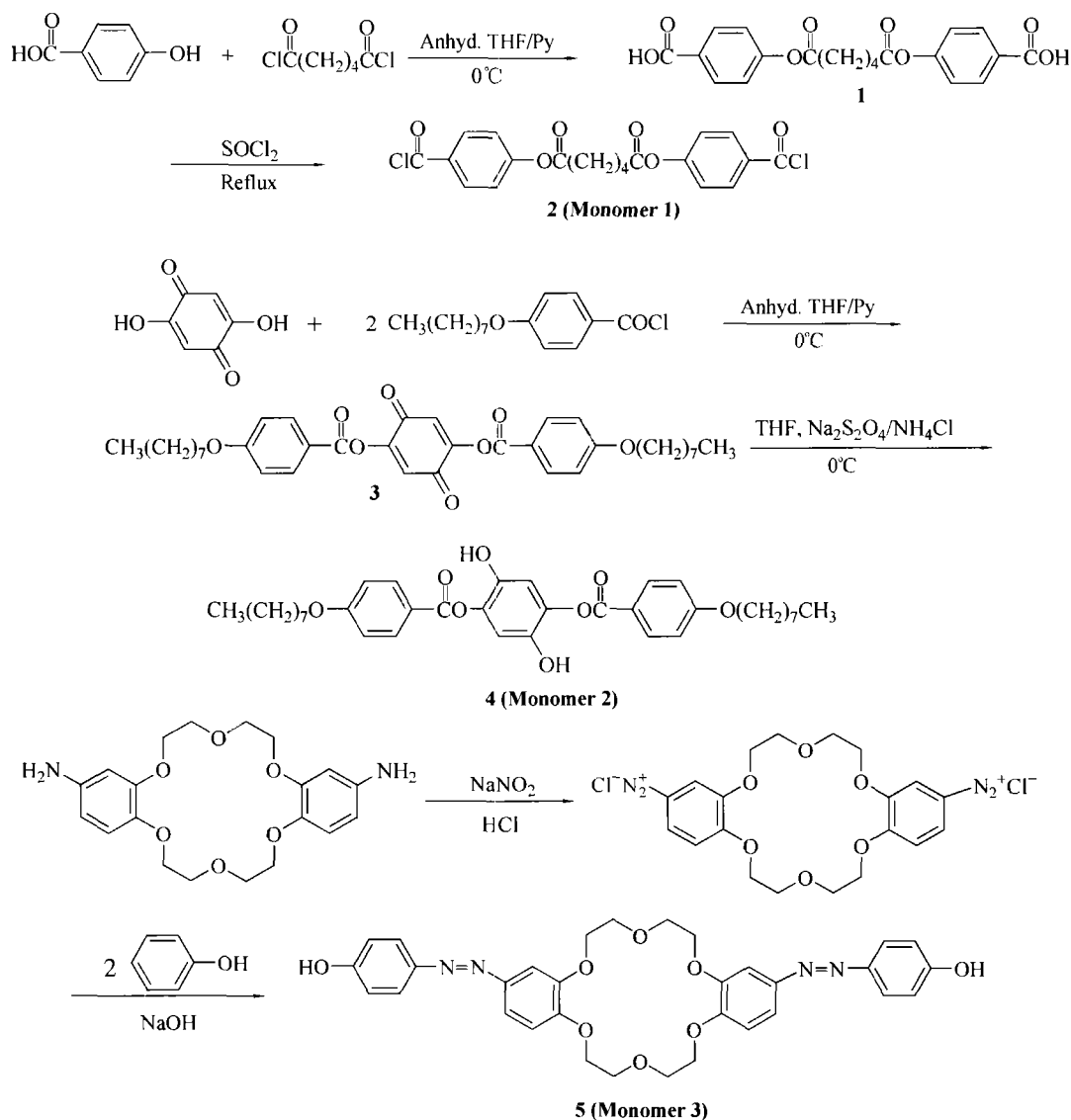
Synthesis of monomers

The synthesis of monomers is shown in Scheme 1.

Synthesis of 4,4'-(α,ω -hexanedioxy) dibenzoyl dichloride (Monomer 1)

It was described previously^[17].

Yield, 83%; m.p. 113.1–114.5°C; ¹H-NMR (DMSO-d₆, 400 MHz) δ : 8.21–7.20 (m, 8H, 2 $\times$ ArH₄), 2.68–2.55 (t, 4H, 2 $\times$ COCH₂), 1.90–1.60 (m, 4H, 2 $\times$ CH₂); IR (KBr, cm⁻¹): 1751, 1782 (C=O), 1595, 1497 (aromatic ring framework), 1033 (C–O–C) and 822 (1,4-Ar); MS (*m/z*): 423 (parent), 121 (base). Elemental analysis: Calc. for C₂₀H₁₆O₆Cl₂ (%): C, 56.76, H, 3.81, Cl, 16.75; Found (%): C, 56.67, H, 3.78, Cl, 16.77.



Scheme 1 Synthetic routes of monomers

Synthesis of 2,5-bis(p-octyloxybenzoyloxy) hydroquinone (Monomer 2)

This compound was synthesized according to a procedure described elsewhere^[5].

Yield, 95%; m.p. 177.5–178.2°C; ¹H-NMR (CF₃COOD, 400 MHz) δ: 9.63 (s, 2 × H, 2 × HO), 8.26–7.10 (m, 8H, 2 × ArH₄), 4.30–4.04 (t, 4H, 2 × ArOCH₂), 1.95–1.36 (m, 24H, 2 × (CH₂)₆) and 0.93 (t, 6H, 2 × CH₃); IR (KBr, cm⁻¹): 3348 (OH), 1710 (C=O), 1600, 1580 (aromatic ring framework), 1328 (C–O–C=), 1260 (C–O–C), 840 (1,4-Ar); MS (m/z): 606 (parent), 233 (base). Elemental analysis: Calc. for C₃₆H₄₆O₈ (%): C, 71.26, H, 7.64; Found (%): C, 71.34, H, 7.60.

Synthesis of cis-4, 4'-bis(4-hydroxyphenylazo) dibenzo-18-crown-6 (Monomer 3)

It was synthesized according to literature [18, 19].

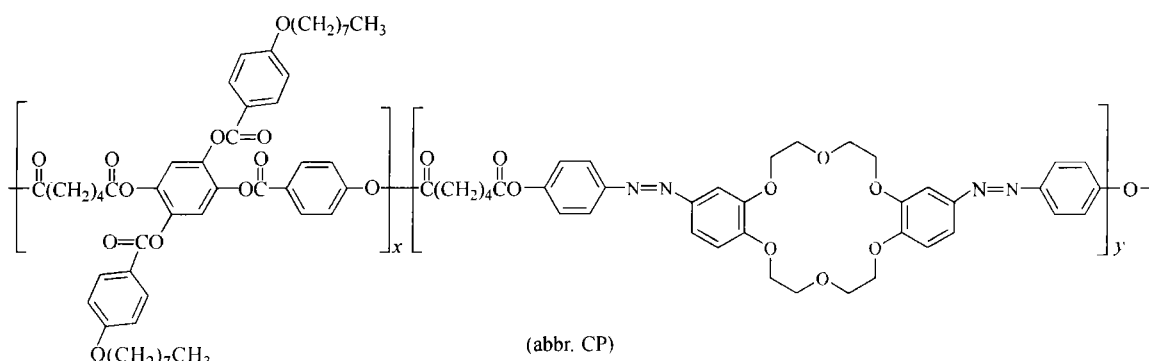
Yield: 67.5%; m.p. 254.5–255.1°C; ¹H-NMR (DMSO-d₆, 400 MHz) δ: 10.22 (s, 2H, 2 × OH), 7.76–6.92 (m, 14H, 2 × ArH₄ + 2 × ArH₃), 4.18 (t, 8H, 4 × ArOCH₂) and 3.89 (t, 8H, 2 × CH₂OCH₂); IR (KBr, cm⁻¹): 3325 (OH), 1589, 1506 (aromatic ring framework), 1452 (–N=N–), 1259 (Ar–O–C) and 843 (1,4-Ar); UV-Vis

(DMF) $\lambda_{\max}$: 372nm; Elemental analysis: Calc. for $C_{32}H_{32}N_4O_8$ (%): C, 63.9, H, 5.37, N, 9.33; Found: (%) C, 63.96, H, 5.42, N, 9.37.

Synthesis of copolyesters

Different ratios of monomers 2 and 3 were dissolved in anhydrous pyridine with stirring under N_2 atmosphere at an ambient temperature and the equimolar monomer 1 was added. The solution was allowed to react for 15 h at room temperature, heated to 65°C and reacted for 8h, followed by pouring the solution into water. The precipitate was filtered, washed with water and dried in vacuo, yellow powders were recrystallized from pyridine to give the product in 90%–95% yield.

The structure of the copolyester is shown in Scheme 2.



Scheme 2 Structure of the copolyester

RESULTS AND DISCUSSION

The monomers were identified by using elemental analysis, UV-Vis, IR, $^1\text{H-NMR}$, MS, etc. Their mesophase properties were studied by using polarized optical microscopy with heating stage and DSC. Monomers 1 and 3 do not show liquid crystalline properties when heated above their melting temperature. On the other hand, monomer 2 exhibits enantiotropic mesophases and shows nematic high strength declination schlieren texture.

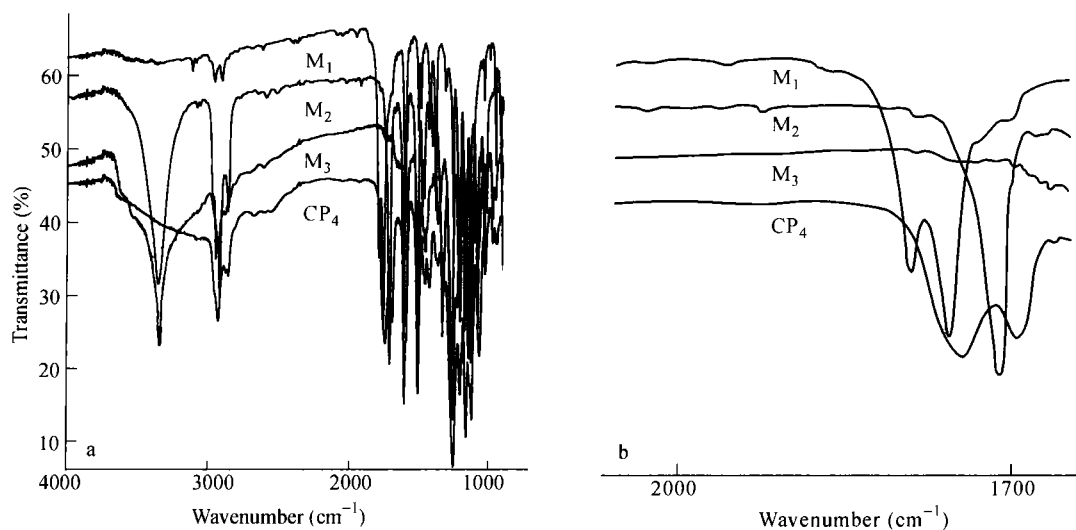


Fig. 1 IR spectra of monomer 1, 2, 3 and CP4

a) IR spectra of monomer 1, 2, 3 and CP4

b) IR spectra of monomer 1, 2, 3 and CP4 (partly zoomed photograph of Fig. 1a)

The copolymerization process was investigated by means of IR spectra. Figure 1(a) shows the IR spectra of monomers 1, 2, 3 and CP4, and Fig. 1(b) shows the partly zoomed photograph of Fig. 1(a). Double peaks at 1782 and 1751 cm^{-1} were the stretching vibration absorption of acyl chloride group in monomer 1, the stretching vibration absorption of hydroxyl of monomers 2 and 3 appeared at 3348 and 3325 cm^{-1} , respectively. After copolymerization, the characteristic absorption bands of all monomers disappeared, indicating that a completing copolymerization has occurred. The copolyesters obtained are fine little yellow powder and do not dissolve in THF and CHCl_3 at room temperature except CP9. The thermal properties of copolyesters were measured with DSC and TG. The phase-transition temperatures and the corresponding transition enthalpy were obtained by using the second heating and first cooling cycles. Molecular weight and intrinsic viscosity were obtained by GPC and Ubbelodhe viscometer. The results are summarized in Table 1.

Table 1. Thermal properties and molecular parameters of the copolyesters

Copolymers	Initial monomer ratio (M_2/M_3)	Phase transition ($^{\circ}\text{C}$) ^a (corresponding enthalpy changes, J/g) [Heating/Cooling]	TG ($^{\circ}\text{C}$) ^b	$[\eta]^c$ (dL/g)	M_n^d	M_w^d
CP1	0.0/1.0	C 174.5(8.73) N 269.5(7.10) I I 262.9(6.53) N 164.1(6.97) C	278.5	0.35		
CP2	0.1/0.9	C 168.7(7.43) N 266.4(6.93) I I 257.1(6.10) N 157.5(6.54) C	281.2	0.34		
CP3	0.2/0.8	C 167.0(7.85) N 254.1(7.36) I I 243.3(6.75) N 154.7(7.10) C	285.1	0.31		
CP4	0.4/0.6	C 163.3(7.72) N 219.0(6.54) I I 207.5(7.10) N 150.4(6.17) C	294.0	0.30		
CP5	0.5/0.5	C 133.7(7.75) N 203.4(6.45) I I 190.6(5.82) N 119.9(6.83) C	296.7	0.27		
CP6	0.6/0.4	C 130.4(7.47) N 195.8 (6.45) I I 182.7(5.93) N 116.3(6.20) C	303.1	0.28		
CP7	0.8/0.2	C 127.0(7.42) S 192.5 (7.20) I I 178.7(8.45) S 112.0(7.45) C	314.4	0.26		
CP8	0.9/0.1	C 126.3(7.48) S 190.7 (7.75) I I 178.5(7.52) S 109.5(7.20) C	326.3	0.25		
CP9	1.0/0.0	C 103.8(7.36) N 187.1 (6.74) I I 174.8(7.74) N 84.5(5.97) C	346.0	—	6900	18000

^a Determined using DSC and proved by using POM, the data are the peak values.

^b Temperature of decomposition = 5% mass loss in N_2 as detected by thermogravimetry

^c Intrinsic viscosity

^d Copolyesters CP1–CP8 are not soluble in THF and their M_n can not be determined by GPC

C: crystal; S: smectic; N: nematic; I: isotropic

As shown in Table 1, CP1 has the highest T_m and T_i among all the copolyesters. The reason is that the flexibility of $-\text{CH}_2\text{OCH}_2-$ chains in comonomer M_3 render the copolymer to build up regular structure easily and increase its degree of ordered arrangement, resulting in better crystallinity which was identified by powder wide angle X-ray diffraction (WAXD) and DSC measurements (Fig. 2). In WAXD profiles, CP1 has the narrowest and the strongest diffraction peaks near $2\theta \approx 20^{\circ}$, indicating it has better ordered arrangement and results in the highest phase transition temperature. The phase transition temperatures of copolyesters decrease with increasing the ratio of comonomer M_2 in feed composition, because M_2 contains X-shaped two-dimensional mesogenic unit that has a bigger steric effect. The steric hindrance decreases the ability of ordered arrangement

leading to the decrease of transition temperatures of copolyesters. The intensities of diffraction peaks become weaker and the diffraction peaks width become broader regularly at $2\theta \approx 20^\circ$ meaning that the ability of order arrangement decreases with an increase in the ratio of X-shaped mesogenic unit in the copolyesters. On the other hand, the temperatures at which weight loss are 5% in TG experiment increase with an increase in the ratio of X-shaped mesogenic unit in the copolyesters. The reason is that the X-shaped two-dimensional mesogenic unit has a very rigid structure and high thermal stability. Increasing the content of M_2 will improve the thermal stability of the copolyesters. The steric hindrance of M_2 also decreases the reactivity of the monomer, resulting in a decrease in the molecular weight of the copolyesters.

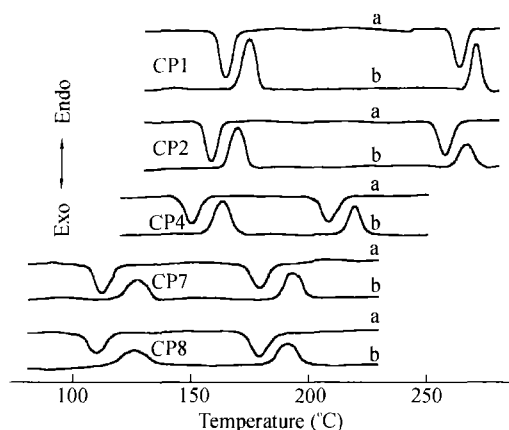


Fig. 2 DSC thermograms of copolyesters CP1, CP2, CP4, CP7 and CP8

Thermotropic liquid crystalline properties of the copolyesters were evaluated by means of DSC measurements and texture observations using a polarizing microscope with a hot stage, which illustrated that the copolyesters form enantiotropic LC phases that expanded over a broad range of temperatures. Figure 2 presents the second heating and first cooling DSC curves of CP1, CP2, CP4, CP7 and CP8. They reveal two clear, reversible, phase transition peaks in the heating and cooling cycles, corresponding to the melting and clearing temperatures.

The results obtained from polarized optical microscope are in a good agreement with those from DSC. At room temperature, weak birefringence can be observed, indicating that the copolyesters have some crystallinity. Above their T_m , birefringence became much more obvious and the typical texture of smectic and nematic phase can be observed. By heating the samples to above their T_i , birefringence disappears. Subsequently, by cooling the copolyesters from the isotropic phase slowly, birefringence reappears. This indicates that the copolyesters are enantiotropic liquid crystals. The typical smectic fan and mosaic texture were observed in the case of CP7 and CP8 on the POM observation. The typical nematic threaded texture and schlieren texture were observed in other copolyesters. Figure 3 exhibits POM photos of CP4 and CP8. In order to identify the mesophase of the copolyesters, WAXD measurements of the copolyesters were conducted by heating up the samples into liquid crystalline state and maintained for enough time, then quenching with ice salt water. The WAXD profiles of selected copolyesters quenched from their liquid crystalline states are shown in Fig. 4. It can be observed that all the copolyesters have a diffuse peak in the wide-angle region, corresponding to short-range intermolecular spacings, which implies a fluid liquid crystalline phase. CP7 and CP8 have not only a diffuse peak in the wide angle region but also a sharp diffraction peak at small angle area. The sharp reflection at the low angle of $2\theta = 2.42^\circ$ and $2\theta = 2.43^\circ$ corresponds to Bragg reflections of CP7 and CP8 respectively, which implies a layer spacing of molecular orientation order. In combination with the results of POM photos, CP7 and CP8 are confirmed to form the smectic phase. By a similar way, other copolyesters are proven to be in the nematic phase.

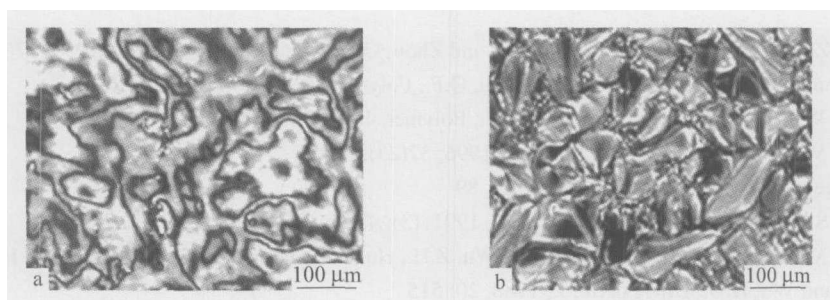


Fig. 3 (a) Threaded texture of CP4 at 179°C; (b) Fan texture of CP8 at 167°C

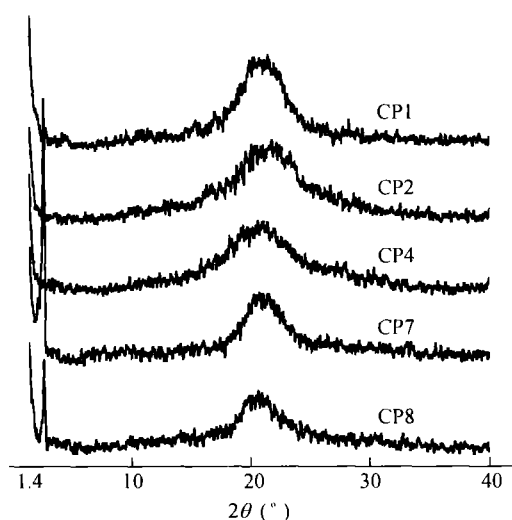


Fig. 4 WAXD pattern of quenched copolyesters CP1, CP2, CP4, CP7 and CP8 from liquid crystal

CONCLUSION

A novel main chain liquid crystalline copolyesters with X-shaped two-dimensional mesogenic unit and crown ether cycle of *cis*-4,4'-bis(4-Hydroxyphenylazo) dibenzo-18-crown-6 were synthesized and their structure and properties were characterized by GPC, DSC, TG, X-ray diffraction and polarizing optical microscope. It was found that all the copolyesters turned to liquid crystalline phase above their T_m . The copolyesters are enantiotropic liquid crystals. The mesophase was also identified by WAXD method. A fan texture and schlieren texture can be observed with typical texture of smectic and nematic phase, respectively. The melt temperature and isotropization temperature of the copolyesters decrease with an increase in the ratio of X-shaped two-dimensional mesogenic unit in the feed composition, but their thermal stability improves with an increase in the ratio of comonomer M_2 in copolyesters.

REFERENCES

- 1 Berg, S., Krone, V. and Ringsdorf, H., *Makromol. Chem. Rapid Commun.*, 1986, 7: 381
- 2 Zhou, Q.F., *Polymer Bull.* (in Chinese), 1991, (3): 160
- 3 Zhou, Q.F., Li, Z.F., Zhang, Z.Y. and Pei, Y.X., *Macromolecules*, 1989, 22: 3821
- 4 Zhang, C.X., Li, Z.F., Zhou, Q.F. and Zhou, H.B., *Chinese J. Polym. Sci.*, 1993, 11(4): 348
- 5 Li, Z.F., Zhang, S.Y., Cao, S.K. and Zhou, Q.F., *Polym. Adv. Technol.*, 1997, 8: 674

- 6 Li, Z.F., Li, L., Zhang, S.Y., Zheng, S.J., Cao, S.K. and Zhou, Q.F., *Chinese J. Polym. Sci.*, 1999, 17(5): 483
- 7 Zhang, S.Y., Deng, G., Li, Z.F., Cao, S.K. and Zhou, Q.F., *Polym. Adv. Technol.*, 2002, 13: 1
- 8 Hou, J.A., Wei, W., Shen, D.Y., Xu, M. and Li, Z.F., *Polymer*, 1994, 35(4): 699
- 9 Hou, J.A., Wei, W., Xu, M. and Li, Z.F., *Polymer*, 1996, 37(23): 5205
- 10 Lehn, J.M., *Angew. Chem. Int. Ed. Engl.*, 1988, 27: 89
- 11 Zhu, Y.M., Jia, S.S. and Nishi, J.M.T., *Chem. Lett.*, 1991, (3): 437
- 12 Zhu, Y.M., Jia, X.B., Xiao, D., Lu, Z.H., Wei, Y., Wu, Z.H., Hu, Z.L. and Xie, M.G., *Phys. Lett. A*, 1994, 188: 287
- 13 Cowie, J.M.G. and Wu, H.H., *Brit. Polym. J.*, 1988, 20: 515
- 14 Percec, V. and Rodemhouse, R., *Macromolecules*, 1989, 22: 2043
- 15 Percec, V., Johansson, G. and Rodemhouse, R., *Macromolecules*, 1992, 25: 2563
- 16 Zhang, S.Y. and Zhao, Y.B., *Chem. J. Chin. Univ.*, 1993, 14: 199
- 17 Li, Z.F., Zhou, Q.F. and Zhang, Z.Y., *Acta Polym. Sinica (in Chinese)*, 1990, (6): 694
- 18 Zhang, S.Y., Deng, G., Li, Z.F., Zheng, S.J. and Zhou, Q.F., *Acta Polym. Sinica (in Chinese)*, 1999, (3): 266
- 19 Dznan, M.F., Marmontov, V.P., Kolesnik, A.A. and Drozdoskya, A.L., *Ukrain. Khim. Zhur.*, 1984, 50: 1285