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## Liquid Crystals

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### Synthesis and properties of three novel series of monomers containing *para*-methoxyazobenzene as the mesogenic group

Guojie Wang<sup>a</sup>; Min Li<sup>a</sup>; Mingming Yu<sup>a</sup>; Chaowei Guo<sup>a</sup>; Xinfang Chen<sup>a</sup>; Gao Li<sup>b</sup>; Enle Zhou<sup>b</sup>

<sup>a</sup> Department of Materials Science, Jilin University, Changchun 130023, PR China, <sup>b</sup> State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China,

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# Synthesis and properties of three novel series of monomers containing *para*-methoxyazobenzene as the mesogenic group

GUOJIE WANG\*, MIN LI, MINGMING YU, CHAOWEI GUO,  
XINFANG CHEN

Department of Materials Science, Jilin University, Changchun 130023, PR China

GAO LI, and ENLE ZHOU

State Key Laboratory of Polymer Physics and Chemistry,  
Changchun Institute of Applied Chemistry, Chinese Academy of Sciences,  
Changchun 130022, PR China

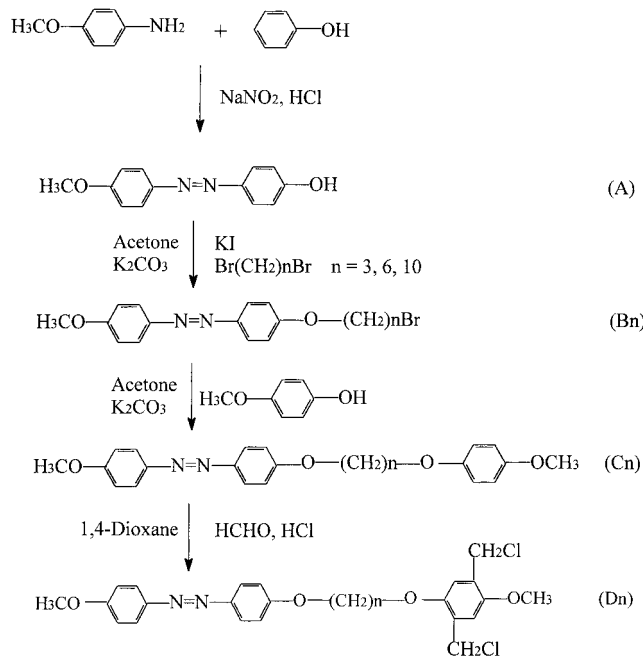
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Three novel series of monomers, namely *n*-1-bromo-[4-(4-methoxyphenylazo)phenoxy]alkanes (*Bn*, *n* = 3, 6, 10), *n*-[4-(4-methoxyphenylazo)phenoxy]alkoxy-4-methoxybenzene (*Cn*, *n* = 3, 6, 10) and *n*-[4-(4-methoxyphenylazo)phenoxy]alkoxy-[4-methoxy-2,5-bis-(chloromethyl)]benzene (*Dn*, *n* = 3, 6, 10) were synthesized and characterized with FTIR, <sup>1</sup>H NMR, UV-visible and fluorescence spectroscopy. Their thermal behaviour was studied by different scanning calorimetry and polarizing optical microscopy. The results show that B3, B6 and C6 exhibit monotropic nematic liquid crystalline behaviour.

## 1. Introduction

The use of liquid crystalline materials in organic light emitting devices has attracted great attention in recent years [1–17]. Although liquid crystal displays (LCDs) have maintained their dominant position in the field of flat panel displays because of their low power consumption, low voltage, and semiconductor compatibility, they still have some disadvantages such as limited brightness and efficiency. These limitations arise mainly from the use of dichroic sheet polarizers and absorbing colour filters, which convert light into thermal energy, and thus lose a significant fraction (as large as >80%) of the incident light [18]. The use of luminescent materials emitting polarized light for backlighting LCDs could enhance their visual performance while removing the need for a polarization filter. For the use of conjugated liquid crystalline polymers in this application, the polymer backbone would be easily oriented in the mesophase, thus exhibiting anisotropic conductivity and emitting polarized light. The incorporation of liquid crystalline materials into light emitting diodes is still in an early state, yet there is no doubt that liquid crystalline materials will play a strong role in the future development of light emitting diodes.

In order to obtain a conjugated liquid crystalline polymer for light emitting diodes, we have prepared monomers *Bn*, *Cn* and *Dn* (*n* = 3, 6, 10) (see the scheme)



Scheme. Synthetic route for monomers *Bn*, *Cn*, and *Dn*.

containing *para*-methoxyazobenzene as the mesogenic group. Azobenzene has been widely used as a mesogenic group in liquid crystalline polymers [19] and it is also a well known photosensitive chromophore which undergoes photoinduced and thermal *cis-trans* isomerization [20]. Amorphous polymers containing a substituted

\*Author for correspondence, e-mail: guojiewang@21cn.com

azobenzene group have been studied as optical storage materials, whose anisotropy can be induced by the orientation of azobenzene groups when exposed to a linearly polarized laser [21]. We chose *para*-methoxyazobenzenes as side chains to prepare poly(1,4-phenylenevinylene) derivatives which could emit polarized light by controlling the state of their azobenzene side chains. In the present paper, the synthesis of the monomers *Bn*, *Cn* and *Dn* ( $n = 3, 6, 10$ ) containing *para*-methoxyazobenzene as mesogenic group is described and the results of physical study of their properties presented.

## 2. Experimental

### 2.1. Synthesis of *Bn*, *Cn* and *Dn* compounds

The synthetic route to these compounds is given in the scheme. The following are typical synthetic procedures.

#### 2.1.1. 4-(4-Methoxyphenylazo)phenol (*A*)

This compound was prepared by a diazonium salt coupling reaction. To 100 ml of 10% aqueous sodium hydroxide containing 0.4 mol of phenol, cooled in an ice bath, an equal molar amount of 4-methoxyaniline diazonium salt was added with vigorous stirring over 1 h; this was followed by neutralization with hydrochloric acid to pH 6–7. After stirring the mixture for a further 0.5 h, the precipitate was filtered, washed twice with water and dried in vacuum. The crude product was recrystallized from 95% ethanol, and dried in vacuum for 48 h, to give pure product as brown-red crystals. Yield: 75%, m.p. 138°C. FTIR (KBr,  $\text{cm}^{-1}$ ): 3414 ( $-\text{OH}$ ,  $\nu_s$ ); 2846 ( $-\text{CH}_3$ ,  $\nu_s$ ); 1599, 1496, 1465 (aromatic  $\nu_{\text{C-C}}$ ); 1439 ( $-\text{CH}_3$ ,  $\delta$ ); 1234, 1016 ( $\text{Ar-O-C}$ ,  $\nu$ ); 845 (aromatic  $\nu_{\text{CH}}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), (ppm, from TMS): 3.88 (s, 3H,  $-\text{OCH}_3$ ), 6.97–7.01 (m, 4H,  $\text{Ar-H}$ , *o*-to  $-\text{O}$ ), 7.85–7.88 (m, 4H,  $\text{Ar-H}$ , *o*-to  $-\text{N=N-}$ ).

#### 2.1.2. 1-Bromo-[4-(4-methoxyphenylazo)phenyloxy]propane (*B3*) and other *Bn* compounds

A mixture of 11.4 g of compound *A* (0.05 mol), 101 g of 1,3-dibromopropane (0.5 mol), 50 g of anhydrous potassium carbonate, and 200 ml of dry acetone was heated under reflux for 20 h in a nitrogen atmosphere. After cooling to room temperature, the mixture was filtered to remove salts and concentrated by evaporating the acetone. The crystalline product was precipitated by addition of excess hexane. Yield: 80%, m.p. 97°C. FTIR (KBr,  $\text{cm}^{-1}$ ): 2931, 2873 ( $-\text{CH}_2-$ ,  $\nu_s$ ); 2840 ( $-\text{CH}_3$ ,  $\nu_s$ ); 1598, 1500, 1468 (aromatic  $\nu_{\text{C-C}}$ ); 1441 ( $-\text{CH}_3$ ,  $\delta$ ); 1255, 1024 ( $\text{Ar-O-C}$ ,  $\nu$ ); 1145, 1105 ( $\text{O-CH}_2$ ,  $\nu_s$ ); 847 (aromatic  $\nu_{\text{CH}}$ ); 667 ( $\text{C-Br}$ ,  $\nu_s$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), (ppm, from TMS): 2.27–2.42 (m, 2H,  $-\text{C-CH}_2-\text{C-}$ ), 3.54–3.69 (t, 2H,  $-\text{CH}_2\text{Br}$ ), 3.87 (s, 3H,  $-\text{OCH}_3$ ), 4.10–4.24 (t, 2H,  $-\text{OCH}_2-$ ), 6.98–7.02 (m, 4H,  $\text{Ar-H}$ , *o*-to  $-\text{O}$ ), 7.86–7.90 (m, 4H,  $\text{Ar-H}$ , *o*-to  $-\text{N=N-}$ ).

Compound *B6* was synthesized using the same method with the appropriate dibromoalkane. Yield: 85%, m.p. 103°C. FTIR (KBr,  $\text{cm}^{-1}$ ): 2937, 2861 ( $-\text{CH}_2-$ ,  $\nu_s$ ); 1601, 1579, 1498, 1466 (aromatic  $\nu_{\text{C-C}}$ ); 1447 ( $-\text{CH}_3$ ,  $\delta$ ); 1245, 1030 ( $\text{Ar-O-C}$ ,  $\nu$ ); 1147, 1109 ( $\text{O-CH}_2$ ,  $\nu_s$ ); 843 (aromatic  $\nu_{\text{CH}}$ ); 644 ( $\text{C-Br}$ ,  $\nu_s$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), (ppm, from TMS): 1.55 (broad, 4H,  $-\text{C-C-CH}_2-\text{CH}_2-\text{C-C-}$ ), 1.87 (broad, 4H,  $-\text{C-CH}_2-\text{C-C-CH}_2-\text{C-}$ ), 3.43–3.46 (t, 2H,  $-\text{CH}_2\text{Br}$ ), 3.87 (s, 3H,  $-\text{OCH}_3$ ), 4.06–4.09 (t, 2H,  $-\text{OCH}_2-$ ), 6.98–7.01 (m, 4H,  $\text{Ar-H}$ , *o*-to  $-\text{O}$ ), 7.85–7.89 (m, 4H,  $\text{Ar-H}$ , *o*-to  $-\text{N=N-}$ ).

Compound *B10* was synthesized using the same method. Yield: 85%, m.p. 112°C. FTIR (KBr,  $\text{cm}^{-1}$ ): 2922, 2850 ( $-\text{CH}_2-$ ,  $\nu_s$ ); 1603, 1579, 1498, 1468 (aromatic  $\nu_{\text{C-C}}$ ); 1425 ( $-\text{CH}_3$ ,  $\delta$ ); 1250, 1030 ( $\text{Ar-O-C}$ ,  $\nu$ ); 1147, 1109 ( $\text{O-CH}_2$ ,  $\nu_s$ ); 843 (aromatic  $\nu_{\text{CH}}$ ); 642 ( $\text{C-Br}$ ,  $\nu_s$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), (ppm, from TMS): 1.32 (broad, 8H,  $-\text{C-C-C-(CH}_2)_4-\text{C-C-C-}$ ), 1.46 (broad, 4H,  $\text{O-C-C-CH}_2-$ ,  $-\text{CH}_2-\text{C-C-Br}$ ), 1.84–1.86 (m, 4H,  $\text{O-C-CH}_2-$ ,  $-\text{CH}_2-\text{C-Br}$ ), 3.40–3.43 (t, 2H,  $-\text{CH}_2\text{Br}$ ), 3.89 (s, 3H,  $-\text{OCH}_3$ ), 4.02–4.05 (t, 2H,  $-\text{OCH}_2-$ ), 6.98–7.02 (m, 4H,  $\text{Ar-H}$ , *o*-to  $-\text{O}$ ), 7.86–7.89 (m, 4H,  $\text{Ar-H}$ , *o*-to  $-\text{N=N-}$ ).

#### 2.1.3. *n*-[4-(4-Methoxyphenylazo)phenyloxy]propoxy-4-methoxybenzene (*C3*) and other *Cn* compounds

A mixture of 17.4 g of compound *B3* (0.05 mol), 6.4 g of *p*-hydroxyanisole (0.052 mol), 50 g of anhydrous potassium carbonate, and 200 ml of dry acetone was heated under reflux for 20 h. After cooling to room temperature, the mixture was poured into excess ice water, and the precipitate solid then recrystallized from methanol. Yield: 75%, m.p. 132°C. FTIR (KBr,  $\text{cm}^{-1}$ ): 2935, 2879 ( $-\text{CH}_2-$ ,  $\nu_s$ ); 2837 ( $-\text{CH}_3$ ,  $\nu_s$ ); 1600, 1509, 1468 (aromatic  $\nu_{\text{C-C}}$ ); 1249, 1031 ( $\text{Ar-O-C}$ ,  $\nu$ ); 1147, 1109 ( $\text{O-CH}_2$ ,  $\nu_s$ ); 843 (aromatic  $\nu_{\text{CH}}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), (ppm, from TMS): 2.26–2.30 (m, 2H,  $-\text{C-CH}_2-\text{C-}$ ), 3.79 (s, 3H,  $-\text{O-Ar-OCH}_3$ ), 3.88 (s, 3H,  $=\text{N-Ar-OCH}_3$ ), 4.11–4.14 (t, 2H,  $-\text{O-Ar-OCH}_2-$ ), 4.22–4.25 (t, 2H,  $-\text{CH}_2\text{O-Ar-N=}$ ), 6.83–6.86 (m, 4H,  $-\text{O-ArH-O-}$ ), 6.99–7.02 (m, 4H,  $-\text{O-ArH-N=}$ , *o*-to  $-\text{O}$ ), 7.85–7.89 (m, 4H,  $-\text{O-ArH-N=}$ , *o*-to  $-\text{N=N-}$ ).

Compound *C6* was prepared in the same way from *B6*. Yield: 80%, m.p. 170°C. FTIR (KBr,  $\text{cm}^{-1}$ ): 2940, 2870 ( $-\text{CH}_2-$ ,  $\nu_s$ ); 2837 ( $-\text{CH}_3$ ,  $\nu_s$ ), 1602, 1510, 1473 (aromatic  $\nu_{\text{C-C}}$ ); 1442 ( $-\text{CH}_3$ ,  $\delta$ ); 1240, 1031 ( $\text{Ar-O-C}$ ,  $\nu$ ); 1151, 1111 ( $\text{O-CH}_2$ ,  $\nu_s$ ); 845 (aromatic  $\nu_{\text{CH}}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ), (ppm, from TMS): 1.56 (broad, 4H,  $-\text{C-C-CH}_2-\text{CH}_2-\text{C-C-}$ ), 1.83 (broad, 4H,  $-\text{C-CH}_2-\text{C-C-CH}_2-\text{C-}$ ), 3.77 (s, 3H,  $-\text{O-Ar-OCH}_3$ ), 3.89 (s, 3H,  $=\text{N-Ar-OCH}_3$ ), 3.91–3.95 (t, 2H,  $-\text{O-Ar-OCH}_2-$ ), 4.03–4.06 (t, 2H,  $-\text{CH}_2\text{O-Ar-N=}$ ),

6.83–6.84 (m, 4H, –O–ArH–O–), 6.98–7.01 (m, 4H, –O–ArH–N=, *o*-to –O–), 7.85–7.89 (m, 4H, –O–ArH–N=, *o*-to –N=N–).

Compound C10 was synthesized from B10 using the same method. Yield: 85%, m.p. 156°C. FTIR (KBr, cm<sup>-1</sup>): 2931, 2856 (–CH<sub>2</sub>–, ν<sub>s</sub>); 1602, 1581, 1508, 1471 (aromatic ν<sub>C–C</sub>); 1442 (–CH<sub>3</sub>, δ); 1246, 1027 (Ar–O–C, ν); 1151, 1111 (O–CH<sub>2</sub>, ν<sub>s</sub>); 843 (aromatic ν<sub>CH</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), (ppm, from TMS): 1.34 (broad, 8H, –C–C–C–(CH<sub>2</sub>)<sub>4</sub>–C–C–C–), 1.46 (broad, 4H, O–C–C–CH<sub>2</sub>–), 1.76–1.82 (m, 4H, O–C–CH<sub>2</sub>–), 3.76 (s, 3H, –O–Ar–OCH<sub>3</sub>), 3.89 (s, 3H, =N–Ar–OCH<sub>3</sub>), 3.90–3.94 (t, 2H, O–Ar–OCH<sub>2</sub>–), 4.01–4.05 (t, 2H, –CH<sub>2</sub>O–Ar–N=), 6.83 (s, 4H, –O–ArH–O–), 6.98–7.01 (m, 4H, –O–ArH–N=, *o*-to –O–), 7.85–7.88 (m, 4H, –O–ArH–N=, *o*-to –N=N–).

#### 2.1.4. *n*-[4-(4-Methoxyphenylazo)phenyloxy]propoxy - [4-methoxy-2,5-bis(chloromethyl)]benzene (D<sub>3</sub>) and other D<sub>n</sub> compounds

A mixture of 3.92 g of compound C3 (0.01 mol), 10 ml of concentrated aqueous HCl and 10 ml of 36% aqueous formaldehyde was dissolved in 1,4-dioxan. This mixture was stirred and heated under reflux at 65°C for 5 h with the continuous addition of dry HCl gas. Upon cooling, the crude product was isolated, neutralized from cold aqueous NaOH, and then recrystallized from methanol. Yield: 85%, m.p. 151°C. FTIR (KBr, cm<sup>-1</sup>): 2939, 2879 (–CH<sub>2</sub>–, ν<sub>s</sub>); 2839 (–CH<sub>3</sub>, ν<sub>s</sub>); 1597, 1500, 1468 (aromatic ν<sub>C–C</sub>); 1414 (–CH<sub>3</sub>, δ), 1255, 1035 (Ar–O–C, ν); 1147, 1107 (O–CH<sub>2</sub>, ν<sub>s</sub>); 873 (aromatic ν<sub>CH</sub>, *o*-to –CH<sub>2</sub>Cl); 696 (ν<sub>C–Cl</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), (ppm, from TMS): 2.33–2.35 (m, 2H, –C–CH<sub>2</sub>–C–), 3.85 (s, 3H, –O–Ar–OCH<sub>3</sub>), 3.89 (s, 3H, =N–Ar–OCH<sub>3</sub>), 4.22–4.24 (t, 2H, –O–Ar–OCH<sub>2</sub>–), 4.27–4.29 (t, 2H, –CH<sub>2</sub>O–Ar–N=), 4.62–4.63 (d, 4H, –CH<sub>2</sub>Cl), 6.91 (s, H, Ar–H, *o*-to –OCH<sub>2</sub>– and –CH<sub>2</sub>Cl), 6.97 (s, H, Ar–H, *o*-to –OCH<sub>3</sub> and –CH<sub>2</sub>Cl), 6.99–7.03 (m, 4H, –O–ArH–N=, *o*-to –O–), 7.86–7.89 (m, 4H, –O–ArH–N=, *o*-to –N=N–).

Compound D<sub>6</sub> was prepared from C6 using the same method. Yield: 85%, m.p. 113°C. FTIR (KBr, cm<sup>-1</sup>): 2937, 2870 (–CH<sub>2</sub>–, ν<sub>s</sub>); 2839 (–CH<sub>3</sub>, ν<sub>s</sub>), 1601, 1500, 1467 (aromatic ν<sub>C–C</sub>); 1414 (–CH<sub>3</sub>, δ); 1248, 1024 (Ar–O–C, ν); 1146, 1105 (O–CH<sub>2</sub>, ν<sub>s</sub>); 874 (aromatic ν<sub>CH</sub>, *o*-to –CH<sub>2</sub>Cl); 688 (ν<sub>C–Cl</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), (ppm, from TMS): 1.58 (broad, 4H, –C–C–CH<sub>2</sub>–CH<sub>2</sub>–C–C–), 1.86 (broad, 4H, –C–CH<sub>2</sub>–C–C–CH<sub>2</sub>–C–), 3.85 (s, 3H, –O–Ar–OCH<sub>3</sub>), 3.89 (s, 3H, =N–Ar–OCH<sub>3</sub>), 4.01–4.03 (t, 2H, –O–Ar–OCH<sub>2</sub>–), 4.04–4.06 (t, 2H, –CH<sub>2</sub>O–Ar–N=), 4.63–4.64 (d, 4H, –CH<sub>2</sub>Cl), 6.91–6.92 (d, 2H, O–ArH–O), 6.99–7.02 (m, 4H, –O–ArH–N=, *o*-to –O–), 7.85–7.88 (m, 4H, –O–ArH–N=, *o*-to –N=N–).

Compound D10 was synthesized from C10 using the same method. Yield: 85%, m.p. 123°C. FTIR (KBr, cm<sup>-1</sup>): 2931, 2854 (–CH<sub>2</sub>–, ν<sub>s</sub>); 1601, 1581, 1508, 1466 (aromatic ν<sub>C–C</sub>); 1415 (–CH<sub>3</sub>, δ); 1250, 1026 (Ar–O–C, ν); 1146, 1105 (O–CH<sub>2</sub>, ν<sub>s</sub>); 690 (C–Cl, ν). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), (ppm, from TMS): 1.35 (broad, 8H, –C–C–C–(CH<sub>2</sub>)<sub>4</sub>–C–C–C–), 1.49 (broad, 4H, O–C–C–CH<sub>2</sub>–), 1.78–1.82 (m, 4H, O–C–CH<sub>2</sub>–), 3.85 (s, 3H, –O–Ar–OCH<sub>3</sub>), 3.89 (s, 3H, =N–Ar–OCH<sub>3</sub>), 3.97–4.00 (t, 2H, O–Ar–OCH<sub>2</sub>–), 4.02–4.05 (t, 2H, –CH<sub>2</sub>O–Ar–N=), 4.62–4.64 (d, 4H, –CH<sub>2</sub>Cl), 6.91–6.92 (d, 2H, –O–ArH–O–), 6.98–7.01 (m, 4H, –O–ArH–N=, *o*-to –O–), 7.85–7.88 (m, 4H, –O–ArH–N=, *o*-to –N=N–).

### 2.2. Characterization

The <sup>1</sup>H NMR spectra of monomers were recorded with a Varian Unity 400 spectrometer (400 MHz), using deuteriated chloroform (CDCl<sub>3</sub>) as solvent and tetramethylsilane (TMS) as an internal chemical shift reference. FTIR spectra were recorded with a BIO-RAD FTS-7 spectrometer; the samples for study were pressed tablets with KBr. The thermotropic properties of the monomers were characterized with a Perkin Elmer DSC-7 instrument. The rate of heating and cooling was 10°C min<sup>-1</sup>, the weight of sample was 10 mg, and indium and zinc were used for calibration. The peak maximum was taken as the phase transition temperature. Optical textures were observed by a Leitz–Wetzlar polarizing optical microscope (POM) equipped with a hot stage and an Option R Pol camera. Samples were cast on the glass slide from a 1% solution of chloroform to form a thin film. UV-vis and fluorescence spectra were measured with a Shimadzu UV-3100 UV-vis spectrophotometer and a Shimadzu RF-5301 PC spectrophotometer, respectively.

## 3. Results and discussion

### 3.1. Synthesis

The synthetic strategy consists of four steps to obtain the desired bis-chloromethyl-type monomers containing *para*-methoxyazobenzene (see the scheme). All the steps are non-critical and have been described in the experimental section. The novel monomers B<sub>n</sub> C<sub>n</sub>, and D<sub>n</sub> (*n* = 3, 6, 10) were obtained in high yield and purity. Structures of the monomers were proved by FTIR and <sup>1</sup>H NMR. The D<sub>n</sub> obtained monomers can be simply polymerized in the presence of a base to form poly(*p*-phenylenevinylenes) used as light emitting materials [22, 23].

### 3.2. Liquid crystalline properties

Figure 1 shows the heating and cooling cycle DSC curves of the B<sub>n</sub> compounds. It can be seen that none of them show liquid crystallinity on heating. Upon cooling,

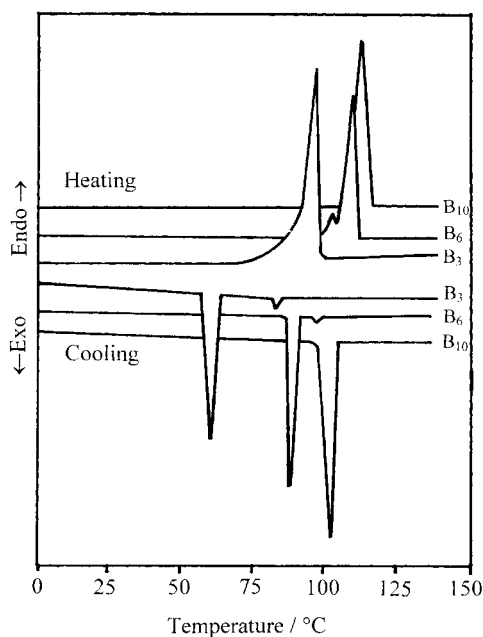


Figure 1. DSC curves of the monomers  $B_n$ .

B3 showed two peaks at 84 and 60°C, corresponding to isotropic–liquid crystalline and liquid crystalline–crystalline transitions, respectively. The phase transitions of B6 on cooling were found at 96 and 87°C. The corresponding enthalpies of the isotropic–liquid crystalline transition of B3 and B6 are both 3% that of liquid crystalline–crystalline transition. The isotropic–liquid crystalline transition enthalpies of B3 and B6 are 0.587 and 1.394 kJ mol<sup>-1</sup>, respectively. According to the literature [24], the isotropic–smectic transition enthalpies always exceed 2.93 kJ mol<sup>-1</sup> and the isotropic–nematic transition enthalpies possess the values of 0.084–9.63 kJ mol. So the liquid crystalline phase of B3 and B6 should be the nematic liquid crystalline phase. In B10, no liquid crystalline–crystalline phase transition was detected upon cooling because of its high crystalline temperature.

The polarized optical micrographs of B3 and B6 observed in their liquid crystalline phase upon cooling are shown in figures 2(a) and 2(b). It is clear that the B3 and B6 LC phase exhibits a schlieren texture with two or four black bands per meeting point, which is a typical nematic texture. Combining the results of DSC and POM analyses, it can be concluded that both B3 and B6 exhibit monotropically nematic liquid crystalline behaviour.

Figure 3 shows the heating and cooling DSC curves of C3, C6 and C10. Clearly, there is only one endothermic peak for them on heating, indicating that none is liquid crystalline on heating. On cooling, C3 and C10 both show only one exothermic peak, while for C6 there are two exothermic peaks at 138 and 115°C, which

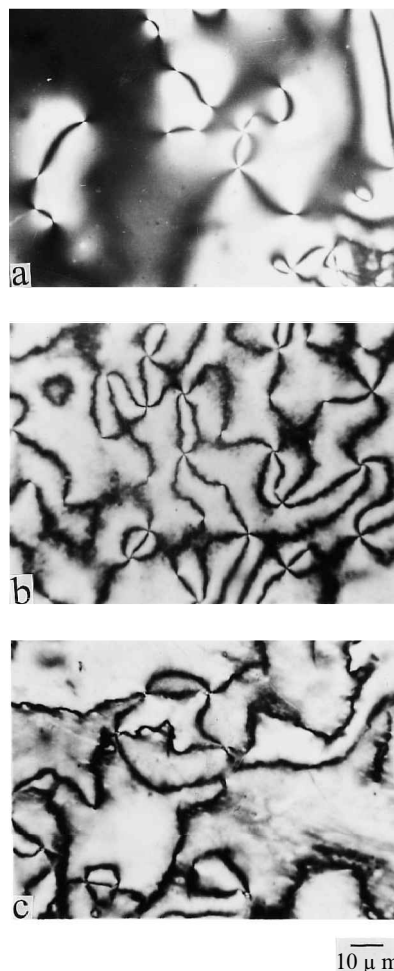


Figure 2. POM photographs of monomers B3, B6 and C6 in their liquid crystalline phases. (a) B3 at 71°C↓; (b) B6 at 85°C↓; (c) C6 at 122°C↓.

correspond to the isotropic–liquid crystalline and the liquid crystalline–crystalline transitions, respectively. The corresponding enthalpy of the isotropic–crystalline transition of C6 is 9% that of liquid crystalline–crystalline transition. The isotropic–liquid crystalline transition enthalpy is 5.19 kJ mol<sup>-1</sup>, which could be the value of the isotropic–nematic or isotropic–smectic transition enthalpy. From the POM observation it can be easily concluded that C6 enters the nematic liquid crystalline phase upon cooling from the isotropic phase, figure 2(c).

No liquid crystalline behaviour of  $D_n$  ( $n = 3, 6, 10$ ) was found by DSC or POM.

### 3.3. Absorption and fluorescence spectra

The photochemical properties of all the compounds  $B_n$ ,  $C_n$  and  $D_n$  were evaluated in chloroform solutions. The compounds all exhibit their absorption maximum at about 359 nm and weak shoulders at about 440 nm which

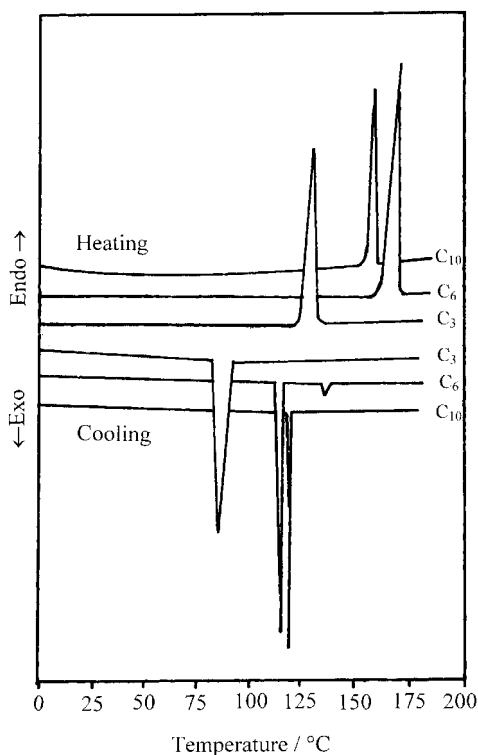


Figure 3. DSC curves of the monomers *C<sub>n</sub>*.

are related to  $\pi$ - $\pi^*$  and  $n$ - $\pi^*$  of the azobenzene *trans*-configuration, respectively (figures 4–6). It was reported that 3-{2-[4-(4-ethoxyphenylazo)phenoxy]ethoxy}-4-methylthiophene and poly{2-[6-[4-(4-cyanophenyl)azo]phenoxy]hexyl}-1,3-propylenetetracarboxate exhibited the  $\pi$ - $\pi^*$  transitions of the azobenzene *trans*-configuration, both at about 365 nm [25, 26]. Comparing the *B<sub>n</sub>*

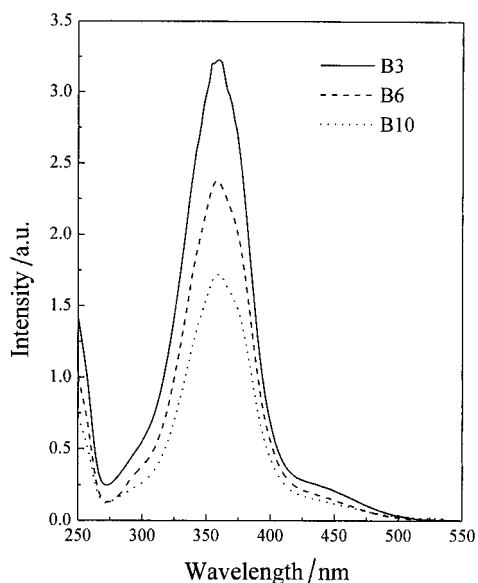


Figure 4. UV-vis spectra of *B<sub>n</sub>* compounds.

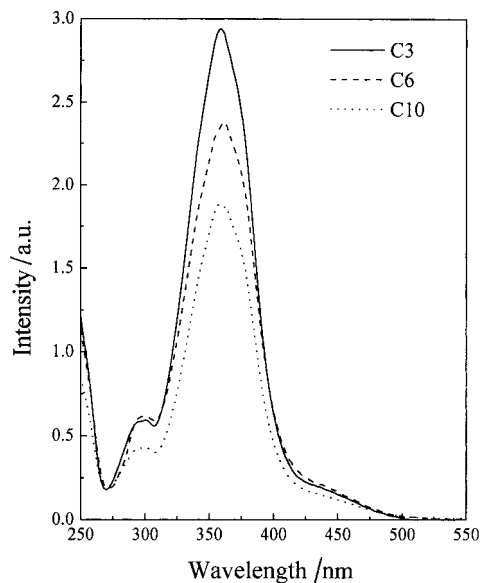


Figure 5. UV-vis spectra of *C<sub>n</sub>* compounds.

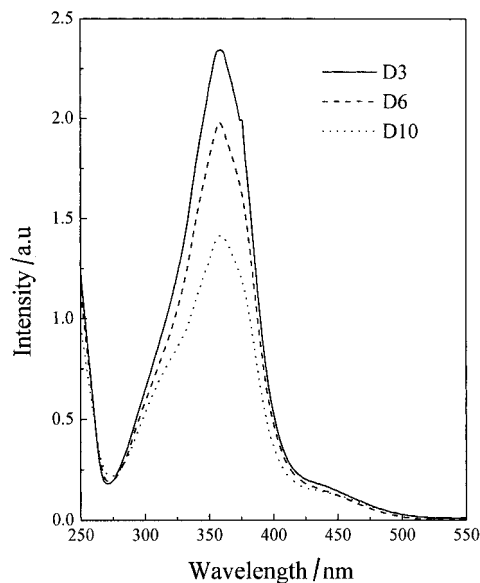
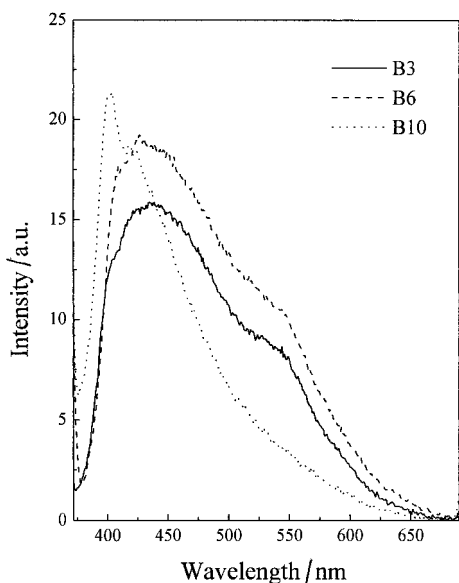
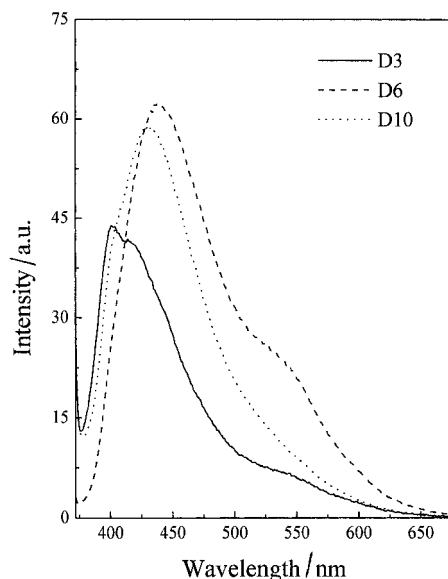
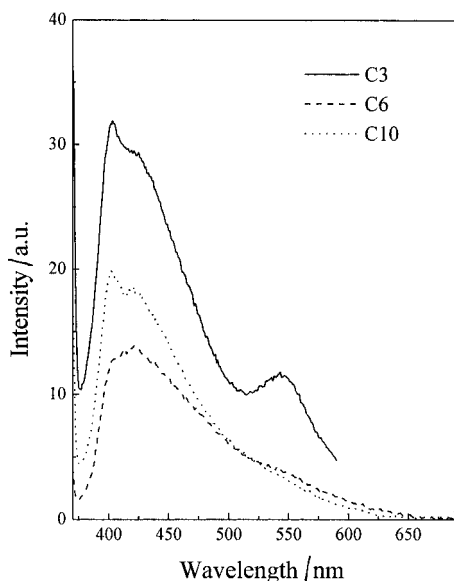


Figure 6. UV-vis spectra of *D<sub>n</sub>* compounds.

and *C<sub>n</sub>* spectra from figures 5 and 6, it can be seen that *C<sub>n</sub>* show extra absorption bands centred at 297 nm, which are related to  $\pi$ - $\pi^*$  transitions of the phenyl units substituted with alkyloxy groups. However, the absorption bands of *D<sub>n</sub>* centred at 297 nm are not as clear as those of *C<sub>n</sub>*, an effect which could be caused by the chloromethylation of *C<sub>n</sub>*.

Most studies on azobenzene are focused on its photochemical reaction, while its fluorescence properties have been paid little attention. The compounds *B<sub>n</sub>*, *C<sub>n</sub>* and *D<sub>n</sub>* can all fluoresce either in chloroform or the solid state. Figures 7–9 present the spectra of the compounds in chloroform, excited at 355 nm. The spectra of B3 and

Figure 7. Fluorescence spectra of *Bn* compounds.Figure 9. Fluorescence spectra of *Dn* compounds.Figure 8. Fluorescence spectra of *Cn* compounds.

B6 show maxima at 437 and 430 nm with shoulders around 540 nm. The spectrum of B10 shows a maximum at 401 nm. The spectra of C3, C6 and C10 exhibit their maximum peaks all around 405 nm, and that of C3 has a shoulder around 543 nm. The spectra of D3, D6 and D10 exhibit their maxima at 402, 431 and 438 nm, respectively, and that of D6 shows a shoulder around 540 nm. Although all the *Bn*, *Cn* and *Dn* compounds can fluoresce, their relative fluorescence quantum yields are less than 0.1% in chloroform as determined employing quinine sulfate in 0.1 M H<sub>2</sub>SO<sub>4</sub> as a standard. The low quantum yields of the compounds may be caused by their photochemical reactivity.

#### 4. Conclusion

Three novel series of monomers *Bn*, *Cn* and *Dn* ( $n = 3, 6, 10$ ) containing *para*-methoxyazobenzene have been synthesized and characterized by FTIR, NMR, DSC, POM and UV-vis and fluorescence spectroscopy. It has been shown that the monomers B3, B6 and C6 exhibit monotropic nematic liquid crystalline phases with schlieren textures. All the compounds *Bn*, *Cn* and *Dn* show absorption maxima at 359 nm, related to  $\pi$ - $\pi^*$  transitions of the azobenzene *trans*-configuration. The fluorescence spectra of the compounds in chloroform exhibit maximum peaks at 400–440 nm. The monomers *Dn* could be polymerized to poly(1,4-phenylenevinylene) derivatives via a dehydrochlorination route. The conjugated polymers synthesized from *Dn* could emit polarized light by controlling the state of their azobenzene side chains, as will be discussed in a later publication.

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