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Synthesis and Photopolymerization of Photoreactive Mesogens Based on Chalcone

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Abstract: A series of photoreactive mesogens based on chalcone were prepared and their morphological behavior and reactivity were studied according to a variable number of alkyloxy tail carbons. The linear ester compounds **3a-h** comprised two chalcone units connected to a benzene ring through ester linkages. All linear ester compounds showed enantiotropic liquid crystalline phases. The X-ray diffractograms for the mesophases of compounds **3a-h** showed a set of reflections in the small-angle region which consisted of more than three sharp diffraction peaks with *d* spacings in the ratio of 1:1/2:1/3, confirming the well defined smectic A structures of the compounds. Compounds **3a-h** were considered to be bifunctional monomers due to the presence of two photoreactive chalcone groups. Upon UV irradiation, its polymerization proceeded through the [2+2] addition reaction between chalcone units in a stepwise manner. An image pattern was obtained by the photopolymerization of the liquid crystal of the compound (**3h**) with decyloxy tails through a photomask. The irradiated part became dark while the masked part remained birefringent under polarized optical microscopy, which was ascribed to the production via the UV irradiation of a polymer or a dimer having cyclobutane rings by [2+2] addition, which thereby disrupted the alignment of the molecules.

Keywords: liquid crystal, chalcone, [2+2] addition, photopolymerization, patterning.

Introduction

Reactive mesogens have many potential applications in display and data storage industries.[1,2] The advantages of reactive mesogens for these applications are associated with their unique phase properties having both fluidity and molecular ordering, which allow better control over alignment. Most mesogens can be macroscopically oriented under electric or magnetic fields, and on mechanically rubbed substrates.[3,4] The polymerization of reactive mesogens in an oriented liquid crystalline state has been used to produce anisotropic polymeric films. The mesogens generally have polymerizable groups attached to both sides of a mesogen through flexible spacers. The polymerization starts by activation of a photoinitiator with light in an LC state to yield a network structure, where a rigid part of a mesogen is still aligned as in an LC state.[1,5-11] There are a few other examples for the polymerizable mesogens, in which photoreactive groups are introduced into mesogens to become parts of rigid rods.[12,13] They are polymerized by light without the aid of a photoinitiator to produce stable anisotropic materials. Significant changes in the aligned structures are often accompanied, resulting in optical property changes.

In a previous communication,[14] we reported a polymerizable liquid crystal molecule with two photoreactive chalcone units and its application for photoimaging. Chalcones consisting of two aromatic rings and an enone group have interesting photochemical reactivities. The [2+2] addition reaction of chalcone units by photoirradiation forms a mixture of cyclobutane rings with different configurations, for example, *cis-cis*, *cis-trans*, and *trans-trans* with respect to the direction of substituents on the ring. Photoirradiation in the liquid crystalline state disrupts an aligned structure to be isotropic. In this work, we prepared a series of photoreactive mesogens based on chalcone. With varying number of alkyloxy tail carbons, we investigated their morphological behavior and reactivity.

Experimental

Materials. 4-Hydroxybenzaldehyde, 4′-hydroxyacetophenone, sodium hydride (95%), terephthaloyl chloride, and 1-bromoalkanes were purchased from Aldrich and used without further purification. Methanol was dried over molecular sieves 4 Å and distilled. Tetrahydrofuran (THF) was dried over sodium metal and distilled.

Measurements. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-LA 300 (300 MHz) spectrometer or a BRUKER Advance DPX-300 (75 MHz) at room temperature. IR spectra were obtained

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*Corresponding Author. E-mail: jichang@snu.ac.kr with a PERKIN ELMER Spectrum 2000 Fourier transform infrared (FTIR) spectrometer. UV-vis spectra were obtained with the use of a SINCO 3150. Thermal analysis was performed with a TA modulated 2920 differential scanning calorimeter (DSC) and 2050 thermogravimetric analyzer (TGA). Powder X-ray diffractograms were obtained by using a Mac Science Mxp 3 (Cu$K\alpha$ radiation, λ = 1.54 Å). The polarized optical microscope (POM) study was performed using a Leica MPS 30 equipped with Mettler Toledo FP82HT heating stage and Mettler Toledo FP 90 controller. Elemental analysis (EA) was performed using an EAGER 200 elemental analyzer.

Synthesis of 4′-Propyloxyacetophenone (1a). To a solution of 4′-hydroxyacetophenone (3.00 g, 22.03 mmol) in tetrahydrofuran (100 mL) was added sodium hydride (95%, 0.56 g), and the mixture was stirred for 2 h under nitrogen. To the reaction mixture was added methanol (30 mL) to dissolve the precipitated salt. To the solution was added 1-bromopropane (2.40 mL, 26.44 mmol), and the solution was refluxed for 24 h under nitrogen. The insoluble precipitates were removed by filtration through a silica gel column (5 cm) with ethyl acetate. After evaporation of the solvent, 4′-propyloxyacetophenone was isolated by column chromatography on silica gel (20% ethyl acetate in hexane) in 82.0% yield. ^{1}H NMR (CDCl$_3$, ppm): δ 7.9 - 6.8 (dd, aromatic proton, 4H), 4.0 (t, -OCH$_2$-, 2H), 2.5 (s, CH$_3$CO-, 3H), 1.9 - 1.1 (m, alkyl proton, 5H). IR (NaCl, cm^{-1}): 3340, 3074, 2943, 2881, 1679, 1600, 1512, 1423, 1361, 1257, 1166. ^{13}C NMR (CDCl$_3$, ppm): δ 195.5, 162.4, 129.8, 129.4, 113.4, 68.9, 25.4, 21.8, 9.8.

Synthesis of 4′-Butyloxyacetophenone (1b). Yield: 88.5%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.9 - 6.8 (dd, aromatic proton, 4H), 4.0 (t, -OCH$_2$-, 2H), 2.5 (s, CH$_3$CO-, 3H), 1.9 - 0.8 (m, alkyl proton, 7H). IR (NaCl, cm^{-1}): 3336, 3074, 2958, 2869, 1679, 1600, 1510, 1421, 1357, 1251, 1170. ^{13}C NMR (CDCl$_3$, ppm): δ 196.1, 162.8, 130.2, 129.7, 113.7, 67.5, 30.8, 25.8, 18.8, 13.8.

Synthesis of 4′-Pentyloxyacetophenone (1c). Yield: 71.4%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.9 - 6.8 (dd, aromatic proton, 4H), 4.0 (t, -OCH$_2$-, 2H), 2.5 (s, CH$_3$CO-, 3H), 1.9 - 0.9 (m, alkyl proton, 9H). IR (NaCl, cm^{-1}): 3340, 3043, 2935, 2874, 1677, 1606, 1515, 1469, 1425, 1361, 1263, 1174. ^{13}C NMR (CDCl$_3$, ppm): δ 196.6, 163.0, 130.5, 129.9, 114.0, 68.1, 28.7, 28.0, 26.2, 22.3, 13.9.

Synthesis of 4′-Hexyloxyacetophenone (1d). Yield: 61.7%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.9 - 6.8 (dd, aromatic proton, 4H), 4.0 (t, -OCH$_2$-, 2H), 2.5 (s, CH$_3$CO-, 3H), 1.9 - 0.8 (m, alkyl proton, 11H). IR (NaCl, cm^{-1}): 3338, 3072, 2935, 2858, 1679, 1604, 1512, 1423, 1361, 1255, 1170. ^{13}C NMR (CDCl$_3$, ppm): δ 196.2, 162.9, 130.3, 129.9, 113.9, 68.0, 31.3, 28.8, 25.9, 25.4, 22.4, 13.8.

Synthesis of 4′-Heptyloxyacetophenone (1e). Yield: 58.1%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.9 - 6.8 (dd, aromatic proton, 4H), 4.0 (t, -OCH$_2$-, 2H), 2.5 (s, CH$_3$CO-, 3H), 1.9 - 0.8 (m, alkyl proton, 13H). IR (NaCl, cm^{-1}): 3327, 3047, 2943, 2854, 1670, 1604, 1508, 1427, 1361, 1255, 1182. ^{13}C NMR (CDCl$_3$, ppm): δ 196.5, 162.9, 130.4, 129.9, 113.9, 68.1, 31.6, 30.0, 28.9, 26.1, 25.8, 22.5, 13.9.

Synthesis of 4′-Octyloxyacetophenone (1f). Yield: 72.2%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.9 - 6.8 (dd, aromatic proton, 4H), 4.0 (t, -OCH$_2$-, 2H), 2.5 (s, CHO$_3$CO-, 3H), 1.9 - 0.9 (m, alkyl proton, 15H). IR (NaCl, cm^{-1}): 3336, 3060, 2925, 2854, 1677, 1606, 1510, 1419, 1357, 1251, 1170. ^{13}C NMR (CDCl$_3$, ppm): δ 195.3, 162.4, 129.8, 129.3, 113.3, 67.5, 31.3, 28.8, 28.7, 28.5, 27.6, 25.5, 22.1, 13.5.

Synthesis of 4′-Nonyloxyacetophenone (1g). Yield: 63.8%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.9 - 6.8 (dd, aromatic proton, 4H), 4.0 (t, -OCH$_2$-, 2H), 2.5 (s, CH$_3$CO-, 3H), 1.9 - 0.8 (m, alkyl proton, 17H). IR (KBr, cm^{-1}): 3143, 2925, 2852, 1676, 1602, 1506, 1419, 1359, 1263, 1174. ^{13}C NMR (CDCl$_3$, ppm): δ 196.6, 163.0, 130.4, 129.9, 114.0, 68.2, 31.8, 29.4, 29.3, 29.2, 29.0, 26.2, 25.9, 22.6, 14.0.

Synthesis of 4′-Decyloxyacetophenone (1h). Yield: 65.3%. ^{1}H NMR (CDCl$_3$, ppm): δ 7.9 - 6.8 (dd, aromatic proton, 4H), 4.0 (t, -OCH$_2$-, 2H), 2.5 (CH$_3$CO-, 3H), 1.9 - 0.8 (m, alkyl proton, 19H). IR (NaCl, cm^{-1}): 3330, 3062, 2918, 2854, 1677, 1606, 1508, 1417, 1363, 1255, 1174. ^{13}C NMR (CDCl$_3$, ppm): δ 196.7, 163.0, 130.5, 129.9, 114.0, 68.2, 31.8, 29.5, 29.3, 29.2, 29.0, 28.8, 26.3, 25.9, 22.6, 14.0.

Synthesis of 4-Hydroxy-4′-Propyloxy-Chalcone (2a). To a solution of 4′-propyloxyacetophenone (3.00 g, 16.83 mmol) in acetic acid (100 mL) was added 4-hydroxybenzaldehyde (2.06 g, 16.83 mmol) and sulfuric acid (98%, 4.13 mL). After stirring under nitrogen for 22 h at room temperature, the solution was neutralized with an aqueous NaOH solution (5 N). The crude product was isolated by filtration and purified by column chromatography on silica gel (25% ethyl acetate in hexane) and recrystallized from ethyl acetate/hexane in 69.0% yield. ^{1}H NMR (CDCl$_3$, ppm): δ 8.1 - 6.8 (dddd, aromatic proton, 8H), 7.8, 7.4 (dd, vinyl proton, 2H), 4.0 (t, -OCH$_2$-, 2H), 1.9 - 1.1 (m, alkyl proton, 5H). IR (KBr, cm^{-1}): 3099, 2945, 2881, 1637, 1600, 1510, 1220, 1166. ^{13}C NMR (CDCl$_3$, ppm): δ 190.2, 163.2, 159.4, 145.4, 130.9, 130.6, 130.4, 126.7, 118.4, 116.1, 114.2, 69.6, 22.2, 10.3. Elemental analysis. Calcd for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.76; H, 6.71.

Synthesis of 4-Hydroxy-4′-Butyloxy-Chalcone (2b). Yield: 77.4%. ^{1}H NMR (CDCl$_3$, ppm): δ 8.1 - 6.8 (dddd, aromatic proton, 8H), 7.8, 7.4 (dd, vinyl proton, 2H), 4.0 (t, -OCH$_2$-, 2H), 1.9 - 1.0 (m, alkyl proton, 7H). IR (KBr, cm^{-1}): 3292, 2949, 2866, 1639, 1602, 1512, 1222, 1168. ^{13}C NMR (CDCl$_3$+ DMSO-d_6, ppm): δ 187.6, 161.9, 159.3, 143.3, 130.1, 129.8, 129.6, 125.4, 117.5, 115.3, 113.4, 66.9, 30.2, 18.3, 13.0. Elemental analysis. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.81. Found: C, 77.30; H, 6.81.

Synthesis of 4-Hydroxy-4′-Pentyloxy-Chalcone (2c). Yield: 75.6%. ^{1}H NMR (CDCl$_3$, ppm): δ 8.1 - 6.8 (dddd, aromatic proton, 8H), 7.8, 7.4 (dd, vinyl proton, 2H), 4.0 (t, -OCH$_2$-, 2H), 1.9 - 0.9 (m, alkyl proton, 9H). IR (KBr, cm^{-1}):

3207, 2956, 2864, 1641, 1604, 1504, 1217, 1172. ^{13}C NMR ($CDCl_3$+DMSO-d_6, ppm): δ 187.2, 161.8, 159.1, 143.1, 129.9, 129.6, 125.2, 117.3, 115.1, 113.2, 67.1, 27.7, 27.0, 21.4, 13.1. Elemental analysis. Calcd for $C_{20}H_{22}O_3$: C, 77.38; H, 7.15. Found: C, 77.19; H, 7.20.

Synthesis of 4-Hydroxy-4′-Hexyloxy-Chalcone (2d). Yield: 69.7%. ^{1}H NMR ($CDCl_3$, ppm): δ8.1 - 6.8 (dddd, aromatic proton, 8H), 7.8, 7.4 (dd, vinyl proton, 2H), 6.4 (s, -OH, 1H), 4.0 (t, $-OCH_2-$, 2H), 1.9 - 0.8 (m, alkyl proton, 11H). IR (KBr, cm^{-1}): 3211, 2947, 2866, 1641, 1603, 1506, 1225, 1167. ^{13}C NMR ($CDCl_3$, ppm): δ190.2, 163.2, 159.3, 145.3, 130.9, 130.8, 130.5, 126.8, 118.7, 116.2, 114.3, 68.4, 31.4, 28.9, 25.5, 13.9. Elemental analysis. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.75; H, 7.64.

Synthesis of 4-Hydroxy-4′-Heptyloxy-Chalcone (2e). Yield: 45.0%. ^{1}H NMR ($CDCl_3$, ppm): δ8.1 - 6.8 (dddd, aromatic proton, 8H), 7.8, 7.4 (dd, vinyl proton, 4H), 6.4 (s, -OH, 1H), 4.0 (t, $-OCH_2-$, 2H), 1.9 - 0.8 (m, alkyl proton, 11H). IR (KBr, cm^{-1}): 3211, 2947, 2866, 1641, 1603, 1506, 1225, 1167. ^{13}C NMR ($CDCl_3$+DMSO-d_6, ppm): δ190.2, 163.2, 159.3, 145.3, 130.9, 130.8, 130.5, 126.8, 118.7. Elemental analysis. Calcd for $C_{22}H_{26}O_3$: C, 78.07; H, 7.74. Found: C, 78.24; H, 7.86.

Synthesis of 4-Hydroxy-4′-Octyloxy-Chalcone (2f). Yield: 54.5% yield. ^{1}H NMR ($CDCl_3$, ppm): δ8.1 - 6.8 (dddd, aromatic proton, 8H), 7.8, 7.4 (dd, vinyl proton, 2H), 7.1 (s, -OH, 1H), 4.0 (t, $-OCH_2-$, 2H), 1.9 - 0.9 (m, alkyl proton, 15H). IR (KBr, cm^{-1}): 3141, 2943, 2854, 1641, 1606, 1550, 1506, 1226, 1164. ^{13}C NMR ($CDCl_3$+DMSO-d_6, ppm): δ 188.1, 162.3, 159.5, 143.8, 130.4, 130.1, 129.9, 125.7, 117.8, 115.6, 113.7, 67.6, 31.2, 28.8, 28.6, 28.5, 25.4, 22.1, 13.6. Elemental analysis. Calcd for $C_{23}H_{28}O_3$: C, 78.38; H, 8.00. Found: C, 78.20; H, 8.24.

Synthesis of 4-Hydroxy-4′-Nonyloxy-Chalcone (2g). Yield: 61.0%. ^{1}H NMR ($CDCl_3$, ppm): δ8.1-6.8 (dddd, aromatic proton, 8H), 7.8, 7.4 (dd, vinyl proton, 2H), 4.0 (t, $-OCH_2-$, 2H), 1.9 - 0.8 (m, alkyl proton, 17H). IR (KBr, cm^{-1}): 3143, 2925, 2852, 1647, 1600, 1512, 1348, 1286, 1218,1166, 1033. ^{13}C NMR ($CDCl_3$+DMSO-d_6, ppm): δ 187.2, 161.8, 159.1, 143.1, 130.0, 129.4, 125.2, 117.3, 115.1, 113.2, 67.2, 30.8, 28.4, 28.2, 28.1, 28.0, 24.9, 21.6, 13.2. Elemental analysis. Calcd for $C_{24}H_{30}O_3$: C, 78.66; H, 8.24. Found: C, 78.59; H, 8.52.

Synthesis of 4-Hydroxy-4′-Decyloxy-Chalcone (2h). Yield: 66.2%. ^{1}H NMR ($CDCl_3$, ppm): δ8.1 - 6.8 (dddd, aromatic proton, 8H), 7.8, 7.4 (dd, vinyl proton, 2H), 4.0 (t, $-OCH_2-$, 2H), 1.9 - 0.8 (m, alkyl proton, 19H). IR (KBr, cm^{-1}): 3253, 2923, 2842, 1645, 1598, 1510, 1222, 1161. ^{13}C NMR ($CDCl_3$+ DMSO-d_6, ppm): δ 196.7, 163.0, 130.5, 129.9, 114.0, 68.2, 31.8, 29.5, 29.3, 29.2, 29.0, 28.8, 26.3, 25.9, 22.6, 14.0. Elemental analysis. Calcd for $C_{25}H_{32}O_3$: C, 78.90; H, 8.48. Found: C, 78.79; H, 8.27.

Synthesis of Compound 3a. To a solution of 4-hydroxy-4′-propyloxy-chalcone (1.00 g, 3.54 mmol) in tetrahydrofuran (100 mL) was added sodium hydride (95%, 0.085 g). After stirring for 2 h at room temperature, terephthaloyl chloride (0.345 g, 1.70 mmol) was added and the mixture was refluxed for 24 h. The precipitated solid was isolated by filtration and washed with methanol and water. The product was isolated by recrystallization from a mixture of chlorform and hexane in 81.0% yield. ^{1}H NMR ($CDCl_3$+CF_3CO_2D, ppm): δ8.3 (s, core aromatic proton, 4H), 8.1 - 6.9 (dddd, side aromatic proton, 16H), 7.8, 7.5 (dd, vinyl proton, 4H), 4.0 (t, $-OCH_2-$, 4H), 1.9 - 1.1 (m, alkyl proton, 10H). IR (KBr, cm^{-1}): 3037, 2962, 2924, 2871, 1749, 1629, 1609, 1504, 1280, 1163, 1072. ^{13}C NMR ($CDCl_3$+CF_3CO_2D, ppm): δ 193.9, 166.1, 164.8, 152.5, 148.5, 133.6, 133.1, 132.3, 130.8, 130.5, 129.2, 122.4, 122.2, 115.1, 70.5, 22.3, 10.1. Elemental analysis. Calcd for $C_{44}H_{38}O_8$: C, 76.06; H, 5.51. Found: C, 76.04; H, 5.40.

Synthesis of Compound 3b. Yield: 64.0%. ^{1}H NMR ($CDCl_3$+CF_3CO_2D, ppm): δ8.4 (s, core aromatic proton, 4H), 8.1 - 7.0 (dddd, side aromatic proton, 16H), 7.8, 7.5 (dd, vinyl proton, 4H), 4.1 (t, $-OCH_2-$, 4H), 1.9 - 1.0 (m, alkyl proton, 14H). IR (KBr, cm^{-1}): 3020, 2952, 2869, 1743, 1629, 1600, 1504, 1278, 1166, 1078. ^{13}C NMR ($CDCl_3$+CF_3CO_2D, ppm): δ 192.5, 164.9, 164.4, 152.4, 145.7, 133.5, 132.8, 131.9, 130.5, 130.1, 129.2, 122.3, 121.7, 114.7, 68.3, 30.9, 19.1, 13.7. Elemental analysis. Calcd for $C_{46}H_{42}O_8$: C, 76.43; H, 5.85. Found: C, 76.65); H, 5.94.

Synthesis of Compound 3c. Yield: 80.0%. ^{1}H NMR ($CDCl_3$+CF_3CO_2D, ppm): δ8.4 (s, core aromatic proton, 4H), 8.1 -7.0 (dddd, side aromatic proton, 16H), 7.8, 7.5 (dd, vinyl proton, 4H), 4.15 (t, $-OCH_2-$, 4H), 2.0 - 0.9 (m, alkyl proton, 18H). IR (KBr, cm^{-1}): 3039, 2927, 2856, 1741, 1631, 1602, 1500, 1280, 1163, 1076. ^{13}C NMR ($CDCl_3$+CF_3CO_2D, ppm): δ 193.3, 165.5, 164.6, 152.4, 146.1, 133.5, 132.9, 132.1, 130.7, 130.3, 129.1, 122.3, 121.9, 114.8, 68.7, 28.6, 28.0, 22.3, 13.8. Elemental analysis. Calcd for $C_{48}H_{46}O_8$: C, 76.77; H, 6.17. Found: C, 76.76; H, 6.35.

Synthesis of Compound 3d. Yield: 64.0%. ^{1}H NMR ($CDCl_3$, ppm): δ8.3 (s, core aromatic proton, 4H), 8.1 - 6.9 (dddd, side aromatic proton, 16H), 7.8, 7.5 (dd, vinyl proton, 4H), 4.0 (t, $-OCH_2-$, 4H), 1.9 - 0.8 (m, alkyl proton, 22H). IR (KBr, cm^{-1}): 3043, 2960, 2924, 2858, 1739, 1629, 1600, 1508, 1278, 1166, 1074. ^{13}C NMR ($CDCl_3$+CF_3CO_2D, ppm): δ 192.4, 164.7, 164.4, 152.5, 145.5, 133.6, 132.8, 131.9, 130.5, 130.1, 129.4, 122.2, 121.8, 114.7, 68.6, 31.5, 28.9, 25.5, 22.5, 13.8. Elemental analysis. Calcd for $C_{50}H_{50}O_8$: C, 77.10; H, 6.47. Found: C, 76.98; H, 6.74.

Synthesis of Compound 3e. Yield: 35.0%. ^{1}H NMR ($CDCl_3$+CF_3CO_2D, ppm): δ 8.4 (s, core aromatic proton, 4H), 8.1 -7.1 (dddd, side aromatic proton, 16H), 7.8, 7.5 (dd, vinyl proton, 4H), 4.0 (t, $-OCH_2-$, 4H), 2.0 - 0.9 (m, alkyl proton, 26H). IR (KBr, cm^{-1}): 3045, 2923, 2856, 1743, 1629, 1600, 1502, 1276, 1164, 1082. ^{13}C NMR ($CDCl_3$+CF_3CO_2D, ppm): δ 193.6, 165.8, 164.6, 152.4, 146.3, 133.5, 133.1, 132.2, 130.8, 130.4, 129.2, 122.4, 122.1, 115.0, 68.9, 31.8, 29.1, 28.9, 25.9, 22.6, 13.9. Elemental analysis. Calcd for $C_{52}H_{54}O_8$: C, 77.39; H, 6.74. Found: C, 77.38; H, 6.71.

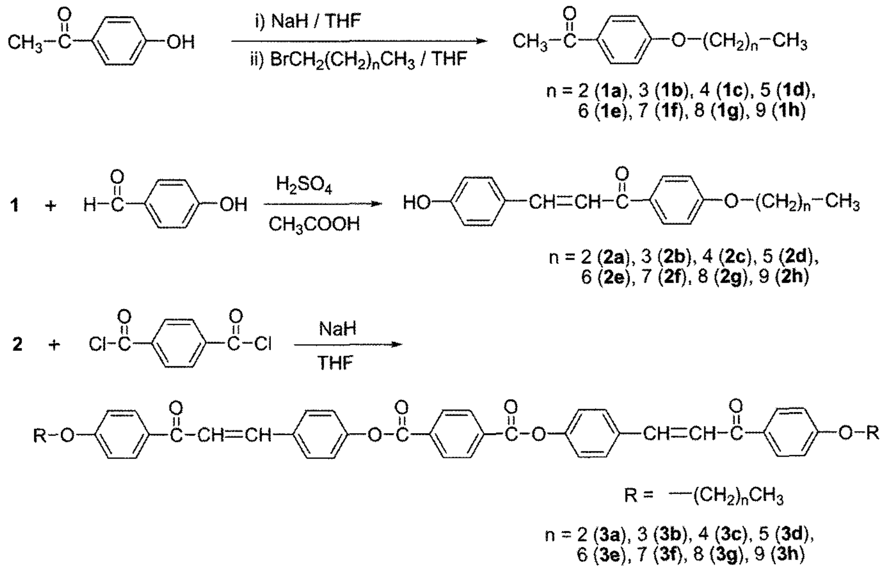
Synthesis of Compound 3f. Yield: 60.0%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.3 (s, core aromatic proton, 4H), 8.1 - 6.9 (dddd, side aromatic proton, 16H), 7.8, 7.5 (dd, vinyl proton, 4H), 4.0 (t, -OCH_2-, 4H), 1.9 - 0.8 (m, alkyl proton, 30H). IR (KBr, cm^{-1}): 3043, 2960, 2924, 2858, 1739, 1629, 1600, 1508, 1278, 1166, 1074. ^{13}C NMR ($CDCl_3$+CF_3CO_2D, ppm): δ 192.4, 164.7, 164.4, 152.5, 145.5, 133.6, 132.8, 131.9, 130.5, 130.1, 129.4, 122.2, 121.8, 114.7, 68.6, 31.5, 28.9, 25.5, 22.5, 13.8. Elemental analysis. Calcd for $C_{54}H_{58}O_8$: C, 77.66; H, 7.00. Found: C, 77.89; H, 6.79.

Synthesis of Compound 3g. Yield: 68.0%. ^{1}H NMR ($CDCl_3$+CF_3CO_2D, ppm): δ 8.4 (s, core aromatic proton, 4H), 8.1 -7.1 (dddd, side aromatic proton, 34H), 7.8, 7.5 (dd, vinyl proton, 4H), 4.0 (t, -OCH_2-, 4H), 2.0 - 0.9 (m, alkyl proton, 26H). IR (KBr, cm^{-1}): 3045, 2923, 2924, 2856, 1743, 1629, 1600, 1502, 1276, 1164, 1082. ^{13}C NMR ($CDCl_3$+CF_3CO_2D, ppm): δ 193.6, 165.8, 164.6, 152.4, 146.3, 133.5, 133.1, 132.2, 130.8, 130.4, 129.2, 122.4, 122.1, 115.0, 68.9, 31.8, 29.1, 28.9, 25.9, 22.6, 13.9. Elemental analysis. Calcd for $C_{56}H_{62}O_8$: C, 77.92; H, 7.24. Found: C, 77.92; H, 7.59.

Synthesis of Compound 3h. Yield: 65.7%. ^{1}H NMR ($CDCl_3$, ppm): δ 8.3 (s, core aromatic proton, 4H), 8.1 - 6.9 (dddd, side aromatic proton, 38H), 7.8, 7.5 (dd, vinyl proton, 4H), 4.0 (t, -OCH_2-, 4H), 1.9 - 0.9 (m, alkyl proton, 30H). IR (KBr, cm^{-1}): 3047, 2920, 2854, 1745, 1625, 1604, 1508, 1276, 1164, 1076. ^{13}C NMR ($CDCl_3$+CF_3CO_2D, ppm): δ 193.3, 165.6, 164.6, 152.4, 146.2, 133.5, 132.9, 132.2, 130.7, 130.4, 129.2, 122.3, 121.9, 114.9, 68.8, 31.8, 29.3, 29.2, 28.9, 25.9, 22.7, 13.9. Elemental analysis. Calcd for $C_{58}H_{66}O_8$: C, 78.17; H, 7.46. Found: C, 78.01; H, 7.58.

Results and Discussion

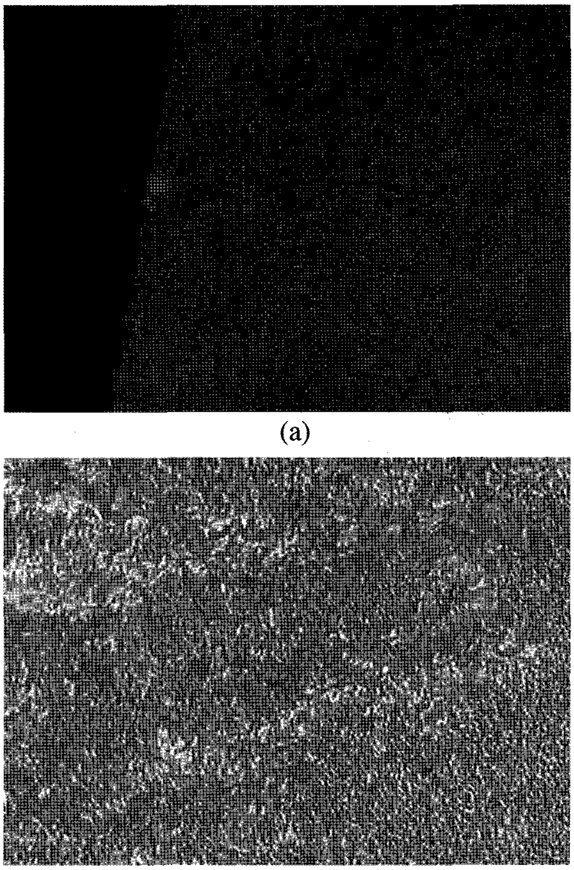
Synthesis. Linear chalcones **3a-h** comprising two chalcone units connected to a benzene ring through ester linkages were prepared according to Scheme I. Chalcones are generally prepared from an aldol condensation between a benzaldehyde and an acetophenone in the presence of a base or acid catalyst. We used 4′-hydroxyacetophenone and 4-hydroxybenzaldehyde as starting materials. Acetophenones with alkyloxy tails were prepepared by sodium salt of 4′-hydroxyacetophenone with 1-bromoalkane (the number of carbon atoms=3-10). A solution of 4′-hydroxyacetophenone in THF became turbid by addition of NaH. Methanol was added to the reaction mixture to dissolve the precipitated salt before the reaction with 1-bromoalkane. Condensation reaction of 4′-alkyloxyacetophenone with 4-hydroxybenzaldehyde was carried out under acidic conditions to give chalcones **2a-h**. The ^{1}H NMR spectra showed two doublet peaks centered at 7.8 and 7.4 ppm for vinyl protons. The coupling constants were about 15 Hz, indicating that the double bonds resulted from the condensation reaction were in the *trans* configuration. Compounds **3a-h** with two chalcone units as a part of a rigid rod were prepared by the reaction of sodium salts of **2a-h** with terephthaloyl chloride in THF. The sodium salts of **2a-h** were partially soluble in THF and the reaction with terephthaloyl chloride was carried out at refluxing temperature. Excess amount of sodium salts were used to complete the reaction. After the reaction, the precipitated products were isolated by filtration and purified by recrystallization from a mixture of chloroform and hexane. Since **3a-h** have two photoreactive groups, the polymerization was expected to proceed in a stepwise manner upon photoirradiation.



Scheme I. Synthesis of linear chalcone esters.

Mesomorphic Properties. We examined morphological changes of the linear ester compounds by differential scanning calorimetry and polarized optical microscope. The transition temperatures and corresponding enthalpy values of the compounds are summarized in Table I. All linear ester compounds (**3a**-**3h**) showed enantiotropic liquid crystalline phases. In DSC analysis of compound **3a** with a propoxy tail, on heating with a rate of 10 °C/min three endothermic peaks were observed at 237 (ΔH=61.3 kJ/mol), 250 (ΔH=0.5 kJ/mol), and 269 °C (ΔH=0.5 kJ/mol). When cooled from isotropic state with a rate of 10 °C/min, three exothermic peaks appeared at 267 (ΔH=-0.4 kJ/mol), 247 (ΔH=-0.4 kJ/mol), and 220 °C (ΔH=-59.4 kJ/mol).

Under a cross-polarized optical microscope, a mesophase with a homeotropic texture on a glass plate was observed above 237 °C on heating (Figure 1(a)). Although a small endothermic peak appeared at 250 °C in DSC analysis, no significant change in the homeotropic texture occurred between 237 and 269 °C. The same texture appeared from 267 °C on cooling and crystals began to form at 220 °C. Compounds **3b** with butoxy tails and **3c** with pentoxy tails also showed mesophases with a stable homeotropic texture. A highly birefringent *Schlieren* texture was observed for compounds **3d**-**3h** (Figure 1(b)). The temperature ranges of liquid crystalline phases became broader as the tail length was increased. It is noteworthy that when the compounds were gently sheared in the liquid crystalline state, the birefringent *Schlieren* texture disappeared. This result suggests that these mesogens can be macroscopically aligned by simple shearing.


(a)

(b)

Figure 1. Polarized optical micrographs of mesophases of (a) compound **3a** at 242 °C and (b) **3h** at 220 °C (All images were obtained on the second cooling).

We further investigated the macroscopic alignment by using a He-Ne laser beam with 632.8 nm wavelength. Figure 2 shows the polar diagram of compound **3d**, which was axially aligned by shearing with a cover glass. The sample was heated to be isotropic and cooled down to exhibit a mesophase. After shearing, it was quenched rapidly to room temperature to yield a film with a glassy liquid crystalline phase. A He-Ne laser beam with 632.8 nm wavelength passed through a polarizer, the sheared film, and a cross-polarizer/analyzer with respect to the surface normal. The transmittance was measured with rotating the sample holder

Table I. Phase Transition Temperatures and Enthalpy Changes for Compounds 3a-h as Determined by DSC (scan rate: 10 °C min^{-1})

Compound	Phase[a] Transition Temperature (°C) and ΔH (kJ/mol) on Heating	Phase Transition Temperature (°C) and ΔH (kJ/mol) on Cooling
3a	K 237.3 (61.3) Sm 250.19 (0.5) Sm 269.4 (0.5) I	I 266.7 (0.4) Sm 247.2 (0.4) Sm 220.2 (59.4) K
3b	K 231.6 (63.3) Sm 262.9 (1.0) Sm 266.0 (0.2) I	I 262.9 (0.4) Sm 258.5 (1.2) Sm 216.8 (65.4) K
3c	K 218.4 (49.6) Sm 260.4 (2.7) I	I 258.4 (2.6) Sm 201.7 (51.1) K
3d	K 213.3 (57.0) Sm 259.9 (3.1) I	I 257.4 (3.4) Sm 195.6 (61.1) K
3e	K 78.9 (5.0) K 205.0 (33.4) Sm 249.5 (3.7) I	I 247.5 (2.6) Sm 187.0 (35.6) K 67.1 (3.0) K
3f	K 86.2 (8.8) K 200.5 (44.1) Sm 251.7 (3.6) I	I 248.8 (3.2) Sm 184.5 (47.2) K 78.7 (6.5) K
3g	K 116.4 (12.7) K 196.7 (45.9) Sm 255.2 (3.4) I	I 252.1 (3.3) Sm 185.3 (47.0) K 112.4 (10.7) K
3h	K 103.4 (9.9) K 198.6 (35.4) Sm 253.5 (2.3) I	I 250.9 (2.6) Sm 182.7 (38.7) K 97.3 (8.4) K

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

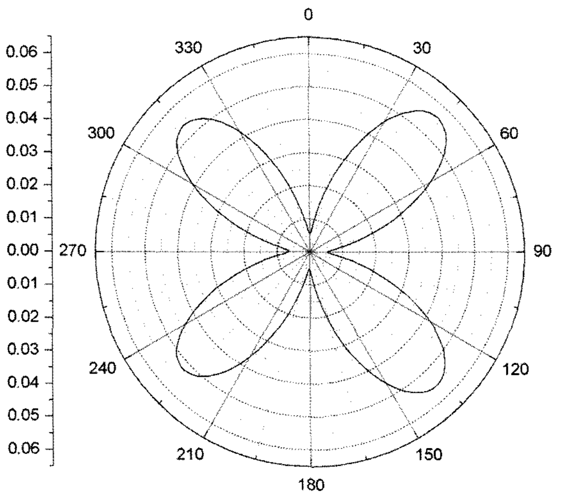


Figure 2. Polar plot of transmittance of a He-Ne laser beam for compound **3d**. The compound was aligned in the LC state (240 °C) by shearing and then quenched to room temperature to obtain a glassy liquid crystalline phase.

around the surface normal. When the shear direction of the sample was parallel or perpendicular to the axis of the cross-polarizer, the minimum transmittance is obtained, indicating that the molecules were macroscopically aligned in the shear direction.

X-Ray Analysis. Figure 3 shows the X-ray diffractograms for the mesophases of compounds **3a-h** obtained at 240 °C on cooling. The X-ray patterns have a set of reflections in the small-angle region. They consist of more than three sharp diffraction peaks with *d* spacings in the ratio of 1:1/2:1/3. These reflections can be indexed as (100), (200), and (300) planes (Table II). No (*kl*) reflections were present in the small angle region indicates a purely two-dimensional smectic-like ordering. The layer distance is increased according to the number of carbon atoms (n) in the alkoxy tails from 38 for **3a** (n=3) to 52 Å for **3h** (n=10). Since the layer distances were comparable to lengths of the corresponding molecules calculated by simple extended molecular modeling as summarized in Table II, we concluded that all the compounds have well defined smectic A structures.

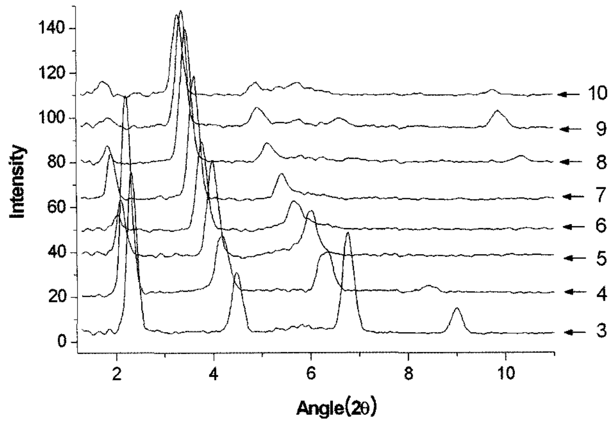


Figure 3. X-ray diffractograms of compounds **3a** (n=3)-**3h** (n=10) obtained in their LC phases on cooling.

Figure 4 shows the UV spectra of compound **3h** measured in a chloroform solution and in the LC state. The maximum absorbance appeared at 324 nm in the solution, which was shifted to 285 nm in the LC state. This blue shift is attributable to H-aggregation of the mesogenic molecules in the LC phase, which is consistent with the proposed smectic A structure.

Photopolymerization. Compounds **3a-h** are considered as bifunctional monomers since they have two photoreactive chalcone groups. Its photopolymerization is expected to proceed through the [2+2] addition reaction between chalcone units in a stepwise manner. A cyclic product could also form by the reaction between two neighboring molecules. Compound **3h** was cast on a glass plate in the LC state (240 °C) and photoirradiated with an UV lamp (high pressure mercury arc lamp, 100 W). Figure 5 shows the IR spectra of

Table II. X-Ray Diffraction Data for the LC Phases of Compounds 3a-h

	Position of Reflection (Å)				Lattice Constant (Å)	
Compound	d_{100}	d_{200}	d_{300}	d_{400}	a	EMM[a]
3a	38.7	19.4	12.9	9.8	38.7	39.2
3b	40.7	20.8	13.9	10.5	40.7	41.4
3c	42.9	21.7	14.5		42.9	43.6
3d	45.3	23.2	15.5		45.3	45.7
3e	48.0	24.2	16.2		48.0	47.9
3f	49.3	25.4	16.9		49.3	49.6
3g	51.0	25.9	17.3		51.0	51.4
3h	52.5	26.6	17.8		52.5	53.1

[a]EMM: Values estimated from an extended molecular model.

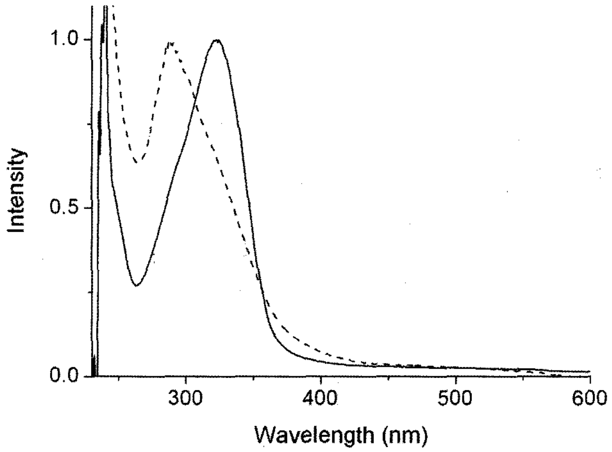


Figure 4. UV spectra of compound **3h** measured in a chloroform solution (solid line) and in the LC state (dotted line).

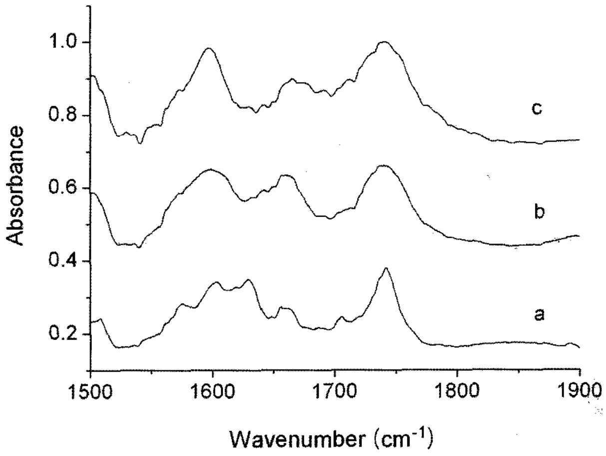


Figure 5. IR spectra of compound **3h** taken (a) in the solid state at room temperature (KBr), (b) in the LC state, and (c) after the photoirradiation in the LC state for 1 h.

compound **3h** taken in the solid state at room temperature (KBr), in the LC state, and after the photoirradiation in the LC state for 1 h. At room temperature, two peaks for carbonyl groups of chalcone units appeared at 1630 and 1660 cm^{-1} corresponding to the carbonyl stretching frequencies of s-*trans* and s-*cis* conformers, respectively. Interestingly only the peak at 1660 cm^{-1} showed up in the LC state, indicating that ketone carbonyl and C-C double bond are in an s-*cis* conformation. After the UV irradiation for 1 h, the intensity of the IR peak for the carbonyl group at 1661 cm^{-1} decreased and a new peak at 1678 cm^{-1} appeared due to the carbonyl group attached to a cyclobutane ring.

In the DSC analysis, compound **3h** showed two endothermic peaks observed at 199 and 253 °C, corresponding to a melting transition into the mesophase and a clearing transition, but no transition occurred after the photopolymerization.

As mentioned above, the photoreaction between two chalcone units produces a cyclobutane ring, which will disrupt the aligned structure of mesogenic molecules in the LC state. An image pattern was obtained by the UV irradiation of the liquid crystal of compound **3h** through a photomask. The sample was prepared according to the procedure we reported previously.[14] Compound **3h** was cast on a glass plate in its LC state (240 °C) and macroscopically oriented by shearing. The thin film was cooled to 160 °C rapidly to solidify with retention of the LC structure and photoirradiated under nitrogen at 160 °C for 1 h through a photomask. Figure 6 shows an image pattern observed in polarized optical microscope. A patterned image was obtained where an irradiated part became dark and a masked part remained birefringent under polarized optical microscope.

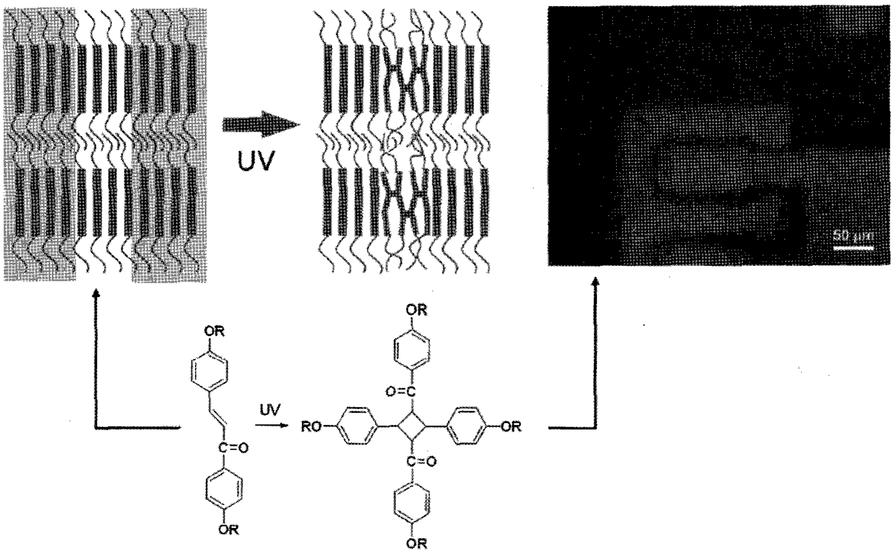


Figure 6. Photoirradiation through a photomask and a resulting image pattern observed under polarized optical microscope.

Conclusions

We prepared a series of LC molecule having two photoreactive chalcone units. The compounds showed smectic A phases and were oriented macroscopically by shearing in the LC state. Photopolymerization was carried out by the UV irradiation through a photomask, resulting in a patterned image. This result can be ascribed to that the UV irradiation produced cyclobutane rings by [2+2] addition, and thereby disrupted the alignment of the molecules, resulting in optical property changes.

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