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Synthesis and properties of novel liquid crystalline materials with super high birefringence: styrene monomers bearing diacetylenes, naphthyl, and nitrogen-containing groups

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Three new liquid crystal asymmetrical styrene monomers bearing diacetylenes, naphthyl, and nitrogen-containing groups were successfully synthesized from 2-(bromoethynyl)-6-(hexyloxy)naphthalene, 4-(4-bromo-2-vinylphenyl)-2-methylbut-3-yn-2-ol, and derivatives of 4-ethynylaniline. The molecular structures of these compounds were confirmed by FTIR, ^{1}H NMR spectroscopy, elemental analysis, and mass spectrometry. The liquid crystalline properties of monomers were characterized by differential scanning calorimetry and polarized light microscopy. Results indicated that all the compounds exhibited the nematic phase in liquid crystal state and super high optical birefringence of 0.5–0.8. The change of terminal nitrogen-containing group affected the birefringence values in the order of $-N(CH_3)_2 < -NH_2 < -NCS$. Moreover, measurements using UV–vis and fluorescence spectroscopy showed their good photoluminescence properties and high quantum efficiency of 0.4–1.0.

1. Introduction

The design and synthesis of novel highly birefringent liquid crystal (LC) material for use in optical devices are greatly desirable in recent years with a rapid expansion of information technology (IT). Nowadays liquid crystals which exhibit high values of birefringence (Δn) are employed not only in conventional display devices such as super twisted nematic (STN) and in high response STN-LCDs with a narrow cell gap as Δn moderators, but also in scattering-type PDLCDs as a reflective LCD, and in spatial light modulators.[1] And they are also widely used as compensation films for improving the viewing angle, reflectors, and polarizers.[2] Besides, more and more new applications of highly birefringent liquid crystals are reported, for example, a new class of liquid crystals with birefringence values greater than 0.5 in the visible region has recently been developed to provide light emission for organic light-emitting diodes (OLEDs).[3]

A large number of researches indicate that the Δn of LCs is mainly determined by π-electron conjugation, molecular shape, and order parameter. Thus, a more linearly conjugated LC would exhibit a larger optical anisotropy. So for, many high Δn materials have been obtained by increasing the molecular π-electron conjugation length and introducing highly polarizable end groups, such as difluoroisothiocyanate, benzene rings, and acetylene linking groups, to give high dielectric anisotropy.[4] Recently, an increasing number of investigations and reports have showed that naphthalene, diacetylene, and nitrogen-containing groups are superior polarizable parts to induce high Δn in a liquid crystal molecule.[5] Therefore, it is reasonable that coupling of these types of groups could lead to high optical and large dielectric anisotropies. However, as we know, there has been no report on high birefringence liquid crystal materials based entirely on the three kinds of groups.

Polymer liquid crystals (PLCs) have attracted much attention during the past decade due to their potential application as high performance photoelectric materials due to their large optical anisotropy and excellent stability.[6] Reactive monomers can be employed for the production of these polymer materials by thermal polymerization or photopolymerization. As a result, the design and synthesis of the relevant liquid crystal monomers with polymerizable group as starting materials for the production of anisotropic polymers are very important.[7] In previous work, we have synthesized two kinds of liquid crystalline monomers with the Δn of 0.2–0.3 (Table 1).[8] In the present work, we attempted to synthesize three new liquid crystal styrene monomers containing

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Table 1

Phase transition temperatures (T/°C), changes in enthalpies (ΔH/kJ/mol in brackets) on the first heating and cooling runs, the thermal polymerization onset temperatures and the thermal polymerization temperatures (T/°C) of three styrene monomers. Cr, crystalline phases; N, nematic

Compd	heating scan[a] / cooling scan	T_0[c]	T_s[d]
7	$\mathrm{Cr} \underset{81.9(16.9)}{\overset{157.4(45.8)}{\rightleftharpoons}} \mathrm{N}$	175	220
8	$\mathrm{Cr} \underset{-}{\overset{128.4(15.1)}{\rightleftharpoons}} \mathrm{N}^{b}$	150	210
9	$\mathrm{Cr} \underset{117.6(15.0)}{\overset{137.4(45.9)}{\rightleftharpoons}} \mathrm{N}$	160	205

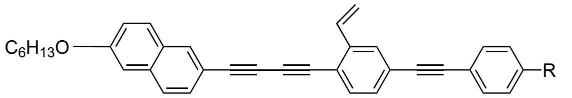
[a] The transition peaks from the nematic phase to isotropic liquid were not observed in DSC because three styrene monomers easily undergoes thermal polymerization during heating.

[b] – indicates value not determined.

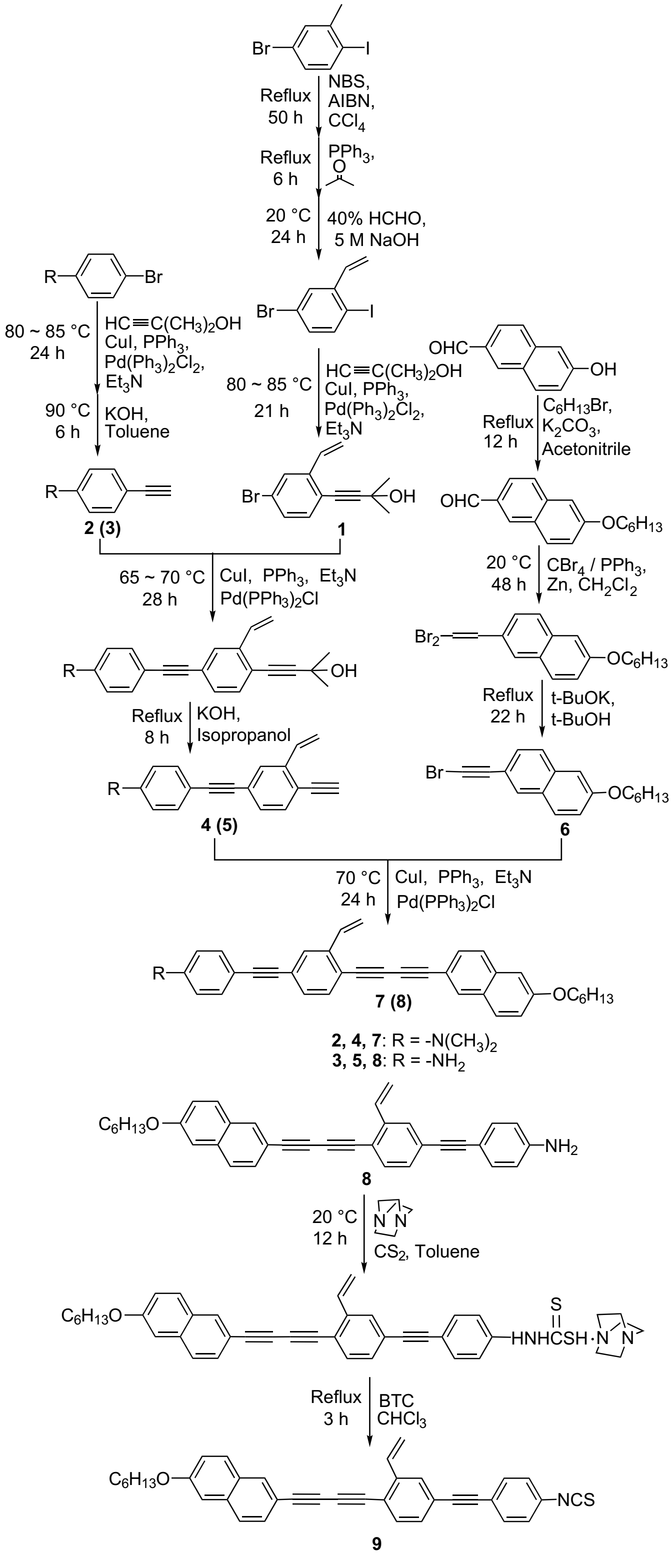
[c] Thermal polymerization onset temperature.

[d] Thermal polymerization temperature.

naphthalene, diacetylene, and nitrogen-containing groups (Scheme 1). Our aim is threefold: (i) to prove the molecular design based on the structure of large linear π-electron conjugation is logical and the synthetic route is viable; (ii) to realize the super high Δn liquid crystal styrene monomers, which could be used for the preparation of mesogen-jacketed liquid crystalline polymers with high Δn; (iii) to learn the liquid crystalline behavior and photophysical property of the newly formed compounds. The polymerization of three monomers and the birefringence properties of the prepared polymers will be described in forthcoming publications.



Scheme 1. The molecular structures of styrene monomers: (1) R=–N(CH$_3$)$_2$; (2) R=–NH$_2$; (3) R=–NCS.



Scheme 2. Synthesis of styrene liquid crystalline monomers.

2. Results and discussion

The synthesis of the asymmetrical monomers **7**, **8**, and **9** is outlined in Scheme 2. These target compounds were mainly synthesized through the coupling of intermediate molecules **1**, **2** (or **3**), and **6**, respectively. The experimental details are described below using **9** as an example. At first, 4-bromo-1-iodo-2-vinylbenzene was synthesized using the similar method previously reported by us[9] and a transparent, viscous liquid, which was very unstable, was obtained through purification by chromatography. Introduction of the protected triple-bonded chain was straightforward by a coupling between the 4-bromo-1-iodo-2-vinylbenzene and 2-methylbut-3-yn-2-ol (the optimal molar ratio was 1:1.1) using Sonogashira conditions to give the 4-bromo-1-(2-methylbut-3-yn-2-ol)-2-vinylbenzene **1**. Similarly, another intermediate molecule 4-ethynylaniline **2** was also synthesized through the introduction of a protected triple-bonded chain and the removal of the protecting group from acetylenes using the same method as reported earlier.[10] The naphthyl-containing compound, 2-(bromoethynyl)-6-(hexyloxy)naphthalene **6**, was obtained from 6-hydroxy-2-naphthaldehyde. Introduction of alkyl chain was accomplished by reacting with bromoalkane in the presence of potassium carbonate (K$_2$CO$_3$) in acetonitrile and the yield was very high, compared with the method used in the previous synthesis of monomers.[11] A variety of methods have been used to prepare the bromoacetylene compound. Our approach converted the aldehyde to the dibromoolefin which then dehydrobrominated to the bromoacetylene and the yellow solid product **6** was successfully obtained.[12] It should be noted that the acetylene intermediates in this work seemed to be sensitive to light and heat and every effort need to be made to protect these materials from light and heat. As shown in Scheme 2, the coupling of styrene fragment **1** with the aniline fragment **2** was carried out in the presence of copper acetate to afford the compound **4** and the method was also used to prepare compound **8**.[13]

However, under the same conditions, each fragment can also self-couple to form the respective dimers. The low yields of **4**, **5**, **7**, and **8** were attributed to these accompanying self-coupling reactions. Then, the conversion from the amino-group to the isothiocyanic ester was accomplished through two-step reactions using triethylenediamine hexahydrate and carbon disulfide in toluene, and bis(trichloromethyl)carbonate (BTC) in chloroform to give the compound **9**, respectively. The resulting crude product was purified by recrystallization from acetone to obtain the target monomer **9**.[14] Compared with a step method of using poisonous thiophosgene to synthesize the isothiocyanic ester in many papers, the two-step method by use of BTC is safer and more environmentally friendly.

The liquid crystalline properties of these three target monomers were investigated primarily by polarized light microscopy (PLM) and differential scanning calorimetry (DSC). The phases were identified through the comparison of the observed textures with reference textures from PLM.[15] Figure 1 shows PLM photographs of monomers **7**, **8**, and **9** observed in their LC phases in the course of heating. It was obvious that all three compounds were mesogenic compounds and exhibited a schlieren texture with two brushes and four brushes in their LC phase, which is the typical texture of the nematic liquid crystalline phase. Furthermore, we found that the three monomers all entered the liquid crystal state at the first phase transition temperature at

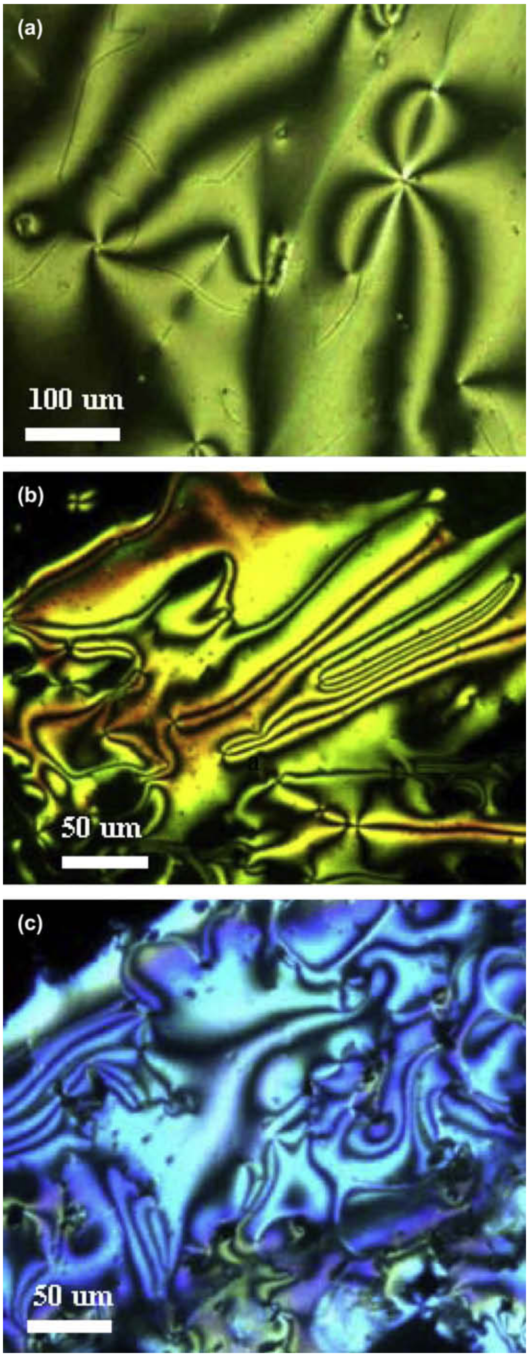


Figure 1. Polarized light microscopy images of monomers. (a) Monomer **7**: schlieren texture of nematic phase at 165 °C. (b) Monomer **8**: schlieren texture of nematic phase at 136 °C. (c) Monomer **9**: schlieren texture of nematic phase at 140 °C.

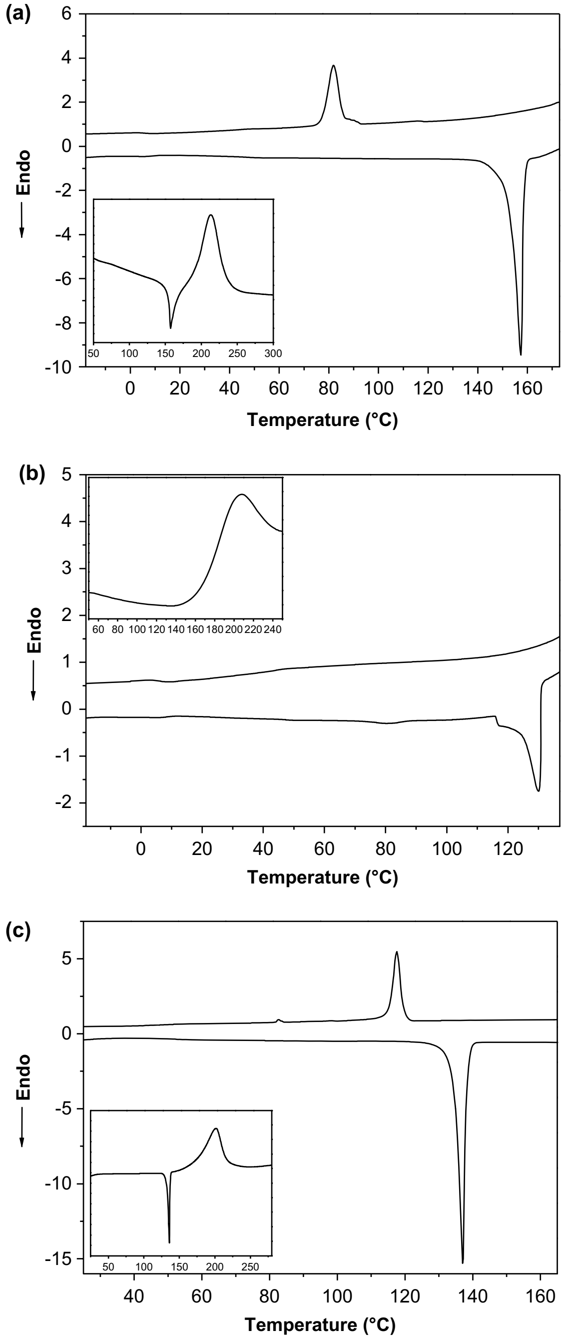


Figure 2. DSC traces for monomers on second heating and subsequent cooling. (a) Monomer **7**: from −20 to 170 °C (scan rate 10 °C min^{-1}). Inset: DSC traces on third heating from 50 to 300 °C. (b) Monomer **8**: from −20 to 138 °C (scan rate 10 °C min^{-1}). Inset: DSC traces on third heating from 50 to 250 °C. (c) Monomer **9**: from 20 to 165 °C (scan rate 10 °C min^{-1}). Inset: DSC traces on third heating from 25 to 300 °C.

approximately 150 °C, when a bright, colorful birefringent texture was observed. However, because of the ready thermal polymerization of the monomers, the mesophase was not stable upon further heating and the field of view turned black at 235, 190, and 228 °C, respectively.

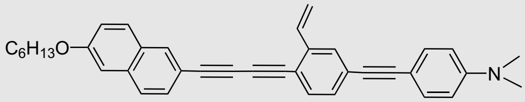
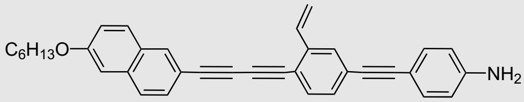
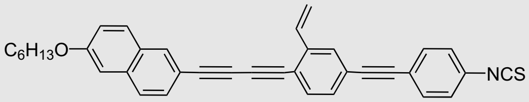
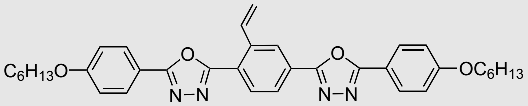
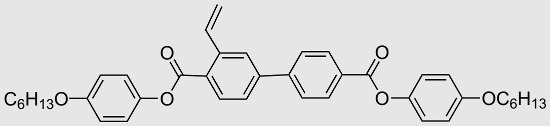
The DSC curves of three compounds are shown in Figure 2 and the phase transitions are summarized in Table 1. Compound **7** exhibited a narrow endothermic peak centered at about 157 °C in the second heating run, corresponding to the transition from the crystal phase (Cr) to the nematic liquid crystalline phase (N), and a transition from the mesophase to the crystal phase at about 82 °C on cooling curve of the DSC, respectively. Furthermore, as shown in the inset of Figure 2a, a broad exothermic process started at about 175 °C and centered at 220 °C indicated that the monomer easily undergoes thermal polymerization once it passed the transition from crystal to liquid crystalline phase. The isotropization process was not observed since the temperature was kept low to avoid polymerization of the monomer during the heating process. For compound **8**, an endothermic peak is at 128 °C in DSC curves and a thermal polymerization peak started at about 150 °C and centered at 210 °C could be observed, similar to the result of compound **7**. But, the DSC curve did not display any transition in the cooling run probably due to higher polymerization activity compared with the activities of compounds **7** and **9**. For compound **9**, the transition from Cr to N was at 137 °C and the mesophase to the crystal phase was at about 118 °C while the thermal polymerization onset temperature was at 160 °C.

Having demonstrated the liquid crystal properties of three monomers, we focused our attention on their Δn properties. Δn was evaluated as extrapolated values from mixtures containing 10 wt % of each test compound in SLC069015 (supplied by Shijiazhuang Yongsheng Huatsing Liquid Crystal Co. Ltd, China).[16] Refractive indices data of compound **7**, **8**, **9**, and some other monomers **10** and **11** synthesized in our previous studies are collected in Table 2. It is well known that high Δn value can be achieved by increasing the molecular conjugation length. Molecules that contain highly polarizable groups with high electron density, such as acetylene linking groups, will therefore have large optical anisotropies. Moreover, high birefringence materials can be obtained by introducing high polar end groups.[10] Firstly, the presence of 1,3,4-oxadiazole and ester groups in molecular **10** and **11** destroyed the linear conjugation degree. Secondly, there were no high polar end groups in molecular **10** and **11**. So, the Δn values of both **10** and **11** were lower than those of **7**, **8**, and **9**. Otherwise, symmetry lowering has also played an important role in increasing the anisotropy of liquid crystals.[17] Compared with **10**, the symmetry of **11** was lower. Therefore, the Δn value of **11** was higher than that of **10**. As expected, three monomers **7**, **8**, and **9** containing high conjugation along the molecular long axis exhibited high Δn values of over 0.4. Moreover, the change of terminal nitrogen-containing group affected the Δn values in the order of $-N(CH_3)_2 < -NH_2 < -NCS$, which was consistent with the order of the electron-withdrawing strength. It was worth noting that compound **9** had an extremely high Δn value of 0.75, which was much higher than most liquid crystal molecules reported before. So, it is expected to be a good candidate for preparation of polymers with high Δn.

It is well known that molecules with large π-electron conjugation length would possess better luminescence ability. So, we also studied the fluorescence property of three monomers. The maximum absorption wavelength in UV–vis spectrum, the maximum excitation and transmitting wavelength in $CHCl_3$ in fluorescence spectrum, and the fluorescence quantum yield in solution are listed in Table 3. The results showed that all compounds emitted blue light and their fluorescence quantum yields (Φ) in solution were high. Noticeably, the Φ of compound **7** (97.5%) was very high and was expected to be useful for

Table 2

n_o, n_e, and Δn values of the synthesized styrene monomers

Compd	Molecular structure	n_o[a]	n_e[a]	Δn[a]
7		1.54	2.01	0.47
8		1.59	2.20	0.61
9		1.57	2.32	0.75
10[b]		1.51	1.71	0.20
11[b]		1.51	1.79	0.28

[a] n_o, n_e, and Δn values (at 25 °C and λ=589 nm) were extrapolated values from the mixture of the liquid crystal monomer (10 wt %) and SLC069015 (90 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] Two styrene monomers synthesized in our previous studies were reported in Ref. 8a and b.

Table 3
The UV–vis and fluorescence spectral data of three styrene monomers (wavelengths in nm)

Monomers	λ_{abs} (UV–vis) (nm)	λ_{ex} (nm)	λ_{em} (nm)	Fluorescence quantum yield[a] Φ (%)
7	381	387	471	97.5
8	360	363	445	51.2
9	338	359	410	38.9

[a] Estimated by using quinine sulfate (dissolved in 0.05% H_2SO_4 with a concentration of 10^{-6} M, assuming Φ_{PL} of 0.55±0.05) as a standard.

photoluminescence, electroluminescence, and organic light-emitting diodes (OLEDs) applications.

3. Conclusion

In conclusion, we had designed and synthesized three new styrene monomers with large π-electron conjugation length bearing diacetylenes, naphthyl, and nitrogen-containing groups, which were very important monomers for the preparation of high Δn polymers. PLM and DSC results indicated their nematic liquid crystalline phases and the good polymerization ability. Measurements of Δn showed that the extrapolated Δn values of these compounds were very high and compound **9** had an extremely high Δn value, much higher than most of those reported before. Moreover, all the compounds exhibited blue fluorescence and better fluorescence quantum yields, making them good candidates for many luminescence applications.

Acknowledgements

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References and notes

1. (a) Meng, H. H. B.; Dalton, L. R.; Wu, S. T. *Mol. Cryst. Liq. Cryst.* **1994**, *259*, 303; (b) Hsu, C. S.; Tsay, K. T.; Chang, A. C.; Wang, S. R. *Liq. Cryst.* **1995**, *19*, 409; (c) Khoshsima, H.; Ghanadzadeh, A.; Tajalli, H.; Dabrowski, R. *J. Mol. Liq.* **2006**, *129*, 169; (d) Yang, D. K.; Lu, Z. J.; Chien, L. C.; Doane, J. W. *SID Tech. Dig.* **2003**, *34*, 959; (e) Yang, D. K.; Doane, J. W. *Appl. Phys. Lett.* **1994**, *64*, 1905; (f) Fergason, J. L. *SID Tech. Dig.* **1985**, *16*, 68; (g) Wu, S. T. *Phys. Rev. A* **1992**, *30*, 1270.
2. Markus, K. T.; Karen, H.; Kim, T. *Thin Solid Films* **2007**, *516*, 107; (b) Klasen, M.; Bremer, M.; Tarumi, K. *Jpn. J. Appl. Phys.* **2000**, *39*, L1180.
3. (a) O'Neill, M.; Kelly, S. M. *Adv. Mater.* **2003**, *15*, 1135; (b) Kunihiko, O.; Atsushi, S.; Tomiki, I. *Adv. Mater.* **2006**, *18*, 523.
4. (a) Takatsu, H.; Takeuchi, K.; Tanaka, Y.; Sasaki, M. *Mol. Cryst. Liq. Cryst.* **1986**, *141*, 279; (b) Wu, S. T.; Margerum, J. D.; Ho, M. S.; Hsu, C. S. *Mol. Cryst. Liq. Cryst.* **1995**, *261*, 79; (c) Wu, S. T.; Hsu, C. S.; Shyu, K. E. *Appl. Phys. Lett.* **1999**, *74*, 344; (d) Wu, S. T.; Hsu, C. S.; Shyu, K. E. *Appl. Phys. Lett.* **2000**, *77*, 957; (e) Gauza, S.; Wen, C. H.; Wu, S. T.; Hsu, C. S. *Jpn. J. Appl. Phys., Part 1* **2004**, *43*, 7634.
5. (a) Sekine, C.; Naoto, K. *Liq. Cryst.* **2001**, *28*, 1361; (b) Michael, H.; Toyne, K. J.; Goodby, J. W. *J. Mater. Chem.* **2004**, *14*, 1731; (c) Gauza, S.; Li, J.; Wu, S. T. *Liq. Cryst.* **2005**, *32*, 1077; (d) Seed, A. J. *J. Mater. Chem.* **2000**, *10*, 2069.
6. (a) Menc, X.; Natansohn, A.; Rochon, P. *J. Polym. Sci., Part B: Polym. Phys.* **1996**, *34*, 1461; (b) Nobuhiro, K.; Tetsuro, K.; Tohei, Y. *Adv. Mater.* **2001**, *13*, 1337; (c) Kunihiko, O.; Atsushi, S.; Osamu, T. *J. Mater. Chem.* **2005**, *15*, 3395; (d) Yan, X.; Rafael, V.; Robert, H. G. *J. Am. Chem. Soc.* **2008**, *130*, 1735.
7. (a) Broer, D. J.; Boven, J.; Mol, G. N. *Makromol. Chem.* **1989**, *190*, 2225; (b) Chain, S. H.; Hwai, L. C. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 3929; (c) Cassano, R.; Dbrowski, R.; Dziaduszek, J. *Tetrahedron Lett.* **2007**, *48*, 1447; (d) Raymond, J. T.; Kenichi, T.; Peter, T. *J. Am. Chem. Soc.* **2006**, *128*, 12084; (e) Williams, B. S.; Leatherman, M. D.; Peter, S. W. *J. Am. Chem. Soc.* **2005**, *127*, 5132.
8. (a) Chen, S.; Gao, L. C.; Zhao, X. D.; Zhou, Q. F. *Macromolecules* **2007**, *40*, 5718; (b) Chai, C. P.; Zhu, X. Q.; Zhou, Q. F. *Macromolecules* **2007**, *40*, 9361.
9. Zhang, D.; Liu, Y. X.; Zhou, Q. F. *Macromolecules* **1999**, *32*, 5183.
10. Catanescu, O.; Chien, L. C. *Liq. Cryst.* **2006**, *33*, 115.
11. Zhang, H.; Yu, Z.; Wan, X.; Zhou, Q.-F.; Woo, E.-M. *Polymer* **2002**, *43*, 2357.
12. Rajesh, A. S.; Marye, N.; David, G. A. *Liq. Cryst.* **2000**, *27*, 801.
13. *Synthesis of* **7**: Solution of compound **4** (2.4 g, 8.85 mmol) dissolved in dry triethylamine (30 ml) was added dropwise to a suspension of compound **6** (2.44 g, 7.38 mmol), $Pd(PPh_3)_2Cl_2$ (0.33 g, 0.47 mmol), triphenylphosphine (0.24 g, 0.93 mmol), and copper(I) iodide (0.12 g, 0.69 mmol) in dry triethylamine (180 ml) at room temperature under nitrogen. The mixture was stirred at near 70 °C for 24 h. After cooled to room temperature, the mixture was filtered and filtrate concentrated in vacuo to remove triethylamine. The crude product was dissolved in dichloromethane and extracted with aqueous ammonium chloride solution. The organic phase was then washed with saturated aqueous sodium chloride and dried over $MgSO_4$. The crude product was isolated by evaporating the solvent and purified by column chromatography using dichloromethane/pet. ether 1:1 as eluant. Pure product as a light yellow needle-like crystal was obtained after being recrystallized in acetone; yield: 1.65 g (42%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.90–0.94 (m, 3H, $-CH_3$), 3.01 (s, 6H, $-N(CH_3)_2$), 4.06–4.10 (m, 2H, Ar-OCH_2-), 5.44 (d, 1H, J=10.7 Hz, $=CH_2$), 5.89 (d, 1H, J=17.5 Hz, $=CH_2$), 7.10–7.15 (m, 1H, $=CH-$), 6.67 (d, 2H, J=7.2 Hz, Ar), 7.18–7.71 (11H, Ar), 8.00 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ 14.45, 23.02, 26.17, 29.55, 31.99, 40.59, 68.54, 74.01, 80.17, 84.46, 87.64, 93.81, 107.00, 112.20, 116.71, 117.20, 119.83, 120.38, 125.50, 127.33, 127.87, 128.60, 129.41, 129.78, 130.49, 133.27, 133.71, 134.54, 135.12, 140.87, 150.68, 158.74. IR (KBr) ν=3088, 3057, 2951, 2926, 2868, 2802, 2194, 1918, 1622, 1591, 1524, 1365, 1225, 1185, 1017, 916, 895, 818 cm^{-1}. Anal. Calcd: C, 87.49; H, 6.76; N, 2.68. Found: C, 87.09; H, 6.64; N, 2.75. MS *m*/*z* (M^+): 521.

    Synthesis of **8**: The synthesis method and purification was similar to that of **7**, and a light yellow needle-like crystal was obtained; yield: ~35%. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.88–0.95 (m, 3H, $-CH_3$), 3.90 (s, 2H, $-NH_2$), 4.03–4.09 (m, 2H, Ar-OCH_2-), 5.44 (d, 1H, J=11.6 Hz, $=CH_2$), 5.89 (d, 1H, J=17.0 Hz, $=CH_2$), 7.09–7.15 (m, 1H, $=CH-$), 6.64 (d, 2H, J=8.4 Hz, Ar), 7.19–7.71 (11H, Ar), 7.99 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ 13.96, 22.52, 25.66, 29.04, 31.50, 68.08, 73.52, 79.62, 79.80, 84.10, 87.09, 92.76, 106.54, 112.08, 114.75, 116.24, 116.89, 119.67, 119.99, 124.83, 126.97, 127.57, 128.20, 129.02, 129.42, 130.18, 132.90, 133.14, 133.36, 134.08, 134.75, 140.50, 147.01, 158.39. IR (KBr) ν=3383, 3081, 3035, 2949, 2924, 2871, 2859, 2199, 1917, 1617, 1592, 1517, 1390, 1296, 1224, 1181, 1026, 909, 889, 832 cm^{-1}. MS *m*/*z* (M^+): 493.
14. *Synthesis of* **9**: Carbon bisulfide (10.0 ml) was added dropwise to a suspension of compound **8** (1.75 g, 3.69 mmol) and triethylenediamine hexahydrate (2.45 g, 21.88 mmol) in toluene (50 ml) at room temperature. The mixture was stirred at room temperature for 12 h and abundant precipitation was produced. A yellow power (2.40 g) was obtained by filtration and drying under vacuum. Then, solution of BTC (0.37 g, 1.26 mmol) dissolved in chloroform (5 ml) was added dropwise to a suspension of the powder in chloroform (20 ml) at room temperature. After stirred at room temperature for 4 h, the mixture was heated under reflux with constant stirring for 2 h. After cooled to room temperature, the mixture was filtered and filtrate concentrated in vacuo to remove chloroform. The crude product was isolated by evaporating the solvent and purified by column chromatography using EtOAc/pet. ether 1:1 as eluant. Pure product as a pale yellow needle-like crystal was obtained after being recrystallized in acetone; yield: 1.30 g (67%). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.90–0.94 (m, 3H, $-CH_3$), 1.35–1.87 (8H, $-CH_2-$), 4.06–4.10 (m, 2H, Ar-OCH_2-), 5.47 (d, 1H, J=11.2 Hz, $=CH_2$), 5.90 (d, 1H, J=17.3 Hz, $=CH_2$), 7.09–7.10 (m, 1H, $=CH-$), 7.20–7.73 (12H, Ar), 8.00 (s, 1H, Ar). ^{13}C NMR ($CDCl_3$): δ 14.03, 22.59, 25.74, 29.12, 31.57, 68.11, 73.46, 79.28, 80.40, 84.47, 90.50, 90.90, 106.55, 116.09, 117.11, 119.97, 120.77, 121.89, 123.46, 125.80, 126.93, 127.89, 128.14, 128.92, 129.35, 130.32, 131.20, 132.80, 132.89, 133.39, 133.87, 134.74, 136.81, 140.56, 158.36. IR (KBr) ν=3089, 3061, 2940, 2922, 2858, 2178, 2037, 1847, 1621, 1597, 1503, 1395, 1223, 1180, 1005, 933, 893, 831 cm^{-1}. Anal. Calcd: C, 82.96; H, 5.46; N, 2.61. Found: C, 82.87; H, 5.51; N, 2.69. MS *m*/*z* (M^+): 535.
15. Hu, J. S.; Zhang, B. Y.; Jia, Y. G.; Chen, S. *Macromolecules* **2003**, *36*, 9060.
16. Sekine, C.; Iwakura, K.; Konya, N.; Minami, M.; Fujisawa, K. *Liq. Cryst.* **2001**, *28*, 1375.
17. Hsu, H. F.; Lin, W. C.; Lai, Y. H.; Lin, A. Y. *Liq. Cryst.* **2003**, *30*, 939.