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含二苯并-18-冠-6冠醚环的主链型液晶共聚酯的设计与合成*

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摘　要　以4,4′-(α,ω-亚烷基二酰氧)二联苯甲酰氯(M1)、顺式-4,4′-双(4-羟基苯基偶氮)二苯并-18-冠-6(M2)、反式-4,4′-双(4-羟基苯基偶氮)二苯并-18-冠-6(M3)和1,10-癸二醇(M4)为单体,通过溶液共缩聚反应,合成了两个系列新的含联苯型液晶基元和偶氮型冠醚环的主链型液晶共聚酯.共聚酯的[η]在0.25~0.35和0.27~0.38之间.单体的化学结构通过IR、UV-Vis、^{1}H-NMR、MS和元素分析等方法确证.共聚酯的性质采用[η]、DSC、TGA、WAXD和POM等方法进行了研究.发现所有的共聚酯加热到各自熔融温度以上都能形成向列相液晶态,可以观察到向列相的丝状织构或纹影织构或球粒织构.共聚酯的熔融温度(T_m)和各向同性温度(T_i)随共聚酯分子中柔性间隔基长度的增加而有规律地降低,含反式冠醚环的共聚酯的T_m和T_i均高于相应含顺式冠醚环的共聚酯的T_m和T_i.

关键词　联苯型液晶基元,冠醚,液晶共聚酯,合成

DESIGN AND SYNTHESIS OF MAIN CHAIN LIQUID CRYSTALLINE COPOLYESTERS CONTAINING DIBENZO-18-CROWN-6 UNITS*

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Abstract　Two series of novel main chain liquid crystalline copolyesters with biphenyl mesogenic units and azo type crown ether cycles were prepared *via* solution polycondensation from 4,4′-(α,ω-alkanedioyloxy) dibiphenylyloyl dichloride (M1), *cis*-4,4′-bis (4-hydroxy-phenylazo) dibenzo-18-crown-6 (M2), *trans*-4,4′-bis-(4-hydroxy-phenylazo)-dibenzo-18-crown-6 (M3) and 1,10-decanediol (M4) as the monomers. The intrinsic viscosity [η] of the two series of copolyesters ranges from 0.25~0.35 dL/g and 0.27~0.38 dL/g, respectively. The structures of monomers were identified by elemental analysis, IR, UV-Vis, ^{1}H-NMR and MS. The properties of copolyesters were investigated by using DSC, TGA, WAXD and POM. All the copolyesters are able to form nematic mesophase after melting. The threaded texture, or ball granul texture or Schlieren texture of nematic phase can be observed on POM. Their melting temperature (T_m) and isotropic temperature (T_i) decrease regularly with increasing the length of flexible spacer in the copolyesters, and the T_m and T_i of copolyesters containing *trans* crown ether cycles are higher than those of the copolyesters containing *cis* crown ether cycles.

Keywords　Biphenyl mesogenic unit, Crown ether, Liquid crystalline copolyesters, Synthesis

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1 INTRODUCTION

It has been paid on great interest the design and synthesis of novel structures of liquid crystal polymers. In 1989 Percec *et al*.[1] first reported thermotropic main chain liquid crystal polyethers and copolyethers with dibenzo-18-crown-6 which are unidirectional nematic liquid crystals and the transition temperatures are low. So far, there are few papers of liquid crystal polymers with crown ether[2~8]. Liquid crystalline polymer with 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 the characteristics of liquid crystal polymers and the select coordination ability of crown ethers. The study of liquid crystalline polymers with crown ether cycles 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.

It is a meaningful work to incorporate the azo type crown ether cycles and biphenyl mesogenic units with different flexible spacers into the copolymer main chain to synthesize main chain liquid crystal copolyesters with both parts, and to investigate whether they are liquid crystalline and the influence of monomers' structures on the properties of copolyesters. In this report, two series of novel main chain liquid crystalline copolyesters with biphenyl mesogenic units and azo type crown ether cycles were prepared *via* solution condensation polymerization from 4,4′-(α,ω-alkanedioyloxy) dibiphenylyloyl dichloride (**M1**), *cis*-4,4′-*bis* (4-hydroxyphenylazo) dibenzo-18-crown-6 (**M2**), *trans*-4,4′-bis-(4-hydroxyphenylazo)-dibenzo-18-crown-6 (**M3**) and 1,10-decanediol (**M4**). The relationship between the structures and liquid crystalline properties of the copolyesters was also investigated.

2 EXPERIMENTAL

2.1 Materials

1,10-Decanediol (Fluka) was analytical pure and used as received. Sulfur oxychloride ($SOCl_2$) was refluxed with triphenyl phoshite for 3 h before distilled and then was collected at 76.5 ~ 77.5℃. Tetrahydrofuran (THF) was refluxed with CaH_2 for 6 h before being distillation and then was collected at 64.5 ~ 65.4℃. Pyridine (Py) was refluxed with KOH for 5 h before distillation and then was collected at 115.0 ~ 116.0℃. All the other reagents are analytical or chemical grade and not purified further before use.

2.2 Synthesis

2.2.1 *Synthesis of* 4,4′-(*α*,*ω-alkanedioyolxy*) *dibiphenylyoyl dichloride* (**M1**)

It was synthesized by the reaction of $SOCl_2$ and 4,4′-(α,ω-alkanedioyloxy) dibiphenylyloyl carboxylic acid, which was prepared by the esterification reaction of 4,4′-hydroxydiphenyl carboxylic acid with alkanedioyl (n = 4,6,8,12) dichloride according literature[3]. Yield: 98.5%, 98.7%, 98.9%, 99.0%; mp 159.1 ~ 160.8℃, 151.2 ~ 152.9℃, 141.9 ~ 143.3℃, 140.4 ~ 141.6℃.

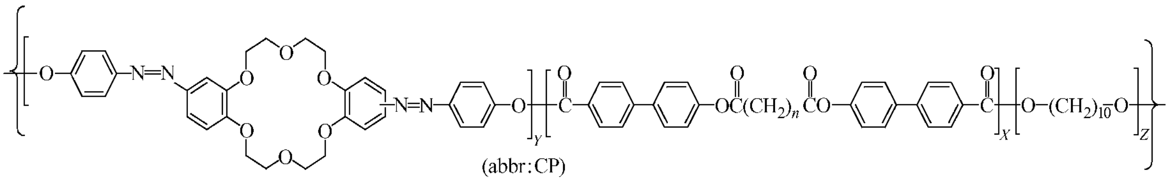
2.2.2 *Synthesis of cis- and trans-*4,4′-*bis* (4-*hydroxyphenylazo*) *dibenzo-*18-*crown-*6 (**M2** and **M3**)

They were synthesized by diazotization and coupling reaction of *cis*-diaminodibenzo-18-crown-6 and *trans*-diaminodibenzo-18-crown-6 with phenol according to literature[9]. Yield: 68.8%, 69.3%, mp 248.2 ~ 249.1℃, 255.1 ~ 255.7℃.

2.2.3 *Synthesis of copolyesters*

In a typical reaction, the equimolar **M2** and **M4** were dissolved in anhydrous pyridine with stirring under N_2 atmosphere at an ambient temperature and **M1** was added dropwise with the molar ratio 2∶1 (**M1**∶**M2**). The solution was allowed to react for 15 h at room temperature, heated to 65℃ and react for 8 h, followed by pouring the solution into methanol. The precipitate was filtered, washed with water, methanol and cold ethanol, then dried in vacuo, yellow powders were recrystallized from *N*-dimethyl-2-pyrrolidone/methanol to give the product. The yield of the copolyesters ranges 91.4% ~ 96.7%.

The structure of the copolyesters is shown in Scheme 1.



CP-Ⅰ (*cis*-), CP-Ⅱ (*trans*-); A: $n = 4$, B: $n = 6$, C: $n = 8$, D: $n = 12$

Scheme 1　Structure of the copolyester

2.3 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. ^{1}H-NMR spectra were measured with a Bruker DPX 400 spectrometer with DMSO-d_6 or CF_3COOD as the solvent and tetramethylsilane as the standard. Mass spectra were recorded with a 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. Thermal gravimetric analysis (TGA) 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-Kα radiation, 35 kV, 30 mA electric current, and a scanning rate of 4 (°)/min. The scanning range of 2θ was from 1.4 ~ 40°. Intrinsic viscosity measurements were performed on an Ubbelodhe viscometer at (40 ± 0.05)℃ 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 Olympus BX51 polarizing microscope equipped with a Linkam Scientific Instruments Ltd 350 hot stage.

3 RESULTS AND DISCUSSION

M1, **M2** and **M3** were identified by using IR, ^{1}H-NMR, UV-Vis, MS, elemental analysis *etc*. The thermotropic liquid crystalline properties of **M1** were identified by DSC and POM observations. The copolyesters are yellowish powders and insoluble at room temperature in ordinary somvents such as $CHCl_3$, THF and Py, so the molecular weight (MW) of the copolyesters could not be determined by GPC method. The thermal properties of the copolyesters were measured by DSC and TGA. The intrinsic viscosity was obtained by Ubbelodhe viscometer. The results are summarized in Table 1.

The intrinsic viscosity of the copolyesters measured in the same conditions could indicate the relative value of the M_w of different copolyesters to some extent. Table 1 shows that the intrinsic viscosities $[\eta]$ of CP-Ⅰ and CP-Ⅱ range from 0.25 ~ 0.35 dL/g and 0.27 ~ 0.38 dL/g, which indicates that the molecular weights of the polymers are not high. The reason is that the big steric hindrance of 4,4′-bis (4-hydroxyphenylazo)-dibenzo-18-crown-6 surely decreases the activity of copolymerization, and the copolymerization is a precipitation polymerization because of the insolubility of the products.

It can also be found that the intrinsic viscosity $[\eta]$ of the copolyesters increases with increasing the length of flexible spacers, which is possibly because that the increased length of flexible spacers will improve the solubility of the corresponding copolyester and then the continuous propagation the polymer chain.

The molecular structures of liquid crystalline polymers have important influences on their liquid crystalline properties. It can be seen from Table 1 that the length of flexible spacers has obvious influences on

T_m and T_i of the copolyesters. For CP-Ⅰ and CP-Ⅱ， T_m and T_i decrease gradually with the increase of the length of flexible spacers from 4 to 12. Moreover， the configuration of crown ether cycle also has influences on phase transition temperatures of the copolyesters. The T_m and T_i of CP-Ⅱ containing *trans*-4，4′-bis-(4-hydroxyphenylazo) dibenzo-18-crown-6 are higher than those of CP-Ⅰ containing *cis*-4，4′-bis-(4-hydroxyphenylazo) dibenzo-18-crown-6. The temperatures of CP-Ⅰ and CP-Ⅱ at which weight loss are 5% in TGA experiment are relatively high， which range from 297.4 ~ 263.8℃ and 298.7 ~ 274.3℃ respectively.

Table 1 Thermal properties and molecular parameters of the copolyesters

Copolyesters	Initial monomer ratio[a] **M1/M2 (or M3)/M4**	Phase transition temperature (℃)[b] (corresponding enthalpy changes， J g^{-1})， [Heating process]	T_d (℃)[c]	[η] (dL/g)[d]
CP-Ⅰ-A	1.0/0.5/0.5	C 189.7 (5.35) N 275.9 (4.46) I I 264.6 (4.35) N 178.0 (5.24) C	297.4	0.25
CP-Ⅰ-B	1.0/0.5/0.5	C 144.1 (5.65) N 263.8 (4.75) I I 253.1 (4.66) N 134.6 (5.54) C	291.7	0.29
CP-Ⅰ-C	1.0/0.5/0.5	C 121.4 (5.27) N 243.7 (4.17) I I 232.5 (4.07) N 111.5 (5.17) C	285.3	0.31
CP-Ⅰ-D	1.0/0.5/0.5	C 102.5 (5.28) N 229.6 (4.10) I I 217.8 (3.98) N 90.7 (5.16) C	263.8	0.35
CP-Ⅱ-A	1.0/0.5/0.5	C 194.5 (5.41) N 278.7 (4.51) I I 268.1 (4.47) N 183.5 (5.32) C	298.7	0.27
CP-Ⅱ-B	1.0/0.5/0.5	C 147.3 (5.60) N 268.8 (4.75) I I 257.1 (4.70) N 137.1 (4.71) C	294.1	0.29
CP-Ⅱ-C	1.0/0.5/0.5	C 125.4 (5.44) N 251.0 (4.38) I I 239.0 (4.34) N 115.7 (5.35) C	287.2	0.30
CP-Ⅱ-D	1.0/0.5/0.5	C 117.7 (5.31) N 245.6 (4.63) I I 232.8 (4.60) N 106.2 (5.31) C	274.3	0.38

[a] Initial monomer ratio：**M1/M2/M4** for CP-Ⅰ， **M1/M3/M4** for CP-Ⅱ； [b] Determined using DSC and proved by using POM； [c] Temperature of decomposition 5% mass loss in N_2 as detected by thermogrvimetry； [d] Intrinsic viscosity；C：crystal，N：nematic，I：isotropic

Thermotropic liquid crystalline properties of CP-Ⅰ and CP-Ⅱ were evaluated by means of DSC measurements and observations using a polarizing microscope with a hot stage. The results show that all the copolyesters are liquid crystalline polymers. Figure 1 presents the second heating and first cooling DSC curves of CP-Ⅰ. It can be seen from Fig. 1 that there are two endotherm peaks in the heating cycles， corresponding to the transition temperatures from solid phase to nematic phase (T_m) and from nematic phase to isotropic phase (T_{n-i})， and two exotherm peaks in the cooling cycles corresponding to the transition temperatures from isotropic phase to nematic phase (T_{i-n}) and from nematic phase to solid phase (T_{n-c}). The highest melting peak and narrowest melting range of CP-Ⅰ-A indicate its good crystallinity. The intensity of the melting peaks becomes weaker and the melting range becomes wider with the sequence of CP-Ⅰ-B， CP-Ⅰ-C and CP-Ⅰ-D. The DSC curves of CP-Ⅱ are similar with those of CP-Ⅰ.

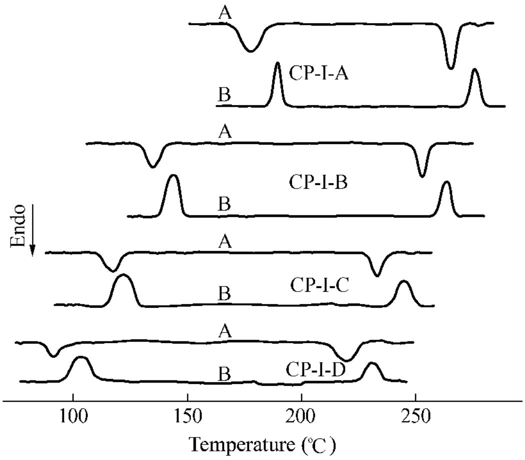
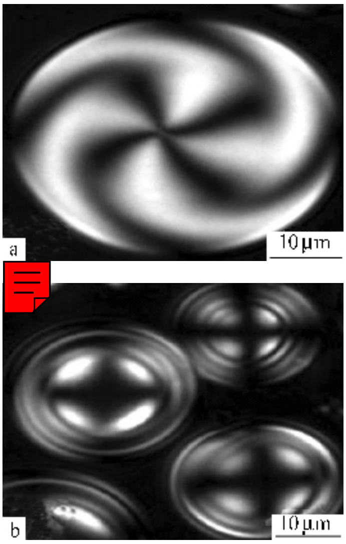


Fig. 1 DSC curves of copolyesters CP-Ⅰ

A) First cooling scan；B) Second heating scan

The phase transition temperatures obtained from POM are in good agreement with those from DSC. The birefringence of the copolyesters can not be observed under POM at room temperature. The order of the copolyesters molecules increases with the heating process and weak birefringence could be observed around T_m. The copolyesters show clear threaded texture，or ball granul 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. It can be observed that viscosities of the copolyesters in liquid crystalline phase decrease with the increase of number of methylene of the copolyesters，which shows that the influence of the length of flexible spacer on the movement of liquid crystalline molecules. Above their T_i，the polymers go into isotropic liquid phase with the disappearance of the birefringence. Figure 2 exhibits liquid crystalline images of CP-Ⅰ-B and CP-Ⅱ-B obtained in the cooling cycles.



. 2　Polarizing optical microcopy photographs of CP-Ⅰ and CP-Ⅱ-B
a) Schlieren texture of CP-Ⅰ-B，obtained after cooling to 197℃；
b) Ball granul texture of CP-Ⅱ-B，obtained after cooling to 241℃

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 bath. The WAXD profiles of CP-Ⅰ 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 $2\theta \approx 20°$ and the value of d is 0.421 ~ 0.425 nm. There is no sharp diffraction peak of the layer structure of smectic phase at small angle area，which is the typical characteristics of nematic phase[0]. The intensity of the diffuse peak decreases with the increase of the length of flexible spacers，which is consistent with the results of DSC curves.

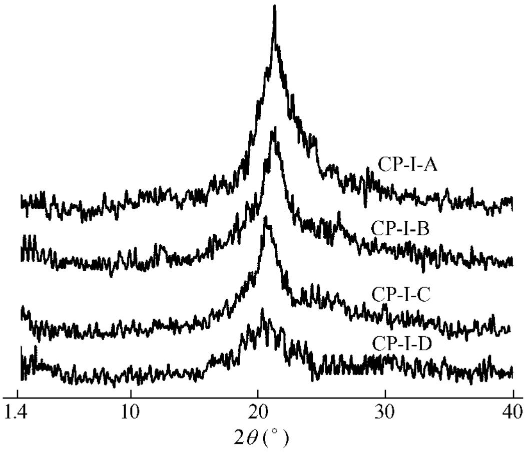


Fig. 3　WAXD patterns of quenched copolyesters CP-Ⅰ

Based on the characteristics of X-ray diffraction peaks and the combined results of DSC and texture images，the liquid crystalline copolyesters CP-Ⅰ and CP-Ⅱ were identified as nematic phase polymers.

4　CONCLUSIONS

Two series of novel main chain liquid crystalline copolyesters with biphenyl mesogenic units and azo type crown ether cycles were prepared *via* solution condensation polymerization from 4，4′-(α，ω-alkanedioyloxy) dibiphenylyloyl dichloride (**M1**)，*cis*-4，4′-bis (4-hydroxyphenylazo) dibenzo-18-crown-6 (**M2**)，*trans*-4，4′-bis-(4-hydroxyphenylazo) dibenzo-18-crown-6 (**M3**) and 1，10-decanediol (**M4**). The properties of copolyesters were investigated by using [η]，DSC，TG，WAXD and POM. It was found that all the copolyesters are thermotropic liquid crystal polymers. The threaded texture，or ball granul texture or schlieren texture of nematic phase can be observed on POM. The nematic mesophase was also identified by WAXD method. Their T_m and isotropic temperature (T_i) decrease regularly with the increase of the length of flexible spacer in the main chain，and the T_m and T_i of CP-Ⅱ containing *trans* crown ether cycles are higher than those of CP-Ⅰ containing *cis* crown ether cycles.

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