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Online publication date: 06 August 2010

To cite this Article Qiu, Hongjin , Li, Min , Chen, Xinfang , Jing, Fengying and Zhou, Enle(1998) 'Synthesis and properties of two series of H-bonded and non-H-bonded thermotropic liquid crystal monomers', Liquid Crystals, 25: 3, 419 — 425

To link to this Article: DOI: 10.1080/026782998206236

URL: http://dx.doi.org/10.1080/026782998206236

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LIQUID CRYSTALS, 1998, VOL. 25, NO. 3, 419–425

Synthesis and properties of two series of H-bonded and non-H-bonded thermotropic liquid crystal monomers

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(*Received 25 February 1998; accepted 9 March 1998*)

Two series of monomers, namely *n*-1-bromo-[4-(4-nitrophenylazo)phenyloxy]alkanes (B*n*, $n = 2, 3, 4, 5, 6, 8, 10$) and *N*-*n*-[4-(4-nitrophenylazo)phenyloxy]alkyl diethanolamines (C*n*, $n = 3, 5, 6, 10$), were synthesized and characterized. Their thermal behaviour was studied by differential scanning calorimetry (DSC), wide angle X-ray diffractometry (WAXD) and polarizing optical microscopy (POM) equipped with a hot stage. The results showed that the B*n*s ($n \geqslant 6$) exhibit monotropic nematic liquid crystalline behaviour; no liquid crystalline phase was found for the B*n*s ($n < 6$), while for the C*n*s, enantiotropic smectic liquid crystallinity for $n = 5, 6, 10$ was seen, and for $n = 3$ monotropic smectic phases were found. This different phase behaviour between B*n* and C*n* compounds is attributed to their different end groups. The FTIR analysis of C*n* indicated that there exists an intermolecular hydrogen bond between hydroxy groups, so that more stable liquid crystalline phase are formed. The effect of the length of the flexible chain on the thermal behaviour is also discussed.

1. Introduction

The study of liquid crystalline materials is of interest due to their potentially wide range of applications, such as in optical [1], electrical [2], and biological medical fields [3]. Many review articles [4, 5] have dealt with the structure–property relationships of liquid crystalline compounds in depth. It is known that liquid crystallinity can be affected by molecular shape and conformation, as well as intermolecular interaction, etc. and it is widely accepted that the introduction of a flexible chain into liquid crystalline molecules can decrease their melting points and thus enhance the stability of the liquid crystalline phases.

Liquid crystalline polymers containing *para*-nitroazobenzene as mesogenic groups are promising for applications in nonlinear optics [6], ferroelectric [7] and opto-electronic [8] materials, and reversible data storage materials areas [9–11]. The synthesis and characterization of side chain liquid crystalline polymers containing *para*-nitroazobenzene have been reported by Li [12–14]. In order to enhance the stability of this kind of polymer, a new synthetic method is proposed by us, and in this article the synthesis and characterization of the monomers are given.

The unique thermotropic behaviour of monomers *N*-*n*-[4-(4-nitrophenylazo)phenyloxy]alkyl diethanolamine (C*n*, $n = 3, 5, 6, 10$) is discussed and the possible molecular arrangement of C*n* compounds in their LC phase given, based on the results of WAXD and the existence of an intermolecular hydrogen-bond which has been confirmed by FTIR analysis.

2. Experimental

2.1. *Synthesis of Bn and Cn compounds*

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

2.1.1. *4-(4-Nitrophenylazo)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-nitroaniline 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 68·5 g pure product as brown red crystals. Yield: 70%, m.p. 219–220°C. IR (KBr, cm^{-1}): 3439 (–OH, ν_s);

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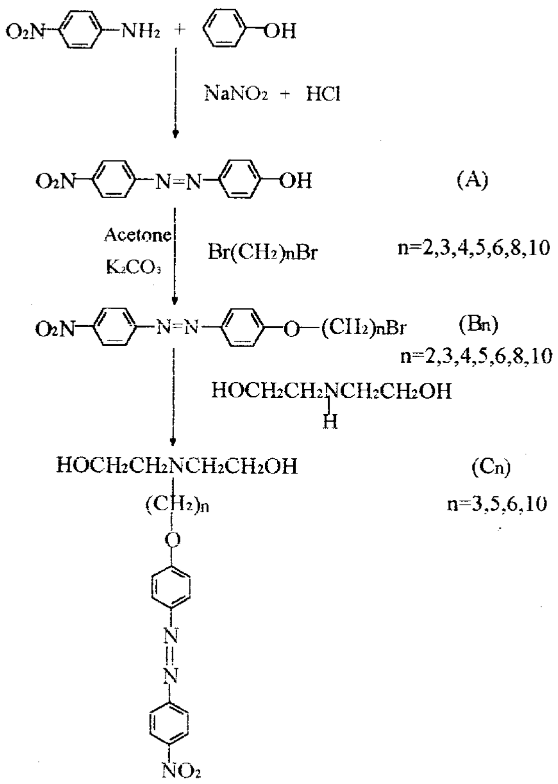
*Author for correspondence.



Scheme. Synthetic route for monomers C*n* and B*n*.

1583, 1500, 1459 (aromatic $\nu_{C\text{–}C}$); 1507 (–NO_2, ν_{as}); 1340 (–NO_2, ν_s); 853 ($\nu_{C\text{–}N}$ and $\delta_{C\text{–}N}$). ^{1}H NMR (400 MHz, $CDCl_3$), (ppm, from TMS): 5·35 (s, H, –OH), 7·01–7·04 (d, 2H, Ar–H, *o*-to –O–), 7·95–7·99 (t, 4H, Ar–H, *o*-to –N=N–), 8·35–8·38 (d, 2H, Ar–H, *o*-to –NO_2).

2.1.2. *1-Bromo-[4-(4-nitrophenylazo)phenyloxy]hexane (B6)*

A mixture of 12·16 g of 4-(4-nitrophenylazo)phenol (0·05 mol), 114·98 g of 1,6-dibromohexane (0·5 mol), 50 g of anhydrous potassium carbonate, and 200 ml of dry acetone was heated under reflux for 24 h in a nitrogen atmosphere. After cooling to room temperature, the mixture was filtered to remove salts and concentrated by evaporating the acetone. A crystalline product was obtained by adding a large amount of hexane. Yield: 78·8%, m.p. 90°C. IR (KBr, cm^{-1}): 2946, 2869 (–CH_2–, ν_s); 1602, 1580, 1500, 1471 (aromatic $\nu_{C\text{–}C}$); 1518 (–NO_2, ν_{as}); 1343 (–NO_2, ν_s); 1252 (Ar–O, ν_s); 1142, 1105 (O–CH_2, ν_s); 856 ($\nu_{C\text{–}N}$ and $\delta_{C\text{–}N}$); 686 (C–Br, ν_s); 540. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm, from TMS): 1·53–1·56 (m, 4H, –C–C–CH_2–CH_2–C–C–), 1·85–1·88 (m, 2H, –CH_2–C–Br), 1·87–1·95 (m, 2H, Ar–O–C–CH_2–), 3·43–3·46 (t, 2H, –CH_2–Br), 4·06–4·09 (t, 2H, Ar–O–CH_2–), 7·02–7·04 (d, 2H, Ar–H, *o*-to –O–), 7·95–7·99 (m, 4H, Ar–H, *o*-to –N=N–), 8·35–8·37 (d, 2H, Ar–H, *o*-to –NO_2).

Using the same method, other B*n* compounds were synthesized and their compositions confirmed. Melting points are given in table 1.

2.1.3. *N[4-(4-nitrophenylazo)phenyloxy]hexyl diethanolamine (C6)*

1-Bromo-[4-(4-nitrophenylazo)phenyloxy]hexane (20 mmol) and diethanolamine (100 mmol) were dissolved in 200 ml of ethanol, and the solution heated under reflux for 10 h. When the reaction was complete, the mixture was concentrated by evaporation and the residue dissolved in chloroform. The chloroform layer was separated from excess diethanolamine, dried and concentrated to give a crude product; this was crystallized from acetonitrile, then dissolved in a mixture of methanol and ethanol (volume ratio 1 : 1). This solution was filtered and the solvent evaporated; the product was recrystallized from acetonitrile. Yield: 74·9%, m.p. 61°C. IR (KBr, cm^{-1}): 3363 (bd, ν_{OH}); 2931, 2855 (–CH_2–, ν_s); 1593, 1458 (aromatic, $\nu_{C\text{–}C}$); 1514 (–NO_2, ν_{as}); 1335 (NO_2, ν_s); 1251; 1135, 1101; 1037, 988; 851 ($\nu_{C\text{–}N}$); 749, 722 (–CH_2–, $\nu_{C\text{–}C}$); 682, 583, 540. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm, from TMS): 1·39–1·41 (m, 4H, –C–C–CH_2–CH_2–C–C–), 1·51–1·54 (m, 2H, –CH_2–C–N$\langle$), 1·82–1·86 (m, 2H, –CH_2–C–O–), 2·54–2·58 (m, 2H, Ar–O–R–CH_2–N$\langle$), 2·66–2·69 (m, 4H, –O–C–CH_2–N–CH_2–C–O), 3·62–3·65 (m, 4H, >N–C–CH_2–O–), 4·05–4·08 (t, 2H, Ar–O–CH_2–), 7·02–7·04 (d, 2H, Ar–H, *o*-to –O–), 7·95–7·99 (m, 4H, Ar–H, *o*-to –N=N–), 8·35–8·38 (d, 2H, Ar–H, *o*-to –NO_2).

Monomers C*n* ($n = 3, 5, 10$) were also successfully synthesized and characterized by IR and ^{1}H NMR. The melting points of C*n* compounds are given in table 1.

2.2. *Characterization*

The ^{1}H NMR spectra of monomers were recorded with a Varian Unity 400 spectrometer (400 MHz), using deuteriated chloroform ($CDCl_3$) 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 general study were pressed tablets with KBr. The sample for hydrogen bond study

Table 1. Melting points (°C) of B*n* and C*n* compounds.

	n						
Monomer	2	3	4	5	6	8	10
B*n*	159	134	104	122	90	78	81
C*n*	—	126	—	89	67	—	70

was cast on a KBr window from a solution of the monomers in chloroform to form thin films, and then covered with another KBr window. This sandwiched sample cell was held on a hot stage, temperature-controlled within 1°C.

The thermotropic properties of the monomers were characterized with a Perkin Elmer DSC-7 instrument. The rate of heating and cooling was $10^{\circ}\mathrm{C\,min^{-1}}$, the weight of the sample was 10 mg, and indium and zinc were used for calibration. The peak maximum were taken as the phase transition temperature.

Optical textures were observed by a Leitz-Wetzlar polarized optical microscope equipped with a hot stage and an Opton R Pol camera. Samples were cast on the glass slide from a 1% solution of chloroform to form a thin film.

Wide angle X-ray diffraction (WAXD) measurements were conducted vs temperature with a Philips X-ray generator (PW 1700), and a flat plate camera using nickel-filtered Cu-K$_{\alpha}$ radiation.

3. Results and discussion

The DSC curves of B*n* compounds in the course of heating and cooling are given in figure 1. It can be seen that there is only one melting peak for all B*n*s studied on heating cycle indicating that none showed liquid crystallinity on heating. On a cooling cycle, only B8 and B10 showed two peaks, corresponding to isotropic–liquid crystalline and liquid crystalline–crystalline transitions. The corresponding enthalpies of the isotropic–liquid crystalline transitions of B8 and B10 are only 1% those of liquid crystalline–crystalline transitions (see figure 1).

Figure 2 shows polarized optical microscopy (POM) photographs of B*n* compounds ($n=6, 8, 10$) observed in their LC phases in the course of cooling. It is obvious that all three compounds exhibited a thread texture in their LC phase which is the typical texture of the nematic liquid crystalline phase. Due to the narrow liquid crystalline temperature range of B6 (only 1°C), no liquid crystalline–crystalline (Cr) phase transition was detected, but B6 did exhibit monotropic liquid crystalline behaviour when observed by POM.

From the above analysis it can be concluded that B*n* compounds exhibit monotropically nematic liquid crystalline behaviour when *n* is larger than five, but when *n* is smaller than six, no liquid crystalline phases are observed due to the short length of the flexible chain resulting in the crystalline temperature being higher than the isotropic temperature.

In order to eliminate the effect of water on the thermal properties of C*n* compounds, the transition temperature of C*n*s was obtained on the second heating and cooling cycle. Figure 3 shows that the DSC curves of C*n* compounds at the second heating and cooling cycle. It can be seen that all the C*n*s except C3 show two transitional peaks in the course of either heating or cooling. The two peaks were assigned to crystalline–liquid crystalline and liquid crystalline–isotropic transitions on heating, and isotropic–liquid crystalline and liquid crystalline–crystalline transitions on cooling. From DSC results, therefore, it can be concluded that C5, C6 and C10 show enantiotropic liquid crystalline behaviour, and C3 monotropic behaviour.

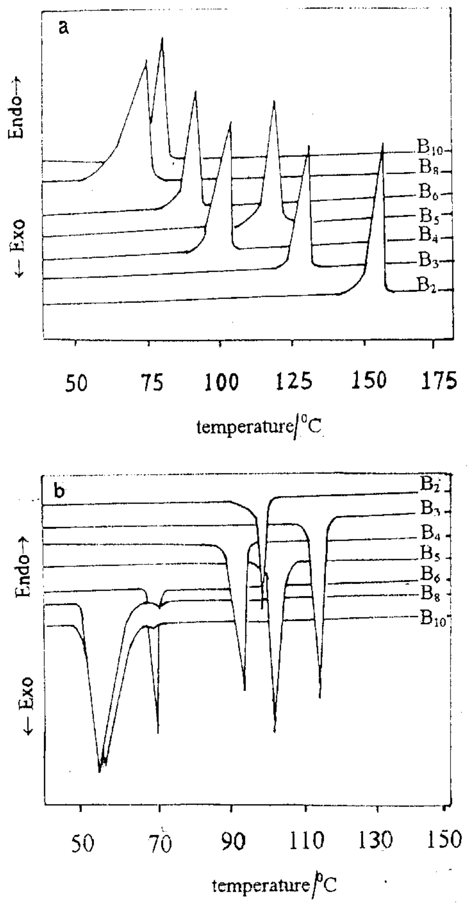
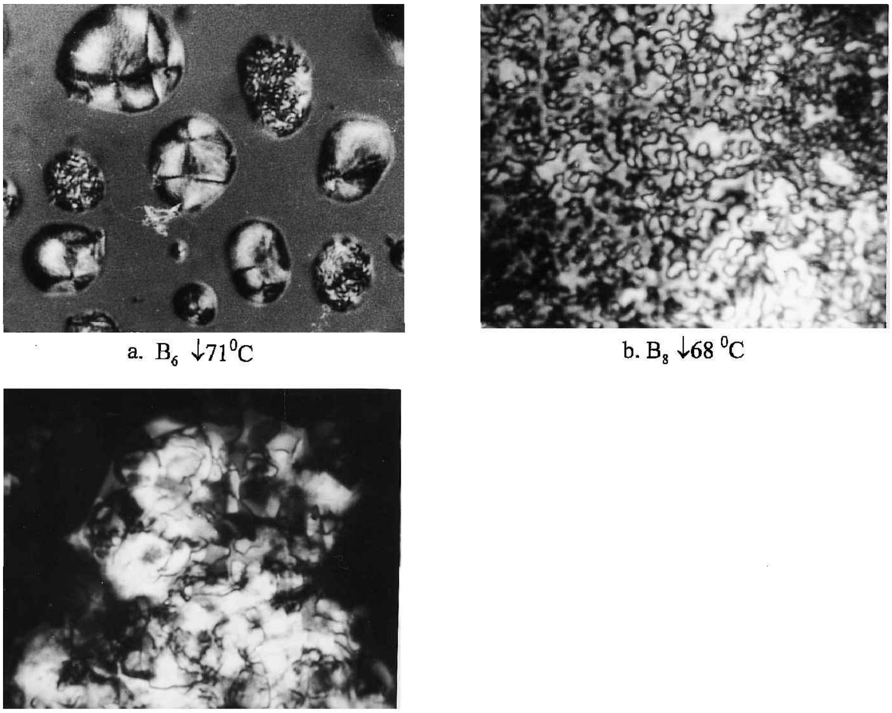


Figure 1. DSC curves of the monomers B*n*: (*a*) first heating; (*b*) first cooling.

Polarized optical microscopy photographs of C*n* compounds in their LC phases are shown in figure 4. It can be seen that all C*n* samples in their LC phases exhibited fan-like textures, regarded as typical smectic phase texture.

Phase transition temperatures and enthalpic changes between isotropic and smectic phases in their heating and cooling cycles are shown in tables 2 and 3. The melting points (T_{CrS}) and isotropic temperature (T_{SI} or T_{IS}) decreased with the increasing of length of flexible chain (*n*), while the temperature range of the smectic C*n* phases was maximized at $n=6$. Therefore, it could be concluded



a. B_6 ↓71 °C

b. B_8 ↓68 °C

c. B_{10} ↓68 °C

Figure 2. POM photographs of the monomers B*n* in their LC phases (×500): (*a*) B6 71°C↓; (*b*) B8 68°C↓; (*c*) B10 68°C↓.

Table 2. Thermal properties of monomer C*n* on second heating.

Monomer	LC phase/°C[a]	Transition temperature/°C[b]		Temperature range of LC phase, ΔT/°C	ΔH_I/kJ mol^{-1} [c]
		T_{CrS}	T_{SI}		
C3	—	126	126	0	0
C5	90–119	89	125	36	4·16
C6	71–115	67/80[d]	119	52	4·41
C10	70–108	70/46[d]	114	44	5·37

[a] POM observations.

[b] Temperature measured by DSC on the second heating (T_{CrS}: melting point; T_{SI}: temperature of smectic to isotropic phase transition).

[c] Change of enthalpy for the smectic to isotropic phase transition.

[d] Double melting peaks.

Table 3. Thermal properties of monomer C*n* on second cooling.

Monomer	LC phase/°C[a]	Transition temperature/°C[b]		Temperature range of LC phase, ΔT/°C	ΔH_I/kJ mol^{-1} [c]
		T_{IS}	T_{SCr}		
C3	97–112	126	119	4	3·09
C5	73–114	124	68	56	5·06
C6	64–113	117	62	55	4·48
C10	59–105	111	59	52	6·06

[a] POM observations.

[b] Temperatures measured by DSC on the second cooling (T_{IS}: temperature of isotropic to smectic phase transition; T_{SCr}: temperature of smectic to crystalline phase transition).

[c] Change of enthalpy for the isotropic to smectic phase transition.

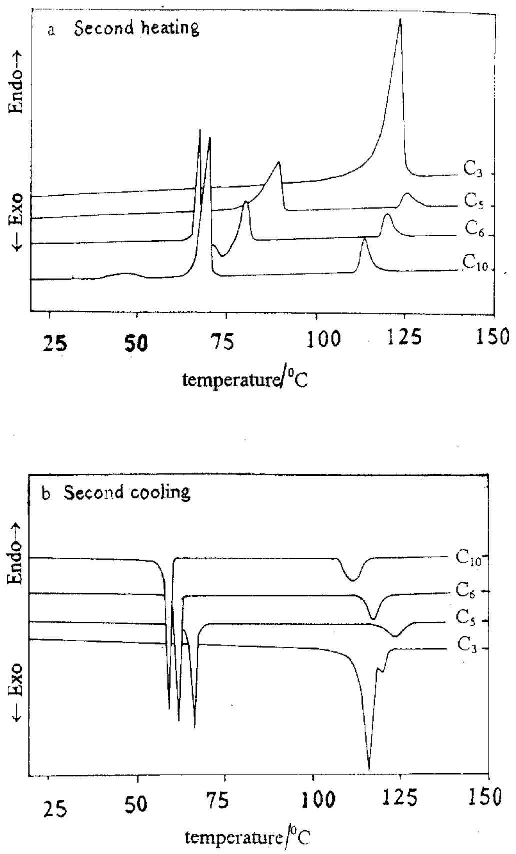


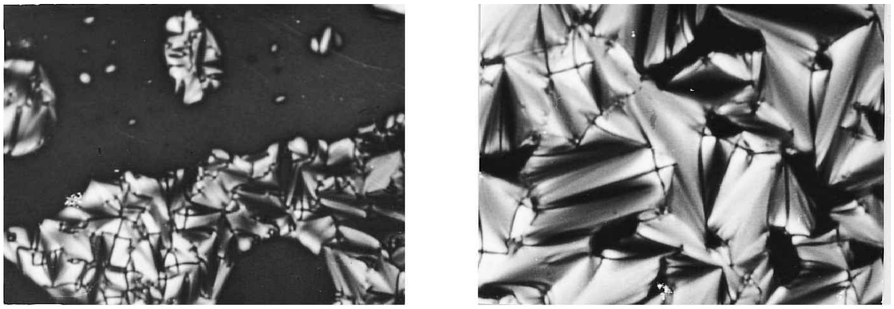
Figure 3. DSC curves of monomers C*n*.

that the mesogenic phase of C6 was more stable than the others. This might be due to the competing effects of the flexible chain on the LC phase range. On the one hand, T_{CrS} decreased with the increase of *n*, so the temperature range of the LC phase should be widened by the increase of *n*; on the other hand, the density of the polar group decreased with the increase of *n*, thus decreasing the interaction of polar groups, which stabilizes the smectic LC phase, and resulting in the narrow temperature range of the LC phase.

WAXD of monomer C10 in its LC phase indicated that the first order diffraction peak ($2\theta = 1{\cdot}99$) corresponds to a *d* spacing of 4·42 nm. The molecular length of monomer C10 was 3·09 nm by calculation (see table 4). In this case, therefore, neighbouring mesogenic groups overlapped each other and the diol parts became associated to form a smectic (S_{Ad}) layer. A schematic illustration of the smectic double layer for the monomer C10 is proposed in figure 5(*a*). For monomer C3 the first order diffraction peak ($2\theta = 3{\cdot}68$) corresponds to a *d* spacing of 2·399 nm, while the molecular length (*l*) is

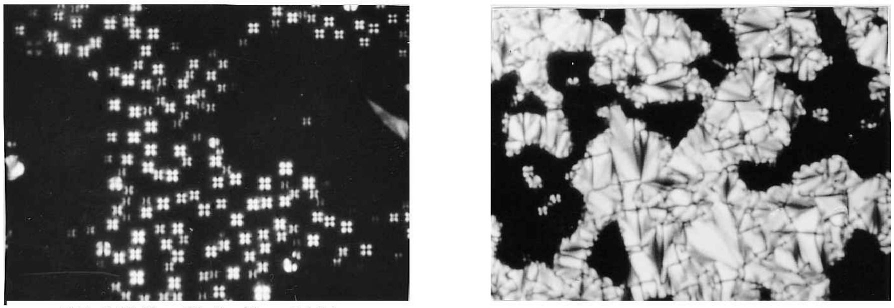
Table 4. WAXD results for C3 and C10 in their LC phase.

Monomer	d_1/nm	l/nm	d/l	S_A phase
C10	4·42	3·090	1·43	S_{Ad}
C3	2·399	2·207	1·07	S_{A1}



a. C$_3$ at 105 °C ↓

b. C$_5$ at 108°C ↓



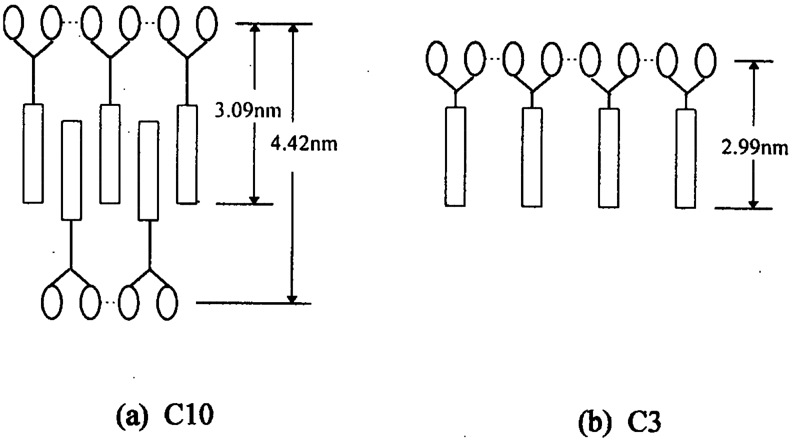
c. C$_{10}$ at 106 °C ↓

d. C$_{10}$ at 104°C ↓

Figure 4. POM photographs of monomers C*n* in their liquid crystalline phases: (*a*) C3 at 105°C↓; (*b*) C5 at 108°C↓; (*c*) C10 at 106°C↓; (*d*) C10 at 104°C↓.

2·207 nm. Therefore, the neighbouring mesogenic groups are parallel to each other and the diol parts associated with each other to form a monolayer smectic ($\mathrm{S_{A1}}$) layer. A schematic illustration of monomer C3 is given in figure 5 (*b*).

The formation of hydrogen bonds between hydroxy groups in monomers C*n*, such as C10 was confirmed by FTIR spectroscopic analysis. There is an absorption peak at 3349 cm^{-1} assigned to associated –OH stretching mode, and an absorption peak at 1519 cm^{-1} assigned to free $-\mathrm{NO_2}$ asymmetric stretching mode (see figure 6). The effect of temperature on hydrogen bonds formed by hydroxy groups was studied from FTIR spectra of monomer C10 at different temperatures. The results are shown in figure 7. With the increase of temperature, the associated –OH absorption band shifts to higher wavenumbers and above the isotropic temperature (T_{I}), a notable absorption band at 3570 cm^{-1} occurs which was assigned to the stretching vibration of free –OH. With the increase of temperature the wave number of the absorption band of associated –OH increased little in the temperature range of the crystalline phase, indicating that the interaction of hydrogen bonds was strong in the crystalline phase. However, there was a remarkable increase in the –OH band wave number with increase of the LC phase temperature, indicating that the interaction of hydrogen bonds decreased with increasing temperature. In the isotropic phase, the interaction of hydrogen bonds was partially destroyed, and there occurred the stretching vibration of free –OH. It is supposed that the formation of hydrogen bonds in C*n* compounds might make molecular arrangement more ordered and stable than that in B*n* compounds, although both have the same mesogenic groups and flexible spacers. More details on hydrogen bonds will be reported separately.



(a) C10

(b) C3

Figure 5. Schematic representation of the molecular arrangement of monomers C*n* at their liquid crystalline phase: (*a*) monomer C10; (*b*) monomer C3. ▭ mesogenic group ○: hydroxy group ···: hydrogen bond.

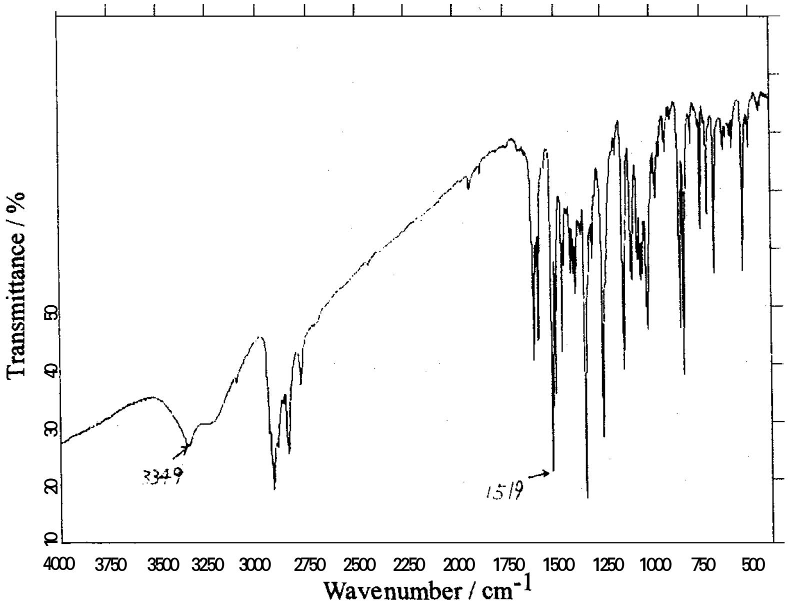


Figure 6. FTIR spectrum of monomer C10 at 30°C.

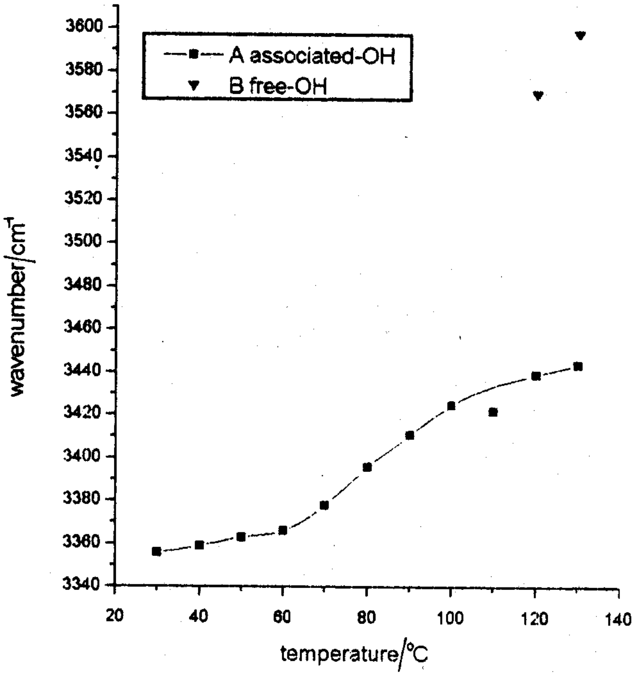


Figure 7. Plot of wave number of the stretching vibration of –OH versus temperature.

4. Conclusion

Two series of monomers C*n* and B*n* have been synthesized and characterized by DSC, POM, WAXD and FTIR. The effect of the length of a flexible chain on the thermal properties of monomers C*n* and B*n* was studied. Results showed that monomer C*n* ($n = 5, 6, 10$) exhibited enantiotropic smectic phases while monomer B*n* ($n = 6, 8, 10$) exhibited monotropic nematic phases. The different phase behaviour of B*n* and C*n* compounds is attributed to the formation of hydrogen bonds in C*n* compounds which makes the C*n* molecular arrangement more stable and more ordered.

The authors are grateful to the National Natural Science Foundation of China for support of this study.

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