Photoimaging through in-Situ Photopolymerization of Heterobifunctional Mesogenic Compounds in Liquid Crystalline State

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ABSTRACT: A series of heterobifunctional mesogenic biphenyl esters having two different polymerizable groups, i.e., acryl and diacetylene groups, were synthesized and their thermal behaviors and polymerization investigated. All compounds showed enantiotropic transitions. Under POM, highly birefringent focal-conic fan textures appeared on heating and cooling from the isotropic melt. Compounds **6**−**8** having a butyl spacer between a biphenyl and a diacetylene group exhibited LC phases even at room temperature. The X-ray diffractograms of compounds **6**−**8** showed a set of reflections in the small-angle region. They consisted of more than three sharp diffraction peaks with *d* spacings in the ratio of 1:1/2:1/3, showing that the compounds had well-defined smectic A structures. For the photoimaging a mixture of **6** and a photoinitiator (2,2-dimethoxy-2-phenylacetophenone, 4 wt %) was cast on a glass plate and sheared with a cover glass at room temperature to result in an LC monodomain. The acryl group was then selectively polymerized by irradiation with low-intensity 365 nm UV light to yield a polymer film. Subsequent UV irradiation at 254 nm using a 100 W high-pressure mercury arc lamp through a photomask produced conjugated polyacetylene chains in the irradiated area. The polydiacetylene chains were fluorescent, and the patterned image was directly visualized by fluorescence microscopy.

Introduction

Polymerization of aligned monomers is an attractive way to obtain anisotropic materials having thermal and mechanical stability since the molecular ordering of monomers offers advantages such as the fact that it proceeds much faster and easier than that of macromolecules. In particular, photopolymerizable liquid crystals (LCs) have attracted considerable attention because of their unique phase properties showing both fluidity and molecular ordering, which allow better control over their alignment.[1−3] LC molecules are macroscopically oriented by electric or magnetic fields, shearing, and on mechanically rubbed substrates,[4−9] and they have been polymerized in nematic, smectic, and discotic phases in order to maintain their aligned structures over a wide range of temperatures.[10−21]

The photopolymerization of oriented polymerizable LC molecules also changes their optical properties and thus has potential applications in imaging. We previously reported photopolymerizable LC molecules having two diacetylene units[22−24] or chalcone groups.[25,26] The LC molecules were aligned macroscopically and polymerized by UV irradiation through a photomask to produce excellent patterned images.[24−26] This result is ascribed to the fact that the photoreaction disrupted ordered structures in an irradiated part. Aligned molecules remained in a masked part.

Here we present the synthesis of novel heterobifunctional mesogenic compounds having two different polymerizable groups, i.e., acryl and diacetylene groups, and selective polymerization in the LC state to produce an image on an anisotropic polymer film. We took advantage of the photoreactivity difference between two groups in the selective polymerization. The acryl groups are known to undergo rapid polymerization upon irradiation even with low-intensity UV light in the presence of a photoinitiator.[27] Photopolymerization of diacetylenes requires relatively high energy for the initiation and proceeds topochemically via 1,4-addition.[28] We were able to polymerize an acryl group first by irradiation with 365 nm UV light in the LC state to form an anisotropic film. A patterned image on the film was obtained by the subsequent polymerization of a diacetylene group through a photomask with 254 nm UV light (Scheme 1). Some of the compounds showed smectic phases even at room temperature, which allowed us to carry out the imaging process without any additional heating step.

Experimental Section

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance DPX-300 (300 MHz) and Avance 500 (125 MHz) spectrometer. Fourier transform infrared (FT-IR) spectra were obtained with a Perkin Elmer Spectrum GX I using a KBr pellet. Elemental analysis was performed using a CE instrument EA 1110 analyzer. The differential scanning calorimetry (DSC) measurements were performed with a TA modulated DSC Q10 at a scanning rate of 10 °C/min. The optical microscopy study was performed using a Leica DM LP equipped with a Mettler Toledo FP 82HT heating stage and a Mettler Toledo FP 90 central process controller. X-ray diffraction (XRD) patterns were recorded by a Bruker NANOSTAR (Cu Kα radiation, $\lambda = 1.54$ Å). UV−vis spectra were obtained with the use of a Sinco 3150 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5301PC spectrofluorometer. Fluorescence images were obtained using Carl Zeiss-LSM510 confocal laser scanning microscope.

Materials. 6-Bromo-1-hexanol (97%), 4′-hydroxy-4-biphenylcarboxylic acid (99%), 1-hexyne (97%), 1-octyne (97%), 1-decyne (98%), 1-dodecyne (98%), 5-hexyn-1-ol (96%), 3-butyn-1-ol (97%), acryloyl chloride (98%), copper(II) acetate (98%), potassium iodide (99%), 2,6-di-*tert*-butylphenol (99%), *N*,*N*-diethylaniline (99%), *N*,*N*-dicyclohexylcarbodiimide (DCC, 99%), and *N*,*N*-(dimethylamino)pyridine (DMAP, 99%) were purchased from Aldrich and

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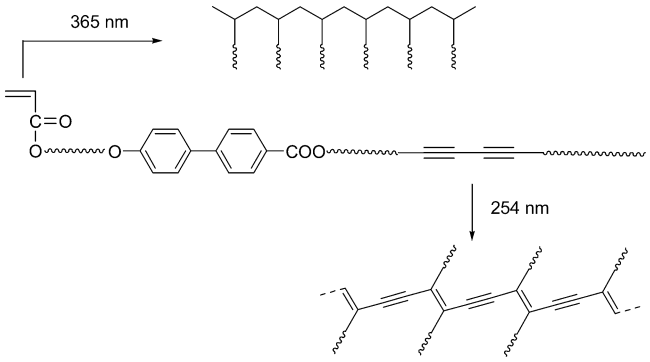
Scheme 1. Selective Photopolymerization of a Heterofunctional LC Molecule



used without further purification. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) was obtained from Ciba Specialty Chemicals. Tetrahydrofuran was dried over sodium metal and distilled. Other reagent-grade solvents were used as received.

Synthesis of Ethyl 4-(4-Hydroxyphenyl)benzoate (1). To a solution of 4′-hydroxy-4-biphenylcarboxylic acid (10 g, 46.7 mmol) in ethanol (200 mL) was added a catalytic amount of sulfuric acid. The reaction mixture was vigorously stirred, heated under reflux for 24 h, and allowed to cool to room temperature. The resulting solution was evaporated, poured into cool water, and neutralized to pH 8. The precipitate was filtered and washed several times with water. The product was purified by recrystallization from ethanol. Yield, 11.3 g (99.8%). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.11 (d, J = 8.3 Hz, −OOCAr−, 2H), 7.62 (d, J = 8.3 Hz, Ar, 2H), 7.54 (d, J = 8.5 Hz, Ar, 2H), 6.98 (d, J = 8.0 Hz, Ar, 2H), 5.30 (s, −OH, 1H), 4.44 (t, $-COOCH_2-$, 2H), 4.05 (t, $-OCH_2$, 2H), 1.44 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 165.6, 158.0, 144.6, 129.7, 129.4, 128.1, 127.6, 125.9, 115.9, 60.6, 14.2. IR (KBr, cm^{-1}): 3331, 3001, 2988, 1682, 1602, 1587, 1532, 1498, 1440, 1404, 1372, 1302, 1277, 1191, 1136, 1116, 1021, 833, 774. Anal. Calcd for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: 74.19; H, 5.86.

Synthesis of Ethyl 4-[4-(6-Hydroxyhexyloxy)phenyl]benzoate (2). To a solution of compound **1** (5.0 g, 20.6 mmol), potassium carbonate (3.7 g, 26.8 mmol), and a pinch of potassium iodide in DMF (50 mL) was added 6-bromo-1-hexanol (4.9 g, 26.8 mmol) slowly dropwise. The reaction mixture was vigorously stirred at 80 °C for 48 h under nitrogen and allowed to cool to room temperature. The resulting solution was poured into distilled water (250 mL). The precipitate was filtered and washed several times with distilled water. The product was purified by recrystallization from ethanol. Yield, 7.0 g (99.1%). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.11 (d, J = 8.3 Hz, −OOCAr−, 2H), 7.62 (dd, overlap, Ar, 4H) 7.00 (d, J = 8.8 Hz, $-OCH_2-$, 2H), 4.44 (t, $-COOCH_2-$, 2H), 4.05 (t, $-OCH_2$, 2H), 1.87−1.40 (m, $-CH_2-$, 11H). ^{13}C NMR ($CDCl_3$, ppm): δ = 166.8, 159.6, 145.4, 132.5, 132.5, 130.3, 128.8, 128.5, 126.6, 115.1, 68.2, 63.1, 61.1, 32.9, 29.4, 26.1, 25.8, 14.6. IR (KBr, cm^{-1}): 3315, 2935, 2860, 1713, 1604, 1528, 1498, 1470, 1400, 1369, 1288, 1254, 1197, 1109, 1029, 829, 772. Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.62; H, 7.66.

Synthesis of 4-[4-(6-Hydroxyhexyloxy)phenyl]benzoic Acid (3). To a solution of compound **2** (5.0 g, 14.6 mmol) in THF (30 mL) was added a solution of potassium hydroxide (1.6 g 29.2 mmol) in ethanol/water (5/1, 60 mL). The reaction mixture was vigorously stirred at reflux temperature for 12 h and allowed to cool to room temperature. The resulting solution was evaporated in vacuo, and the residue was poured into distilled water. The precipitate was filtered and washed several times with distilled water. The product was purified by recrystallization from ethanol. Yield, 4.5 g (98.6%). ^{1}H NMR (DMSO-d_6, ppm): δ = 7.86 (d, J = 7.9 Hz, −OOCAr−, 2H), 7.59 (d, J = 8.5 Hz, Ar, 2H), 7.47 (d, J = 8.1 Hz, Ar, 2H), 7.00 (d, J = 8.5 Hz, $-OCH_2-$, 2H), 4.36 (s, −OH, 1H), 4.02 (t, $-COOCH_2-$, 2H), 3.45 (t, $-OCH_2$, 4H), 1.75−1.65 (m, $-OCH_2-CH_2-$, 4H), 1.54−1.27 (m, $-CH_2-$, 4H). ^{13}C NMR (DMSO-d_6, ppm): δ = 166.8, 159.6, 145.4, 132.5, 130.3, 128.8, 128.5, 126.6, 115.1, 68.2, 63.1, 61.1, 32.9, 29.4, 26.1, 25.8, 14.6. IR (KBr, cm^{-1}): 3254, 2941, 2862, 1594, 1574, 1546, 1527, 1476, 1389, 1277, 1192, 1030, 830, 789. Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.39; H, 7.10.

Synthesis of 4-[4-(6-Acryloyloxyhexyloxy)phenyl]benzoic Acid (4). To a solution of compound **3** (5.0 g, 15.9 mmol), *N*,*N*-diethylaniline (2.0 g, 16.7 mmol), and a catalytic amount of 2,6-di-*tert*-butylphenol in 1,4-dioxane (50 mL) was added acryloyl chloride (4.3 g, 47.7 mmol) slowly dropwise. The reaction mixture was stirred at 25 °C for 24 h. The resulting solution was poured into cold water. The precipitate was filtered and washed several times with distilled water. The product was purified by recrystallization from ethanol. Yield, 4.1 g (70.0%). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.17 (d, J = 8.4 Hz, −OOCAr−, 2H), 7.67 (d, J = 8.4 Hz, Ar, 2H), 7.59 (d, J = 8.7 Hz, Ar, 2H), 7.00 (d, J = 8.8 Hz, −OAr−, 2H), 6.44 (d, J = 17.3 Hz, ═CH, 1H), 6.17 (dd, J = 10.4, 6.9 Hz, ═CH, 1H), 5.84 (d, J = 10.4 Hz, ═CH, 1H), 4.21 (t, $-OCH_2-$, 2H), 4.04 (t, $-ArOCH_2-$, 2H), 1.84−1.70 (m, $-OCH_2-CH_2-$, 4H), 1.60−1.47 (m, $-CH_2-$, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ = 166.6, 159.7, 146.4, 132.3, 131.0, 130.8, 128.8, 128.6, 126.8, 115.2, 104.8, 68.1, 64.7, 29.4, 28.8, 26.0. IR (KBr, cm^{-1}): 2938, 2865, 1724, 1694, 1678, 1635, 1604, 1431, 1409, 1292, 1248, 1194, 1009, 985, 832, 810, 774. Anal. Calcd for $C_{22}H_{24}O_5$: C, 71.72; H, 6.57. Found: C, 71.77; H, 6.72.

Synthesis of Dodeca-5,7-diyn-1-ol (5a). To a solution of 5-hexyn-1-ol (3.0 g, 30.5 mmol) and 1-hexyne (3.7 g, 45.8 mmol) in pyridine/methanol (80/80 mL) was added copper(II) acetate (11.1 g, 61.1 mmol). The reaction mixture was vigorously stirred at 60 °C for 18 h under nitrogen. Insoluble solids were removed by filtration. After evaporating the solvent, the product was isolated as an oil by column chromatography on silica gel using ethyl acetate and *n*-hexane (1/3) as eluent. Yield, 2.2 g (40.4%). ^{1}H NMR ($CDCl_3$, ppm): δ = 3.69 (t, $-OCH_2$, 2H), 2.34 (m, ≡CCH_2, 4H), 1.70−1.62 (m, $-CH_2-$, 4H), 1.52−1.41 (m, $-CH_2-$, 4H), 0.94 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 78.0, 77.0, 65.9, 65.3, 62.4, 31.8, 25.7, 24.5, 22.7, 19.3, 19.2, 14.2. IR (KBr, cm^{-1}): 3334, 2934, 2873, 2257, 2167, 1456, 1428, 1323, 1254, 1062, 982, 935. Anal. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.57; H, 10.32.

Synthesis of Tetradeca-5,7-diyn-1-ol (5b). This compound was prepared from 5-hexyn-1-ol (2.5 g, 26.0 mmol) and 1-octyne (4.2 g, 39.0 mmol) as described for compound **5a**. The product was isolated as an oil by column chromatography on silica gel using ethyl acetate and *n*-hexane (1/2) as eluent. Yield, 2.4 g (45.7%). ^{1}H NMR ($CDCl_3$, ppm): δ = 3.69 (t, $-OCH_2$, 2H), 2.34 (m, ≡CCH_2, 4H), 1.70−1.26 (m, $-CH_2-$, 12H), 0.91 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 78.0, 77.0, 65.9, 65.3, 62.4, 31.8, 28.7, 28.5, 24.8, 22.7, 19.3, 19.2, 14.2. IR (KBr, cm^{-1}): 3335, 2934, 2873, 2257, 2167, 1455, 1429, 1323, 1254, 1062, 982, 935. Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.73; H, 10.75.

Synthesis of Hexadeca-5,7-diyn-1-ol (5c). This compound was prepared from 5-hexyn-1-ol (1.8 g, 18.3 mmol) and 1-decyne (3.8 g, 27.5 mmol) as described for compound **5a**. The product was isolated as an oil by column chromatography on silica gel using ethyl acetate and *n*-hexane (1/2) as eluent. Yield, 2.3 g (53.6%). ^{1}H NMR ($CDCl_3$, ppm): δ = 3.69 (t, $-OCH_2$, 2H), 2.34 (m, ≡CCH_2, 4H), 1.70−1.24 (m, $-CH_2-$, 16H), 0.90 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 78.0, 77.0, 65.9, 65.3, 62.4, 32.0, 31.9, 29.3, 29.2, 29.0, 28.5, 24.8, 22.8, 19.4, 19.2, 14.2. IR (KBr, cm^{-1}): 3334, 2934, 2873, 2257, 2166, 1456, 1428, 1323, 1255, 1061, 982, 933. Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 82.18; H, 11.04.

Synthesis of Icosa-5,7-diyn-1-ol (5d). This compound was prepared from 5-hexyn-1-ol (6.0 g, 61.1 mmol) and 1-tetradecyne (17.8 g, 91.7 mmol) as described for compound **5a**. The product was isolated as a solid powder by column chromatography on silica gel using ethyl acetate and hexane (1/3) as eluent. Yield, 6.5 g (36.6%). ^{1}H NMR ($CDCl_3$, ppm): δ = 3.68 (t, $-OCH_2$, 2H), 2.34 (m, ≡CCH_2, 4H), 1.70−1.24 (m, $-CH_2-$, 24H), 0.90 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 78.0, 77.0, 65.9, 65.3, 62.5, 32.1, 32.0, 29.9, 29.8, 29.7, 29.5 29.3, 29.1, 28.5, 24.8, 22.9, 19.4, 19.2, 14.3. IR (KBr, cm^{-1}): 3334, 2935, 2873, 2257, 2166, 1456,

1428, 1323, 1254, 1062, 982, 935. Anal. Calcd for $C_{20}H_{34}O$: C, 82.69; H, 11.80. Found: C, 82.81; H, 11.68.

Synthesis of Deca-3,5-diyn-1-ol (5e). This compound was prepared from 3-butyn-1-ol (3.0 g, 42.8 mmol) and 1-hexyne (5.3 g, 64.2 mmol) as described for compound **5a**. The product was isolated as an oil by column chromatography on silica gel using ethyl acetate and hexane (1/3) as eluent. Yield, 3.0 g (46.7%). ^{1}H NMR ($CDCl_3$, ppm): δ = 3.69 (t, $-OCH_2$, 2H), 2.34 (m, $\equiv CCH_2$, 4H), 1.70−1.62 (m, $-CH_2-$, 4H), 1.52−1.41 (m, $-CH_2-$, 4H), 0.94 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 78.0, 77.0, 65.9, 65.3, 62.4, 31.9, 28.5, 22.7, 19.3, 14.2. IR (KBr, cm^{-1}): 3330, 2933, 2873, 2257, 2167, 1456, 1425, 1323, 1254, 1060, 980, 936. Anal. Calcd for $C_{10}H_{14}O$: C, 79.96; H, 9.39. Found: C, 80.10; H, 9.25.

Synthesis of Octadeca-3,5-diyn-1-ol (5f). This compound was prepared from 3-butyn-1-ol (4.0 g, 40.8 mmol) and 1-tetradecyne (11.9 g, 61.1 mmol) as described for compound **5a**. The product was isolated as a solid powder by column chromatography on silica gel using ethyl acetate and hexane (1/3) as eluent. Yield, 7.0 g (46.2%). ^{1}H NMR ($CDCl_3$, ppm): δ = 3.69 (t, $-OCH_2$, 2H), 2.34 (m, $\equiv CCH_2$, 4H), 1.70−1.41 (m, $-CH_2-$, 20H), 0.94 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 78.0, 77.0, 65.9, 65.3, 62.5, 32.1, 32.0, 29.9, 29.7, 29.3, 29.1, 28.5, 24.8, 22.9, 19.4, 19.2, 14.3. IR (KBr, cm^{-1}): 3334, 2933, 2873, 2257, 2166, 1456, 1425, 1323, 1254, 1060, 980, 936. Anal. Calcd for $C_{18}H_{30}O$: C, 82.38; H, 11.52. Found: C, 82.04; H, 11.63.

Synthesis of Dodeca-5,7-diynyl 4-[4-(6-Acryloyloxyhexyloxy)-phenyl]benzoate (6). To a solution of compound **4** (2.5 g, 6.8 mmol) and compound **5a** (1.2 g, 6.8 mmol) in CH_2Cl_2 and THF (20/20 mL) were added DCC (1.7 g, 8.2 mmol) and DMAP (0.17 g, 1.36 mmol). The reaction mixture was stirred at room temperature for 24 h. After filtration and evaporation, the product was isolated as a solid powder by column chromatography on silica gel using ethyl acetate and hexane (1/3) as eluent. Yield, 1.8 g (50.2%). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.10 (d, J = 8.3 Hz, −OOCAr−, 2H), 7.63 (dd, overlap, Ar, 4H), 7.00 (d, J = 8.8 Hz, −OAr−, 2H), 6.44 (d, J = 17.3 Hz, =CH, 1H), 6.17 (dd, J = 10.3, 7.0 Hz, =CH, 1H), 5.84 (d, J = 10.3 Hz, =CH, 1H), 4.37 (t, $-COOCH_2-$, 2H), 4.20 (t, $-OCH_2-$, 2H), 4.04 (t, $-ArOCH_2-$, 2H), 2.39 (t, $\equiv CCH_2-$, 2H), 2.28 (t, $\equiv CCH_2-$, 2H), 1.91−1.83 (m, $-OCH_2CH_2-$, 6H), 1.75−1.70 (m, $\equiv CCH_2CH_2-$, 4H), 1.49−1.42 (m, $-CH_2-$, 6H), 0.93 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 166.6, 166.4, 159.6, 145.6, 132.4, 130.7, 130.4, 128.8, 128.5, 128.1, 126.6, 115.1, 78.7, 72.8, 68.1, 67.2, 65.2, 64.7, 62.6, 30.5, 29.3, 28.8, 26.0, 22.1, 20.1, 19.1, 13.7. IR (KBr, cm^{-1}): 2942, 2871, 2243, 2145, 1727, 1713, 1634, 1604, 1480, 1407, 1279, 1195, 1118, 1000, 986, 825, 810. Anal. Calcd for $C_{34}H_{40}O_5$: C, 77.24; H, 7.63. Found: C, 77.25; H, 7.66.

Synthesis of Tetradeca-5,7-diynyl 4-[4-(6-Acryloyloxyhexyloxy)phenyl]benzoate (7). This compound was prepared from compound **4** (1.5 g, 4.1 mmol) and compound **5b** (0.8 g, 4.1 mmol) as described for compound **6**. The product was isolated as a solid powder by column chromatography on silica gel using ethyl acetate and hexane (1/3) as eluent. Yield, 7.0 g (46.2%). ^{1}H NMR (CDCl3, ppm): δ = 8.10 (dd, J = 8.3 Hz, −OOCAr−, 2H), 7.63 (dddd, overlap, Ar, 4H), 7.00 (dd, J = 8.8 Hz, −OAr−, 2H), 6.44 (d, J = 17.3 Hz, =CH, 1H), 6.17 (dd, J = 10.3, 7.0 Hz, =CH, 1H), 5.84 (d, J = 10.3 Hz, =CH, 1H), 4.37 (t, $-COOCH_2-$, 2H), 4.20 (t, $-OCH_2-$, 2H), 4.04 (t, $-ArOCH_2-$, 2H), 2.39 (t, $\equiv CCH_2-$, 2H), 2.28 (t, $\equiv CCH_2-$, 2H), 1.91−1.83 (m, $-OCH_2CH_2-$, 6H), 1.75−1.70 (m, $\equiv CCH_2CH_2-$, 4H), 1.57−1.28 (m, $-CH_2-$, 10H), 0.91 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 166.7, 166.5, 159.5, 145.4, 132.5, 130.7, 130.3, 128.8, 128.6, 128.5, 126.6, 115.1, 78.1, 76.7, 68.1, 66.1, 65.3, 64.7, 64.5, 31.5, 29.3, 28.8, 28.7, 28.5, 28.1, 26.0, 25.2, 22.7, 19.4, 19.2, 14.2. IR (KBr, cm^{-1}): 2944, 2870, 2243, 2145, 1729, 1713, 1635, 1604, 1480, 1407, 1279, 1195, 1118, 1002, 981, 825, 808. Anal. Calcd for $C_{36}H_{44}O_5$: C, 77.66; H, 7.97. Found: C, 77.51; H, 8.08.

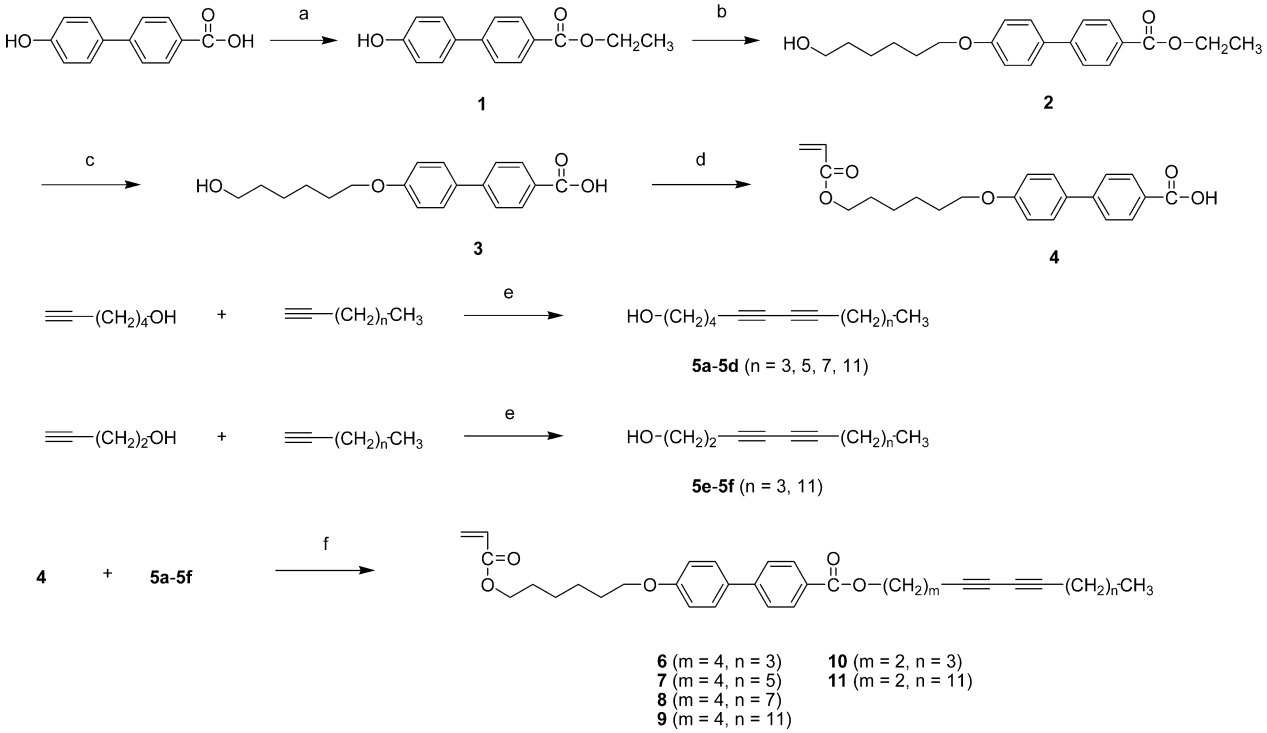
Synthesis of Hexadeca-5,7-diynyl 4-[4-(6-Acryloyloxyhexyloxy)phenyl]benzoate (8). This compound was prepared from compound **4** (1.5 g, 4.1 mmol) and compound **5c** (1.0 g, 4.1 mmol) as described for compound **6**. The product was isolated as a solid powder by column chromatography on silica gel using ethyl acetate and hexane (1/3) as eluent. Yield, 1.3 g (54.0%). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.10 (dd, J = 8.3 Hz, −OOCAr−, 2H), 7.63 (dddd, overlap, Ar, 4H), 7.00 (dd, J = 8.8 Hz, −OAr−, 2H), 6.44 (d, J = 17.3 Hz, =CH, 1H), 6.17 (dd, J = 10.3, 7.0 Hz, =CH, 1H), 5.84 (d, J = 10.3 Hz, =CH, 1H), 4.37 (t, $-COOCH_2-$, 2H), 4.20 (t, $-OCH_2-$, 2H), 4.04 (t, $-ArOCH_2-$, 2H), 2.39 (t, $\equiv CCH_2-$, 2H), 2.28 (t, $\equiv CCH_2-$, 2H), 1.91−1.83 (m, $-OCH_2CH_2-$, 6H), 1.75−1.70 (m, $\equiv CCH_2CH_2-$, 4H), 1.57−1.28 (m, $-CH_2-$, 14H), 0.90 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 166.7, 166.5, 159.5, 145.4, 132.5, 130.7, 130.3, 128.8, 128.6, 128.5, 126.6, 115.1, 78.1, 76.7, 68.1, 66.1, 65.3, 64.7, 64.5, 32.0, 29.2, 29.1, 28.8, 28.5, 28.1, 26.0, 25.2, 22.8, 19.4, 19.2, 14.3. IR (KBr, cm^{-1}): 2945, 2870, 2242, 2145, 1729, 1713, 1633, 1606, 1480, 1408, 1279, 1195, 1118, 1000, 980, 825, 808. Anal. Calcd for $C_{38}H_{48}O_5$: C, 78.05; H, 8.27. Found: C, 78.06; H, 8.40.

Synthesis of Icosa-5,7-diynyl 4-[4-(6-Acryloyloxyhexyloxy)-phenyl]benzoate (9). This compound was prepared from compound **4** (1.2 g, 3.4 mmol) and compound **5d** (1.0 g, 3.4 mmol) as described for compound **6**. The product was isolated as a solid powder by column chromatography on silica gel using ethyl acetate and hexane (1/3) as eluent. Yield, 2.2 g (41.1%). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.10 (dd, J = 8.3 Hz, −OOCAr−, 2H), 7.63 (dddd, overlap, Ar, 4H), 7.00 (dd, J = 8.8 Hz, −OAr−, 2H), 6.44 (d, J = 17.3 Hz, =CH, 1H), 6.17 (dd, J = 10.3, 7.0 Hz, =CH, 1H), 5.84 (d, J = 10.3 Hz, =CH, 1H), 4.37 (t, $-COOCH_2-$, 2H), 4.20 (t, $-OCH_2-$, 2H), 4.04 (t, $-ArOCH_2-$, 2H), 2.39 (t, $\equiv CCH_2-$, 2H), 2.28 (t, $\equiv CCH_2-$, 2H), 1.91−1.83 (m, $-OCH_2CH_2-$, 6H), 1.75−1.70 (m, $\equiv CCH_2CH_2-$, 4H), 1.57−1.25 (m, $-CH_2-$, 22H), 0.90 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 166.7, 166.5, 159.6, 145.5, 132.5, 130.7, 130.3, 128.8, 128.6, 128.5, 126.6, 115.1, 78.1, 76.7, 68.1, 66.1, 65.3, 64.7, 64.5, 32.1, 29.9, 29.8, 29.7, 29.5, 29.4, 29.3, 29.1, 28.8, 28.5, 28.1, 26.0, 25.2, 19.4, 19.2, 14.2. IR (KBr, cm^{-1}): 2945, 2870, 2243, 2145, 1729, 1713, 1635, 1604, 1480, 1407, 1276, 1195, 1118, 1000, 981, 825, 808. Anal. Calcd for $C_{42}H_{56}O_5$: C, 78.71; H, 8.81. Found: C, 78.48; H, 8.87.

Synthesis of Deca-3,5-diynyl 4-[4-(6-Acryloyloxyhexyloxy)-phenyl]benzoate (10). This compound was prepared from compound **4** (1.0 g, 2.7 mmol) and compound **5e** (0.4 g, 2.7 mmol) as described for compound **6**. The product was isolated as a solid powder by column chromatography on silica gel using ethyl acetate and hexane (1/3) as eluent. Yield, 0.7 g (51.5%). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.10 (d, J = 8.3 Hz, −OOCAr−, 2H), 7.63 (dd, overlap, Ar, 4H), 7.00 (d, J = 8.8 Hz, −OAr−, 2H), 6.44 (d, J = 17.3 Hz, =CH, 1H), 6.17 (dd, J = 10.3, 7.0 Hz, =CH, 1H), 5.84 (d, J = 10.3 Hz, =CH, 1H), 4.43 (t, $-COOCH_2-$, 2H), 4.20 (t, $-OCH_2-$, 2H), 4.00 (t, $-ArOCH_2-$, 2H), 2.77 (t, $\equiv CCH_2-$, 2H), 2.28 (t, $\equiv CCH_2-$, 2H), 1.83−1.70 (m, $-OCH_2CH_2-$, 4H), 1.53−1.42 (m, $-CH_2-$, 8H), 0.93 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 166.6, 166.4, 159.6, 145.6, 132.4, 130.7, 130.4, 128.8, 128.5, 128.1, 126.6, 115.1, 78.7, 72.8, 68.1, 67.2, 65.2, 64.7, 62.6, 30.5, 29.3, 28.8, 26.0, 22.1, 20.1, 19.1, 14.2. IR (KBr, cm^{-1}): 2931, 2854, 2243, 2145, 1737, 1723, 1635, 1606, 1408, 1000, 985, 875, 844, 811. Anal. Calcd for $C_{32}H_{36}O_5$: C, 76.77; H, 7.25. Found: C, 76.74; H, 7.29.

Synthesis of Octadeca-3,5-diynyl 4-[4-(6-Acryloyloxyhexyloxy)phenyl]benzoate (11). This compound was prepared from compound **4** (1.3 g, 3.4 mmol) and compound **5f** (0.9 g, 3.4 mmol) as described for compound **6**. The product was isolated as a solid powder by column chromatography on silica gel using ethyl acetate and hexane (1/3) as eluent. Yield, 1.2 g (59.3%). ^{1}H NMR ($CDCl_3$, ppm): δ = 8.10 (d, J = 8.3 Hz, −OOCAr−, 2H), 7.63 (dd, overlap, Ar, 4H), 7.00 (d, J = 8.8 Hz, −OAr−, 2H), 6.44 (d, J = 17.3 Hz, =CH, 1H), 6.17 (dd, J = 10.3, 7.0 Hz, =CH, 1H), 5.84 (d, J = 10.3 Hz, =CH, 1H), 4.43 (t, $-COOCH_2-$, 2H), 4.20 (t, $-OCH_2-$, 2H), 4.00 (t, $-ArOCH_2-$, 2H), 2.77 (t, $\equiv CCH_2-$, 2H), 2.28 (t, $\equiv CCH_2-$, 2H), 1.83−1.70 (m, $-OCH_2CH_2-$, 4H), 1.53−1.25 (m, $-CH_2-$, 24H), 0.93 (t, $-CH_3$, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ = 166.6, 166.5, 159.6, 145.6, 132.5, 130.7, 130.3, 128.8, 128.6, 128.5, 126.6, 115.1, 78.1, 76.7, 68.1, 66.1, 65.3, 64.7, 64.5, 32.1, 29.9, 29.7, 29.5, 29.4, 29.3, 29.1, 28.8, 28.5, 28.1, 26.0, 25.2, 19.4, 19.2,

Scheme 2. Synthesis of Heterobifunctional Monomers (6−11)[a]



[a] Conditions: (a) ethanol, H_2SO_4, reflux; (b) 6-bromo-1-hexanol, K_2CO_3, KI, DMF, 80 °C; (c) KOH, THF, ethanol, H_2O, reflux; (d) acryloyl chloride, *N*,*N*-diethylaniline, 2,6-di-*tert*-butylphenol, 1,4-dioxane, 25 °C; (e) copper(II) acetate, pyridine, methanol, 60 °C, (f) DCC, DMAP, CH_2Cl_2, THF, rt.

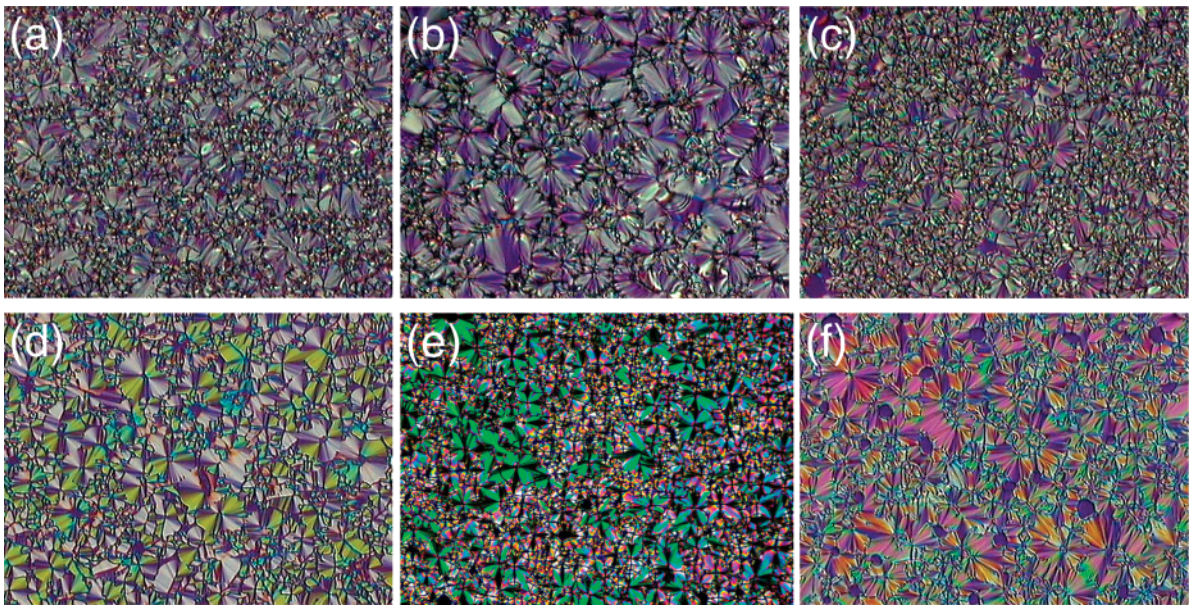


Figure 1. Photomicrographs of mesophase textures taken under POM: (a) **6** (25 °C on second cooling), (b) **7** (25 °C on second cooling), (c) **8** (25 °C on second cooling), (d) **9** (42 °C on second cooling), (e) **10** (88 °C on second heating), and (f) **11** (88 °C on second heating).

14.2. IR (KBr, cm^{-1}): 2935, 2854, 2243, 2145, 1736, 1723, 1634, 1606, 1408, 1000, 985, 875, 844, 810. Anal. Calcd for $C_{40}H_{52}O_5$: C, 78.39; H, 8.55. Found: C, 78.15; H, 8.62.

Results and Discussion

Heterobifunctional mesogenic compounds **6**−**11** were synthesized according to Scheme 2. 4-[4-(6-Hydroxyhexyloxy)-phenyl]benzoic acid (**3**) was prepared by reaction of ethyl 4-(4-hydroxyphenyl)benzoate (**1**) with 6-bromo-1-hexanol and subsequent hydrolysis. An acryl group was connected to compound **3** to yield acryl monomer **4**. Hydroxyl-functionalized diacetylene **5a**−**f** were prepared by the coupling reaction of 5-hexyn-1-ol or 3-butyn-1-ol with 1-alkynes. Diacetylenes (**5**) were connected to the acryl monomer (**4**) through an esterification reaction using DCC, resulting in compounds **6**−**11**. The structures of all of the products were identified by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis.

The mesomorphic properties of compounds **6**−**11** were investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffractometry (Cu Kα radiation). All compounds showed enantiotropic transitions. Under POM, highly birefringent focal-conic fan textures appeared on heating and cooling from the isotropic melt (Figure

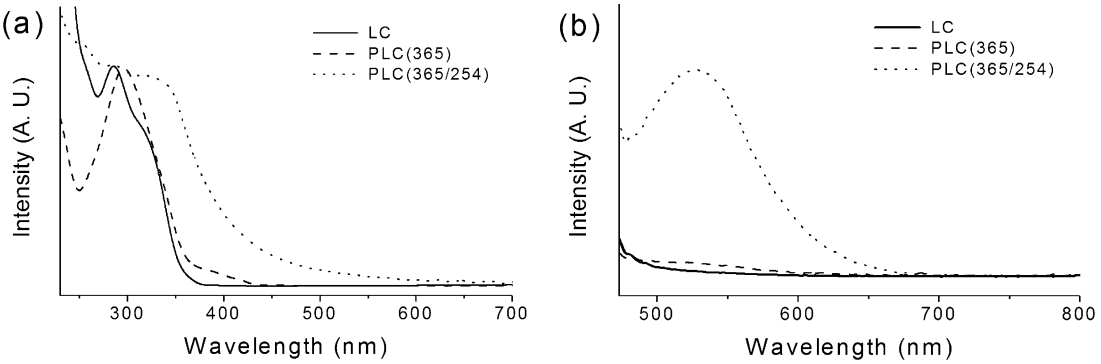


Figure 2. (a) UV−vis and (b) photoluminescence spectra of **6** taken in the LC state (solid line) after irradiation with 365 nm UV light for 10 min (dashed line) and after subsequent irradiation with 254 nm UV for 2 h (dotted line).

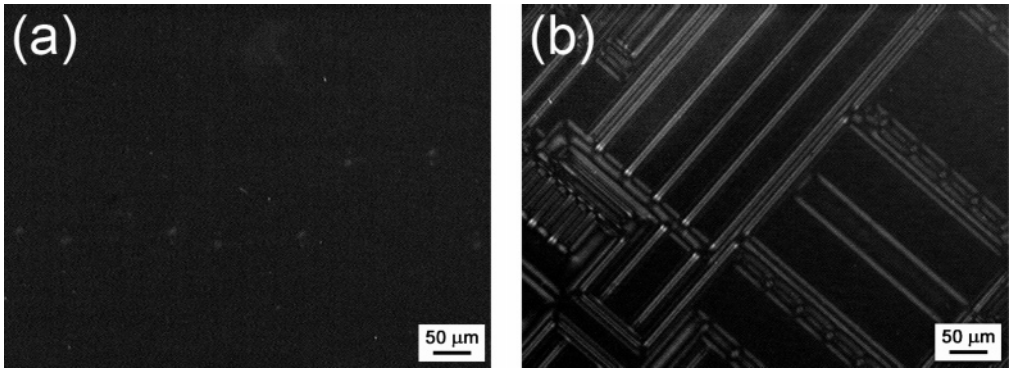


Figure 3. Image patterns observed under polarizing microscopy; the angle between the shear direction of the sample and the axis of the cross-polarizer was 0° (a) and 45° (b). The patterns were obtained by irradiation of **6** with a 365 nm UV light for 10 min and with a 100 W high-pressure mercury arc lamp at 254 nm through a photomask for 2 h at 30 °C.

Table 1. Phase-Transition Temperatures (°C) and Enthalpy Values (in brackets, kJ/mol) of Compounds 6−11 As Determined by DSC (scan rate 10 °C min^{-1})[a]

compound	second heating	second cooling
6	K 26.4 [13.4] Sm 44.9 [8.1] I	I 39.6 [7.8] Sm 12.9 [12.0] K
7	K 30.4 [16.4] Sm 41.8 [10.4] I	I 38.2 [9.0] Sm 17.4 [15.3] K
8	K 34.7 [15.4] Sm 43.1 [8.4] I	I 38.5 [8.7] Sm 19.9 [13.7] K
9	K 47.4 [9.8] Sm 55.5 [42.9] I	I 43.5 [10.3] Sm 33.9 [32.3] K
10	K 87.7 [9.6] Sm 96.4 [9.4] I	I 91.9 [9.6] Sm 83.1 [9.8] K
11	K 13.1 [4.9] K 81.0 [12.3] Sm 88.6 [12.4] I	I 87.8 [13.6] Sm 79.1 [13.4] K 21.2 [3.5] K

[a] K = crystal; Sm = smectic; I = isotropic.

1). For example, compound **6** showed two endothermic peaks at 26.4 (13.4 kJ/mol) and 44.9 °C (8.1 kJ/mol) during the second heating and two exothermic peaks at 39.6 (−7.8 kJ/mol) and 12.9 °C (−12.0 kJ/mol) during the second cooling. A focal-conic fan texture began to appear at 39.6 °C during cooling from the isotropic melt and persisted below room temperature. Compounds **6**−**9** having a butyl spacer between a biphenyl and a diacetylene group showed lower crystal to liquid crystal transition temperatures than compounds **10** and **11** having an ethyl spacer. The crystal to liquid crystal transition temperature decreased as the alkyl tail length decreased, so that compounds **6**−**8** exhibited LC phases even at room temperature. The thermal transitions of the compounds are summarized in Table 1.

An XRD study was carried out to obtain more detailed information on the liquid crystalline structure. Compound **6** showed four sharp peaks with *d* spacings of 33.2, 16.6, 11.1, and 8.3 Å in the small-angle region, corresponding to the (100), (200), (300), and (400) Bragg reflections, respectively. The (100) spacing of 33.2 Å was almost the same as the length of the extended structure of **6** (33.5 Å) determined using simple molecular modeling, suggesting that the compound had a monolayered smectic A structure. The X-ray diffraction data

Table 2. X-ray Diffraction Data for the LC Phases of Compounds 6−11

compound	(*hkl*)	d_{exp} (Å)	d_{calcd} (Å)	compound	(*hkl*)	d_{exp} (Å)	d_{calcd} (Å)
6	(100)	33.2	33.5	**7**	(100)	35.6	35.8
	(200)	16.6	16.8		(200)	17.6	17.6
	(300)	11.1	11.2		(300)	11.8	11.9
	(400)	8.3	8.4		(400)	8.8	9.0
8	(100)	38.0	38.0	**9**	(100)	73.6	43.2
	(200)	18.9	19.0		(200)	37.0	21.6
	(300)	12.6	12.7		(300)	24.9	14.4
	(400)	9.5	9.5				
10	(100)	32.7	32.0	**11**	(100)	40.5	41.0
	(200)	16.4	16.0		(200)	20.3	20.5
	(300)	10.9	10.7		(300)	13.5	13.7
	(400)	8.2	8.0				

are summarized in Table 2. All compounds except **9** seemed to form monolayered smectic A structures. Compound **9** having the longest tail among the series showed a (100) spacing of 73.6 Å, which was much larger than the calculated length (43.2 Å) of the molecule. We presume that compound **9** had a double-layered smectic structure.

Photopolymerization of compound **6** in the LC state was studied by FT-IR.[15,25] A mixture of **6** and a photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA, 4 wt %), was cast on a KBr window. When irradiated with 365 nm UV light (1 mW/cm^2), the intensities of the representative absorption peaks of the acryl group at 1636 (C═C stretching mode) and 1408 cm^{-1} (vinyl CH_2 in plane deformation mode) gradually decreased with increasing irradiation time. After irradiation for 10 min, about 50% conversion of the acryl group was calculated from the intensity change of the peak at 1636 cm^{-1}. The sample was irradiated subsequently with 254 nm UV light (3 mW/cm^2), resulting in a decrease in the intensity of the two peaks at 2241

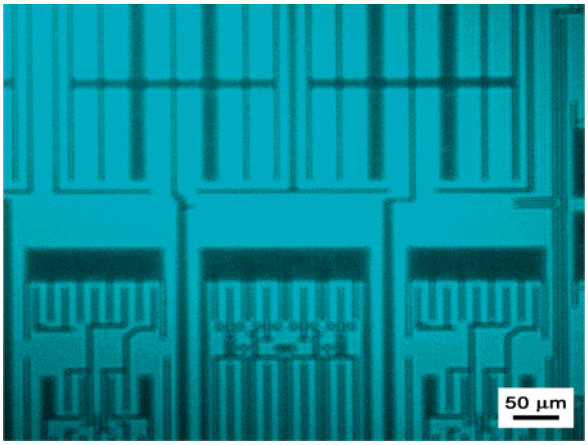


Figure 4. Fluorescence image obtained from **6** excited at 458 nm and recorded emission above 475 nm.

and 2142 cm^{-1} (C−C triple bond stretching) and the appearance of a weak peak at 2201 cm^{-1} as a consequence of the 1,4-addition reaction.

Figure 2 shows the UV−vis and photoluminescence (λ_{ex} = 458 nm) spectra of compound **6**, which had an absorption maximum at 286 nm in the LC state. The absorption maximum was slightly red shifted to 296 nm by the UV irradiation at 365 nm. When excited at 458 nm, neither sample showed any fluorescence emission, since no absorption occurred at this wavelength. However, after UV irradiation at 254 nm, absorption occurred up to about 600 nm with a λ_{max} of 333 nm due to the presence of the short conjugated polydiacetylene chains. The fluorescence emission occurred at a wavelength of up to 650 nm when excited at 458 nm.

For the photoimaging a mixture of **6** and a photoinitiator (DMPA, 4 wt %) was cast on a glass plate and sheared with a cover glass at room temperature to result in an LC monodomain. The sample was then partially polymerized to form a polymeric thin film by irradiation with 365 nm UV light (1 mW/cm^2) for 10 min. Subsequent UV irradiation at 254 nm using a 100 W high-pressure mercury arc lamp (3 mW/cm^2) through a photomask was carried out for 2 h. At this stage, the diacetylene groups in addition to the remnant vinyl groups were polymerized. Figure 3 shows an image pattern observed under polarizing microscopy. When the shear direction of the sample was parallel or perpendicular to the axis of the cross-polarizer, minimum transmittance was obtained, indicating that the molecules were macroscopically aligned in the shear direction. A bright birefringence pattern was obtained by rotating the sample by 45°. The masked part remained birefringent under polarizing microscopy. On the other hand, the irradiated part appeared dark. This result is ascribed to the polymerization of both the acryl and diacetylene groups, resulting in a cross-linked structure in which the long range order was lost.

Figure 4 shows the fluorescence image observed by confocal laser scanning microscopy (CLSM). The sample was prepared in the same manner as that described above. The part of the sample irradiated by a high-pressure mercury arc lamp was highly fluorescent due to the presence of the polydiacetylene chains, while the masked part exhibited little fluorescence. Bluish fluorescence was observed when the 458 nm line of an argon-ion laser was used for excitation and the emission was collected above 475 nm.

Conclusions

We prepared heterobifunctional mesogenic compounds having two photopolymerizable groups, i.e., acryl and diacetylene groups. Among the series, compounds **6**−**8** formed smectic phases even at room temperature. An anisotropic polymer thin film was obtained by the photopolymerization of compound **6** with 365 nm UV light, where the acryl group was selectively polymerized. Photoimaging was performed on the film by the subsequent photopolymerization of the diacetylene group through a photomask. The selective photopolymerization of the heterobifunctional liquid crystals will be useful for achieving more sophisticated micropatterning.

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