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Preparation and properties of highly birefringent liquid crystalline materials: styrene monomers with acetylenes, naphthyl, and isothiocyanate groups

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Preparation and properties of highly birefringent liquid crystalline materials: styrene monomers with acetylenes, naphthyl, and isothiocyanate groups

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Two new series of styrene monomers with different alkyl chain length were successfully synthesised. The chemical structures of synthetic intermediates and monomers were confirmed by Fourier transform infrared spectroscopy, ^{1}H nuclear magnetic resonance spectroscopy, mass spectrometry and elemental analysis. Their thermal stability, transition temperatures and phase sequences were investigated by polarised light microscopy, thermogravimetric analysis, differential scanning calorimetry and one-dimensional wide-angle X-ray diffraction. The birefringent and photoelectric properties, UV–vis and fluorescence spectroscopy were also measured using Abbe refractometer and fluorescent apparatus. The results indicated that all the monomers exhibited a liquid crystalline phase at higher temperature, high birefringence values between 0.4 and 0.7, and good photoluminescence properties. Optical anisotropy of homologous molecules was reduced with the increase of alkyl chain length due to the decrease of molecular polarisation. Moreover, a significant effect of the chemical structure on the photoluminescence properties was also found and discussed according to the length of π-conjugation.

Key words: liquid crystal; birefringent; photoelectric properties; mesogen-jacketed liquid crystalline polymers

1. Introduction

The work reported here is part of an ongoing programme focused on the synthesis and evaluation of mesogen-jacketed liquid crystalline polymers with high optical anisotropy. With the development of information technology, design and synthesis of highly birefringent liquid crystalline materials has become an important issue due to the fact that highly birefringent (Δn) liquid crystals are urgently needed for fast third-order non-linear switching devices [1, 2] and extensively employed in not only conventional display devices such as super-twisted nematic liquid crystal displays (STN-LCDs), but also in scattering type displays such as polymer-dispersed liquid crystals (PDLCs), in light modulators, in compensation for extending viewing angle [3, 4], in cholesteric liquid crystal displays (Ch-LCDs) [5, 6] and so on. Moreover, recent studies on liquid crystals with high birefringence values also focus their applications on organic light emitting diodes (OLEDs) [7] and optical devices [8].

Birefringence (Δn), which is one of the most important properties of liquid crystalline materials, was defined as $\Delta n = n_e$- n_o, proposed by Vuks [9], as a formula defining the relationship between the refractive index n and the mean molecular polarisability α in isotropic systems given by Lorenz-Lorentz expression [10] for anisotropic systems. In 1986, Wu [11] proposed a birefringence equation of liquid crystals according to quantum mechanics; he pointed out that high n values can be achieved by increasing the molecular linear conjugation length:

$$\Delta n = n_e - n_o \tag{1}$$

$$\Delta n = \frac{4\pi\langle n^2\rangle + 2}{3n_e + n_o} N(\alpha_e - \alpha_o) \tag{2}$$

$$n^2 = \frac{(n_e^2 + 2n_o^2)}{3} \tag{3}$$

$$\Delta n(\lambda, T) = gNZS\left(f^*|| - f_\perp^*\right)(\lambda^*)^2 \left[1 + (\lambda^*/\lambda)^2 + (\lambda^*/\lambda)^4 + ...\right] \tag{4}$$

where n_e and n_o are the refractive indices related to the extraordinary and the ordinary ray, respectively, α denotes the anisotropy of the molecular, g is a constant, N is the number of molecules per unit volume, Z represents electron number of σ or π electrons, S is the Saupe orientation order parameter, $f^*//$ and $f^*_\perp$ are vibration intensities of electrons along the axial direction and radial direction of molecules, respectively, λ^* is the transition wavelengths of electronic vibration, and λ is the wavelength of light irradiation.

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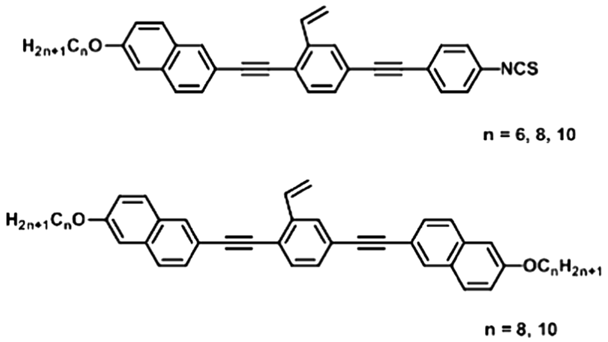
It is well known that structural units must be introduced into the molecules to achieve a high birefringence (Δn) suitable for practical use in a mesogenic material. It is reported that a high Δn value can be realised by increasing the molecular conjugation length and designing the molecular shape [12–25]; representative functional groups that contribute to the molecular conjugation length include unsaturated rings such as phenyl, naphthalene, thiophene or other fused rings, and unsaturated bonds, carbon–carbon double or triple bonds, for example, and high polarisability groups such as cyano or isothiocyanate groups. For the molecules with unsaturated carbon–carbon bonds, diacetylene [26, 27] and stilbene groups [28, 29] should be avoided due to their instability under ultraviolet illumination. According to this principle, many small molecules with high Δn have been synthesised during the past few years; e.g. Yokokoji *et al.* [12] focused on the 5,6-difluoro-1H-indene derivatives and 5,6-difluoroindan derivatives for the novel liquid crystal core structure, and obtained compounds with high optical anisotropy values, low viscosity and high dielectric anisotropy. Gauza *et al.* [13] synthesised and evaluated a series of lateral difluoro terphenyl compounds and mixtures with high birefringence in the visible spectral range and a relatively low viscosity, and found that the mixtures had attractive applications for achieving fast response times in thin-cell liquid crystal displays. Sekine *et al.* [14–16] designed and synthesised a series of phenylacetylene-based and thiophenylacetylene-based nematic liquid crystals with Δn of around 0.3–0.5. Wu *et al.* [17, 18] and Catanescu and Chien [19] introduced highly polarisable isothiocyanate (-NCS) groups into molecules and obtained compounds with high birefringence, relatively low viscosity, high resistivity, good photo and thermal stabilities. Seed *et al.* designed and synthesised a series of compounds with 4-butylsulfanylphenyl and 4-cyano- or 4-isothiocyanato-phenyl units connected by —CH=CH—, —COO—, —C≡C—, —C≡C—COO—, —COS—, —CSO—, —CSS— linking groups, and showed that different substituted groups had great effects on optical anisotropy and polarisability anisotropy [20–23], and also synthesised compounds with mesogenic isothiocyanatonaphthalenes groups [24]; the newly synthesised compounds had high nematic phase thermal stabilities and relatively low melting points compared with compounds where the naphthalene and benzene rings were interchanged, and the analogous compounds where a cyano group replaced the isothiocyanate. Hird *et al.* [25] pointed out that a construction of alkoxy-naphthyl-phenyl-ethynylisothiocyanato has ultra-high birefringence (up to 0.63).



Scheme 1. The molecular structures of styrene monomers.

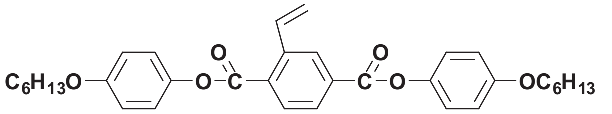
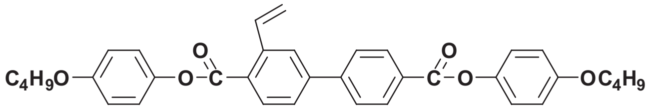
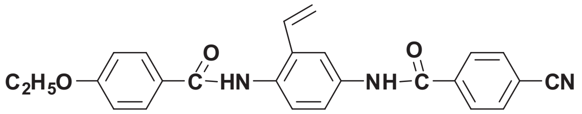
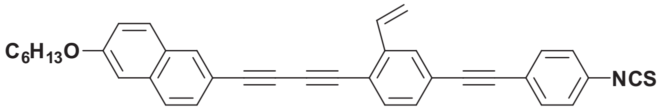
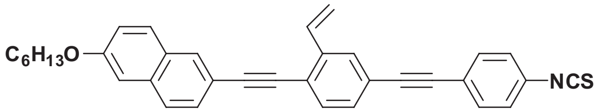
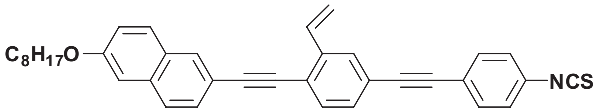
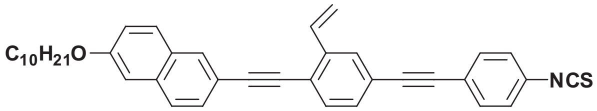
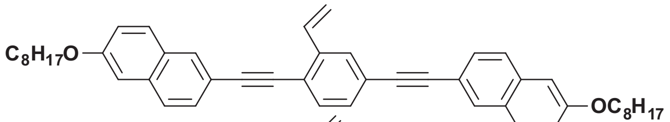
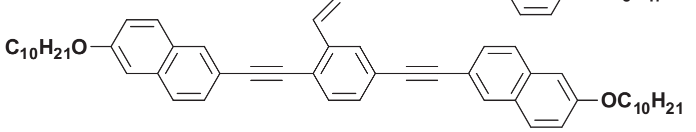
Liquid crystalline polymers (LCPs) have attracted longstanding attention for their outstanding applications in optic, electroptic, magnetic, non-linear optic devices, and so on, [30] because of their optical or thermal stability, large optical anisotropy, and other excellent characteristics. While most polymers are obtained by polymerisation of monomers with reactive groups, design and synthesis of such reactive monomers with specific functionality is important. Harris *et al.* [31] pointed that for the birefringence of polymer films, there are three determinant factors, one of which is the birefringence of the reactive monomers. Thus, design and evaluation of highly birefringent reactive monomers is essential. However, most molecules reported previously do not contain reactive groups, although they have relatively high birefringence values. In our previous work, a number of liquid crystalline monomers with moderate birefringence were designed and synthesised, as well as molecules with super high birefringence (see Table 1), but these monomers were unstable to light and heat, and were also susceptible to 1,4-topopolymerisation when exposed to ultraviolet light, heat, and irradiation [32–34], although their birefringence values were very high. In this work, two series of new liquid crystalline styrene monomers with high birefringence were projected and synthesised. Considering the principle of high π-electron conjugation length, naphthalene, acetylene, and isothiocyanato groups were introduced into one molecular structure to obtain highly birefringent monomers and also preserve its thermal and light stabilities (see Scheme 1), so that highly birefringent mesogen-jacketed liquid crystalline polymers can be achieved.

2. Results and discussion

2.1 Synthesis and Characterisation of the Monomers and intermediates

The synthetic route to the monomers and intermediates is shown in Scheme 2, and the detailed synthetic processes are available elsewhere in references. These targeted precursors were mainly synthesised through a

Table 1. n_o, n_e, and Δn values of synthesised styrene monomers.

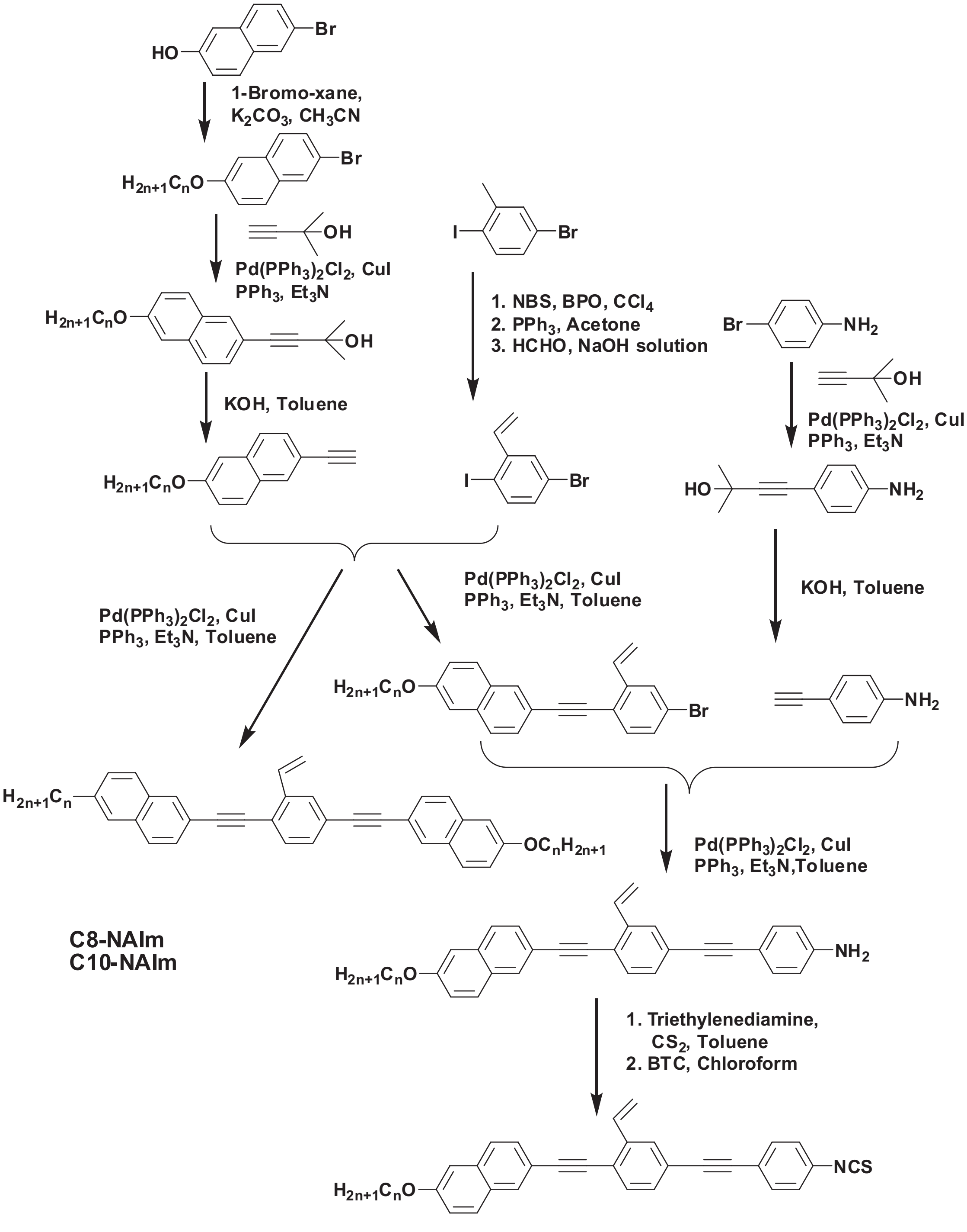
Structure of monomers	n_e	n_o	Δn
	1.5199	1.6932	0.169[a] [41]
	1.5196	1.6997	0.304[a] [42]
	1.5204	1.6989	0.271[a]
	1.5700	2.3200	0.750[b] [43]
	1.5190	1.7706	0.588
	1.5180	1.7655	0.547
	1.5189	1.7642	0.532
	1.5151	1.7398	0.503
	1.5162	1.7542	0.454

Notes: [a] n_o, n_e, and Δn values (at 25°C and $\lambda = 589$ nm) were extrapolated values from the mixture of the liquid crystal monomer (5 wt%) and TEB30A ($\Delta n = 0.1735$)(95 wt%) from an equation: $(\Delta n)_{gh} = x(\Delta n)_g + (1 - x)\,(\Delta n)_h$, where the subscripts g, h and gh denote guest, host, and guest–host cells, respectively; x is the concentration (in wt%) of the guest compound.

[b] The monomer was dissolved in host liquid crystalline materials named slc069015 ($\Delta n = 0.214$). The monomers above were synthesised in our previous studies and reported in reference 41–43. The Δn of the C6-NAIm was not determined.

key Sonogashira coupling reaction with a palladium catalyst, a copper (I) co-catalyst, and an amine base as the solvent. The detailed synthetic procedure and characterisation data of the six monomers are illustrated below in the experimental part. It is worthy of note that the series of Cn-NAIm were obtained during separation of the intermediates in moderate yield. For the series of Cn-NCSm, the conversion from the amino group to the isothiocyanate was accomplished according to our previous work, through two-step reactions using triethylenediamine hexahydrate and carbon disulfide in toluene, and bis(trichloromethyl)carbonate (BTC) in chloroform to give the crude products. The resulting crude products were purified by recrystallisation from acetone to obtain the targeted monomer. The yield of each step was moderate or relatively high. The chemical structures of the monomers were confirmed by ^{1}H nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FT-IR) spectroscopy, mass spectroscopy, and elemental analysis (see experimental details).

The representative ^{1}H NMR and ^{13}C NMR spectra ($CDCl_3$-d) of the C8-NCSm and C8-NAIm are illustrated in Figure 1. The monomers show the characteristic resonances of the vinyl group at 5.42–6.00 and 7.20–7.25 ppm.



C8-NAIm
C10-NAIm

C6-NCSm
C8-NCSm
C10-NCSm

Scheme 2. Synthetic route to styrene liquid crystalline monomers.

2.2 Phase characterisation of the monomers

The melting points, phase transition temperatures and the temperature at which the monomers began thermal polymerisation are listed in Table 2. The melting points of the monomer series Cn-NAIm are much higher than that of the monomer series Cn-NCSm due to the fact that the naphthalene ring can effectively increase the melting points. A typical thermogram obtained by differential scanning calorimetry (DSC) of phase transitions of the monomers (C10-NCSm) during

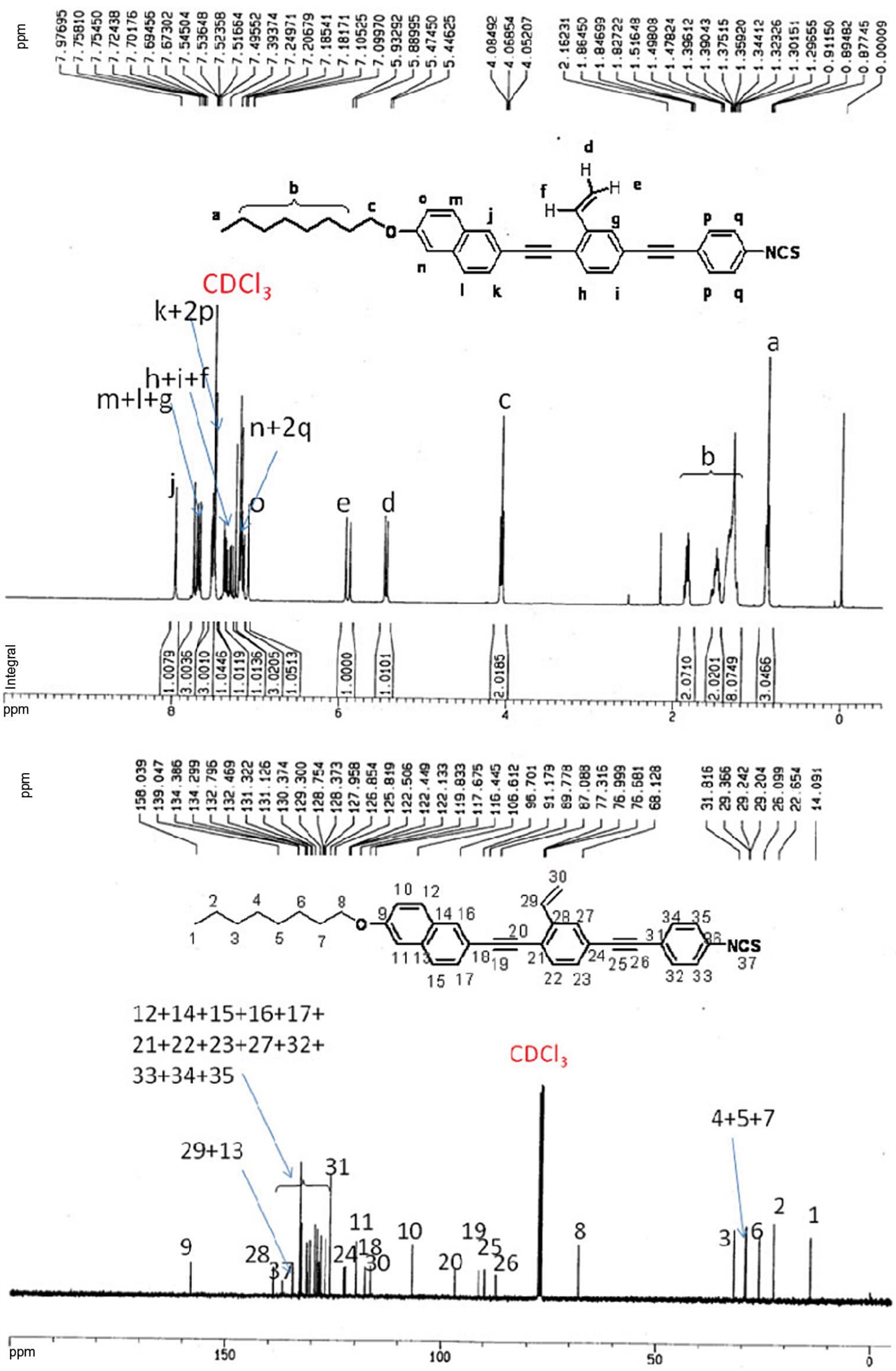


Figure 1. ^{1}H NMR and ^{13}C NMR of the representative monomers: C8-NCSm; C8-NAIm.

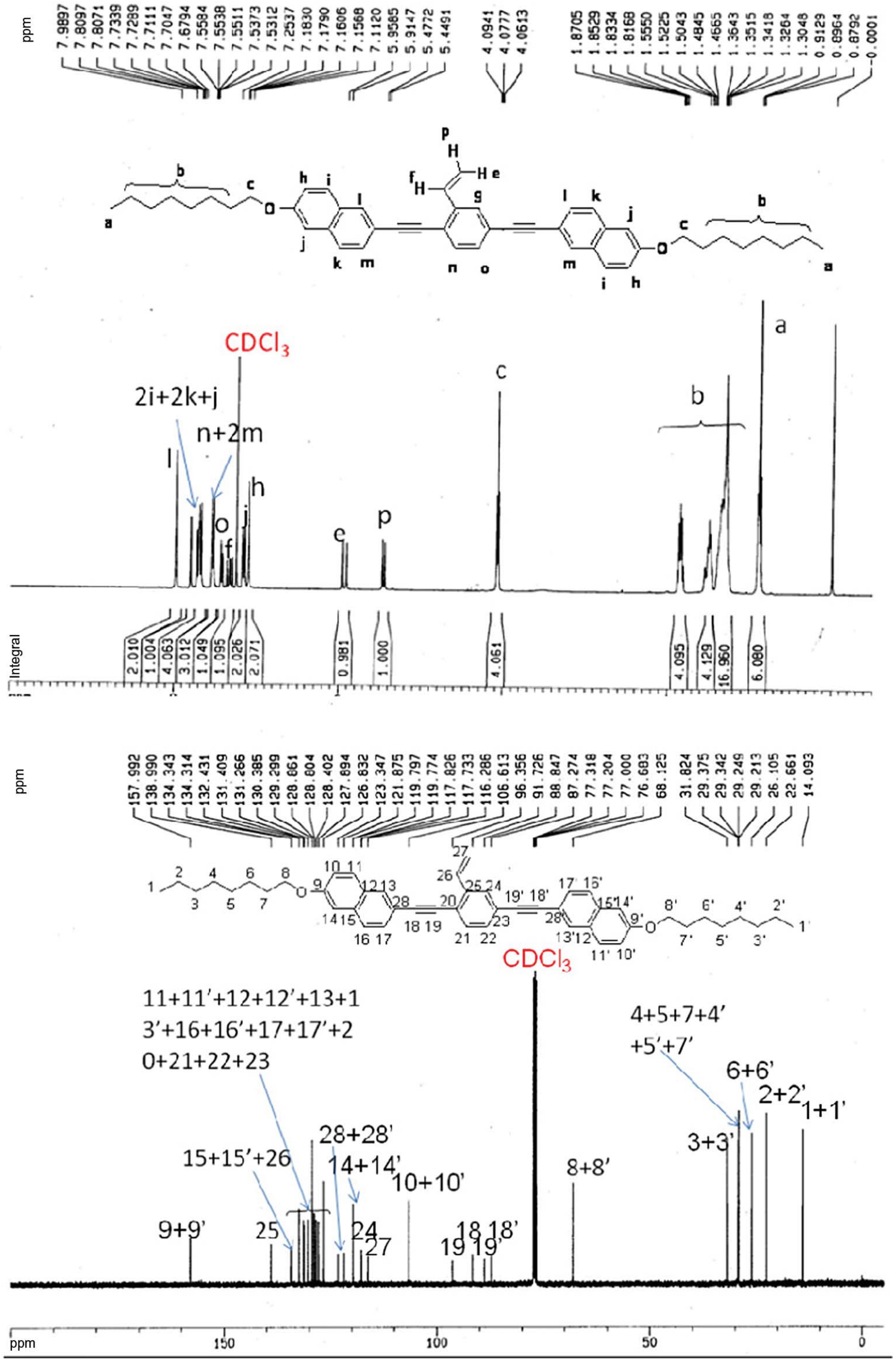
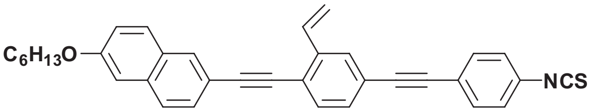
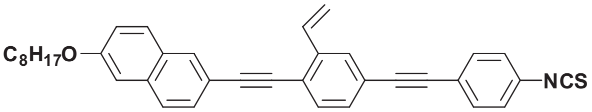
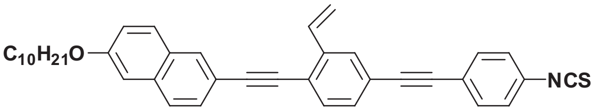
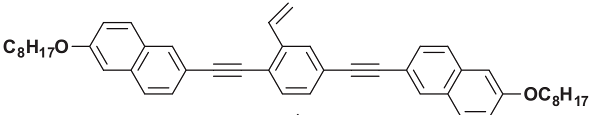
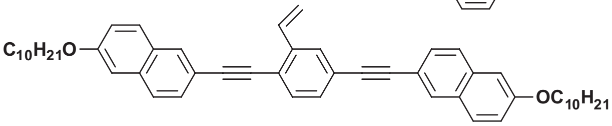


Figure 1. (*Continued*).

the first cooling and second heating, and thermogravimetric analysis-differential scanning calorimetry (TGA-DSC) is shown in Figure 2. For the three monomers containing an isothiocyanato (–NCS) group, no phase transition appears when they are under cooling, while there are exothermic peaks at low temperatures and endothermic peaks at high temperatures when heating, which correspond to crystallisation and crystal–liquid crystal transitions, respectively. For the monomers without an isothiocyanato (–NCS) group, the exothermic

Table 2. Phase transition temperatures (°C) for the monomers obtained by DSC experiment. T_N = the temperature at which the monomer enters into the nematic phase, T_p: temperature at which the monomers began thermal polymerisation, which was obtained from DSC-TGA.

Molecular structure	T_N/°C	T_p/°C
	96	170
	75	178
	79	185
	134	201
	128	178

peaks and endothermic peaks that appear during the cooling and heating scan are complex, making interpretation dificult. Polarised light microscopy (PLM) and one-dimensional wide-angle X-ray diffraction (1D WAXD) confirm that all the monomers exhibited liquid crystalline phase after they melted. Owing to our emphasis of optical anisotropy and photophysical properties, we did not investigate the corresponding peaks in detail. From TGA-DSC, all the monomers could be thermally polymerised, indicating they could be easily thermally polymerised when heated above a specific temperature.

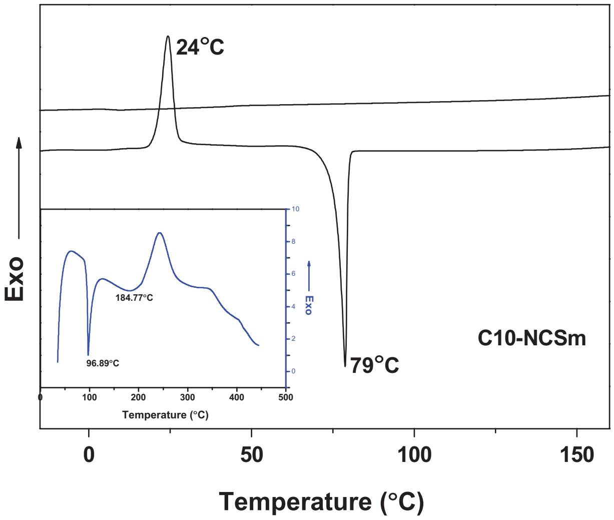


Figure 2. Differential scanning calorimetry curves of the monomers: C10-NCSm during the first cooling and second heating at the scanning rate of 2°C min^{-1}. Inset: TGA-DSC traces on heating from 0°C to 500°C.

The thermotropic mesophases and typical polarised optical photographs observed for the monomers are presented in Figure 3 and listed in Table 2. From the photographs, it is obvious that all the monomers exhibited liquid crystalline properties and showed a schlieren texture with two-fold brushes and four-fold brushes in their liquid crystal phase when they were heated below the polymerisation temperature, which is a typical texture of the nematic liquid crystalline phase [35]. When cooled, the monomers may all be crystallised.

In order to confirm the phase transition of all the monomers, a 1D WAXD experiment was also conducted. Typical powder WAXD patterns of the monomers (C10-NCSm) are presented in Figure 4. When the mesogenic compounds are heated into the liquid crystalline phase, a diffraction peak developed at a low 2θ° appears. For the monomers with a terminal isothiocyanato (–NCS) group, their phase transition behaviours were similar, exhibiting a nematic phase at higher temperatures; it is worth noting that these three monomers crystallised slowly, which was manifested in DSC and 1D WAXD. However, for the Cn-NAIm series, there existed multiple phase transition peaks in the DSC thermogram and the results by

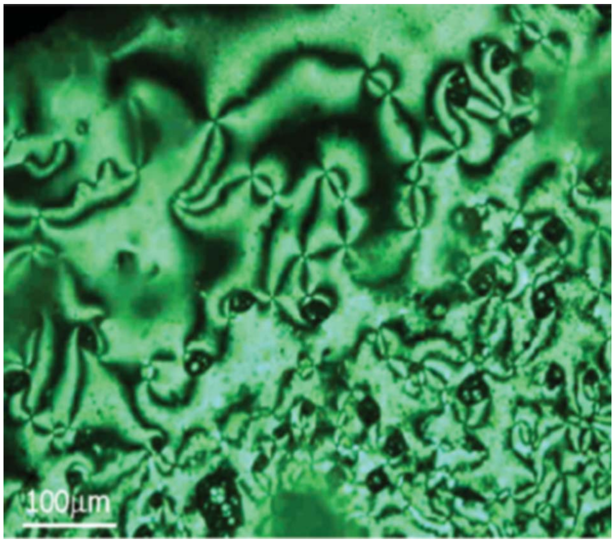


Figure 3. Polarised light microscope images of C10-NCSm (200×), heating rate: 10°C min^{-1}. C10-NCSm at 129°C.

1D WAXD were also complicated, so we did not further investigate their detailed properties.

2.3 *Optical anisotropy and photophysical properties*

After confirming the liquid crystalline phase of all the monomers, we turned our attention to their birefringent (Δn) properties. The Δn value, defined as the differences between the two principal refractive indices of a uniaxial material, is estimated by the host-guest method [36]. A fixed amount (10 wt%) of every monomer was dissolved in a standard liquid crystalline host (SLC069015, $\Delta n = 0.214$, supplied by Shijiazhuang Yong sheng Huatsing Liquid Crystal Co. Ltd, China); Δn values of the monomers were evaluated as extrapolated values from host-guest mixtures.

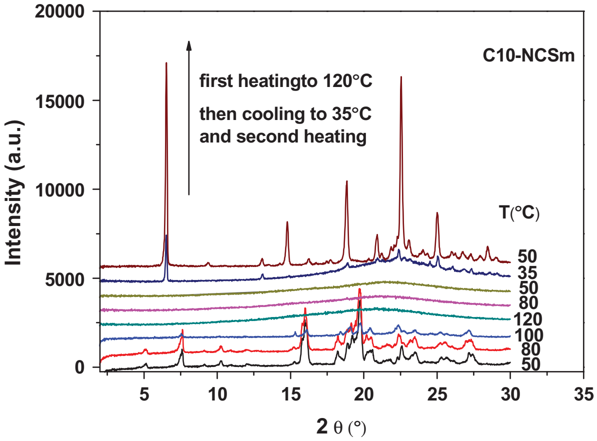


Figure 4. Powder WAXD patterns of the monomer C10-NCSm obtained during the first heating and first cooling.

Table 3. The UV-vis and fluorescence spectral data of the monomers.

Monomers	λ_{abs} (UV-*vis*)/nm	λ_{ex}/nm	λ_{em}/nm	Φ/%
C6-NCSm	352	419	362	15.5
C8-NCSm	351	420	362	15.9
C10-NCSm	352	417	363	16.7
C8-NAIm	348	393	354	83.2
C10-NAIm	338	394	354	53.9

Note: Φ: Fluorescence quantum yield, which was estimated by using quinine sulphate (dissolved in 0.05% H_2SO_4, assuming Φ_{PL} of 0.55±0.05) as a standard.

Refractive indices data of all the monomers and some other representative monomers synthesised in our previous studies are collected in Table 1; as expected, all the monomers with long π-conjugation along the molecular long axis and high polarisability display high birefringent values (0.4–0.7), especially the ones containing an isothiocyanato (–NCS) group, due to its high polarisability. The large optical anisotropies of all the monomers suggest that they could be good candidates for synthesis of highly birefringent LCPs. In addition, from the values of high birefringence, optical anisotropy of the molecules with the same chemical structures was reduced with the increase of alkyl chain length due to the decrease of molecular polarisability, which was also reported in previous investigations [37].

It is well known that molecules with large π-electron conjugation length have the best luminescence properties [38–40] and photophysical properties of all the monomers. The maximum absorption wavelength λ_{abs} (UV-vis) in the UV–vis spectrum, the maximum excitation λ_{ex} and transmitting wavelength λ_{em} in $CHCl_3$ in the fluorescence spectrum, and the fluorescence quantum yield Φ in solution are illustrated in Table 3. The monomers containing a terminal isothiocyanato (–NCS) group had moderate fluorescence quantum yields (Φ) in solution, while Φ values of the other series were very high (between 0.54–0.84) because they had longer π-conjugation lengths. All the results indicated that they had potential applications in photoluminescence, electroluminescence, and other fields.

3. Conclusion

Two series of monomers with high optical anisotropy (Δn) were successfully synthesised and studied. Their chemical structures were confirmed by various characterisation techniques. The mesophase morphology and transitions of the monomers were investigated by DSC, PLM and 1D WAXD. All the results indicated that the monomers had good thermal stabilities, polymerisation abilities, especially high optical anisotropy (0.4–0.7) and good luminescent properties (for the series of Cn-NAIm, up to 0.54–0.84 of Φ were obtained), making them good candidates for the preparation of highly birefringent mesogen-jacketed liquid LCPs and potential applications in display applications and electroluminescent apparatus. Moreover, the easy polymerisation and high optical anisotropy of the monomers provided us an effective tool to investigate the properties of the corresponding mesogen-jacketed LCPs.

4. Experimental

4.1 Characterisation

^{1}H NMR (400 MHz) spectra were recorded on a Bruker ARX400 spectrometer using deuterated chloroform ($CDCl_3$) with tetramethylsilane as the internal standard at room temperature for monomers, and deuterated chloroform ($CDCl_3$) without tetramethylsilane at room temperature for the polymers. FT-IR was performed using a Nicolet Magna-IR 750 Fourier transform infrared spectrometer.

TGA was performed on a TA SDT 2960 instrument at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. A DSC examination was carried out on a TA DSC Q100 calorimeter with a programmed heating procedure in nitrogen. The sample size was about 5 mg and encapsulated in hermetically sealed aluminium pans, whose weights were kept constant. The temperature and heat flow scale at different cooling and heating rates were calibrated using standard materials such as indium and benzoic acid.

PLM observation was performed on a Leitz Laborlux 12 microscope with a Leitz 350 hot stage in order to observe the liquid crystalline textures of the polymers. 1D WAXD experiments were performed on a Philips X'Pert Pro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu Kα) and an X'celerator detector. The reflection peak positions were calibrated with silicon powder ($2\theta > 15°$) and silver behenate ($2\theta < 10°$). The sample stage was set horizontally, and a temperature control unit (Paar Physica TCU 100) in conjunction with the diffractometer was utilised to study the structure evolutions as a function of temperature. The heating and cooling rates in the WAXD experiments were 5°C min^{-1}.

4.2 Synthesis

Synthesis of C6-NCSm: the conversion from the amino-group to the isothiocyanato (–NCS) group was accomplished through two-step reactions. The monomer precursor with -NH_2 group (1.543 g, 0.0033 mol) and triethylenediamine hexahydrate (2.194 g, 0.0196 mol) were dissolved in toluene (16 ml) and stirred at room temperature. Carbon disulfide (0.7577 g, 0.00998 mol) in toluene was added dropwise and the reaction mixture was stirred for 4 h (a yellow solid precipitated during this period). The mixture was filtered and the obtained precipitate was dried. The yellow solid (2.000 g) obtained above was dissolved in chloroform, ice-bathed to 0°C, bis(trichloromethyl)carbonate (BTC, 0.344 g, 0.00117 mol) in chloroform was added dropwise into the system, the mixture was stirred at room temperature for 1 h, then stirred at reflux for 1 h. The mixture was filtered and the solvent removed under a vacuum, concentrated and purified by column chromatography (silica gel, petroleum/ethyl acetate = 6:1); the resulting crude product was purified by recrystallisation from acetone to obtain the targeted monomer as a light yellow crystal. Yield: 68%.

^{1}H NMR ($CDCl_3$, TMS as internal standards, δ): 7.99(s, 1H, Ar-H), 7.68–7.77 (m, 3H, Ar-H), 7.51–7.56 (m, 4H, Ar-H), 7.20–7.26 (m, 5H, Ar-H, CH=), 7.12 (s, 1H, Ar-H), 5.89–5.94, 5.45-5.48 (d, 2H, =CH_2), 4.07–4.10 (t, 2H, OCH_2), 1.82–1.87 (m, 2H, aliphatic-H), 1.25–1.82 (m, 6H, aliphatic-H), 0.90–0.94 (t, 3H, terminal CH_3). IR ν_{max}: 2958, 2930, 2857, 2033, 1601, 1506, 1464, 1257, 1210. MS *m*/*z*: 511(M^+). Elemental analysis: found (calcd.): C: 82.04 (82.16), H: 5.67 (5.71) S: 6.35 (6.27) N:2.71 (2.78).

The synthesis of C8-NCSm used the same method as described for the preparation of C6-NCSm. Yellow crystal. Yield: 72%.

^{1}H NMR ($CDCl_3$, TMS as internal standards, δ): 7.98 (s, 1H, Ar-H), 7.67–7.76 (m, 3H, Ar-H), 7.50–7.55 (m, 4H, Ar-H), 7.10–7.39 (m, 5H, Ar-H, CH=), 7.09 (s, 1H, Ar-H), 5.89–5.93, 5.45–5.47 (d, 2H, =CH_2), 4.05–4.08 (t, 2H, OCH_2), 1.83–1.86 (m, 2H, aliphatic-H), 1.30–1.52 (m, 10H, aliphatic-H), 0.87–0.91 (t, 3H, terminal CH_3). IR ν_{max}: 2952, 2935, 2856, 2125, 1601, 1505, 1470, 1256, 1210. MS *m*/*z*: 539 (M^+). Elemental analysis: found (calcd.): C: 82.33 (82.34), H: 6.21 (6.06) S: 5.99 (5.94) N: 2.50 (2.60).

The synthesis of C10-NCSm used the same method as described for the preparation of C6-NCSm. Yellow crystal. Yield: 63%.

^{1}H NMR ($CDCl_3$, TMS as internal standards, δ): 7.99 (s, 1H, Ar-H), 7.69–7.77 (m, 3H, Ar-H), 7.51–7.56 (m, 4H, Ar-H), 7.21–7.26 (m, 5H, Ar-H, CH=), 7.12 (s, 1H, Ar-H), 5.90–5.94, 5.45–5.48 (d, 2H, =CH_2), 4.07–4.10 (t, 2H, OCH_2), 1.84–1.88 (m, 2H, aliphatic-H), 1.25–1.82 (m, 14H, aliphatic-H), 0.90–0.94 (t, 3H, terminal CH_3).IR ν_{max}: 2953, 2926, 2853, 2044, 1602, 1504, 1467, 1256, 1211. MS *m*/*z*: 567 (M^+). Elemental analysis: found (calcd.): C: 82.41 (82.50), H: 6.63 (6.57) S: 5.58 (5.65) N: 2.39 (2.47).

Synthesis of monomers C8-NAIm: the monomer was obtained during the preparation of 2-((4-bromo-2-vinylphenyl)ethynyl)-6-(octanoxy)naphthalene. Light yellow flake crystal. Yield: 28%.

^{1}H NMR ($CDCl_3$, TMS as internal standards, δ): 7.99 (s, 2H, Ar-H), 7.68–7.81 (m, 5H, Ar-H), 7.53–7.56

(m, 4H, Ar-H), 7.11–7.25 (m, 5H, Ar-H, CH=), 5.91–5.96, 5.45–5.48 (d, 2H, $=CH_2$), 4.06–4.09 (t, 4H, OCH_2), 1.82–1.87 (m, 4H, aliphatic-H), 1.30–1.36 (m, 4H, aliphatic-H), 1.470–1.56 (m, 16H, aliphatic-H), 0.88–0.91 (t, 6H, terminal CH_3). IR ν_{max}: 2955, 2931, 2855, 2209, 1600, 1500, 1469, 1254, 1211. MS *m/z*: 660 (M^+). Elemental analysis: found (calcd.): C: 87.06 (87.23), H: 7.84 (7.93).

The synthesis of C10-NAIm used the same method as described for the preparation of C8-NCSm. Light yellow crystal. Yield: 26%.

^{1}H NMR ($CDCl_3$, TMS as internal standards, δ): 7.98 (s, 2H, Ar-H), 7.67–7.80 (m, 5H, Ar-H), 7.52–7.55 (m, 4H, Ar-H), 7.10–7.43 (m, 5H, Ar-H, CH=), 5.91–5.95, 5.45–5.47 (d, 2H, $=CH_2$), 4.06–4.08 (t, 4H, OCH_2), 1.80–1.88 (m, 4H, aliphatic-H), 1.25–1.34 (m, 4H, aliphatic-H), 1.46–1.53 (m, 24H, aliphatic-H), 0.87–0.90 (t, 6H, terminal CH_3). IR ν_{max}: 2955, 2931, 2920, 2852, 2204, 1600, 1496, 1471, 1257, 1215. MS *m/z*: 716 (M^+). Elemental analysis: found (calcd.): C: 86.86 (87.10), H: 8.36 (8.43).

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