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Preparation and Characterization of Crosslinked Azobenzene Liquid-Crystalline Polymer Fibers

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We report the synthesis and physical properties of crosslinked liquid-crystalline polymer (CLCP) fibers consisting of a liquid-crystalline monomer and an acrylate monomer with a hydroxyl group that acts as a reactive site for crosslinking. By differential scanning calorimetry, the CLCP fibers showed a glass transition temperature around 60°C. Polarizing optical microscopy revealed that we obtained fibers with high orientation of mesogens along the fiber axis. The CLCP fibers showed deformations induced by heated the fiber to an isotropic phase.

Keywords: azobenzene; fiber; liquid crystal; photoinduced bending

INTRODUCTION

Human's muscles are made of many bundles of fibers and their anisotropic contractions are induced by electric stimuli. Recently, there has been a considerable effort to develop artificial actuator materials that can mimic muscle performance. To construct artificial muscles, it is desirable to use soft materials with high mechanical flexibility. Crosslinked liquid-crystalline polymers (CLCPs) are superior soft materials that possess both LC orders and elasticity due to polymer networks. CLCPs have been intensively investigated over the last two decades

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[1–3]. One of the most characteristic properties of the CLCPs was theoretically proposed by de Gennes *et al.* [4,5]. They suggested that a change in temperature across an isotropic to nematic transition is able to cause a strong uniaxial deformation of CLCPs at nearly constant volume (thermomechanical effects). In fact, nematic CLCPs showed anisotropic contraction along the director axis experimentally when heated above the nematic to isotropic phase transition temperature [6]. Naciri *et al.* described a synthesis and physical properties of CLCP fibers containing two side-chain mesogens. The fibers showed an anisotropic contraction induced by the nematic-isotropic phase transition [7]. Also self-assembled shape-memory fibers using triblock main-chain LC polymers showed a contraction upon heating and an elongation on cooling reversibly [8].

The phase transition of CLCPs from an LC to isotropic phase is usually induced by heating the samples to high temperature. Some photochromic molecules such as azobenzene could isothermally trigger the phase transition of LCs through the photochemical reaction of the chromophores [9]. The driving force of the photochemical phase transition is interpreted in terms of the changes in geometrical structure of the chromophores: the *trans* azobenzene, for instance, has a rod-like shape, which stabilizes the phase structure of the LC phase, while its isomer (*cis* form) is bent form and acted as an impurity that disrupts the orientational order. Finkelmann *et al.* achieved a large photocontraction by using azobenzene-containing CLCPs, which is ascribed to the change in the nematic order [10]. Recently, we have realized photoinduced bending behavior of CLCP gels and films containing azobenzene moieties [11–17]. The mechanism of the photoinduced bending behavior is the difference of volume contractions between the sample's surface and the bulk of the sample.

The aim of this paper is the preparation of photoresponsive CLCP fibers containing azobenzene moieties and to investigate their thermal and optical properties.

EXPERIMENTAL

Materials

The structures of monofunctional LC monomers, 6-[4-(4-hexyloxyphenylazo)phenoxy]hexyl acrylate (**A6AB6**), and 6-{4-[4-(6-hydroxyhexyloxy)phenylazo]phenoxy}hexyl acrylate (**A6AB6OH**) and a crosslinker 4,4'-methylenebis(phenyl isocyanate) (MDI) used in this study are shown in Figure 1. **A6AB6** was synthesized according to the method reported previously [18]. Scheme 1 shows the synthetic

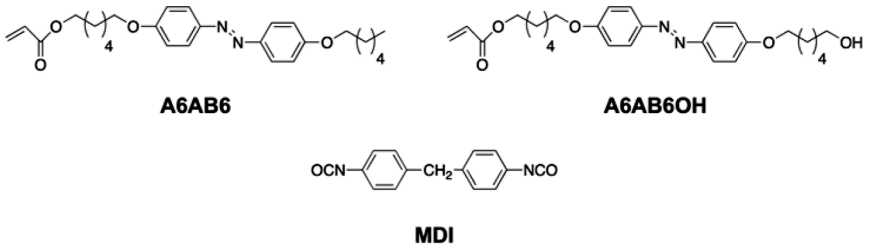
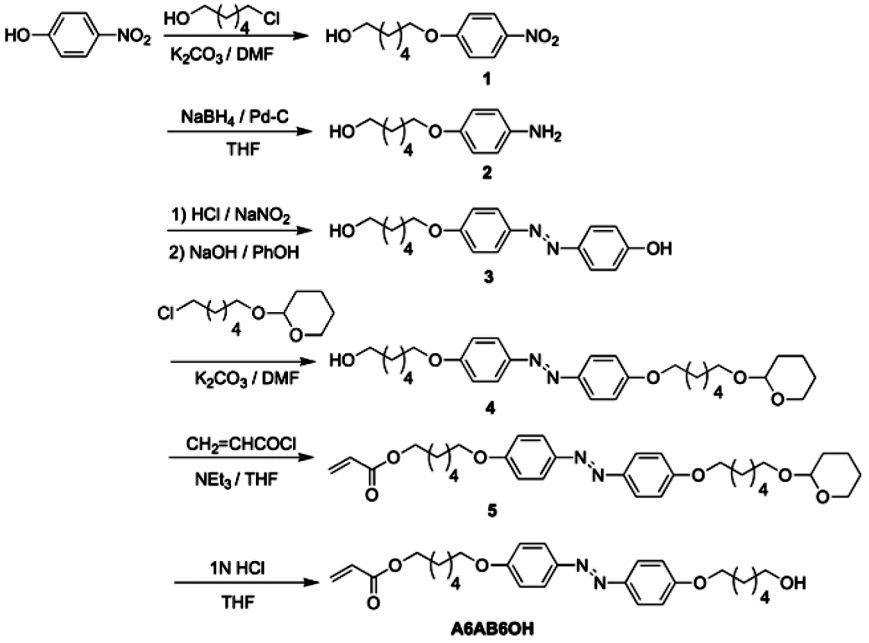


FIGURE 1 Structures and abbreviations of the LC monomers and the crosslinker used in this study.

routes of **A6AB6OH**. All reagents were purchased from Tokyo Kasei Co. or Wako Pure Chemical Industries, Ltd. The compounds synthesized were identified by means of ^{1}H NMR (JEOL, JNM-LA300), fast atom bombardment mass spectrometry (FABMS, JEOL, JMS-AX505W). Molecular weight of a copolymer was determined by gel permeation chromatography (GPC, JASCO, DG-980-50; column, Shodex GPC K802 + K804 + K805; eluent, chloroform) calibrated with standard polystyrenes.



SCHEME 1 Synthetic route for the LC monomer **A6AB6OH**.

Synthesis of an LC Monomer

4-(6-Hydroxyhexyloxy)nitrobenzene (1). A mixture of 4-nitrophenol (5.0 g, 36 mmol) and 6-chloro-1-hexanol (5.2 g, 38 mmol) was dissolved in 5 ml of DMF, and potassium carbonate (4.7 g, 34 mmol) and a trace amount of potassium iodide were added to the solution. The resulting solution was heated at 120°C for 4 h. After the reaction mixture was cooled to room temperature, 100 ml of water was added to the mixture. The precipitate was collected and extracted with ethyl acetate. The ethyl acetate solution was washed with water and dried with magnesium sulfate. After the solvent was evaporated, **1** (8.1 g, 34 mmol) was obtained in 94% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.37–1.86 (m, 8H, $-O-CH_2-(\underline{CH_2})_4-CH_2-OH$), 3.65 (t, $J = 6$ Hz, 2H, $-\underline{CH_2}OH$), 4.03 (t, $J = 6$ Hz, Hz, 2H, $-O-CH_2-$), 6.91–6.97 (m, 2H, –Ar), 8.17–8.22 (m, 2H, –Ar).

4-(6-Hydroxyhexyloxy)aniline (2). A mixture of **1** (8.1 g, 34 mmol) and Pd/C (1.6 g) was added to 55 ml of THF, and the resulting suspension was stirred vigorously at 0°C. Sodium boronhydride (5.5 g, 145 mmol) was added to the solution. The suspension was stirred at room temperature for 2 h. About 110 ml of hydrochloric acid (1 M) was added to the mixture at 0°C. The precipitate was removed and an aqueous solution of potassium carbonate was added to the mixture to give pH 10. The mixture solution was extracted with ethyl acetate and washed with water. Then the solution was dried with sodium sulfate. After the solvent was removed, **2** (6.5 g, 31 mmol) was obtained in 91% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.23–1.77 (m, 8H, $-O-CH_2-(\underline{CH_2})_4-CH_2-OH$), 3.38 (br, 2H, $-NH_2$), 3.63 (t, $J = 6$ Hz, 2H, $-\underline{CH_2}-\underline{OH}$), 3.88 (t, $J = 6$ Hz, 2H, $-O-CH_2-$), 6.55–6.64 (m, 2H, –Ar), 6.70–6.74 (m, 2H, –Ar).

4′-Hydroxy-4-(6-hydroxyhexyloxy)azobenzene (3). **2** (6.5 g, 31 mmol) was dissolved in 120 ml of hydrochloric acid (1 M) and the resulting solution was cooled at 0°C. With stirring, 2.5 g (36 mmol) of sodium nitrite in water (40 ml) was added dropwise into the solution to produce diazonium salt. A mixture of phenol (3.5 g, 37 mmol) and sodium hydroxide (2.4 g, 60 mmol) in water (100 ml) was added slowly at 0°C. An aqueous solution of potassium carbonate was added to the mixture to give pH 7, and then a yellow solid precipitated. The reaction mixture was stirred at 0°C for 3 h. After hydrochloric acid (1 M) was added to the reaction mixture to give pH 3, the precipitated solid was collected and washed with water. The crude product was recrystallized from a mixture of *n*-hexane and ethyl acetate to give **3** (6.8 g, 22 mmol) in 71% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38–1.58 (m, 6H, $-O-CH_2-CH_2-(CH_2)_3-CH_2-OH$), 1.74–1.79 (m, 2H, $-O-CH_2-CH_2-$), 3.68 (t, $J = 6$ Hz, 2H, $-CH_2-OH$), 4.04 (t, $J = 6$ Hz, 2H, $-O-CH_2-$), 6.92–7.00 (m, 4H, −Ar), 7.82–7.87 (m, 4H, −Ar).

6-(4-{4-[6-(2-Tetrahydropyranyloxy)hexyloxy]phenylazo}phenoxy)-hexanol (4). A mixture of **3** (5.0 g, 16 mmol) and 2-(6-chlorohexyloxy)-tetrahydropyran (4.0 g, 19 mmol) was dissolved in 10 ml of DMF, and potassium carbonate (3.3 g, 24 mmol) and a trace amount of potassium iodide were added to the solution. The resulting solution was heated at 120°C for 3 h. After the reaction mixture was cooled to room temperature, 100 ml of water was added to the mixture. The precipitate was collected and extracted with ethyl acetate. The ethyl acetate solution was washed with water and dried with magnesium sulfate. After the solvent was removed, the crude product was purified by recrystallization from *n*-hexane and ethyl acetate to give **4** (6.0 g, 12 mmol) in 76%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.42–1.84 (m, 22H, $-Ar-O-CH_2-(CH_2)_4-CH_2-O-$, $-O-CH_2-(CH_2)_3-CH-O-$), 3.37–3.41 (m, 2H, $-O-CH_2-(CH_2)_4-CH_2-O-CH-$), 3.65 (t, $J = 6$ Hz, 2H, $-CH_2-OH$), 3.73–3.82 (m, 2H, $-O-CH_2-(CH_2)_3-CH-O-$), 4.02 (t, $J = 7$ Hz, Hz, 4H, $-Ar-O-CH_2-$), 4.57 (t, $J = 4$ Hz, 1H, $-O-CH_2-(CH_2)_3-CH-O-$), 6.95–6.99 (m, 4H, −Ar), 7.82–7.87 (m, 4H, −Ar).

6-(4-{4-[6-(2-Tetrahydropyranyloxy)hexyloxy]phenylazo}phenoxy)-hexyl acrylate (5). A mixture of **4** (4.0 g, 8.0 mmol), triethylamine (15 ml, 108 mmol) and a trace amount of hydroquinone were dissolved in dehydrated THF (100 ml), and the resulting solution was cooled at 0°C. With stirring, 2.0 ml (24 mmol) of acryloyl chloride in dehydrated THF (40 ml) was added dropwise to the solution, and the reaction mixture was stirred at room temperature for 48 h. The reaction mixture was poured into saturated sodium hydrogen carbonate solution, and the product was extracted with chloroform. The chloroform solution was washed with water and dried with magnesium sulfate. After the solvent was removed, a yellow solid obtained was purified by column chromatography on silica gel (chloroform) and recrystallized from ethyl acetate and methanol to give **5** (3.6 g, 6.6 mmol) in 82%.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40–1.79 (m, 22H, $-Ar-O-CH_2-(CH_2)_4-CH_2-O-$, $-O-CH_2-(CH_2)_3-CH-O-$), 3.30–3.47 (m, 2H, $-O-CH_2-(CH_2)_4-CH_2-O-CH-$), 3.66–3.83 (m, 2H, $-O-CH_2-(CH_2)_3-CH-O-$), 3.99 (t, $J = 6$ Hz, 4H, $-Ar-O-CH_2-$), 4.11 (t, $J = 7$ Hz, 2H, $CH_2=CH-O-CH_2-$), 5.74 (dd, $J = 2$, 10 Hz, 1H, *cis*$-CH_2=CH-$), 6.07 (dd, $J = 10$, 17 Hz, 1H, $CH_2=CH-$), 6.33 (dd, $J = 2$, 17 Hz, 1H, *trans*$-CH_2=CH-$), 6.90–6.93 (m, 4H, −Ar), 7.79–7.82 (m, 4H, −Ar).

6-{4-[4-(6-Hydroxyhexyloxy)phenylazo]phenoxy}hexyl acrylate (A6AB6OH). **5** (3.0 g, 5.4 mmol) was dissolved in 150 ml of THF, and the resulting solution was cooled at 0°C. With stirring, 60 ml of hydrochloric acid (1 M) was added dropwise to the solution, and the reaction mixture was stirred at room temperature for 24 h. The mixture solution was extracted with ethyl acetate and washed with water. The ethyl acetate solution was dried with sodium sulfate. After the solvent was removed, a yellow solid obtained was purified by column chromatography on silica gel (chloroform) and recrystallized twice from methanol to give 2.3 g (4.8 mmol) of **A6AB6OH** in 89% yield.

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.38–1.79 (m, 16H, $-O-CH_2-(CH_2)_4-CH_2-O-$), 3.60 (t, $J = 6$ Hz, 2H, $-CH_2-OH$), 3.97 (t, $J = 7$ Hz, 4H, $-Ar-O-CH_2-$), 4.13 (t, $J = 7$ Hz, 2H, $CH_2=CHCOOCH_2-$), 5.75 (dd, $J = 2$, 10 Hz, 1H, *cis*$-CH_2-CH-$), 6.05 (dd, $J = 10$, 17 Hz, 1H, $CH_2=CH-$), 6.33 (dd, $J = 2$, 17 Hz, 1H, *trans*-$CH_2=CH-$), 6.90–6.93 (m, 4H, $-Ar$), 7.78–7.82 (m, 4H, $-Ar$). MS (FAB+) m/z: 469 (M^+). Anal. Calcd for $C_{27}H_{36}N_2O_5$: C, 69.21; H, 7.74; N, 5.98. Found: C, 69.06; H, 7.62; N, 5.94.

Polymerization of Monomers

A mixture of **A6AB6** (0.48 g, 1.1 mmol), **A6AB6OH** (0.21 g, 0.45 mmol) and 5.0 mg (0.015 mmol, 1 mol% of monomers) of azobis(isobutyronitrile) (AIBN) were dissolved in 10 ml of dry toluene. The mixture was degassed by five freeze-pump-thaw cycles and then sealed off. The mixture was stirred and heated in an oil bath at 60°C for 48 h. The cooled solution was poured into 300 ml of methanol with stirring to obtain a copolymer. The copolymer obtained was purified by reprecipitation from THF into methanol three times and dried under vacuum for 24 h to give 0.30 g of the copolymer **PAB70** in 44% yield. The number-average molecular weights (M_n) and the molecular weight distribution (M_w/M_n) determined by GPC were 7,000 and 1.2.

Characterization Methods

The thermodynamic properties of the monomers and the copolymer were determined by differential scanning calorimetry (DSC, Seiko I&E, SSC-5200 and DSC220C) at heating and cooling rates of 3°C/min for the monomers and 10°C/min for the copolymer. At least three scans were performed to check the reproducibility. The mesomorphic properties and phase transition behavior were examined with a polarizing optical microscope (POM, Olympus, BH-2) equipped with a hot

stage (Mettler, FP-90 and FP-82). The X-ray diffraction measurement of the copolymer was performed by X-ray diffractctomertry (MAC Science MXP with a thermal controller, model 5301).

RESULTS AND DISCUSSION

Mesomorphic Properties of Monomers and a Copolymer

The mesomorphic properties of the monomers and the copolymer were studied by POM, DSC and X-ray diffraction measurement. For **A6AB6**, a typical schlieren texture of a nematic phase was observed at 86°C and then isotropization occurred at 92°C upon heating. When cooled from the isotropic phase, the nematic phase appeared at 92°C and then a monotropic smectic phase at 85°C. Crystallization started at 77°C. **A6AB6OH** also exhibited an LC phase from 93 to 106°C upon heating. In addition, it was found that **PAB70** exhibited an LC phase from 71 to 140°C. X-ray diffraction measurements at 90°C for **A6AB6OH** or 100°C for **PAB70** revealed that both compounds exhibited a diffuse halo in a wide-angle region, meaning that they showed a nematic phase (Fig. 2). Thermodynamic properties of the monomers and the copolymer are summarized in Table 1.

Preparation of CLCP Fibers

The CLCP fibers were prepared from a mixture of **PAB70** and the MDI crosslinker. A small amount of **PAB70** (20 mg) was heated to

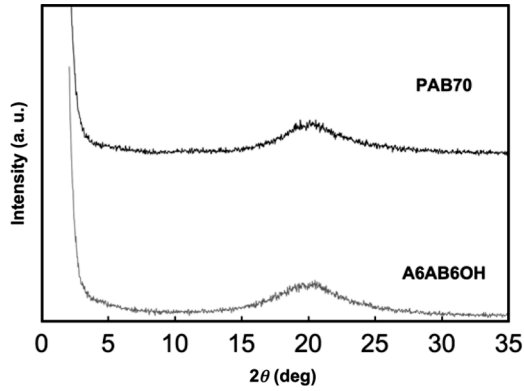


FIGURE 2 X-ray patterns of the liquid-crystalline monomer **A6AB6OH** and the copolymer **PAB70**.

TABLE 1 Phase Transition Temperature and Thermodynamic Parameters of the Monomers and the Copolymer

Compound	Phase transition temperature[a] (°C)	ΔH_{NI} (kJ/mol)	ΔS_{NI} (J/mol·K)	ΔH_{SN} (kJ/mol)	ΔS_{SN} (J/mol·K)
A6AB6	I 92 N (85 S) 77 K	1.1	3.1	1.3	3.7
A6AB6OH	I 103 N 77 K	5.6	14.7	–	–
PAB70	I 140 N 71 G	0.95	2.3	–	–

[a]I, isotropic; N, nematic; S, smectic; K, crystal; G, glass; ΔH_{NI}, change in enthalpy of N-I phase transition; ΔS_{NI}, change in entropy of N-I phase transition; ΔH_{SN}, change in enthalpy of S-N phase transition; ΔS_{SN}, change in entropy of S-N phase transition.

145°C on a glass substrate placed on a hot stage. 2 mg of MDI was added at this temperature, and then the temperature was lowered to around 125°C where **PAB70** showed a nematic phase. The sample was mixed well at this temperature for several seconds until the mixture appeared homogeneous. At this point, the mixture became viscous, indicating that the crosslinking had started to occur. The CLCP fibers were formed by dipping a tip of a pick and pulling the mixture with it as quickly as possible.

Thermal and Optical Properties of the CLCP Fiber

The DSC thermogram of the CLCP fibers is shown in Figure 3. The glass transition temperature (T_g) of the CLCP fibers appeared around 60°C. The CLCP fiber was observed by POM (Fig. 4). This figure shows the CLCP fiber placed between crossed polarizers at room

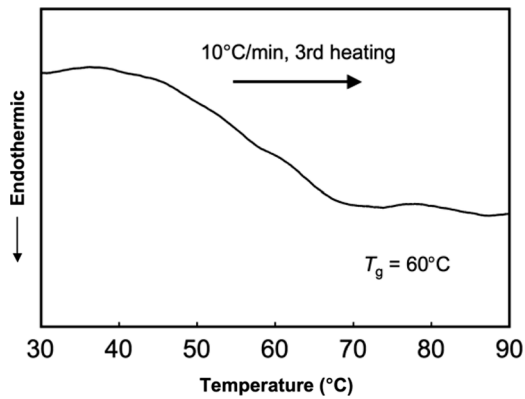


FIGURE 3 DSC thermogram of the CLCP fibers.

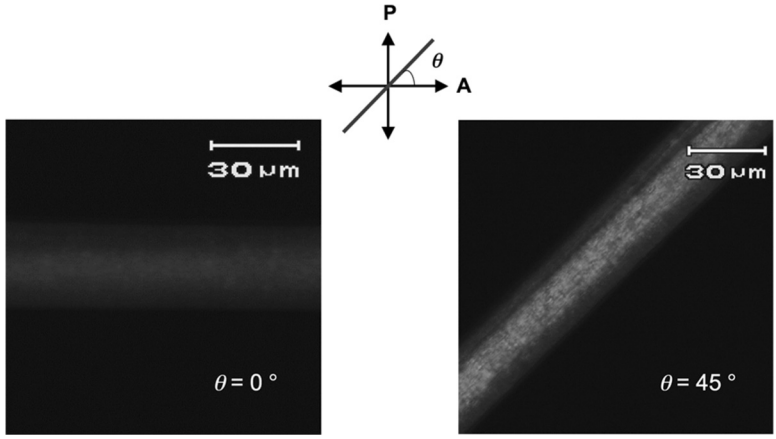


FIGURE 4 Polarizing optical micrographs of the texture of the CLCP fiber. Sample angle to the analyzer: $\theta = 0^\circ$ (a); $\theta = 45^\circ$ (b). The textures were observed at room temperature.

temperature. The CLCP fiber showed a contrast inversion upon rotating the sample to every $\pm 45^\circ$ position with respect to the analyzer. This means that the CLCP fibers have high orientation of mesogens. When the CLCP fiber was dipped in a chloroform solution as shown in Figure 5, the fiber was undissolved to the solution,

FIGURE 5 Photographs of the CLCP fiber dipping in chloroform solution.

(a) (b)

FIGURE 6 Photographs of the deformation behavior of the CLCP fibers. Temperature: 60°C (a); 180°C (b). Size of the fiber: 1.3 mm × 30 μm (a); 0.75 mm × 60 μm (b).

indicating that the CLCP fiber formed network structures by urethane bonding.

Thermomechanical Behavior of the CLCP Fiber

When the CLCP fibers were heated from an LC phase to an isotropic phase, the length of the fiber along the fiber axis was decreased, and when the fibers were cooled to room temperature, the fibers regained their original length as shown in Figure 6. The contraction of the fiber is induced by the change in the nematic order [7].

CONCLUSIONS

The CLCP fibers containing azobenzene moieties were obtained by mixing a copolymer and a crosslinker in the nematic phase. From DSC measurement, it was found that the CLCP fiber showed a T_g around 60°C. The CLCP fiber showed a contrast inversion upon rotating the sample to every $\pm 45^\circ$ position with respect to the analyzer. Also the CLCP fibers showed contractions when the fibers were heated to an isotropic phase. Furthermore, we expect that the CLCP fibers may show photoinduced bending behavior as the CLCP films previously reported. This is now under investigation.

REFERENCES

[1] Finkelmann, H., Kock, H.-J., & Rehage, G. (1981). *Makromol. Chem., Rapid Commun.*, *2*, 317.
[2] Zentel, R. (1989). *Angew. Chem. Adv. Mater.*, *101*, 1437.
[3] Terentjev, E. M. (1999). *J. Phys.-Condes. Matter*, *11*, R239.
[4] de Gennes, P.-G. (1975). *C. R. Acad. Sci. B*, *281*, 101.
[5] de Gennes, P.-G., Hebert, M., & Kant, R. (1997). *Macromol. Symp.*, *113*, 39.
[6] Küpfer, J. & Finkelmann (1994). *Macromol. Chem. Phys.*, *195*, 1353.
[7] Naciri, J., Srinvasan, A., Jeon, H., Nikolov, N., Keller, P., & Ratna, B. R. (2003). *Macromolecules*, *36*, 8499.

[8] Ahir, S. V., Tajbakhsh, A. R., & Terentjev, E. M. (2006). *Adv. Funct. Mater.*, *16*, 556.
[9] Ikeda, T. (2003). *J. Mater. Chem.*, *13*, 2037.
[10] Finkelmann, H., Nishikawa, E., Pereira, G. G., & Warner, M. (2001). *Phys. Rev. Lett.*, *87*, 015501.
[11] Ikeda, T., Nakano, M., Yu, Y., Tsutsumi, O., & Kanazawa, A. (2003). *Adv. Mater.*, *15*, 201.
[12] Yu, Y., Nakano, M., & Ikeda, T. (2003). *Nature*, *425*, 145.
[13] Yu, Y., Nakano, M., Shishido, A., Shiono, T., & Ikeda, T. (2004). *Chem. Mater.*, *16*, 1637.
[14] Yu, Y., Nakano, M., & Ikeda, T. (2004). *Pure Appl. Chem.*, *76*, 1435.
[15] Kondo, M., Yu, Y., & Ikeda, T. (2006). *Angew. Chem. Int. Ed.*, *45*, 1378.
[16] Yu, Y., Maeda, T., Mamiya, J., & Ikeda, T. (2007). *Angew. Chem. Int. Ed.*, *46*, 881.
[17] Ikeda, T., Mamiya, J., & Yu, Y. (2007). *Angew. Chem. Int. Ed.*, *46*, 506.
[18] Angeloni, A., Caretti, D., Carlini, C., Chiellini, E., Galli, G., Altomare, A., Solaro, R., & Laus, M. (1989). *Liq. Cryst.*, *4*, 513.