

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

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Abstract A novel series of liquid crystalline copolyesters with T-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 -hexanedioxy)dibenzoyl dichloride (M_1), 2-(4'-ethoxyphenyl)hydroquinone (M_2) and *cis*-4,4'-bis(4-hydroxyphenylazo)dibenzo-18-crown-6 (M_3). The molecular weights of copolyesters are not high, and the intrinsic viscosity $[\eta]$ of copolyesters ranges from 0.29–0.43. The monomers' structures were identified by elemental analysis, IR, UV, ¹H-NMR, MS, *etc.* All the copolyesters are yellowish powders and insoluble in THF and CHCl₃ at room temperature except CP-9. 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 crystalline phase when they were heated to above their melting temperature (T_m). The threaded texture and schlieren texture of nematic phase can be observed on POM. Their T_m and isotropic temperature (T_i) decrease gradually, while thermal stability increase with varying the content of T-shaped two-dimensional mesogenic unit in the copolyesters.

Keywords: T-shaped two-dimensional mesogenic unit; Crown ether; Liquid Crystalline copolyesters; Synthesis.

INTRODUCTION

The concept of liquid crystal polymers with two-dimensional mesogenic units (LCPTDMU) was formally proposed by Zhou when he was invited by Du Pont Company to give a lecture in 1990, then the paper titled by this concept was published in Polymer Bulletin^[1]. The main point is that the main chain liquid crystal polymers based on one-dimensional rod-like mesogenic units could be processed to obtain highly orientation of the molecular chain and good mechanical strength in the orientation direction; If one-dimensional rod-like mesogenic units are changed into T-shaped or X-shaped two-dimensional mesogenic units, then one dimension part of the two-dimensional mesogenic structure could be embedded in the polymer main chain, another dimension part would extend out from the main chain; The resulted liquid crystal polymers will possess high mechanical strength in the main chain and other directions, which are promising isotropic mechanical materials with high strength and modulus.

In 1993, Rotz *et al.*^[2] reported LCPTDMU that are called by us today, but the concept of it was not proposed and the comparison of LCPTDMU and other liquid crystal polymers about the relationships between structures and properties was not done yet.

Inspired by this concept, Li *et al.*^[3–9] have successfully synthesized many LCPTDMU since 1993, and the relationships of their structures and properties have been investigated systematically.

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It has been paid on great interest that the design and synthesis of novel structures of liquid crystal polymers. Liquid crystalline polymer with T-shaped two-dimensional mesogenic unit and crown ether cycle is a kind of system with ordered structures and incorporated functionalities. It is also a novel kind of materials that possess both characteristic of liquid crystal polymers and the select coordination ability of crown ethers. There are few papers of liquid crystal polymers with crown ether^[10–15] since Percec *et al.*^[10] first reported thermotropic main chain liquid crystal copolyethers with dibenzo-18-crown-6 in 1989. It is a new study to incorporate the crown ether cycle and T-shaped mesogenic unit into the copolymer main chain to synthesize main chain liquid crystal copolyesters with both parts. In this report, the liquid crystal properties of this kind of copolyesters and the influence of different monomers on the properties of the copolyesters have been investigated. Although the assumption that the preparation of materials with good properties from this kind of liquid crystal polymers has not been realized yet, it is important to widen new research fields of liquid crystal polymers and crown ether functional materials and develop host-guest chemistry in academic meaning and promising applications.

EXPERIMENTAL

Materials

Thionyl chloride (SOCl₂) was refluxed with triphenyl phosphite for 3 h before distilled and then was collected at 76.5–77°C. Pyridine was fluxed with KOH for 5 h before distilled and then was collected at 115.0–116.0°C. All the other reagents are analytical or chemical grade and not purified further before use.

Synthesis

Synthesis of 4,4'-(α,ω -hexanedioxy)dibenzoyl dichloride (M₁)

It was synthesized by the reaction of SOCl₂ and 4,4'-(α,ω -hexanedioxy)dibenzoyl carboxylic acid, which was prepared by the esterification reaction of *p*-hydroxybenzoic acid with hexanedioyl chloride according literature [3]. Yield: 85.8%; m.p. 113.0–114.6°C.

Synthesis of 2-(4'-ethoxyphenyl)hydroquinone (M₂)

It was synthesized by the reaction of Na₂SO₄ and 2-(4'-ethoxyphenyl)quinone, which was prepared by the reaction of quinone with *p*-ethoxyaniline according literature [5]. Yield: 83.7%; m.p. 95.5–95.6°C.

Synthesis of cis-4,4'-bis(4-hydroxyphenylazo)dibenzo-18-crown-6 (M₃)

It was synthesized by diazotization and coupling reaction of *cis*-diaminodibenzo-18-crown-6 and phenol according to literature [16]. Yield: 67.8 %, m.p. 248.3–249.3°C.

Synthesis of copolyesters

Different ratios of monomers 2 and 3 were dissolved in anhydrous pyridine with stirring under N₂ 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 react for 8 h, 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.

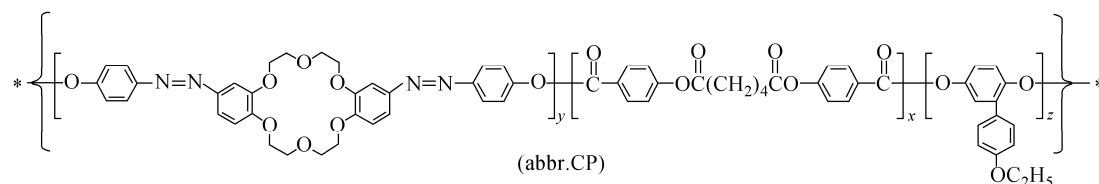
Characterization

The monomers and copolyesters were characterized by the following techniques.

Melting points were measured on a WRS-1 melting point apparatus and the heating rate was controlled at 1 K/min. Elemental analysis was obtained with MOD1106 elemental analyzer. IR spectra were recorded on a Nicolet 460 FT-IR spectrometer using KBr pellet. Ultraviolet-visible spectra were obtained on an UV-2401 PC spectrophotometer in DMF. ¹H-NMR spectra were measured with a Bruker DPX 400 spectrometer with DMSO-d₆ or CF₃COOD as the solvent and tetramethylsilane as the standard. Mass spectra were recorded with VG-ZAB-HS spectrometer in EI. The phase-transition temperatures were determined as the maximum position of the endotherm peak of the first cooling cycle and the exotherm peak of the second heating cycle with a NETZSCH DSC-204 calorimeter equipped with a liquid-nitrogen cooling accessory. The heating and cooling rates were controlled at 10 K/min. Thermalgravimetric (TG) analysis was performed on a NETZSCH TG-204 thermal analysis instrument 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 2θ was from 1.4–40°. Gel permeation chromatography (GPC) measurement of CP-9 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/tetrachloroethane/4-chlorophenol mixed solvent (25/35/45 by volume) in a 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.

The structure of the copolyesters is shown in Scheme 1.



Scheme 1 Structure of the copolyesters

RESULTS AND DISCUSSION

The monomers were identified by using elemental analysis, UV-Vis, IR, $^1\text{H-NMR}$, MS, *etc.* The copolyesters are yellow powders and insoluble in THF and chloroform solvents except CP-9. The thermal properties of the copolyesters were measured by DSC and TG. 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 ($M_1/M_2/M_3$)	Phase transition temperature (°C) ^a (corresponding enthalpy changes, J/g)	TG (°C) ^b	$[\eta]^c$ (dL/g)	M_n^d	M_w^d
		[Heating / Cooling]				
CP-1	1.0/0.0/1.0	<u>C 184.8 (5.89) N 235.9 (4.95) I</u> I 228.6 (4.57) N 176.4 (5.52) C	248.5	0.43		
CP-2	1.0/0.1/0.9	<u>C 171.4 (5.66) N 233.6 (5.43) I</u> I 225.4 (5.11) N 161.1 (5.18) C	249.1	0.42		
CP-3	1.0/0.2/0.8	<u>C 167.0 (5.08) N 231.7 (4.94) I</u> I 222.2 (4.59) N 154.9 (4.77) C	251.8	0.37		
CP-4	1.0/0.4/0.6	<u>C 163.5 (5.83) N 227.1 (4.96) I</u> I 216.6 (4.61) N 149.6 (5.22) C	254.9	0.37		
CP-5	1.0/0.5/0.5	<u>C 147.7 (5.44) N 225.8 (5.06) I</u> I 214.9 (4.98) N 132.5 (5.10) C	263.2	0.35		
CP-6	1.0/0.6/0.4	<u>C 146.1 (5.76) N 224.0 (5.20) I</u> I 211.8 (4.82) N 130.2 (5.19) C	271.7	0.33		
CP-7	1.0/0.8/0.2	<u>C 138.9 (4.85) N 220.9 (4.72) I</u> I 207.1 (4.33) N 121.7 (4.53) C	285.6	0.31		
CP-8	1.0/0.9/0.1	<u>C 130.2 (5.39) N 216.5 (5.07) I</u> I 202.6 (4.66) N 111.3 (5.01) C	293.5	0.29		
CP-9	1.0/1.0/0.0	<u>C 121.5 (5.22) N 193.8 (4.88) I</u> I 178.7 (4.55) N 100.9 (4.98) C	297.3	–	7800	15000

^a Determined using DSC and proved by using POM, the data are the peak values; ^b Temperature of decomposition 5% mass loss in N₂ as detected by thermogravimetry; ^c Intrinsic viscosity; ^d Copolyserters CP-1–CP-8 are not soluble in THF, M_n of these copolyserters not determined by GPC; C: crystal, N: nematic, I: isotropic

As shown in Table 1, CP-1 has the highest T_m and T_i among all the copolyesters. The reason is that the flexibility of $-\text{OCH}_2\text{OCH}_2-$ chains in comonomer M_3 renders the copolymer to build up regular structure easily and increase its degree of ordered arrangement, resulting in better crystallinity which was identified by

DSC curves. From this table, it can also be seen that the phase transition temperatures of copolyesters decrease with increasing the ratio of comonomer M_2 in feed composition, because M_2 contains T-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 temperature of copolyesters. The temperatures at which weight loss are 5% in TG experiment range from 248.5–297.3°C and increase with an increase on the ratio of T-shaped mesogenic unit in the copolyesters. The reason is that the T-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 intrinsic viscosity $[\eta]$ of copolyesters ranging from 0.29–0.43 dL/g indicates the molecular weights of the polymers are not high, the reason of which is that the steric hindrance of M_2 also decrease the reactivity of the monomer, resulting in a decrease in the molecular weights of the copolyesters.

Thermotropic liquid crystalline properties of all the copolyesters were evaluated by means of DSC measurements and observations using a polarizing microscope with a hot stage. Figure 1 presents the second heating and first cooling DSC curves of CP-1, CP-3, CP-5 and CP-7.

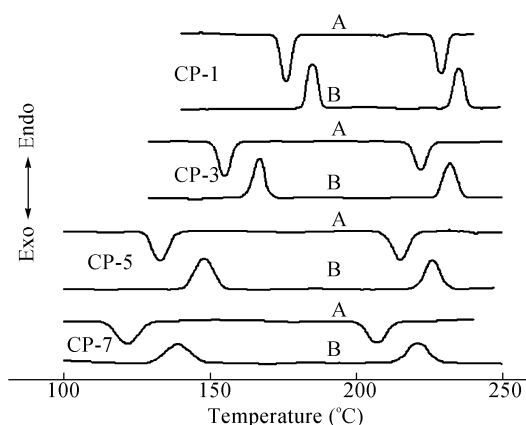


Fig. 1 DSC thermograms of copolyesters CP-1, CP-3, CP-5 and CP-7
A) First cooling scan; B) Second heating scan

It can be seen from Fig. 1 that there are two endotherm peaks in the heating cycles, corresponding to the melting and clearing temperatures, and two exotherm peaks in the cooling cycles corresponding to the liquid crystalline and crystalline temperatures. The highest melting peak and narrowest melting range of CP-1 indicate its good crystallinity. The intensity of the melting peaks becomes weaker and the melting range becomes wider with the sequence of CP-3, CP-5 and CP-7. The phase transition temperatures obtained from polarized optical microscope are in a good agreement with those from DSC. The copolyesters have weak double reflections at room temperature and show clear threaded texture or schlieren texture when heated to above their T_m into liquid crystalline phase, which indicates that all of them are nematic thermotropic liquid crystalline polymers. Above their T_i , the polymers go into isotropic liquid phase with the disappearance of the double reflection and the double reflection reappears during the slow cooling cycle. CP-1, CP-2, CP-3, CP-5 and CP-9 show threaded texture of nematic phase and CP-4, CP-6, CP-7 and CP-8 show schlieren texture of nematic phase on POM observations. Figure 2 exhibits liquid crystalline images of CP-2 and CP-8.

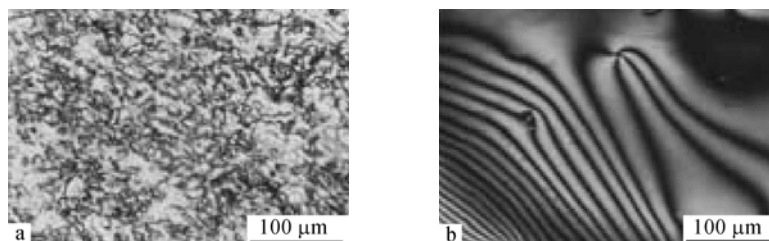


Fig. 2 Polarizing optical micrographs of copolyesters CP-2 (a) and CP-8 (b)
a) Threaded texture, obtained at 205°C; b) Schlieren texture, obtained at 175°C

Besides the texture images obtained from POM, which were not adequate to define the liquid crystalline phase, WAXD study was combined to identify the liquid crystalline phase further. WAXD measurements of the copolyesters were conducted by heating up the samples into liquid crystalline state and maintained for 10 min, then quenching with ice salt water. The WAXD profiles of selected copolyesters quenched from their liquid crystalline states are shown in Fig. 3. It can be observed that the copolyesters have a diffuse peak in the wide-angle region. The center of the diffuse peak is around $2\theta \approx 20^\circ$ and the value of d is 0.409–0.440 nm, corresponding to transverse stacking. There is no sharp diffraction peak of the layer structure of smectic phase at small angle area, which is the typical characteristic of nematic phase^[17]. The intensity of the diffuse peak decreases with the increase of the content of T-shaped mesogenic unit, which is consistent with the results of DSC curves.

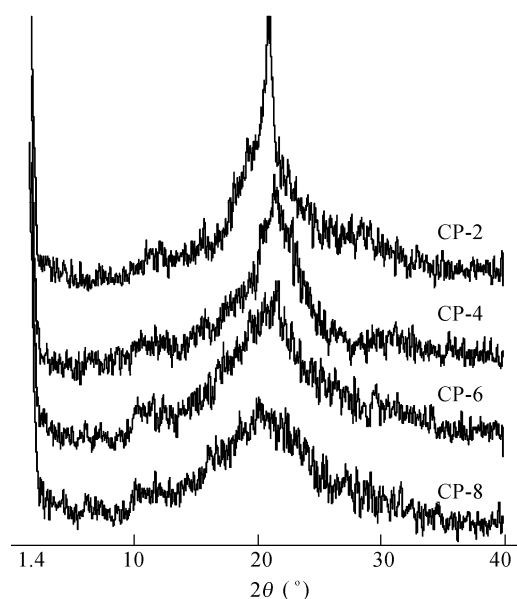


Fig. 3 WAXD pattern of quenched copolyesters CP-2, CP-4, CP-6 and CP-8

Based on the characteristic of X-ray diffraction peaks and the combined results of DSC and texture images, the liquid crystalline copolyesters CP-1–CP-9 were identified as nematic phase.

CONCLUSIONS

A novel series of liquid crystalline copolyesters with T-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. 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 crystalline phase when they were heated to above

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