

Synthesis and Characterization of Photopolymerizable Liquid Crystalline Compounds Having Two Reactive Sites

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Rod-like polymerizable LC molecules having two different reactive groups, *i.e.* acryl and diacetylene groups were prepared. 4-Hydroxyphenyldiacetylenes were synthesized by the coupling reaction of 1-bromoalkynes with 4-ethynylphenol and then reacted with 4-(6-acryloyloxyalkyloxy)benzoic acid to give polymerizable LC molecules **4a-d**. The mesomorphic properties of compounds **4a-d** were investigated by differential scanning calorimetry, polarized optical microscopy and X-ray diffractometry. Compounds **4a-c** exhibited smectic and nematic phases, but compound **4d** having a longest alkyl tail among the series formed only a smectic phase. Photopolymerizability of acryl and diacetylene groups was investigated by IR spectroscopy. An anisotropic polymer film could be prepared by selective polymerization of acryl groups with 365 nm UV light in the presence of a photoinitiator (2,2-dimethoxy-2-phenylacetophenone). The subsequent reaction of diacetylene groups with 254 nm UV light disrupted the anisotropic structure, suggesting that these LC molecules could be used for imaging on the film.

Key Words : Polymerizable liquid crystal, Diacetylene, UV irradiation, Photopolymerization

Introduction

Photopolymerizable liquid crystal (LC) monomers are of great interest because of their potential applications in display and data storage industries.¹⁻³ They can be macroscopically oriented under electric or magnetic fields, and on mechanically rubbed substrates. Their *in-situ* photopolymerization in the LC state produces an anisotropic film having an aligned structure of LC molecules.⁴⁻¹⁰

There are two general methods for preparing an LC monomer. Firstly vinyl groups can be attached to both sides of a mesogen through flexible spacers. In the second method, photoreactive groups are introduced into mesogens to become parts of rigid rods. We previously reported LC molecules having two chalcone units^{11,12} or two diacetylene groups¹³ as parts of rigid rods. A chalcone is known to form a dimer by [2 + 2] addition reaction when exposed to UV light. The polymerization of the LC molecules having two chalcone units proceeds in a stepwise manner. The polymerization of diacetylenes occurs topochemically *via* 1,4-addition by irradiation.¹⁴⁻¹⁷ Since these molecules had two reactive sites within one structure, the photopolymerization in the LC state disrupted an aligned structure, resulting in optical property changes. When the photopolymerization was carried out through a photomask, an excellent-patterned image was obtained.

In this work, we prepared rod-like LC molecules having two different photopolymerizable groups, *i.e.* acryl and diacetylene groups. We introduced an acryl group at one end of a mesogen through a flexible spacer and a phenyl diacetylene group as a part of rigid rod. Since two functional groups have different photoreactivity, we expected the selective reaction of each group, depending on irradiation

conditions. We report here the synthesis and polymerization of heterobifunctional LC molecules.

Experimental Section

Measurements. ¹H and ¹³C NMR spectra were recorded on a BRUKER Avance DPX-300 and Avance 500 spectrometer. FT-IR spectra were obtained with PERKIN ELMER Spectrum GX I using a KBr window. The differential scanning calorimetry (DSC) measurements were performed with a TA modulated DSC 2090. X-ray diffractograms were obtained by using a Mac Science M18XHF-SRA (Cu K radiation, $\lambda = 1.54 \text{ \AA}$). The optical microscopy study was performed using a Leica DM LP equipped with Mettler Toledo FP 82HT heating stage and Mettler Toledo FP 90 central process controller. Elemental analysis was performed using a CE instrument EA 1110 analyzer.

Synthesis of 4-(6-Hydroxyhexyloxy)benzoic acid (1). 4-Hydroxybenzoic acid (10 g, 72.40 mmol) was dissolved in a mixture of ethanol (30 mL) and water (20 mL) along with potassium hydroxide (10.78 g, 192 mmol) and a pinch of potassium iodide. 1-Chloro-6-hydroxyhexane (9.01 g, 66 mmol) was added slowly to the mixture at room temperature while stirring vigorously, and then the mixture was refluxed for 48 h. After evaporation of the solvents, the solid residue was dissolved in water (120 mL) and washed with diethyl ether (3 \times 30 mL). The aqueous layer was acidified with concentrated HCl until the pH was 2. The precipitates were isolated by filtration, washed with water, and recrystallized from ethanol to give compound **1** in 54% yield. ¹H NMR (CDCl₃, ppm): $\delta = 8.08, 6.95$ (dd, aromatic protons, 4H), 4.20 (s, -OH, 1H), 4.05 (t, -OCH₂, 2H), 1.87-1.48 (m, alkyl chain protons, 8H).

Synthesis of 4-(6-Acryloyloxyhexyloxy)benzoic Acid (2). Compound **1** (5 g, 21.53 mmol), acrylic acid (5.71 mL, 83.3 mmol), *p*-toluene sulfonic acid (1.40 g, 7.35 mmol), and hydroquinone (0.47 g, 4.27 mmol) were dissolved in toluene. The solution was refluxed for 12 h in a flask equipped with a Dean-stark trap. After evaporation of the solvent, the residue was dissolved in chloroform (40 mL), diluted with diethyl ether (200 mL), and washed with warm water until no more acrylic acid was detected. The organic layer was dried over anhydrous MgSO_4 . After filtration and evaporation of the solvent, the solid residue was recrystallized from isopropanol to give compound **2** in 48% yield. ^1H NMR (CDCl_3 , ppm): δ = 8.08, 6.95 (dd, aromatic protons, 4H), 6.45, 6.19, 5.86 (m, vinyl protons, 3H), 4.22, 4.07 (t, $-\text{OCH}_2$, 4H), 1.87–1.46 (m, alkyl chain protons, 8H).

Synthesis of Compound 3. Compound **3** was prepared according to our previous report.¹³

Synthesis of Compound 4. A typical procedure is as follows. To compound **2** (1.84 g, 6.32 mmol) were added thionyl chloride (2.79 g, 23.48 mmol), 2,6-di-*t*-butyl 4-methylphenol (0.44 g, 1.99 mmol) as an inhibitor, and a catalytic amount of dimethylformamide (DMF) (two drops). After stirring for 40 min, the excess thionyl chloride was removed under reduced pressure. The residue was dissolved in chloroform (8 mL), and to the solution was added dropwise a solution of compound **3** ($n = 5$) (1.10 g, 4.86 mmol) and triethylamine (0.54 g, 5.35 mmol) in chloroform (15 mL) at 0 °C. After stirring for 16 h at room temperature, chloroform (100 mL) was added to the mixture and the resulting solution was washed with water (30 mL), 2 *N* sodium hydroxide (3 \times 60 mL), and water (2 \times 40 mL). The organic layer was dried over anhydrous MgSO_4 . After filtration and evaporation of the solvent, the product was isolated by column chromatography on silica gel (20% ethyl acetate in hexane) and further purified by recrystallization from ethanol to give compound **4b** in 41% yield. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 8.07, 7.63, 7.32, 7.12 (dddd, aromatic protons, 8H), 6.33, 6.22, 5.96 (m, vinyl protons, 3H), 4.14 (m, $-\text{OCH}_2$, 4H), 2.46 (t, CCH_2 , 2H), 1.62–1.22 (m, alkyl chain protons, 16H), 0.89 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2935, 2860, 2244, 2145, 1739, 1719, 1636, 1608, 1408, 989, 879, 844, 814. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.3, 122.1, 121.5, 119.8, 114.6, 114.5, 85.2, 74.7, 74.2, 68.3, 65.2, 64.7, 31.5, 29.8, 29.2, 28.8, 28.6, 28.4, 25.9, 22.7, 19.5, 13.8. Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{O}_5$: C, 76.77; H, 7.25. Found: C, 76.75; H, 7.32.

For **4a**: Yield, 53%. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 8.07, 7.64, 7.33, 7.12 (dddd, aromatic protons, 8H), 6.32, 6.20, 5.88 (m, vinyl protons, 3H), 4.11 (m, $-\text{OCH}_2$, 4H), 2.43 (t, CCH_2 , 2H), 1.51–1.38 (m, alkyl chain protons, 12H), 0.92 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2958, 2865, 2242, 2148, 1744, 1713, 1636, 1600, 1409, 1006, 987, 875, 851, 814, 805. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.4, 122.3, 121.7, 120.0, 114.9, 114.6, 85.2, 74.7, 74.2, 68.3, 65.3, 64.7, 30.5, 29.8, 29.2, 28.8, 25.9, 22.2, 19.5, 13.8. Anal. Calcd for

$\text{C}_{30}\text{H}_{32}\text{O}_5$: C, 76.25; H, 6.83. Found: C, 75.94; H, 6.82.

For **4c**: Yield, 48%. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 7.96, 7.53, 7.22, 7.02 (dddd, aromatic protons, 8H), 6.19, 6.11, 5.85 (m, vinyl protons, 3H), 4.03 (m, $-\text{OCH}_2$, 4H), 2.34 (t, CCH_2 , 2H), 1.64–1.15 (m, alkyl chain protons, 20H), 0.76 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2931, 2854, 2243, 2145, 1737, 1723, 1635, 1606, 1408, 1000, 985, 875, 844, 811. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.4, 122.1, 121.4, 119.8, 114.8, 114.6, 85.2, 74.7, 74.2, 68.3, 65.2, 64.7, 32.1, 29.7, 29.4, 29.3, 29.2, 29.1, 28.8, 28.5, 25.9, 22.9, 19.8, 14.3. Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{O}_5$: C, 77.24; H, 7.63. Found: C, 77.25; H, 7.66.

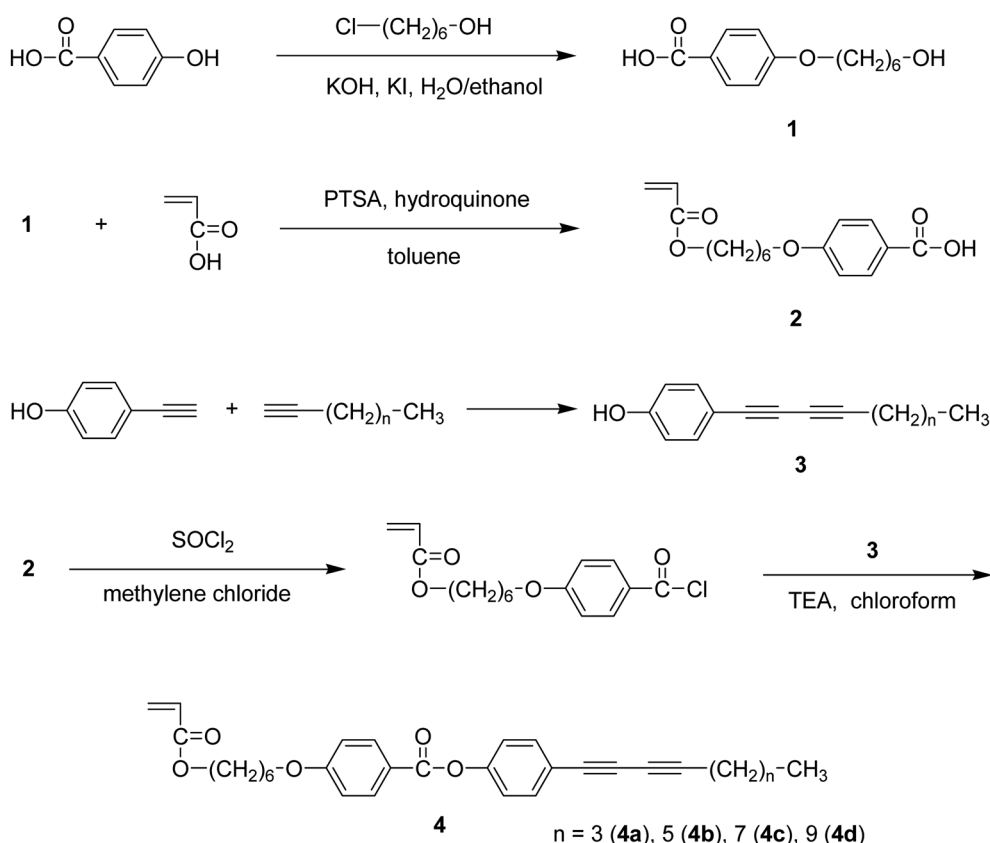
For **4d**: Yield, 47%. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 8.07, 7.64, 7.32, 7.12 (dddd, aromatic protons, 8H), 6.30, 6.21, 5.95 (m, vinyl protons, 3H), 4.13 (m, $-\text{OCH}_2$, 4H), 2.44 (t, CCH_2 , 2H), 1.75–1.33 (m, alkyl chain protons, 24H), 0.88 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2924, 2854, 2244, 2144, 1742, 1721, 1634, 1602, 1409, 1006, 990, 875, 853, 813, 802. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.3, 122.1, 121.4, 119.8, 114.6, 114.5, 85.2, 74.7, 74.2, 68.3, 65.2, 64.7, 32.1, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 28.8, 28.5, 25.9, 22.9, 19.8, 14.3. Anal. Calcd for $\text{C}_{36}\text{H}_{44}\text{O}_5$: C, 77.66; H, 7.97. Found: C, 77.77; H, 8.00.

Radical Polymerization of Compound 4b. In a 10 mL polymerization tube, compound **4b** (0.3 g, 0.56 mmol) and AIBN (0.0046 g, 0.028 mmol) were dissolved in dry THF (3 mL). The reaction mixture was degassed by a freeze-thaw method to remove oxygen. After sealing the ampule, the mixture was heated with stirring at 60 °C for 48 h. The polymer was isolated and dropped into *n*-hexane to precipitate the polymer. The polymer was dried for 24 h in vacuum oven. Yield, 36.7%. ^1H NMR (CDCl_3 , 300 MHz): δ = 8.15–6.9 (8H, Ar-H), 4.22–2.35 (6H, $-\text{OCH}_2$, CCH_2), 1.82–1.25 (m, 19H, polymer backbone and alkyl chain protons), 0.83 (3H, $-\text{CH}_3$).

Results and Discussion

Synthesis of Polymerizable Mesogens. The rod-like mesogenic monomers were prepared according to Scheme 1. 4-Hydroxybenzoic acid was reacted with 6-chlorohexanol to yield compound **1**. An acryl group was introduced to compound **1** by esterification reaction with acrylic acid. The carboxyl end group of acryl compound **2** was converted to acid chloride with thionyl chloride and then reacted with 4-hydroxyphenyldiacetylenes **3**, which were synthesized by the coupling reaction of 1-bromoalkynes with 4-ethynylphenol, to give compounds **4a–d**. The structures of all products were identified by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis.

Mesomorphic Properties. The mesomorphic properties of compounds **4a–d** were investigated by DSC, polarized optical microscopy (POM) and X-ray diffractometry. The compounds showed enantiotropic transitions. In the DSC study, sharp phase transitions were observed upon heating



Scheme 1

and cooling with a scan rate of 5 °C/min. For example, compound **4b** showed three endothermic peaks at 55.4 °C ($\Delta H = 31.5$ kJ/mol), 79.7 °C ($\Delta H = 1.67$ kJ/mol), and 86.1 °C ($\Delta H = 0.38$ kJ/mol) during the 2nd heating, and three exothermic peaks at 84.8 °C ($\Delta H = 0.76$ kJ/mol), 78.4 °C ($\Delta H = 1.66$ kJ/mol), and 3.7 °C ($\Delta H = 20.6$ kJ/mol) during

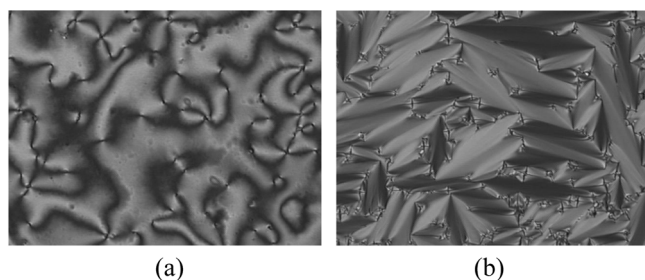


Figure 1. Polarizing optical micrographs of **4b** taken (a) at 83 °C and (b) at 50 °C on cooling.

the 2nd cooling. In POM analysis, a focal conic fan-type texture appeared from 55.4 °C and then a Schlieren texture above 79.7 °C on heating, corresponding to a smectic and a nematic phase, respectively (Figure 1). The same textures were observed on cooling. Compounds **4a** and **4c** also exhibited two LC phases, but compound **4d** having a longest alkyl tail among the series formed only a smectic phase. The thermal transitions of **4a-d** are summarized in Table 1.

The structures of the smectic phases of **4a-d** were further investigated by using an X-ray diffraction technique. Figure 2 shows the X-ray diffractogram of **4b** measured at 50 °C. In the small-angle region, three sharp peaks with d spacings of 35.9, 17.8, and 11.8 Å appeared, corresponding to the (100), (200), and (300) Bragg reflections, respectively. Since the length of the molecule was calculated to be 35.7 Å, which was almost the same as the (100) spacing of 35.9 Å, it seems that the compound had a monolayered smectic A structure. Other compounds also showed similar results. The X-ray

Table 1. Phase transition temperatures (°C) and enthalpy values (in parentheses, kJ/mol) of compounds **4a-d** determined by DSC at a rate of 5 °C min⁻¹

Compound	2 nd heating	2 nd cooling
4a	K 63.8 (33.1) Sm 83.8 (4.36) N 92.1 (0.77) I	I 91.7 (0.60) N 83.3 (2.16) Sm 27.2 (19.5) K
4b	K 55.4 (31.5) Sm 79.7 (1.67) N 86.1 (0.38) I	I 84.8 (0.76) N 78.4 (1.66) Sm 3.7 (20.6) K
4c	K 21.2 (0.8) Sm 81.5 (3.37) N 84.8 (0.95) I	I 83.0 (0.89) N 80.0 (1.86) Sm -11.5 (0.6) K
4d	K 47.7 (26.3) Sm 82.4 (8.27) I	I 80.3 (7.90) Sm -6.6 (20.4) K

^aK = crystal; Sm = smectic; N = nematic; I = isotropic.

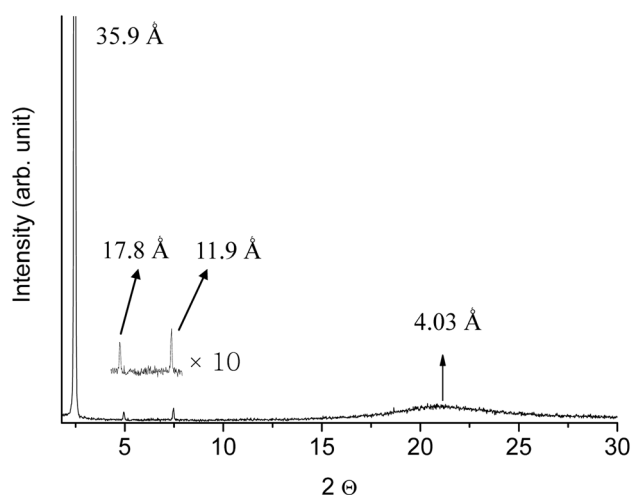


Figure 2. X-ray diffractogram of compound **4b**, obtained at 50 °C.

Table 2. X-ray diffraction data of the smectic phases of compounds **4a-d** obtained at 50 °C

Compound	d_{exp} (Å) ^a	d_{calc} (Å) ^b	(hkl)
4a	33.2	33.5	(100)
	16.5	16.7	(200)
	10.9	11.1	(300)
4b	35.9	35.7	(100)
	17.8	17.8	(200)
	11.8	11.9	(300)
4c	38.7	38.3	(100)
	18.8	19.1	(200)
	12.6	12.7	(300)
4d	40.9	40.9	(100)
	21.5	20.5	(200)
	14.2	13.7	(300)

^aObserved from XRD analysis. ^bEstimated from an extended molecular model.

diffraction data are summarized in Table 2.

Photopolymerization. Photopolymerizability of an acryl and a diacetylene groups was investigated by IR spectroscopy. A solution of **4b** (0.1 g) and a photoinitiator (2,2-dimethoxy-2-phenylacetophenone, 4 wt %) in toluene (0.4 mL) was cast on a KBr window, dried *in vacuo*, and sheared with a cover glass at 50 °C. The sample was first irradiated with 365 nm UV light (1 mW/cm²). The IR band intensity at 1636 cm⁻¹ for C=C stretching of a vinyl group gradually decreased with increasing irradiation time, while the intensity of the band at 2241 cm⁻¹ for a diacetylene group changed little, indicating the selective polymerization of the vinyl group (Figure 3). When irradiated with 254 nm UV light (3 mW/cm²), the diacetylene group was polymerized, resulting in a decrease in the intensity of the band at 2241 cm⁻¹. Figure 4 shows a polar plot of the absorbance of the IR peak at 1731 cm⁻¹ versus polarization angle. After shearing in the LC state, the molecules were oriented mostly parallel to the shearing direction. The oriented LC structure was maintained when about 50% of vinyl groups were polymerized by irradiation with 365 nm UV light. The

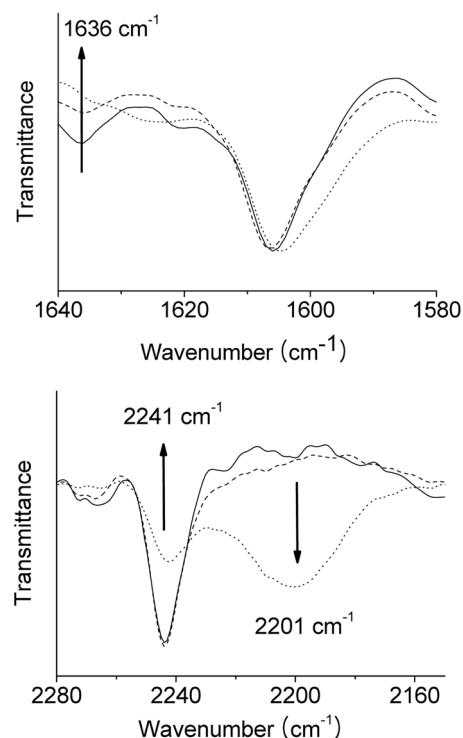


Figure 3. FT-IR spectral changes of compound **4b**; before UV irradiation (solid line), after 365 nm UV irradiation for 10 min (dashed line), and after 365 nm UV irradiation for 10 min and 254 nm UV irradiation for 60 min (dotted line).

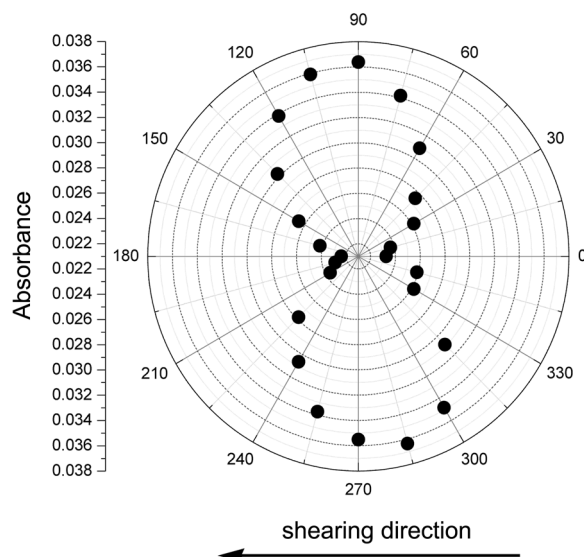


Figure 4. Polar plot of the absorbance of the IR peak for the C=O stretch at 1731 cm⁻¹ versus polarization angle for **4b**.

aligned structure was disrupted by irradiation with 254 nm UV light, which caused cross-linking.

Radical Polymerization. The acryl group of compound **4b** could be radically polymerized by initiation with AIBN in THF at 60 °C. Number average molecular weight and weight average molecular weight of the polymer measured by GPC were 7000 and 9790, respectively. The polymer formed a smectic phase. In DSC analysis, an endothermic

peak corresponding to isotropization was observed at 96.0 °C on 2nd heating. On cooling, a weak exothermic peak appeared at 92.0 °C. A birefringent phase began to form at 92.0 °C and persisted to room temperature. In the X-ray diffractogram, a relatively sharp peak with *d* spacing of 35.2 Å appeared. We examined the miscibility of **4b** and the acryl polymer by POM. The 7:3 mixture of **4b** and the polymer showed isotropization at 94 °C. On cooling from the isotropic state with a rate of 5 °C/min, however, phase separation occurred. This result is in contrast to the observation that the LC structure was maintained during in-situ polymerization of the vinyl group with 365 nm UV light in the LC state.

In summary, we prepared LC molecules having two different photopolymerizable groups, *i.e.* an acryl and a diacetylene group and examined their photoreactivity. An anisotropic polymer film could be prepared by selective polymerization of the acryl group with 365 nm UV light in the presence of a photoinitiator. The subsequent reaction of diacetylene groups with 254 nm UV light disrupted the anisotropic structure, suggesting that these LC molecules could be used for imaging on the film.

Acknowledgement. Financial support from the Korea Science and Engineering Foundation, through the Hyperstructured Organic Materials Center is gratefully acknowledged.

References

1. Broer, D. J.; Mol, G. N. *Makromol. Chem.* **1989**, *190*, 19.
2. Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.
3. Yoshio, M.; Kagata, T.; Hoshino, K.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2006**, *128*, 5570.
4. Penterman, R.; Klink, S. I.; de Koning, H.; Nisato, G.; Broer, D. J. *Nature* **2002**, *417*, 55.
5. Kondo, M.; Yu, Y.; Ikeda, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 1378.
6. Ree, M. *Macromol. Res.* **2006**, *14*, 1.
7. Baxter, B. C.; Gin, D. L. *Macromolecules* **1998**, *31*, 4419.
8. Hoag, B. P.; Gin, D. L. *Macromolecules* **2000**, *33*, 8549.
9. Vlachos, P.; Kelly, S. M.; Mansoor, B.; ÓNeill, M. *Chem. Commun.* **2002**, 874.
10. Beyer, P.; Krueger, M.; Giesselmann, F.; Zentel, R. *Adv. Funct. Mater.* **2007**, *17*, 109.
11. Chang, J. Y.; Nam, S. W.; Hong, C. G.; Im, J.-H.; Kim, J.-H.; Han, M. J. *Adv. Mater.* **2001**, *13*, 1298.
12. Nam, S. W.; Kang, S. H.; Chang, J. Y. *Macromol. Res.* **2007**, *15*, 74.
13. Cho, H. J.; Seo, K.; Lee, C. J.; Yun, H.; Chang, J. Y. *J. Mater. Chem.* **2003**, *13*, 986.
14. Lee, C. J.; Lee, S. J.; Chang, J. Y. *Tetrahedron Lett.* **2002**, *43*, 3863.
15. Hwang, I. H.; Lee, S. J.; Chang, J. Y. *J. Polym. Sci., Polym. Chem. Ed.* **2003**, *41*, 1881.
16. Chang, J. Y.; Baik, J. H.; Lee, C. B.; Han, M. J.; Hong, S.-K. *J. Am. Chem. Soc.* **1997**, *119*, 3197.
17. Chang, J. Y.; Yeon, J. R.; Shin, Y. S.; Han, M. J.; Hong, S.-K. *Chem. Mater.* **2000**, *12*, 1076.

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Measurements. ¹H and ¹³C NMR spectra were recorded on a BRUKER Avance DPX-300 and Avance 500 spectrometer. FT-IR spectra were obtained with PERKIN ELMER Spectrum GX I using a KBr window. The differential scanning calorimetry (DSC) measurements were performed with a TA modulated DSC 2090. X-ray diffractograms were obtained by using a Mac Science M18XHF-SRA (Cu K radiation, $\lambda = 1.54 \text{ \AA}$). The optical microscopy study was performed using a Leica DM LP equipped with Mettler Toledo FP 82HT heating stage and Mettler Toledo FP 90 central process controller. Elemental analysis was performed using a CE instrument EA 1110 analyzer.

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Synthesis of 4-(6-Acryloyloxyhexyloxy)benzoic Acid (2). Compound **1** (5 g, 21.53 mmol), acrylic acid (5.71 mL, 83.3 mmol), *p*-toluene sulfonic acid (1.40 g, 7.35 mmol), and hydroquinone (0.47 g, 4.27 mmol) were dissolved in toluene. The solution was refluxed for 12 h in a flask equipped with a Dean-stark trap. After evaporation of the solvent, the residue was dissolved in chloroform (40 mL), diluted with diethyl ether (200 mL), and washed with warm water until no more acrylic acid was detected. The organic layer was dried over anhydrous MgSO_4 . After filtration and evaporation of the solvent, the solid residue was recrystallized from isopropanol to give compound **2** in 48% yield. ^1H NMR (CDCl_3 , ppm): δ = 8.08, 6.95 (dd, aromatic protons, 4H), 6.45, 6.19, 5.86 (m, vinyl protons, 3H), 4.22, 4.07 (t, $-\text{OCH}_2$, 4H), 1.87–1.46 (m, alkyl chain protons, 8H).

Synthesis of Compound 3. Compound **3** was prepared according to our previous report.¹³

Synthesis of Compound 4. A typical procedure is as follows. To compound **2** (1.84 g, 6.32 mmol) were added thionyl chloride (2.79 g, 23.48 mmol), 2,6-di-*t*-butyl 4-methylphenol (0.44 g, 1.99 mmol) as an inhibitor, and a catalytic amount of dimethylformamide (DMF) (two drops). After stirring for 40 min, the excess thionyl chloride was removed under reduced pressure. The residue was dissolved in chloroform (8 mL), and to the solution was added dropwise a solution of compound **3** ($n = 5$) (1.10 g, 4.86 mmol) and triethylamine (0.54 g, 5.35 mmol) in chloroform (15 mL) at 0 °C. After stirring for 16 h at room temperature, chloroform (100 mL) was added to the mixture and the resulting solution was washed with water (30 mL), 2 *N* sodium hydroxide (3×60 mL), and water (2×40 mL). The organic layer was dried over anhydrous MgSO_4 . After filtration and evaporation of the solvent, the product was isolated by column chromatography on silica gel (20% ethyl acetate in hexane) and further purified by recrystallization from ethanol to give compound **4b** in 41% yield. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 8.07, 7.63, 7.32, 7.12 (dddd, aromatic protons, 8H), 6.33, 6.22, 5.96 (m, vinyl protons, 3H), 4.14 (m, $-\text{OCH}_2$, 4H), 2.46 (t, CCH_2 , 2H), 1.62–1.22 (m, alkyl chain protons, 16H), 0.89 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2935, 2860, 2244, 2145, 1739, 1719, 1636, 1608, 1408, 989, 879, 844, 814. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.3, 122.1, 121.5, 119.8, 114.6, 114.5, 85.2, 74.7, 74.2, 68.3, 65.2, 64.7, 31.5, 29.8, 29.2, 28.8, 28.6, 28.4, 25.9, 22.7, 19.5, 13.8. Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{O}_5$: C, 76.77; H, 7.25. Found: C, 76.75; H, 7.32.

For **4a**: Yield, 53%. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 8.07, 7.64, 7.33, 7.12 (dddd, aromatic protons, 8H), 6.32, 6.20, 5.88 (m, vinyl protons, 3H), 4.11 (m, $-\text{OCH}_2$, 4H), 2.43 (t, CCH_2 , 2H), 1.51–1.38 (m, alkyl chain protons, 12H), 0.92 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2958, 2865, 2242, 2148, 1744, 1713, 1636, 1600, 1409, 1006, 987, 875, 851, 814, 805. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.4, 122.3, 121.7, 120.0, 114.9, 114.6, 85.2, 74.7, 74.2, 68.3, 65.3, 64.7, 30.5, 29.8, 29.2, 28.8, 25.9, 22.2, 19.5, 13.8. Anal. Calcd for

$\text{C}_{30}\text{H}_{32}\text{O}_5$: C, 76.25; H, 6.83. Found: C, 75.94; H, 6.82.

For **4c**: Yield, 48%. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 7.96, 7.53, 7.22, 7.02 (dddd, aromatic protons, 8H), 6.19, 6.11, 5.85 (m, vinyl protons, 3H), 4.03 (m, $-\text{OCH}_2$, 4H), 2.34 (t, CCH_2 , 2H), 1.64–1.15 (m, alkyl chain protons, 20H), 0.76 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2931, 2854, 2243, 2145, 1737, 1723, 1635, 1606, 1408, 1000, 985, 875, 844, 811. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.4, 122.1, 121.4, 119.8, 114.8, 114.6, 85.2, 74.7, 74.2, 68.3, 65.2, 64.7, 32.1, 29.7, 29.4, 29.3, 29.2, 29.1, 28.8, 28.5, 25.9, 22.9, 19.8, 14.3. Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{O}_5$: C, 77.24; H, 7.63. Found: C, 77.25; H, 7.66.

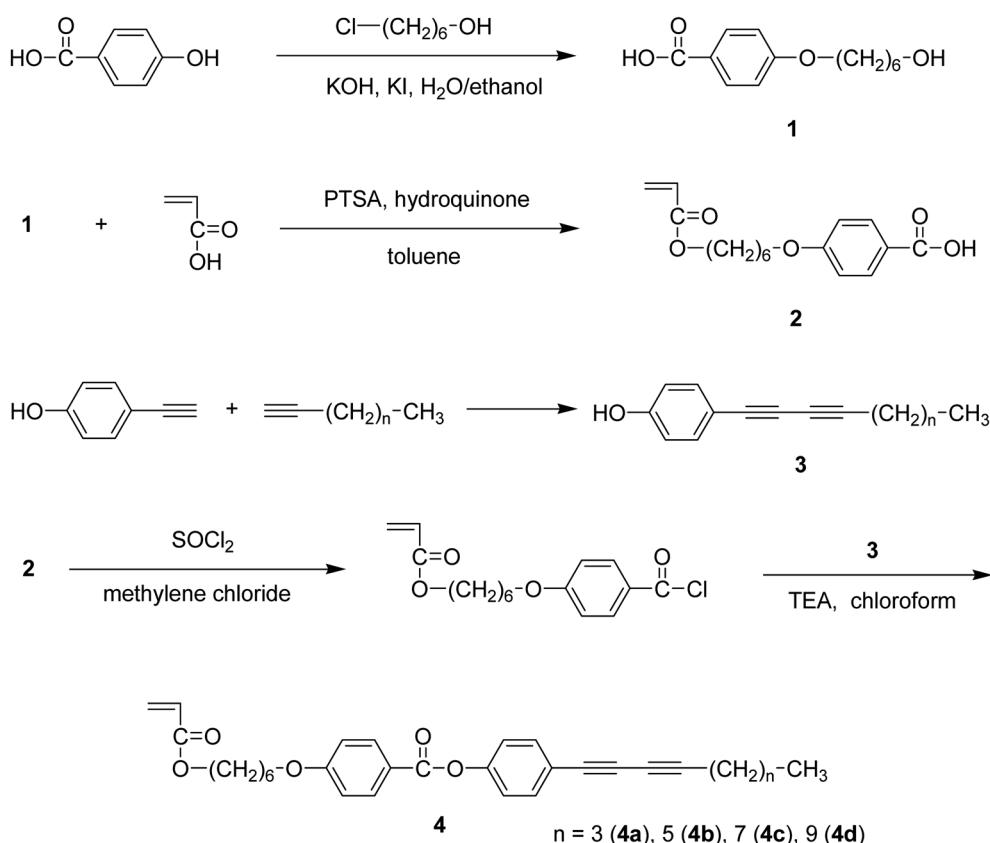
For **4d**: Yield, 47%. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 8.07, 7.64, 7.32, 7.12 (dddd, aromatic protons, 8H), 6.30, 6.21, 5.95 (m, vinyl protons, 3H), 4.13 (m, $-\text{OCH}_2$, 4H), 2.44 (t, CCH_2 , 2H), 1.75–1.33 (m, alkyl chain protons, 24H), 0.88 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2924, 2854, 2244, 2144, 1742, 1721, 1634, 1602, 1409, 1006, 990, 875, 853, 813, 802. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.3, 122.1, 121.4, 119.8, 114.6, 114.5, 85.2, 74.7, 74.2, 68.3, 65.2, 64.7, 32.1, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 28.8, 28.5, 25.9, 22.9, 19.8, 14.3. Anal. Calcd for $\text{C}_{36}\text{H}_{44}\text{O}_5$: C, 77.66; H, 7.97. Found: C, 77.77; H, 8.00.

Radical Polymerization of Compound 4b. In a 10 mL polymerization tube, compound **4b** (0.3 g, 0.56 mmol) and AIBN (0.0046 g, 0.028 mmol) were dissolved in dry THF (3 mL). The reaction mixture was degassed by a freeze-thaw method to remove oxygen. After sealing the ampule, the mixture was heated with stirring at 60 °C for 48 h. The polymer was isolated and dropped into *n*-hexane to precipitate the polymer. The polymer was dried for 24 h in vacuum oven. Yield, 36.7%. ^1H NMR (CDCl_3 , 300 MHz): δ = 8.15–6.9 (8H, Ar-H), 4.22–2.35 (6H, $-\text{OCH}_2$, CCH_2), 1.82–1.25 (m, 19H, polymer backbone and alkyl chain protons), 0.83 (3H, $-\text{CH}_3$).

Results and Discussion

Synthesis of Polymerizable Mesogens. The rod-like mesogenic monomers were prepared according to Scheme 1. 4-Hydroxybenzoic acid was reacted with 6-chlorohexanol to yield compound **1**. An acryl group was introduced to compound **1** by esterification reaction with acrylic acid. The carboxyl end group of acryl compound **2** was converted to acid chloride with thionyl chloride and then reacted with 4-hydroxyphenyldiacetylenes **3**, which were synthesized by the coupling reaction of 1-bromoalkynes with 4-ethynylphenol, to give compounds **4a–d**. The structures of all products were identified by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis.

Mesomorphic Properties. The mesomorphic properties of compounds **4a–d** were investigated by DSC, polarized optical microscopy (POM) and X-ray diffractometry. The compounds showed enantiotropic transitions. In the DSC study, sharp phase transitions were observed upon heating



Scheme 1

and cooling with a scan rate of 5 °C/min. For example, compound **4b** showed three endothermic peaks at 55.4 °C ($\Delta H = 31.5$ kJ/mol), 79.7 °C ($\Delta H = 1.67$ kJ/mol), and 86.1 °C ($\Delta H = 0.38$ kJ/mol) during the 2nd heating, and three exothermic peaks at 84.8 °C ($\Delta H = 0.76$ kJ/mol), 78.4 °C ($\Delta H = 1.66$ kJ/mol), and 3.7 °C ($\Delta H = 20.6$ kJ/mol) during

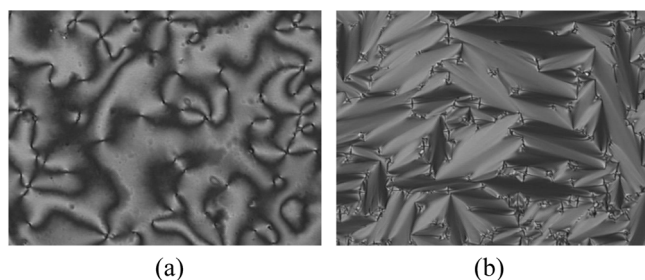


Figure 1. Polarizing optical micrographs of **4b** taken (a) at 83 °C and (b) at 50 °C on cooling.

the 2nd cooling. In POM analysis, a focal conic fan-type texture appeared from 55.4 °C and then a Schlieren texture above 79.7 °C on heating, corresponding to a smectic and a nematic phase, respectively (Figure 1). The same textures were observed on cooling. Compounds **4a** and **4c** also exhibited two LC phases, but compound **4d** having a longest alkyl tail among the series formed only a smectic phase. The thermal transitions of **4a-d** are summarized in Table 1.

The structures of the smectic phases of **4a-d** were further investigated by using an X-ray diffraction technique. Figure 2 shows the X-ray diffractogram of **4b** measured at 50 °C. In the small-angle region, three sharp peaks with d spacings of 35.9, 17.8, and 11.8 Å appeared, corresponding to the (100), (200), and (300) Bragg reflections, respectively. Since the length of the molecule was calculated to be 35.7 Å, which was almost the same as the (100) spacing of 35.9 Å, it seems that the compound had a monolayered smectic A structure. Other compounds also showed similar results. The X-ray

Table 1. Phase transition temperatures (°C) and enthalpy values (in parentheses, kJ/mol) of compounds **4a-d** determined by DSC at a rate of 5 °C min⁻¹

Compound	2 nd heating	2 nd cooling
4a	K 63.8 (33.1) Sm 83.8 (4.36) N 92.1 (0.77) I	I 91.7 (0.60) N 83.3 (2.16) Sm 27.2 (19.5) K
4b	K 55.4 (31.5) Sm 79.7 (1.67) N 86.1 (0.38) I	I 84.8 (0.76) N 78.4 (1.66) Sm 3.7 (20.6) K
4c	K 21.2 (0.8) Sm 81.5 (3.37) N 84.8 (0.95) I	I 83.0 (0.89) N 80.0 (1.86) Sm -11.5 (0.6) K
4d	K 47.7 (26.3) Sm 82.4 (8.27) I	I 80.3 (7.90) Sm -6.6 (20.4) K

^aK = crystal; Sm = smectic; N = nematic; I = isotropic.

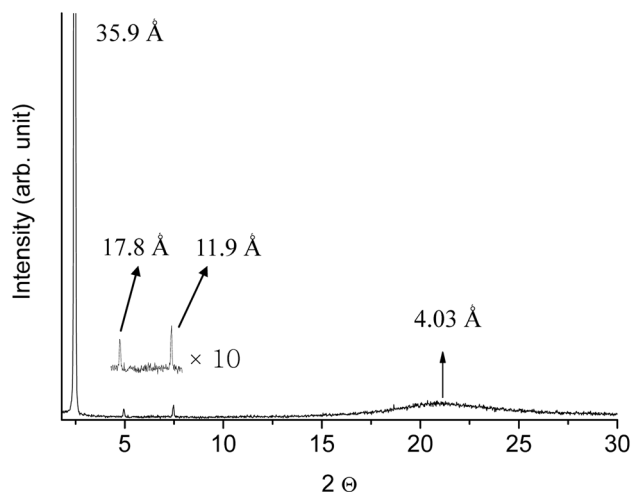


Figure 2. X-ray diffractogram of compound **4b**, obtained at 50 °C.

Table 2. X-ray diffraction data of the smectic phases of compounds **4a-d** obtained at 50 °C

Compound	d_{exp} (Å) ^a	d_{calc} (Å) ^b	(hkl)
4a	33.2	33.5	(100)
	16.5	16.7	(200)
	10.9	11.1	(300)
4b	35.9	35.7	(100)
	17.8	17.8	(200)
	11.8	11.9	(300)
4c	38.7	38.3	(100)
	18.8	19.1	(200)
	12.6	12.7	(300)
4d	40.9	40.9	(100)
	21.5	20.5	(200)
	14.2	13.7	(300)

^aObserved from XRD analysis. ^bEstimated from an extended molecular model.

diffraction data are summarized in Table 2.

Photopolymerization. Photopolymerizability of an acryl and a diacetylene groups was investigated by IR spectroscopy. A solution of **4b** (0.1 g) and a photoinitiator (2,2-dimethoxy-2-phenylacetophenone, 4 wt %) in toluene (0.4 mL) was cast on a KBr window, dried *in vacuo*, and sheared with a cover glass at 50 °C. The sample was first irradiated with 365 nm UV light (1 mW/cm²). The IR band intensity at 1636 cm⁻¹ for C=C stretching of a vinyl group gradually decreased with increasing irradiation time, while the intensity of the band at 2241 cm⁻¹ for a diacetylene group changed little, indicating the selective polymerization of the vinyl group (Figure 3). When irradiated with 254 nm UV light (3 mW/cm²), the diacetylene group was polymerized, resulting in a decrease in the intensity of the band at 2241 cm⁻¹. Figure 4 shows a polar plot of the absorbance of the IR peak at 1731 cm⁻¹ versus polarization angle. After shearing in the LC state, the molecules were oriented mostly parallel to the shearing direction. The oriented LC structure was maintained when about 50% of vinyl groups were polymerized by irradiation with 365 nm UV light. The

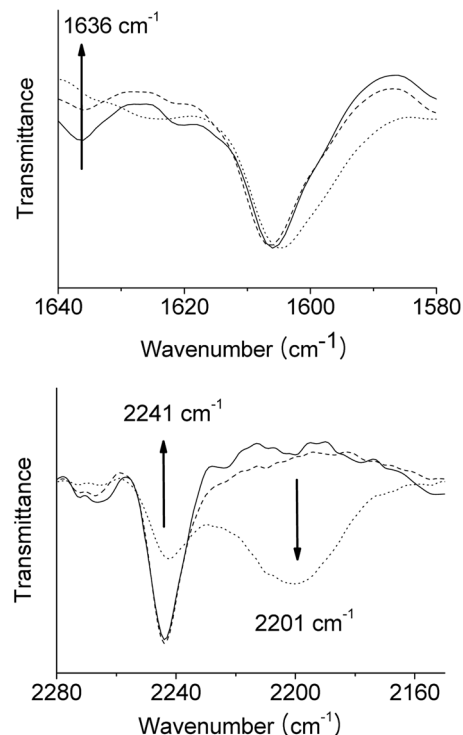


Figure 3. FT-IR spectral changes of compound **4b**; before UV irradiation (solid line), after 365 nm UV irradiation for 10 min (dashed line), and after 365 nm UV irradiation for 10 min and 254 nm UV irradiation for 60 min (dotted line).

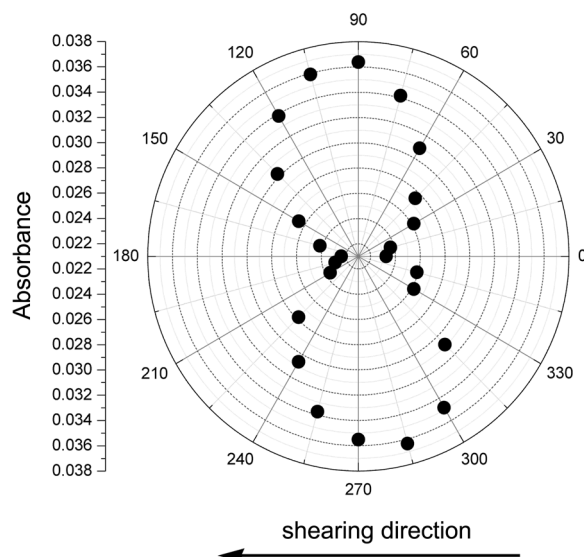


Figure 4. Polar plot of the absorbance of the IR peak for the C=O stretch at 1731 cm⁻¹ versus polarization angle for **4b**.

aligned structure was disrupted by irradiation with 254 nm UV light, which caused cross-linking.

Radical Polymerization. The acryl group of compound **4b** could be radically polymerized by initiation with AIBN in THF at 60 °C. Number average molecular weight and weight average molecular weight of the polymer measured by GPC were 7000 and 9790, respectively. The polymer formed a smectic phase. In DSC analysis, an endothermic

peak corresponding to isotropization was observed at 96.0 °C on 2nd heating. On cooling, a weak exothermic peak appeared at 92.0 °C. A birefringent phase began to form at 92.0 °C and persisted to room temperature. In the X-ray diffractogram, a relatively sharp peak with *d* spacing of 35.2 Å appeared. We examined the miscibility of **4b** and the acryl polymer by POM. The 7:3 mixture of **4b** and the polymer showed isotropization at 94 °C. On cooling from the isotropic state with a rate of 5 °C/min, however, phase separation occurred. This result is in contrast to the observation that the LC structure was maintained during in-situ polymerization of the vinyl group with 365 nm UV light in the LC state.

In summary, we prepared LC molecules having two different photopolymerizable groups, *i.e.* an acryl and a diacetylene group and examined their photoreactivity. An anisotropic polymer film could be prepared by selective polymerization of the acryl group with 365 nm UV light in the presence of a photoinitiator. The subsequent reaction of diacetylene groups with 254 nm UV light disrupted the anisotropic structure, suggesting that these LC molecules could be used for imaging on the film.

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References

1. Broer, D. J.; Mol, G. N. *Makromol. Chem.* **1989**, *190*, 19.
2. Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.
3. Yoshio, M.; Kagata, T.; Hoshino, K.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2006**, *128*, 5570.
4. Penterman, R.; Klink, S. I.; de Koning, H.; Nisato, G.; Broer, D. J. *Nature* **2002**, *417*, 55.
5. Kondo, M.; Yu, Y.; Ikeda, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 1378.
6. Ree, M. *Macromol. Res.* **2006**, *14*, 1.
7. Baxter, B. C.; Gin, D. L. *Macromolecules* **1998**, *31*, 4419.
8. Hoag, B. P.; Gin, D. L. *Macromolecules* **2000**, *33*, 8549.
9. Vlachos, P.; Kelly, S. M.; Mansoor, B.; ÓNeill, M. *Chem. Commun.* **2002**, 874.
10. Beyer, P.; Krueger, M.; Giesselmann, F.; Zentel, R. *Adv. Funct. Mater.* **2007**, *17*, 109.
11. Chang, J. Y.; Nam, S. W.; Hong, C. G.; Im, J.-H.; Kim, J.-H.; Han, M. J. *Adv. Mater.* **2001**, *13*, 1298.
12. Nam, S. W.; Kang, S. H.; Chang, J. Y. *Macromol. Res.* **2007**, *15*, 74.
13. Cho, H. J.; Seo, K.; Lee, C. J.; Yun, H.; Chang, J. Y. *J. Mater. Chem.* **2003**, *13*, 986.
14. Lee, C. J.; Lee, S. J.; Chang, J. Y. *Tetrahedron Lett.* **2002**, *43*, 3863.
15. Hwang, I. H.; Lee, S. J.; Chang, J. Y. *J. Polym. Sci., Polym. Chem. Ed.* **2003**, *41*, 1881.
16. Chang, J. Y.; Baik, J. H.; Lee, C. B.; Han, M. J.; Hong, S.-K. *J. Am. Chem. Soc.* **1997**, *119*, 3197.
17. Chang, J. Y.; Yeon, J. R.; Shin, Y. S.; Han, M. J.; Hong, S.-K. *Chem. Mater.* **2000**, *12*, 1076.

Synthesis and Characterization of Photopolymerizable Liquid Crystalline Compounds Having Two Reactive Sites

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Rod-like polymerizable LC molecules having two different reactive groups, *i.e.* acryl and diacetylene groups were prepared. 4-Hydroxyphenyldiacetylenes were synthesized by the coupling reaction of 1-bromoalkynes with 4-ethynylphenol and then reacted with 4-(6-acryloyloxyalkyloxy)benzoic acid to give polymerizable LC molecules **4a-d**. The mesomorphic properties of compounds **4a-d** were investigated by differential scanning calorimetry, polarized optical microscopy and X-ray diffractometry. Compounds **4a-c** exhibited smectic and nematic phases, but compound **4d** having a longest alkyl tail among the series formed only a smectic phase. Photopolymerizability of acryl and diacetylene groups was investigated by IR spectroscopy. An anisotropic polymer film could be prepared by selective polymerization of acryl groups with 365 nm UV light in the presence of a photoinitiator (2,2-dimethoxy-2-phenylacetophenone). The subsequent reaction of diacetylene groups with 254 nm UV light disrupted the anisotropic structure, suggesting that these LC molecules could be used for imaging on the film.

Key Words : Polymerizable liquid crystal, Diacetylene, UV irradiation, Photopolymerization

Introduction

Photopolymerizable liquid crystal (LC) monomers are of great interest because of their potential applications in display and data storage industries.¹⁻³ They can be macroscopically oriented under electric or magnetic fields, and on mechanically rubbed substrates. Their *in-situ* photopolymerization in the LC state produces an anisotropic film having an aligned structure of LC molecules.⁴⁻¹⁰

There are two general methods for preparing an LC monomer. Firstly vinyl groups can be attached to both sides of a mesogen through flexible spacers. In the second method, photoreactive groups are introduced into mesogens to become parts of rigid rods. We previously reported LC molecules having two chalcone units^{11,12} or two diacetylene groups¹³ as parts of rigid rods. A chalcone is known to form a dimer by [2 + 2] addition reaction when exposed to UV light. The polymerization of the LC molecules having two chalcone units proceeds in a stepwise manner. The polymerization of diacetylenes occurs topochemically *via* 1,4-addition by irradiation.¹⁴⁻¹⁷ Since these molecules had two reactive sites within one structure, the photopolymerization in the LC state disrupted an aligned structure, resulting in optical property changes. When the photopolymerization was carried out through a photomask, an excellent-patterned image was obtained.

In this work, we prepared rod-like LC molecules having two different photopolymerizable groups, *i.e.* acryl and diacetylene groups. We introduced an acryl group at one end of a mesogen through a flexible spacer and a phenyl diacetylene group as a part of rigid rod. Since two functional groups have different photoreactivity, we expected the selective reaction of each group, depending on irradiation

conditions. We report here the synthesis and polymerization of heterobifunctional LC molecules.

Experimental Section

Measurements. ¹H and ¹³C NMR spectra were recorded on a BRUKER Avance DPX-300 and Avance 500 spectrometer. FT-IR spectra were obtained with PERKIN ELMER Spectrum GX I using a KBr window. The differential scanning calorimetry (DSC) measurements were performed with a TA modulated DSC 2090. X-ray diffractograms were obtained by using a Mac Science M18XHF-SRA (Cu K radiation, $\lambda = 1.54 \text{ \AA}$). The optical microscopy study was performed using a Leica DM LP equipped with Mettler Toledo FP 82HT heating stage and Mettler Toledo FP 90 central process controller. Elemental analysis was performed using a CE instrument EA 1110 analyzer.

Synthesis of 4-(6-Hydroxyhexyloxy)benzoic acid (1). 4-Hydroxybenzoic acid (10 g, 72.40 mmol) was dissolved in a mixture of ethanol (30 mL) and water (20 mL) along with potassium hydroxide (10.78 g, 192 mmol) and a pinch of potassium iodide. 1-Chloro-6-hydroxyhexane (9.01 g, 66 mmol) was added slowly to the mixture at room temperature while stirring vigorously, and then the mixture was refluxed for 48 h. After evaporation of the solvents, the solid residue was dissolved in water (120 mL) and washed with diethyl ether (3 \times 30 mL). The aqueous layer was acidified with concentrated HCl until the pH was 2. The precipitates were isolated by filtration, washed with water, and recrystallized from ethanol to give compound **1** in 54% yield. ¹H NMR (CDCl₃, ppm): $\delta = 8.08, 6.95$ (dd, aromatic protons, 4H), 4.20 (s, -OH, 1H), 4.05 (t, -OCH₂, 2H), 1.87-1.48 (m, alkyl chain protons, 8H).

Synthesis of 4-(6-Acryloyloxyhexyloxy)benzoic Acid (2). Compound **1** (5 g, 21.53 mmol), acrylic acid (5.71 mL, 83.3 mmol), *p*-toluene sulfonic acid (1.40 g, 7.35 mmol), and hydroquinone (0.47 g, 4.27 mmol) were dissolved in toluene. The solution was refluxed for 12 h in a flask equipped with a Dean-stark trap. After evaporation of the solvent, the residue was dissolved in chloroform (40 mL), diluted with diethyl ether (200 mL), and washed with warm water until no more acrylic acid was detected. The organic layer was dried over anhydrous MgSO_4 . After filtration and evaporation of the solvent, the solid residue was recrystallized from isopropanol to give compound **2** in 48% yield. ^1H NMR (CDCl_3 , ppm): δ = 8.08, 6.95 (dd, aromatic protons, 4H), 6.45, 6.19, 5.86 (m, vinyl protons, 3H), 4.22, 4.07 (t, $-\text{OCH}_2$, 4H), 1.87–1.46 (m, alkyl chain protons, 8H).

Synthesis of Compound 3. Compound **3** was prepared according to our previous report.¹³

Synthesis of Compound 4. A typical procedure is as follows. To compound **2** (1.84 g, 6.32 mmol) were added thionyl chloride (2.79 g, 23.48 mmol), 2,6-di-*t*-butyl 4-methylphenol (0.44 g, 1.99 mmol) as an inhibitor, and a catalytic amount of dimethylformamide (DMF) (two drops). After stirring for 40 min, the excess thionyl chloride was removed under reduced pressure. The residue was dissolved in chloroform (8 mL), and to the solution was added dropwise a solution of compound **3** ($n = 5$) (1.10 g, 4.86 mmol) and triethylamine (0.54 g, 5.35 mmol) in chloroform (15 mL) at 0 °C. After stirring for 16 h at room temperature, chloroform (100 mL) was added to the mixture and the resulting solution was washed with water (30 mL), 2 *N* sodium hydroxide (3×60 mL), and water (2×40 mL). The organic layer was dried over anhydrous MgSO_4 . After filtration and evaporation of the solvent, the product was isolated by column chromatography on silica gel (20% ethyl acetate in hexane) and further purified by recrystallization from ethanol to give compound **4b** in 41% yield. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 8.07, 7.63, 7.32, 7.12 (dddd, aromatic protons, 8H), 6.33, 6.22, 5.96 (m, vinyl protons, 3H), 4.14 (m, $-\text{OCH}_2$, 4H), 2.46 (t, CCH_2 , 2H), 1.62–1.22 (m, alkyl chain protons, 16H), 0.89 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2935, 2860, 2244, 2145, 1739, 1719, 1636, 1608, 1408, 989, 879, 844, 814. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.3, 122.1, 121.5, 119.8, 114.6, 114.5, 85.2, 74.7, 74.2, 68.3, 65.2, 64.7, 31.5, 29.8, 29.2, 28.8, 28.6, 28.4, 25.9, 22.7, 19.5, 13.8. Anal. Calcd for $\text{C}_{32}\text{H}_{36}\text{O}_5$: C, 76.77; H, 7.25. Found: C, 76.75; H, 7.32.

For **4a**: Yield, 53%. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 8.07, 7.64, 7.33, 7.12 (dddd, aromatic protons, 8H), 6.32, 6.20, 5.88 (m, vinyl protons, 3H), 4.11 (m, $-\text{OCH}_2$, 4H), 2.43 (t, CCH_2 , 2H), 1.51–1.38 (m, alkyl chain protons, 12H), 0.92 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2958, 2865, 2242, 2148, 1744, 1713, 1636, 1600, 1409, 1006, 987, 875, 851, 814, 805. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.4, 122.3, 121.7, 120.0, 114.9, 114.6, 85.2, 74.7, 74.2, 68.3, 65.3, 64.7, 30.5, 29.8, 29.2, 28.8, 25.9, 22.2, 19.5, 13.8. Anal. Calcd for

$\text{C}_{30}\text{H}_{32}\text{O}_5$: C, 76.25; H, 6.83. Found: C, 75.94; H, 6.82.

For **4c**: Yield, 48%. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 7.96, 7.53, 7.22, 7.02 (dddd, aromatic protons, 8H), 6.19, 6.11, 5.85 (m, vinyl protons, 3H), 4.03 (m, $-\text{OCH}_2$, 4H), 2.34 (t, CCH_2 , 2H), 1.64–1.15 (m, alkyl chain protons, 20H), 0.76 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2931, 2854, 2243, 2145, 1737, 1723, 1635, 1606, 1408, 1000, 985, 875, 844, 811. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.4, 122.1, 121.4, 119.8, 114.8, 114.6, 85.2, 74.7, 74.2, 68.3, 65.2, 64.7, 32.1, 29.7, 29.4, 29.3, 29.2, 29.1, 28.8, 28.5, 25.9, 22.9, 19.8, 14.3. Anal. Calcd for $\text{C}_{34}\text{H}_{40}\text{O}_5$: C, 77.24; H, 7.63. Found: C, 77.25; H, 7.66.

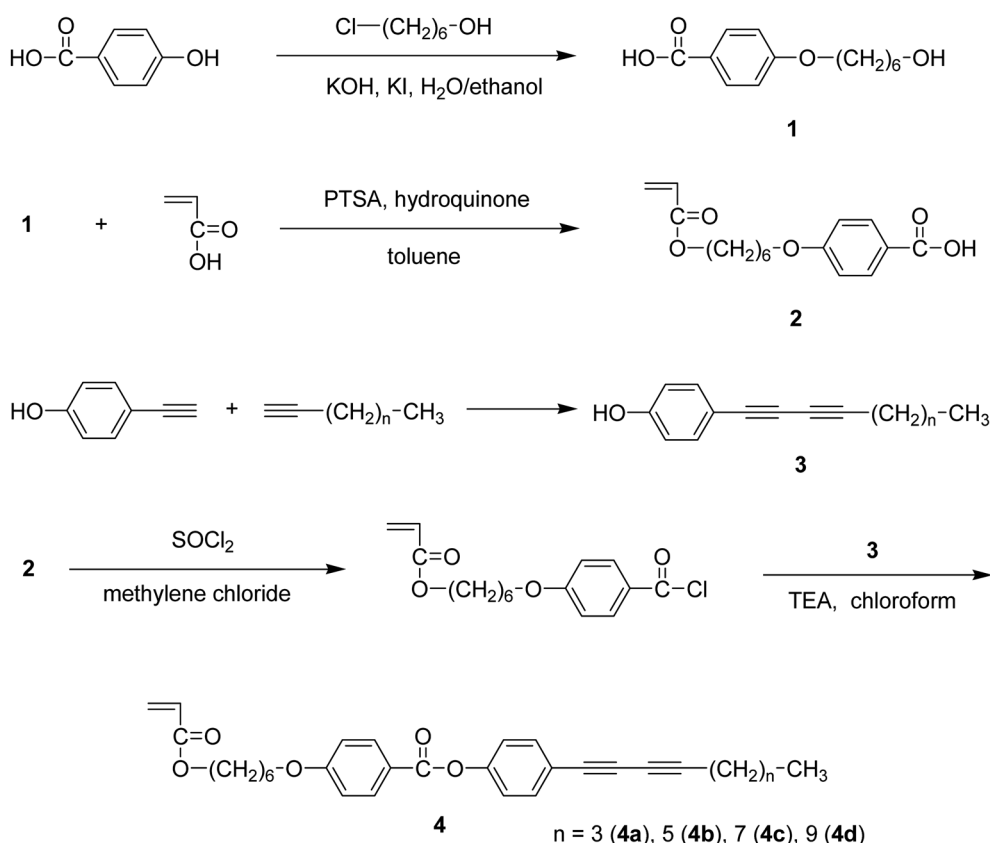
For **4d**: Yield, 47%. ^1H NMR ($\text{DMSO}-d_6$, ppm): δ = 8.07, 7.64, 7.32, 7.12 (dddd, aromatic protons, 8H), 6.30, 6.21, 5.95 (m, vinyl protons, 3H), 4.13 (m, $-\text{OCH}_2$, 4H), 2.44 (t, CCH_2 , 2H), 1.75–1.33 (m, alkyl chain protons, 24H), 0.88 (t, $-\text{CH}_3$, 3H). IR (KBr, cm^{-1}): 2924, 2854, 2244, 2144, 1742, 1721, 1634, 1602, 1409, 1006, 990, 875, 853, 813, 802. ^{13}C NMR (CDCl_3 , ppm): δ = 166.5, 164.7, 163.8, 151.6, 134.0, 133.8, 132.6, 132.5, 130.2, 128.5, 122.3, 122.1, 121.4, 119.8, 114.6, 114.5, 85.2, 74.7, 74.2, 68.3, 65.2, 64.7, 32.1, 29.8, 29.7, 29.6, 29.5, 29.3, 29.2, 29.1, 28.8, 28.5, 25.9, 22.9, 19.8, 14.3. Anal. Calcd for $\text{C}_{36}\text{H}_{44}\text{O}_5$: C, 77.66; H, 7.97. Found: C, 77.77; H, 8.00.

Radical Polymerization of Compound 4b. In a 10 mL polymerization tube, compound **4b** (0.3 g, 0.56 mmol) and AIBN (0.0046 g, 0.028 mmol) were dissolved in dry THF (3 mL). The reaction mixture was degassed by a freeze-thaw method to remove oxygen. After sealing the ampule, the mixture was heated with stirring at 60 °C for 48 h. The polymer was isolated and dropped into *n*-hexane to precipitate the polymer. The polymer was dried for 24 h in vacuum oven. Yield, 36.7%. ^1H NMR (CDCl_3 , 300 MHz): δ = 8.15–6.9 (8H, Ar-H), 4.22–2.35 (6H, $-\text{OCH}_2$, CCH_2), 1.82–1.25 (m, 19H, polymer backbone and alkyl chain protons), 0.83 (3H, $-\text{CH}_3$).

Results and Discussion

Synthesis of Polymerizable Mesogens. The rod-like mesogenic monomers were prepared according to Scheme 1. 4-Hydroxybenzoic acid was reacted with 6-chlorohexanol to yield compound **1**. An acryl group was introduced to compound **1** by esterification reaction with acrylic acid. The carboxyl end group of acryl compound **2** was converted to acid chloride with thionyl chloride and then reacted with 4-hydroxyphenyldiacetylenes **3**, which were synthesized by the coupling reaction of 1-bromoalkynes with 4-ethynylphenol, to give compounds **4a–d**. The structures of all products were identified by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis.

Mesomorphic Properties. The mesomorphic properties of compounds **4a–d** were investigated by DSC, polarized optical microscopy (POM) and X-ray diffractometry. The compounds showed enantiotropic transitions. In the DSC study, sharp phase transitions were observed upon heating



Scheme 1

and cooling with a scan rate of 5 °C/min. For example, compound **4b** showed three endothermic peaks at 55.4 °C ($\Delta H = 31.5$ kJ/mol), 79.7 °C ($\Delta H = 1.67$ kJ/mol), and 86.1 °C ($\Delta H = 0.38$ kJ/mol) during the 2nd heating, and three exothermic peaks at 84.8 °C ($\Delta H = 0.76$ kJ/mol), 78.4 °C ($\Delta H = 1.66$ kJ/mol), and 3.7 °C ($\Delta H = 20.6$ kJ/mol) during

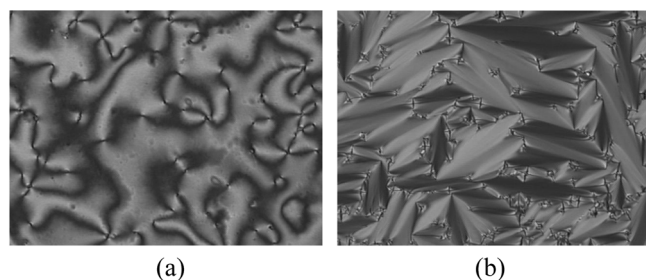


Figure 1. Polarizing optical micrographs of **4b** taken (a) at 83 °C and (b) at 50 °C on cooling.

the 2nd cooling. In POM analysis, a focal conic fan-type texture appeared from 55.4 °C and then a Schlieren texture above 79.7 °C on heating, corresponding to a smectic and a nematic phase, respectively (Figure 1). The same textures were observed on cooling. Compounds **4a** and **4c** also exhibited two LC phases, but compound **4d** having a longest alkyl tail among the series formed only a smectic phase. The thermal transitions of **4a-d** are summarized in Table 1.

The structures of the smectic phases of **4a-d** were further investigated by using an X-ray diffraction technique. Figure 2 shows the X-ray diffractogram of **4b** measured at 50 °C. In the small-angle region, three sharp peaks with d spacings of 35.9, 17.8, and 11.8 Å appeared, corresponding to the (100), (200), and (300) Bragg reflections, respectively. Since the length of the molecule was calculated to be 35.7 Å, which was almost the same as the (100) spacing of 35.9 Å, it seems that the compound had a monolayered smectic A structure. Other compounds also showed similar results. The X-ray

Table 1. Phase transition temperatures (°C) and enthalpy values (in parentheses, kJ/mol) of compounds **4a-d** determined by DSC at a rate of 5 °C min⁻¹

Compound	2 nd heating	2 nd cooling
4a	K 63.8 (33.1) Sm 83.8 (4.36) N 92.1 (0.77) I	I 91.7 (0.60) N 83.3 (2.16) Sm 27.2 (19.5) K
4b	K 55.4 (31.5) Sm 79.7 (1.67) N 86.1 (0.38) I	I 84.8 (0.76) N 78.4 (1.66) Sm 3.7 (20.6) K
4c	K 21.2 (0.8) Sm 81.5 (3.37) N 84.8 (0.95) I	I 83.0 (0.89) N 80.0 (1.86) Sm -11.5 (0.6) K
4d	K 47.7 (26.3) Sm 82.4 (8.27) I	I 80.3 (7.90) Sm -6.6 (20.4) K

^aK = crystal; Sm = smectic; N = nematic; I = isotropic.

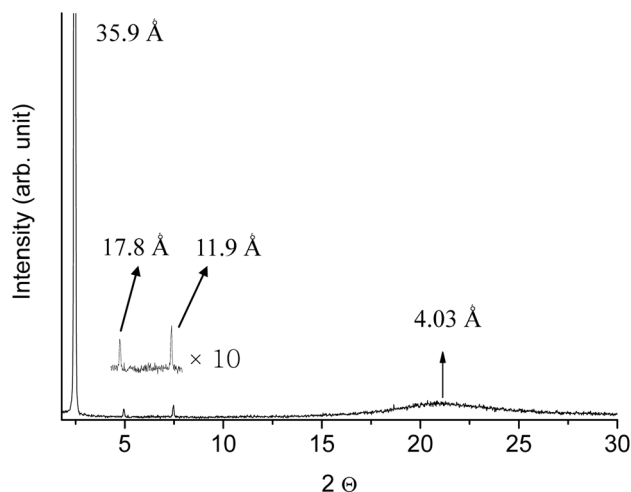


Figure 2. X-ray diffractogram of compound **4b**, obtained at 50 °C.

Table 2. X-ray diffraction data of the smectic phases of compounds **4a-d** obtained at 50 °C

Compound	d_{exp} (Å) ^a	d_{calc} (Å) ^b	(hkl)
4a	33.2	33.5	(100)
	16.5	16.7	(200)
	10.9	11.1	(300)
4b	35.9	35.7	(100)
	17.8	17.8	(200)
	11.8	11.9	(300)
4c	38.7	38.3	(100)
	18.8	19.1	(200)
	12.6	12.7	(300)
4d	40.9	40.9	(100)
	21.5	20.5	(200)
	14.2	13.7	(300)

^aObserved from XRD analysis. ^bEstimated from an extended molecular model.

diffraction data are summarized in Table 2.

Photopolymerization. Photopolymerizability of an acryl and a diacetylene groups was investigated by IR spectroscopy. A solution of **4b** (0.1 g) and a photoinitiator (2,2-dimethoxy-2-phenylacetophenone, 4 wt %) in toluene (0.4 mL) was cast on a KBr window, dried *in vacuo*, and sheared with a cover glass at 50 °C. The sample was first irradiated with 365 nm UV light (1 mW/cm²). The IR band intensity at 1636 cm⁻¹ for C=C stretching of a vinyl group gradually decreased with increasing irradiation time, while the intensity of the band at 2241 cm⁻¹ for a diacetylene group changed little, indicating the selective polymerization of the vinyl group (Figure 3). When irradiated with 254 nm UV light (3 mW/cm²), the diacetylene group was polymerized, resulting in a decrease in the intensity of the band at 2241 cm⁻¹. Figure 4 shows a polar plot of the absorbance of the IR peak at 1731 cm⁻¹ versus polarization angle. After shearing in the LC state, the molecules were oriented mostly parallel to the shearing direction. The oriented LC structure was maintained when about 50% of vinyl groups were polymerized by irradiation with 365 nm UV light. The

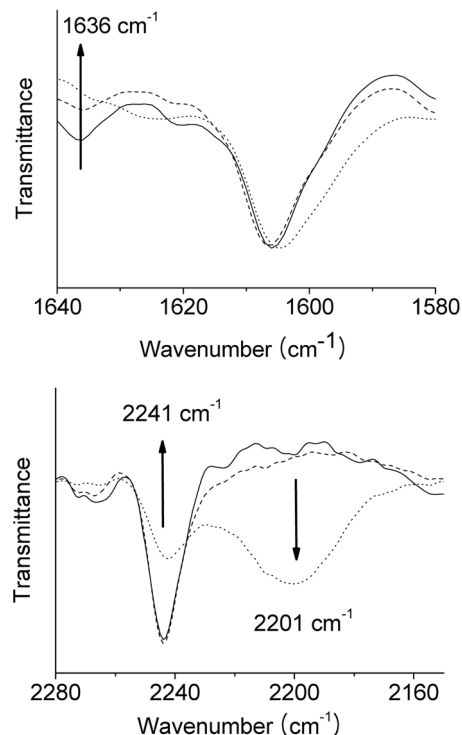


Figure 3. FT-IR spectral changes of compound **4b**; before UV irradiation (solid line), after 365 nm UV irradiation for 10 min (dashed line), and after 365 nm UV irradiation for 10 min and 254 nm UV irradiation for 60 min (dotted line).

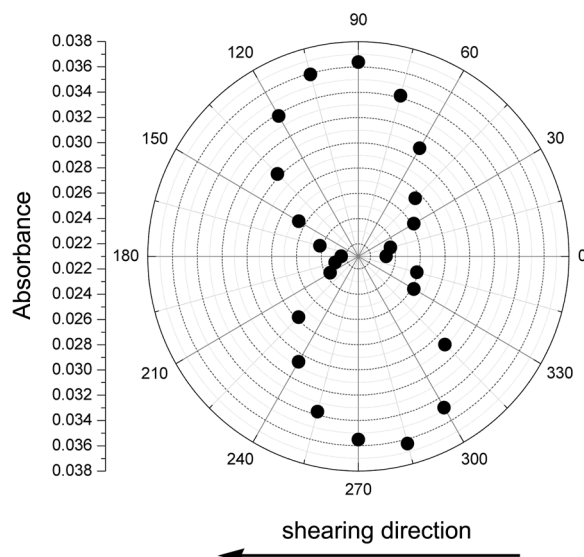


Figure 4. Polar plot of the absorbance of the IR peak for the C=O stretch at 1731 cm⁻¹ versus polarization angle for **4b**.

aligned structure was disrupted by irradiation with 254 nm UV light, which caused cross-linking.

Radical Polymerization. The acryl group of compound **4b** could be radically polymerized by initiation with AIBN in THF at 60 °C. Number average molecular weight and weight average molecular weight of the polymer measured by GPC were 7000 and 9790, respectively. The polymer formed a smectic phase. In DSC analysis, an endothermic

peak corresponding to isotropization was observed at 96.0 °C on 2nd heating. On cooling, a weak exothermic peak appeared at 92.0 °C. A birefringent phase began to form at 92.0 °C and persisted to room temperature. In the X-ray diffractogram, a relatively sharp peak with *d* spacing of 35.2 Å appeared. We examined the miscibility of **4b** and the acryl polymer by POM. The 7:3 mixture of **4b** and the polymer showed isotropization at 94 °C. On cooling from the isotropic state with a rate of 5 °C/min, however, phase separation occurred. This result is in contrast to the observation that the LC structure was maintained during in-situ polymerization of the vinyl group with 365 nm UV light in the LC state.

In summary, we prepared LC molecules having two different photopolymerizable groups, *i.e.* an acryl and a diacetylene group and examined their photoreactivity. An anisotropic polymer film could be prepared by selective polymerization of the acryl group with 365 nm UV light in the presence of a photoinitiator. The subsequent reaction of diacetylene groups with 254 nm UV light disrupted the anisotropic structure, suggesting that these LC molecules could be used for imaging on the film.

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References

1. Broer, D. J.; Mol, G. N. *Makromol. Chem.* **1989**, *190*, 19.
2. Ichimura, K. *Chem. Rev.* **2000**, *100*, 1847.
3. Yoshio, M.; Kagata, T.; Hoshino, K.; Mukai, T.; Ohno, H.; Kato, T. *J. Am. Chem. Soc.* **2006**, *128*, 5570.
4. Penterman, R.; Klink, S. I.; de Koning, H.; Nisato, G.; Broer, D. J. *Nature* **2002**, *417*, 55.
5. Kondo, M.; Yu, Y.; Ikeda, T. *Angew. Chem., Int. Ed.* **2006**, *45*, 1378.
6. Ree, M. *Macromol. Res.* **2006**, *14*, 1.
7. Baxter, B. C.; Gin, D. L. *Macromolecules* **1998**, *31*, 4419.
8. Hoag, B. P.; Gin, D. L. *Macromolecules* **2000**, *33*, 8549.
9. Vlachos, P.; Kelly, S. M.; Mansoor, B.; ÓNeill, M. *Chem. Commun.* **2002**, 874.
10. Beyer, P.; Krueger, M.; Giesselmann, F.; Zentel, R. *Adv. Funct. Mater.* **2007**, *17*, 109.
11. Chang, J. Y.; Nam, S. W.; Hong, C. G.; Im, J.-H.; Kim, J.-H.; Han, M. J. *Adv. Mater.* **2001**, *13*, 1298.
12. Nam, S. W.; Kang, S. H.; Chang, J. Y. *Macromol. Res.* **2007**, *15*, 74.
13. Cho, H. J.; Seo, K.; Lee, C. J.; Yun, H.; Chang, J. Y. *J. Mater. Chem.* **2003**, *13*, 986.
14. Lee, C. J.; Lee, S. J.; Chang, J. Y. *Tetrahedron Lett.* **2002**, *43*, 3863.
15. Hwang, I. H.; Lee, S. J.; Chang, J. Y. *J. Polym. Sci., Polym. Chem. Ed.* **2003**, *41*, 1881.
16. Chang, J. Y.; Baik, J. H.; Lee, C. B.; Han, M. J.; Hong, S.-K. *J. Am. Chem. Soc.* **1997**, *119*, 3197.
17. Chang, J. Y.; Yeon, J. R.; Shin, Y. S.; Han, M. J.; Hong, S.-K. *Chem. Mater.* **2000**, *12*, 1076.