Synthesis and Characterization of Mesogenic Disklike Benzenetricarboxylates Containing Diacetylenic Groups and Their Polymerization

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Polymerizable disklike compounds that have a benzene ring core and three rigid diacetylenic units were prepared. The diacetylenic units were attached to the benzene ring via ester linkages. By varying number of alkoxy tail carbons and benzene rings of the disk, the morphological change of the compounds and their polymerization were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy, infrared spectroscopy (IR), and powder X-ray diffraction (XRD). Compound **7** with no alkoxy tail was glassy or small crystals at room temperature and showed crystal-to-crystal phase transition when heated. Compounds **8** with butyloxy tails, **9** with hexyloxy tails, and **10** with octyloxy tails showed monotropic transitions. When the compounds were cooled from the isotropic liquid states, birefringent phases with mosaic textures were observed. XRD study showed that compounds **9** and **10** had hexagonal columnar structures in their liquid crystalline (LC) states. The diacetylene compounds were polymerized by irradiation with UV in solid states or LC states. IR and UV−vis studies showed that the polymerization proceeded by 1,4-addition.

Introduction

The topochemical polymerization of diacetylenes by irradiation or thermal annealing has been widely used for preparing ordered macromolecules.[1,2] Most topochemical polymerization of diacetylenes has been carried out in the solid state. Monomers with molecular arrangements suitable for polymerization are prepared as single crystals, Langmuir−Blodgett films,[3−5] self-assembling monolayers,[6,7] and vesicles.[8,9] Recently the liquid crystalline (LC) state polymerization of diacetylenes was also found to proceed by a 1,4-polymerization pathway as the solid-state polymerization.[10−15] In an LC state, molecules are self-organized into ordered arrays comparable to those in Langmuir−Blodgett or self-assembling processes. Several mesogenic linear diacetylenes have been polymerized in nematic or smetic phases.[10−21]

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In the previous communication,[22] we reported mesogenic disklike diacetylenes with ester or amide linkages and their LC state polymerization. The molecules we designed contained diacetylenic groups as a part of the rigid disks and thereby their LC state structure could be maintained even after polymerization. Molecular ordering on heating was influenced by intermolecular interactions such as $\pi-\pi$ interaction between benzene rings and hydrogen bondings between amide groups. Aliphatic tails provided the mobility necessary for molecular arrangement into ordered form. Disklike mesogenic diacetylenes are of particular interest as they stack in columns, and zipping of diacetylenes along the column axis by polymerization will lead to supramolecules with columnar structures. In this work, we prepared a series of disklike diacetylenes with ester linkages. By varying number of alkoxy tail carbons and benzene rings of the disk, we investigated morphological changes of the compounds and their polymerization. Since no hydrogen bondings were expected between the molecules, $\pi-\pi$ interaction would play an important role for molecular stacking.

Experimental Section

Materials and Instrumentation. 4-Iodophenol, trimethylsilylacetylene, dichlorobis(triphenylphosphine)palladium(II), copper(I) iodide, phenylacetylene, copper(II) acetate, 1,3,5-benzenetricarbonyl trichloride, and phloroglucinol were purchased from Aldrich and used as received. Reagent-grade solvents were dried and purified as follows. *N*,*N*-Dimethylformamide (DMF) was dried over anhydrous P_2O_5 and purified by distillation. Triethylamine and pyridine were distilled over potassium hydroxide. Methanol was dried over molecular sieves 4 Å and distilled. Tetrahydrofuran (THF) and 1,4-dioxane were dried over sodium metal and distilled. ^1H and ^{13}C NMR spectra were recorded on a Varian-Gemini 200 spectrometer. IR spectra were obtained with the use of a Nicolet Magna-IR 550 spectrometer. UV−vis spectra were obtained with the use of a Guided Wave model 260. Thermal analyses were performed by a Dupont 2010 differential scanning calorimeter and a 2050 thermogravimetric analyzer. Powder X-ray diffractograms were obtained with the use of a Mac Science Mxp 3 (Cu Kα radiation, $\lambda = 1.54$ Å). An optical microscopy study was performed with a Carl Zeiss optical polarizing microscope equipped with a Linkam heating stage and a Linkam TP92 controller. Elemental analyses were performed at the Korea Research Institute of Chemical Technology and the Korea Basic Research Center.

4-Trimethylsilylethynylphenol. This compound was prepared according to our previous report.[23] To a solution of 4-iodophenol (10 g, 45.5 mmol) and (trimethylsilyl)acetylene (9.6 mL, 68.1 mmol) in triethylamine (200 mL) under nitrogen were added dichlorobis(triphenylphosphine)palladium(II) (1.8 g, 2.56 mmol) and copper(I) iodide (0.3 g, 1.58 mmol) at −4 °C. The reaction mixture was stirred at the same temperature for 2 h. After stirring at room temperature for additional 10 h, the reaction mixture was concentrated to dryness by evaporation under reduced pressure. The crude product was isolated by sublimation (35−45 °C, 0.1 mmHg) and further purified by column chromatography on silica gel (20% ethyl acetate in hexane) to yield 6.6 g (76%), mp 60−62 °C.

Ethynylphenol. 4-Trimethylsilylethynylphenol (2.57 g, 13.5 mmol) was dissolved in methanol (100 mL) in the presence of KOH (1.45 g, 25.8 mmol). The solution was stirred at room temperature for 4 h under nitrogen. After filtration of undissolved KOH, the solvent was removed by evaporation. The product (1.13 g, 9.57 mmol, yield 71%) was isolated by column chromatography on silica gel (25% ethyl acetate in hexane), mp 129−130 °C.

^1H NMR (acetone-d_6): δ 7.5−6.9 (dd, 4H, aromatic), 3.7 (s, 1H, −CH). IR (KBr pellet, cm^{-1}): 3388, 3285, 2966, 2923, 2846, 2105, 1607, 1509.

1-(4-Hydroxyphenyl)-4-phenylbutadiyne (1). 4-Ethynylphenol (1.13 g, 9.56 mmol) was dissolved in pyridine/methanol (1:1, v/v). To the solution were added phenylacetylene (2.1 mL, 19.12 mmol) and copper acetate (5.83 g, 32.1 mmol), and the reaction mixture was refluxed for 12 h under nitrogen. After the mixture was concentrated to 50 mL, copper acetate was removed by filtration through a silica gel column (3 cm). The solvents were removed by evaporation, and the product (1.6 g, 7.33 mmol, yield 77%) was isolated by column chromatography on silica gel (17% ethyl acetate in hexane), mp 119−120 °C.

Anal. Calcd for $C_{16}H_{10}O$: C, 88.05; H, 4.62. Found: C, 87.90; H, 4.61. ^1H NMR (DMSO-d_6): δ 10.2 (s, −OH, 1H), 7.65−6.7 (m, aromatic, 9H). IR (KBr pellet, cm^{-1}): 3263, 3068, 2938, 2213, 2154, 1601, 1515, 1239.

1-Butyloxy-4-iodobenzene. To a solution of 4-iodophenol (3.0 g, 13.66 mmol) in tetrahydrofuran (THF, 100 mL) was added sodium hydride (0.328 g, 13.66 mmol). After the mixture was stirred for 3 h at room temperature, 1-bromobutane (1.47 mL, 13.66 mmol) was added and the reaction mixture was refluxed for 36 h under nitrogen. After evaporation of the solvent, the product was isolated by column chromatography on silica gel (10% ethyl acetate in hexane) as an oil (yield 66%).

^1H NMR ($CDCl_3$, 200 MHz): δ 7.25, 6.25 (dd, 4H, C_6H_4), 3.9 (t, 2H, OCH_2), 1.9−0.8 (m, 7H, alkyl chain protons).

1-Hexyloxy-4-iodobenzene. This compound was prepared from 4-iodophenol and 1-bromohexane as described for 1-butyloxy-4-iodobenzene as an oil (yield 69%).

Anal. Calcd for $C_{12}H_{17}IO$: C, 47.39; H, 5.63. Found: C, 47.79; H, 5.82. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.6, 6.6 (dd, 4H, C_6H_4), 3.9 (t, 2H, OCH_2), 1.9−0.8 (m, 11H, alkyl chain protons).

1-Octyloxy-4-iodobenzene. This compound was prepared from 4-iodophenol and 1-bromooctane as described for 1-butyloxy-4-iodobenzene as an oil (yield 85%).

Anal. Calcd for $C_{14}H_{21}IO$: C, 50.61; H, 6.37. Found: C, 50.09; H, 6.40. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.6, 6.8 (dd, 4H, C_6H_4), 3.9 (t, 2H, OCH_2), 1.9−0.8 (m, 15H, alkyl chain protons).

1-Dodecyloxy-4-iodobenzene. This compound was prepared from 4-iodophenol and 1-iodododecane as described for 1-butyloxy-4-iodobenzene (mp 37−38 °C, yield 91%).

^1H NMR ($CDCl_3$, 200 MHz): δ 7.55, 6.68 (dd, 4H, C_6H_4), 3.9 (t, 2H, OCH_2), 1.9−0.8 (m, 23H, alkyl chain protons).

1-Butyloxy-4-(trimethylsilylethynyl)benzene. To a solution of 1-butyloxy-4-iodobenzene (5 g, 18.11 mmol) and (trimethylsilyl)acetylene (3.84 mL, 27.17 mmol) in triethylamine (100 mL) were added dichlorobis(triphenylphosphine)-palladium(II) (0.73 g, 1.04 mmol) and copper(I) iodide (0.12 g, 0.63 mmol) at 0 °C. The reaction mixture was stirred for 20 h at the same temperature under nitrogen. After evaporation of the solvent, the product was isolated by column chromatography on silica gel (10% ethyl acetate in hexane) as an oil (yield 90%).

^1H NMR ($CDCl_3$, 200 MHz): δ 7.4, 6.8 (dd, 4H, C_6H_4), 3.95 (t, 2H, OCH_2), 1.9−0.8 (m, 7H, alkyl chain protons), 0.25 (s, 9H, $SiCH_3$).

1-Hexyloxy-4-(trimethylsilylethynyl)benzene. This compound was prepared following the procedure for 1-butyloxy-4-(trimethylsilylethynyl)benzene as an oil (yield 89%).

Anal. Calcd for $C_{17}H_{26}SiO$: C, 74.39; H, 9.55. Found: C, 74.15; H, 9.82. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.4, 6.8 (dd, 4H, C_6H_4), 3.95 (t, 2H, OCH_2), 1.9−0.8 (m, 11H, alkyl chain protons), 0.25 (s, 9H, $SiCH_3$).

1-Octyloxy-4-(trimethylsilylethynyl)benzene. This compound was prepared following the procedure for 1-butyloxy-4-(trimethylsilylethynyl)benzene as an oil (yield 92%).

Anal. Calcd for $C_{19}H_{30}SiO$: C, 75.43; H, 10.00. Found: C, 75.76; H, 10.12. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.5, 6.7 (dd,

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4H, C_6H_4), 3.95 (t, 2H, OCH_2), 1.9−0.8 (m, 15H, alkyl chain protons), 0.25 (s, 9H, $SiCH_3$).

1-Dodecyloxy-4-(trimethylsilylethynyl)benzene. This compound was prepared following the procedure for 1-butyloxy-4-(trimethylsilylethynyl)benzene (mp 35−36 °C, yield 82%).

^1H NMR ($CDCl_3$, 200 MHz): δ 7.4, 6.8 (dd, 4H, C_6H_4), 3.95 (t, 2H, OCH_2), 1.9−0.8 (m, 23H, alkyl chain protons), 0.25 (s, 9H, $SiCH_3$).

1-Butyloxy-4-ethynylbenzene. To a solution of 1-butyloxy-4-(trimethylsilylethynyl)benzene (3.7 g, 16.06 mmol) in methanol (100 mL) was added a solution of KOH (1.2 g, 21.39 mmol) in methanol (50 mL). The solution was stirred for 10 h at room temperature and passed through a silica gel column (5 cm high). After evaporation of the solvent, the product was isolated by column chromatography on silica gel (25% ethyl acetate in hexane) as an oil (yield 94%). The compound was susceptible to hydration.

^1H NMR ($CDCl_3$, 200 MHz): δ 7.40, 6.85 (dd, 4H, C_6H_4), 3.95 (t, 2H, OCH_2), 3.0 (s, 1H, ethynyl proton), 1.9−0.8 (m, 7H, alkyl chain protons).

1-Hexyloxy-4-ethynylbenzene, 1-octyloxy-4-ethynylbenzene, and 1-dodecyloxy-4-ethynylbenzene were prepared with the same method as above.

1-(4-Hydroxyphenyl)-4-(4-butyloxyphenyl)butadiyne (2). To a solution of 4-ethynylphenol (2.1 g, 17.18 mmol) and 1-butyloxy-4-ethynylbenzene (2.4 g, 13.77 mmol) in pyridine/methanol (1:1 v/v, 100 mL) was added copper(II) acetate (4.83 g, 26.58 mmol), and the reaction mixture was refluxed for 18 h under nitrogen. Insoluble solids were removed by filtration. After evaporation of the solvent, the product was isolated by column chromatography on silica gel (10% ethyl acetate in hexane) and further purified by recrystallization from ethyl acetate/methanol (mp 101−104 °C, yield 31%).

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25. Found: C, 82.92; H, 6.31. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.44, 6.83 (dd, 4H, C_6H_4), 7.40, 6.79 (dd, 4H, C_6H_4), 5.12 (s, 1H, OH), 3.94 (t, 2H, OCH_2), 1.82−0.92 (m, 7H, alkyl chain protons). IR (KBr pellet, cm^{-1}): 3407, 2940, 2868, 2217, 2144, 1604, 1512, 1256.

1-(4-Hydroxyphenyl)-4-(4-hexyloxyphenyl)butadiyne (3). This compound was prepared from 4-ethynylphenol and 1-hexyloxy-4-ethynylbenzene as described for compound **2** (mp 122−123 °C, yield 35%).

Anal. Calcd for $C_{22}H_{22}O_2$: C, 82.99; H, 6.96. Found: C, 82.79; H, 7.10. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.45, 6.83 (dd, 4H, C_6H_4), 7.40, 6.77 (dd, 4H, C_6H_4), 5.2 (s, 1H, OH), 3.96 (t, 2H, OCH_2), 1.8−0.9 (m, 15H, alkyl chain protons). IR (KBr pellet, cm^{-1}): 3414, 2927, 2861, 2216, 2144, 1604, 1505.

1-(4-Hydroxyphenyl)-4-(4-octyloxyphenyl)butadiyne (4). This compound was prepared from 4-ethynylphenol and 1-octyloxy-4-ethynylbenzene as described for compound **2** (mp 110−111 °C, yield 45%).

Anal. Calcd for $C_{24}H_{26}O_2$: C, 83.19; H, 7.57. Found: C, 82.45; H, 7.49. ^1H NMR ($CDCl_3$, 200 MHz): δ 7.44, 6.83 (dd, 4H, C_6H_4), 7.40, 6.79 (dd, 4H, C_6H_4), 5.1 (s, 1H, OH), 3.94 (t, 2H, OCH_2), 1.8−0.8 (m, 15H, alkyl chain protons). IR (KBr pellet, cm^{-1}): 3406, 2928, 2860, 2213, 2146, 1606, 1512, 1256.

1-(4-Hydroxyphenyl)-4-(4-dodecyloxyphenyl)butadiyne (5). This compound was prepared from 4-ethynylphenol and 1-dodecyloxy-4-ethynylbenzene as described for compound **2** (mp 113−114 °C, yield 54%).

^1H NMR ($CDCl_3$, 200 MHz): δ 7.44, 6.83 (dd, 4H, C_6H_4), 7.40, 6.79 (dd, 4H, C_6H_4), 5.1 (s, 1H, OH), 3.94 (t, 2H, OCH_2), 1.9−0.8 (m, 23H, alkyl chain protons). IR (KBr pellet, cm^{-1}): 3387, 2923, 2842, 2216, 2136, 1611, 1503, 1254, 1167.

1-(4-Hydroxyphenyl)-4-hexylbutadiyne (6). This compound was prepared from 4-ethynylphenol and 1-octyne as described for compound **2** (yield 31%).

^1H NMR ($CDCl_3$, 200 MHz): δ 7.35, 6.75 (dd, 4H, C_6H_4), 5.85 (s, 1H, OH), 2.32 (t, 2H, CCH_2), 1.65−0.85 (m, 11H, alkyl chain protons). IR (NaCl crystal pellet, cm^{-1}): 2934, 2861, 2243, 2144, 1611, 1512, 1275.

Tris(4-phenylbutadiynylphenyl)-1,3,5-benzenetricarboxylate (7). To a solution of compound **1** (1 g, 4.58 mmol) in THF (60 mL) was added NaH (0.11 g, 4.58 mmol). After the mixture was stirred for 2 h at room temperature, a solution of 1,3,5-benzenetricarbonyl trichloride (0.32 g, 1.2 mmol) in THF (50 mL) was added dropwise. The solution was refluxed for 72 h. After evaporation, the product was isolated by column chromatography on silica gel (methylene chloride/hexane = 1:1 v/v) and further purified by recrystallization from ethyl acetate/methanol to give 0.85 g (mp 198−200 °C, yield 70%).

Anal. Calcd for $C_{57}H_{30}O_6$: C, 84.43; H, 3.73. Found: C, 83.95; H, 3.96. ^1H NMR (DMSO-d_6, 200 MHz): δ 9.06 (s, 3H, C_6H_3), 7.79, 7.54 (dd, 12H, C_6H_4), 7.64−7.52 (m, 15H, C_6H_5). ^{13}C NMR (DMSO-d_6, 50 MHz): δ 162.7, 151.5, 135.5, 134.1, 132.5, 130.8, 130.2, 129.0, 122.8, 120.4, 118.7, 82.2, 81.2, 73.8, 73.5. IR (KBr pellet, cm^{-1}): 3073, 2925, 2859, 2222, 2157, 1749, 1499.

Tris[4-(4-butyloxyphenyl)butadiynylphenyl]-1,3,5-benzenetricarboxylate (8). This compound was prepared from 1,3,5-benzenetricarbonyl trichloride and 1-(4-hydroxyphenyl)-4-(4-butyloxyphenyl)butadiyne as described for compound **7** (mp 183−185 °C, yield 48%).

Anal. Calcd for $C_{69}H_{30}O_9$: C, 80.68; H, 5.30. Found: C, 80.45; H, 5.14. ^1H NMR ($CDCl_3$, 200 MHz): δ 9.23 (s, 3H, C_6H_3), 7.62, 7.25 (dd, 12H, C_6H_4), 7.45, 6.82 (dd, 12H, C_6H_4), 3.94 (t, 6H, OCH_2), 1.82−0.92 (m, 21H, alkyl chain protons). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 162.8, 160.1, 150.8, 136.2, 134.1, 133.8, 131.0, 121.8, 120.0, 114.7, 113.2, 82.3, 79.9, 74.8, 72.5, 67.8, 31.2, 19.2, 13.8. IR (KBr pellet, cm^{-1}): 3072, 2938, 2874, 2223, 2151, 1760, 1607, 1505.

Tris[4-(4-hexyloxyphenyl)butadiynylphenyl]-1,3,5-benzenetricarboxylate (9). This compound was prepared from 1,3,5-benzenetricarbonyl trichloride and 1-(4-hydroxyphenyl)-4-(4-hexyloxyphenyl)butadiyne as described for compound **7** (mp 149−150 °C, yield 51%).

Anal. Calcd for $C_{75}H_{66}O_9$: C, 81.06; H, 5.99. Found: C, 80.86; H, 6.06. ^1H NMR ($CDCl_3$, 200 MHz): δ 9.2 (s, 3H, C_6H_3), 7.6, 7.28 (dd, 12H, C_6H_4), 7.45, 6.85 (dd, 12H, C_6H_4), 3.94 (t, 6H, OCH_2), 1.9−0.85 (m, 33H, alkyl chain protons). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 162.7, 160.1, 150.7, 136.2, 134.1, 133.8, 131.0, 121.7, 120.3, 114.7, 113.2, 82.3, 79.9, 74.8, 72.5, 68.1, 31.5, 29.1, 25.6, 22.6, 14.0. IR (KBr pellet, cm^{-1}): 2934, 2855, 2223, 2144, 1756, 1604, 1506, 1196.

Tris[4-(4-octyloxyphenyl)butadiynylphenyl]-1,3,5-benzenetricarboxylate (10). This compound was prepared from 1,3,5-benzenetricarbonyl trichloride and 1-(4-hydroxyphenyl)-4-(4-octyloxyphenyl)butadiyne as described for compound **7** (mp 140−141 °C, yield 36%).

Anal. Calcd for $C_{81}H_{78}O_9$: C, 81.37; H, 6.57. Found: C, 80.90; H, 6.71. ^1H NMR ($CDCl_3$, 200 MHz): δ 9.25 (s, 3H, C_6H_3), 7.65, 7.25 (dd, 12H, C_6H_4), 7.50, 6.85 (dd, 12H, C_6H_4), 3.95 (t, 6H, OCH_2), 1.90−0.80 (m, 45H, alkyl chain protons). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 162.8, 160.1, 150.8, 136.2, 134.2, 133.8, 131.1, 121.8, 120.4, 114.7, 113.2, 82.4, 79.9, 74.8, 72.5, 68.2, 31.8, 29.3, 29.2, 29.1, 26.0, 22.6, 14.1. IR (KBr pellet, cm^{-1}): 3088, 2934, 2860, 2223, 2149, 1754, 1606, 1512, 1204.

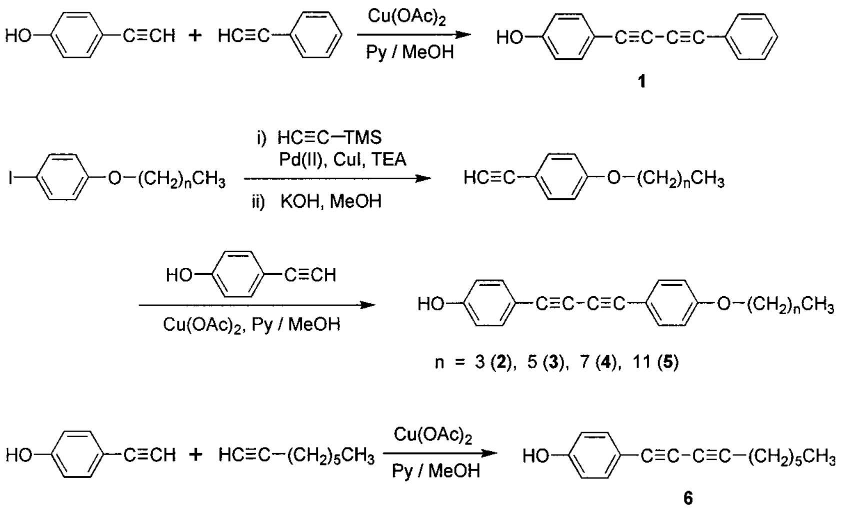
Tris[4-(4-dodecyloxyphenyl)butadiynylphenyl]-1,3,5-benzenetricarboxylate (11). This compound was prepared from 1,3,5-benzenetricarbonyl trichloride and 1-(4-hydroxyphenyl)-4-(4-dodecyloxyphenyl)butadiyne as described for compound **7** (mp 146−147 °C, yield 46%).

Anal. Calcd for $C_{93}H_{102}O_9$: C, 81.90; H, 7.54. Found: C, 82.12; H, 7.70. ^1H NMR ($CDCl_3$, 200 MHz): δ 9.25 (s, 3H, C_6H_3), 7.6, 7.22 (dd, 12H, C_6H_4), 7.42, 6.83 (dd, 12H, C_6H_4), 3.95 (t, 6H, OCH_2), 1.9−0.8 (m, 69H, alkyl chain protons). IR (KBr pellet, cm^{-1}): 2929, 2849, 2220, 2139, 1751, 1611, 1504, 1223.

Tris(4-hexylbutadiynylphenyl)-1,3,5-benzenetricarboxylate (12). This compound was prepared from 1,3,5-benzenetricarbonyl trichloride and 1-(4-hydroxyphenyl)-4-hexylbutadiyne as described for compound **7** (mp 120−121 °C, yield 57%).

Anal. Calcd for $C_{57}H_{30}O_6$: C, 881.89; H, 6.75. Found: C, 81.67; H, 6.75. ^1H NMR ($CDCl_3$, 200 MHz): δ 9.2 (s, 3H, C_6H_3), 7.56, 7.23 (dd, 12H, C_6H_4), 2.35 (t, 6H, CCH_2), 1.65−0.85 (m, 33H, alkyl chain protons). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 162.7, 150.6, 136.1, 133.8, 131.0, 124.6, 120.5, 85.3, 75.0, 73.6, 64.9, 31.3, 28.5, 28.2, 22.5, 19.6, 14.0. IR (KBr pellet, cm^{-1}): 2933, 2863, 2252, 1761, 1509, 1228.

Scheme 1



Methyl 4-Trimethylsilylethynylbenzoate. To a solution of 4-bromobenzoate (2.47 g, 11.49 mmol) and (trimethylsilyl)-acetylene (1.95 mL, 13.80 mmol) in triethylamine/pyridine (5:2 v/v, 35 mL) under nitrogen were added dichlorobis(triphenylphosphine)palladium(II) (0.46 g, 0.66 mmol) and copper-(I) iodide (0.076 g, 0.40 mmol) at −4 °C. The reaction mixture was stirred at the same temperature for 2 h. After stirring at room temperature for additional 24 h, the reaction mixture was filtered through a silica gel column. The filtrate was concentrated to dryness by evaporation under reduced pressure. The product was isolated by column chromatography on silica gel (17% ethyl acetate in hexane) to yield 2.18 g (82%).

Anal. Calcd for $C_{13}H_{16}SiO_2$: C, 67.20; H, 6.94. Found: C, 67.23; H, 7.05. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.98, 7.52 (dd, 4H, C_6H_4), 3.91 (s, 3H, OCH_3), 0.3 (s, 9H, $SiCH_3$).

Methyl 4-Ethynylbenzoate. This compound was prepared as described for 1-butyloxy-4-ethynylbenzene (yield 69%).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.05, 7.56 (dd, 4H, C_6H_4), 3.92 (s, 3H, OCH_3), 3.25 (s, 1H, ethynyl proton).

Methyl 4-[(4-Octyloxyphenyl)butadiynyl]benzoate (13). This compound was prepared from methyl 4-ethynylbenzoate and 1-octyloxy-4-ethynylbenzene as described for compound **2** (yield 32%).

Anal. Calcd for $C_{26}H_{28}O_3$: C, 80.38; H, 7.26. Found: C, 80.56; H, 7.48. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.05, 7.56 (dd, 4H, C_6H_4), 7.46, 6.86 (dd, 4H, C_6H_4), 3.96 (t, 2H, OCH_2), 3.92 (s, 3H, OCH_3), 1.82−0.92 (m, 15H, alkyl chain protons). IR (KBr pellet, cm^{-1}): 2955, 2929, 2862, 2214, 2142, 1727, 1603, 1512, 1256.

1,3,5-Tris[4-(4-octyloxyphenyl)butadinylbenzenecarboxy]benzene (15). Compound **13** (1 g, 2.57 mmol) was dissolved in a solution of sodium hydroxide (0.41 g, 10.25 mmol) in butanol (100 mL). After the mixture was refluxed for 20 min, the precipitated salt was isolated by filtration and washed with diethyl ether. To a mixture of the salt (0. 8 g, 2.02 mmol) in chloroform (30 mL) were added dropwise a solution of thionyl chloride (0.5 mL) in chloroform (15 mL) for 3 h at 0 °C and then DMF (5 mL). The mixture was stirred for 12 h at room temperature. After filtration, the filtrate was evaporated under reduced pressure to give acyl chloride **14**, which was dissolved in THF (30 mL). A mixture of phloroglucinol (0.076 g, 0.47 mmol) and sodium hydride (0.068 g, 2.83 mmol) in THF (15 mL) was stirred for 3 h at room temperature and then added dropwise to the acyl chloride solution in THF at the same temperature. The reaction mixture was stirred for 3 days at room temperature and the insoluble precipitates were removed by filtration through a silica gel column. After evaporation, compound **15** was isolated by column chromatography on silica gel (25% THF in hexane) and further purified by recrystallization from chloroform/hexane to give 0.21 g (mp 149−151 °C, yield 38%).

Anal. Calcd for $C_{81}H_{78}O_9$: C, 81.38; H, 6.58. Found: C, 81.20; H, 6.59. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.16, 7.65 (dd, 12H, C_6H_4), 7.45, 6.86 (dd, 12H, C_6H_4), 7.17 (s, 3H, C_6H_3), 4.0 (t, 6H, OCH_2), 1.9−0.85 (m, 45H, alkyl chain protons). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 163.6, 160.3, 151.4, 134.2, 132.5, 130.1, 128.7, 127.9, 114.7, 113.2, 112.9, 84.0, 79.7, 72.3, 68.2, 31.8, 29.3, 29.1, 26.0, 22.6, 14.0. IR (KBr pellet, cm^{-1}): 2934, 2861, 2217, 2124, 1749, 1604, 1512, 1256.

UV Polymerization. Thin films of the compounds prepared on glass plates by melt or solution casting were placed on a hot stage (Linkam THM 600 with a TP 92 controller) under an UV lamp (high-pressure mercury arc lamp, 50 W). The polymerization was carried out under nitrogen.

Results and Discussion

Linear diacetylenic side groups were synthesized according to Scheme 1. 4-Trimethylsilylethynylphenol was prepared by coupling reaction of 4-iodophenol with trimethylsilylacetylene in the presence of a palladium catalyst.[22−28] The addition of all reagents and the initial reaction was carried out below 0 °C, otherwise there was a considerable occurrence of the coupling reaction between acetylenes to produce a diacetylene compound. The trimethylsilyl group was removed easily under basic conditions to give 4-ethynylphenol, which was very susceptible to hydration. Even during storage as solids at room temperature, 4-acetylphenol was formed. Alkoxy tails with various lengths were introduced to the benzene rings by the reaction of sodium 4-iodophenoxide with alkyl bromides. After acetylation with trimethylsilylacetylene in the presence of a palladium catalyst, the resulting (4-alkoxyphenyl)acetylenes were subjected to oxidative coupling reaction with 4-ethynylphenol to give diacetylene products. Each reaction yielded three different diacetylene products, and the desired unsymmetric diacetylene was isolated by column chromatography on silica gel. Diacetylene **1** with no alkoxy tail and diacetylene **6** with only one benzene ring were also

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(24) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

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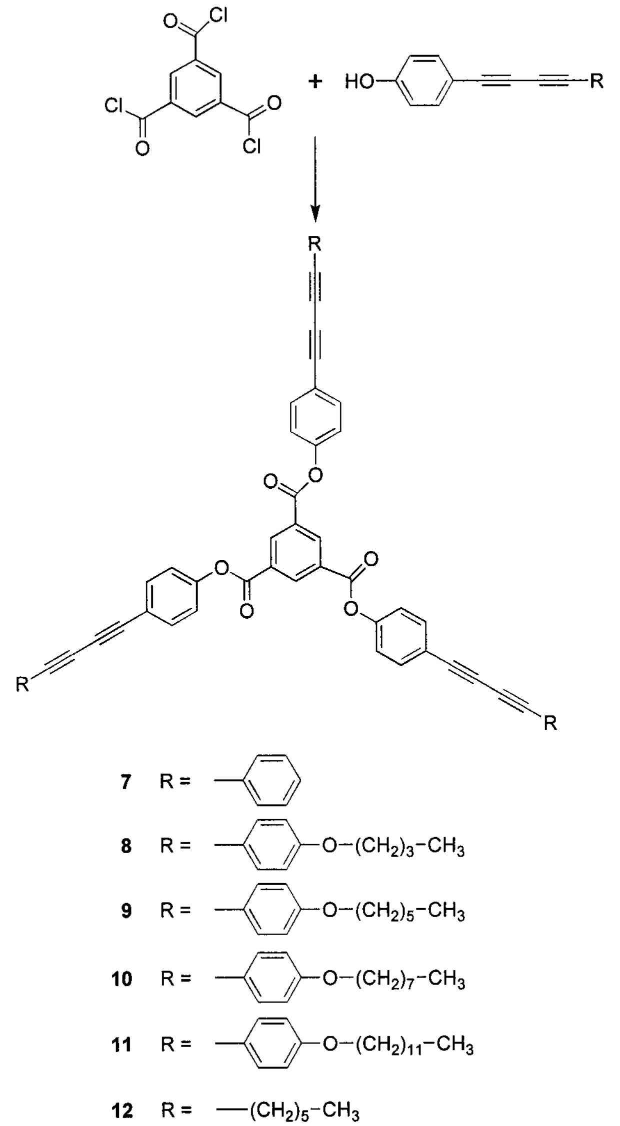
(26) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

(27) Austin, W. B.; Bilow, N.; Kellaghan, W. J.; Lau, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280.

(28) Chang, J. Y.; Rhee, S. B.; Cheong, S.; Yoon, M. *Macromolecules* **1992**, *25*, 2666.

Scheme 2



prepared by the oxidative coupling reaction of 4-ethynylphenol with ethynylbenzene and 1-octyne, respectively. The linear diacetylenes **1**–**6** were linked to benzene cores by an esterification reaction with benzenetricarbonyl trichloride in THF (Scheme 2). The products were characterized by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. ^{1}H NMR spectroscopy showed singlet peaks for the core ring protons around 9.2 ppm in $CDCl_3$ and 9.1 ppm in DMSO-d_6. And also only two peaks appeared around 131 and 136 ppm in $CDCl_3$ for the core ring carbons in the ^{13}C NMR spectra, indicating that all chloro groups were replaced.

While compounds **7**–**12** are benzenetricarboxylates, compound **15** is a tribenzoate of phloroglucinol (Scheme 3). This time the linear diacetylene with a carboxylic group was prepared as a side group. For acetylation, methyl 4-bromobenzoate was used instead of the acid which gave poor yield.[29] The methyl group was not removed until the oxidative coupling reaction with 1-octyloxy-4-ethynylbenzene. Deprotection of diacetylene **13** under basic conditions, activation with thionyl chloride to give compound **14**, and esterification with phloroglucinol were carried out in one pot successfully.

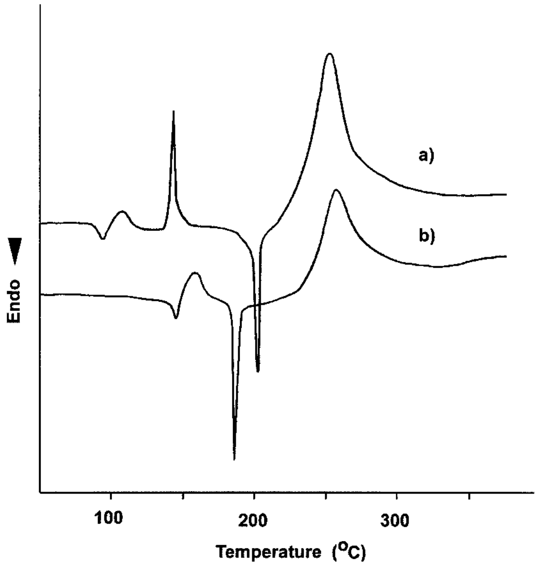


Figure 1. DSC thermograms of (a) compound **7** and (b) compound **8** obtained with a heating rate of 10 °C/min under nitrogen.

All ester compounds have a planar benzene ring core to which three rigid diphenyl diacetylenic units or alkylphenyl diacetylenic units (compound **12**) are linked via ester bonds. Simple molecular modeling showed that three side groups were placed on the nearly same plane as the core, forming a flat structure like a disk. We examined morphological changes of the ester compounds on heating by differential scanning calorimetry (DSC), polarizing optical microscopy, and powder X-ray diffraction (XRD).

Compound **7** was purified by recrystallization from ethyl acetate/methanol and dried under vacuum at 60 °C for 10 h. The compound showed a very interesting DSC thermogram (Figure 1). Around 90 °C, a small endotherm was observed, corresponding to glass transition or melt of small crystals, followed by a small exotherm for crystallization. A strong exotherm (ΔH = 25.1 kJ mol^{-1}) appeared at 140 °C before a strong endotherm (ΔH = 61.2 kJ mol^{-1}) around 200 °C for melt transition. As IR and ^{1}H and ^{13}C NMR spectroscopies did not show any structural change when compound **7** was heated above 140 °C, the exotherm at 140 °C was ascribed to crystallization. This was also confirmed by polarizing optical microscopy, which showed marble textures at 115 °C and rapid crystal growth at 140 °C. Crystallization rather than disordering at such a high temperature is very peculiar. The disklike structure of compound **7** is likely responsible for this unusual result. On melting, the compound began to polymerize thermally. A strong exotherm around 250 °C for the polymerization was also observed in the DSC thermogram. When the sample was cooled to room temperature from the isotropic state and reheated, only melt transition above 200 °C was observed. This was attributable to the partial thermal polymerization occurring immediately after melting.

XRD showed that compound **7** had very low crystallinity at room temperature. When quenched from 115

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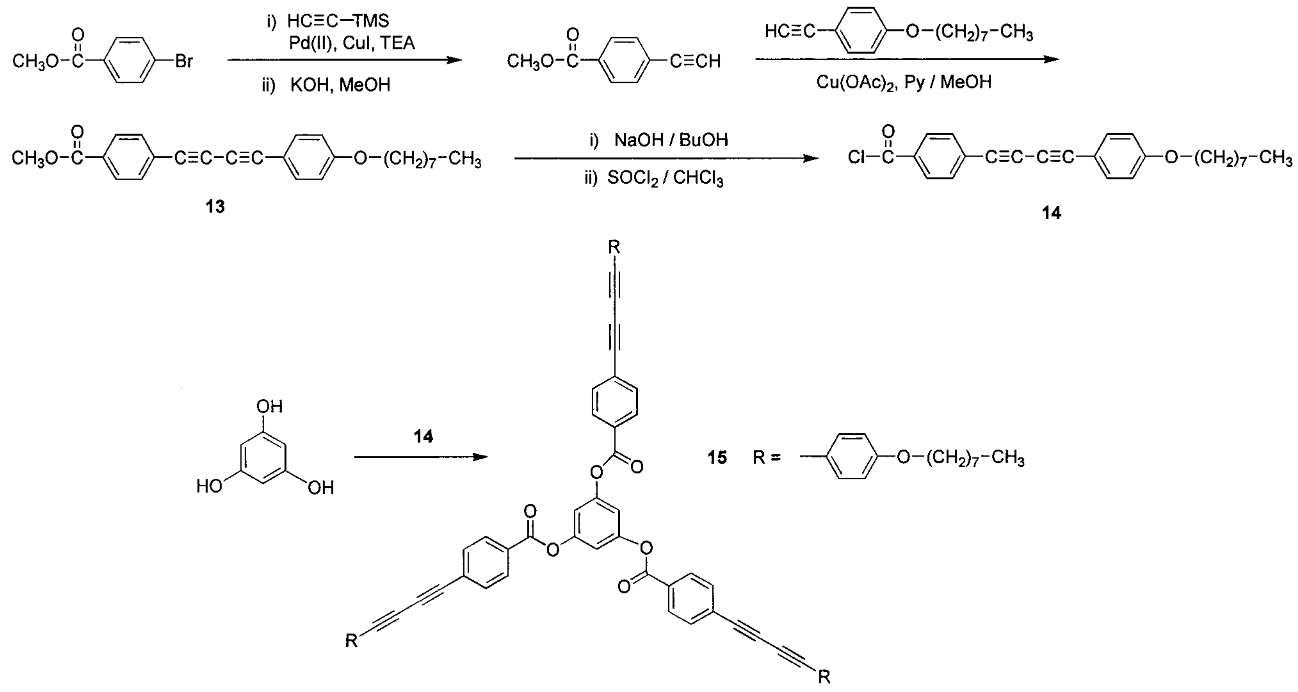
[29] Melissaris, A. P.; Litt, M. H. *J. Org. Chem.* **1992**, *57*, 6998.

Scheme 3



°C to room temperature, sharp peaks with *d* spacings of 20.8 and 10. 5 Å appeared in the small angle region and small peaks with *d* spacings of 4.9, 3.9, and 3.4 Å atop the diffuse peaks in the wide-angle region, corresponding to the ordered structure. When the sample was heated above 140 °C, the broad and diffuse peaks almost disappeared. The small angle region peaks shifted to 23.2 and 11.1 Å. Several other sharp peaks also appeared at 7.3, 5.6, 3.8, 3.7, and 3.5 Å. DSC, polarizing optical microscopy, and XRD results suggested that by heating, molecules in glassy state or small crystals at room temperature were self-organized to solids with two-dimensional order and eventually crystals with three-dimensional order. The crystal structure is not known at this point.

By introducing short alkoxy tails (C_4) to compound **7**, the melt transition temperature was lowered by 15 °C. The resulting compound (**8**) still showed a broad endothermic peak for crystal to crystal phase transition around 159 °C. When cooled from isotropic state with a rate of 10 °C/min, the compound was frozen as a glass. However, with a cooling rate of 1 °C/min, a birefringent phase with mosaic textures began to form at 123 °C (Figure 2). DSC also showed a small endothermic peak ($\Delta H = -4.10$ kJ mol^{-1}) at 120 °C. Mosaic textures were observed more clearly in compound **9** with hexyloxy tails and compound **10** with octyloxy tails.[22] Both compounds showed no crystal-to-crystal or crystal-to-liquid crystal phase transition before clearing transition on heating. When cooled from the isotropic liquid state to room temperature, compound **9** exhibited one exothermic transition at 140 °C ($\Delta H = -10.97$ kJ/mol). A birefringent phase with mosaic textures began to form at 144 °C and persisted to room temperature. That no further crystallization occurred is attributable to the high viscosity of the compound in its LC phase. After the textures were fully developed at 140 °C, the compound was quenched to room temperature for XRD experiments. In the small-angle region, at least three peaks corresponding to *d* spacings of 25.6, 22.3, and 17.1 Å appeared. They are in the ratio of $1:\sqrt{3}/2:2/3$, which is in good agreement with a hexagonal lattice. In addition, the peak with a *d* spacing of 106.3 Å appeared. Wide-angle XRD showed a peak with a *d* spacing of 3.9 Å atop a diffuse peak, which resulted from stacking of the disks. In the case of compound **10**, the peaks with *d* spacings of 30.3, 26.5, and 20.4 Å for a hexagonal lattice were observed. [22]

Compound **11** with longer alkoxy tails (C_{12}) did not show a monotropic transition. When cooled from isotropic state, crystals formed. This was attributable to the fact that long alkyl chains induce crystallization more easily. Compound **12** had only four benzene rings and octyloxy tails. It was crystallized without showing meso phases when cooled from isotropic state. Absence of the second benzene ring in the diacetylenic unit seems to be responsible in part for this result.

Compound **15** has a very similar structure to that of compound **10** and many mesogenic disklike compounds have been prepared as benzoates of multihydroxyben-

Figure 2. Optical polarized micrograph of compound **8**.

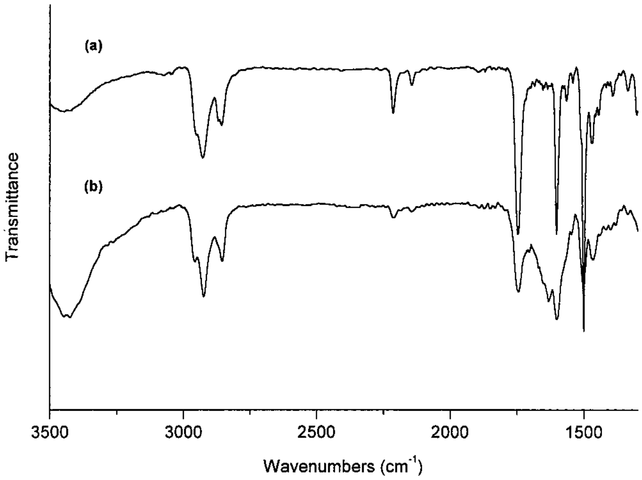


Figure 3. IR spectra of (a) compound **9** and (b) the polymer (KBr).

Table 1. Phase Transition Temperatures and Polymerization Results of Diacetylene Compounds

compd	transition *T* (°C)	polymerization *T* (°C)	phase	*t* (h)	convn %
7	115 (K1−K2)	120	solid	24	71
8	120 (K-LC)	135	LC	24	51
9	140 (K-LC)	143	LC	24	58
11		80	solid	24	22
12		80	solid	24	15
15		80	solid	24	17

zenes. Therefore, compound **15** was expected to show discotic mesophases. However, no birefringent phases were observed on heating or cooling. Presumably atomic position changes in ester linkages acted against π stacking favorable to molecular ordering.

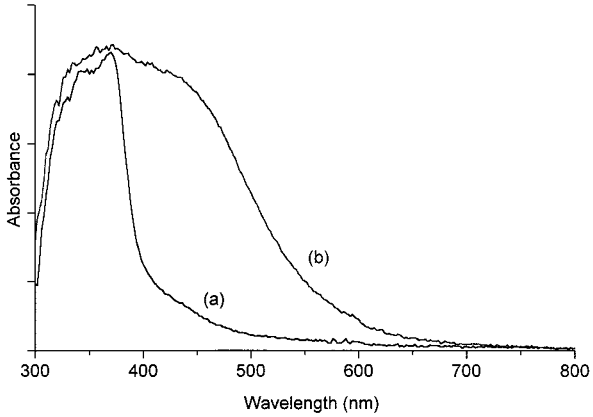


Figure 4. UV spectra of (a) compound **9** and (b) the polymer.

The diacetylene compounds were polymerized by irradiation with UV light (50-W mercury arc lamp). Compounds **8**, **9**, **11**, **12**, and **15** were fabricated into films on glass plates by melt casting, while compound **7** was fabricated by solution casting in a mixture of ethyl acetate and methanol. The polymerization results are summarized in Table 1. Compounds **7**, **11**, **12**, and **15** were polymerized in the solid states, while compounds **8** and **9** in the LC states. Monomer conversion percents were estimated by intensity decreases of the peaks for the diacetylenic groups in the IR spectra. The polymerization in the solid state gave the polymers in low yields except that of compound **7** at 120 °C, where the molecules were likely organized into a two dimensionally ordered form as mentioned above. The LC state polymerization showed relatively high yields. After polymerization in the LC state by irradiation with UV light, compound **9** turned dark red and the phase was still birefringent. In the IR spectrum of compound **9**, two weak bands at 2149 and 2223 cm^{-1} from symmetric and asymmetric stretching vibrations of carbon−carbon triple bonds appeared (Figure 3). After polymerization, the absorbances of two bands decreased in the same proportion by 58% and a weak band at 2186 cm^{-1} for C−C triple bonds showed up. The band at 1630 cm^{-1} became broader and stronger by overlapping with the band from C−C double bonds. This result suggested that the polymerization proceeded by 1,4-addition. Since the stacking distance of the disks was suitable for the topochemical polymerization in the hexagonal columnar structure, the polymerization likely proceeded in a vertical direction with respect to the disk plane. In the XRD study, the polymerized compound **9** showed peaks with *d* spacings of 24.7, 21.6, and 85.8 Å, indicating that the LC structure was maintained. In the wide-angle region, the peak at 3.9 Å was shifted to 4.1 Å after polymerization. The backbone structures of the polymers were also confirmed by UV−vis spectroscopy. Figure 4 shows the UV−vis spectra of compound **9** obtained with a waveguided UV−vis spectrometer. The sample was prepared as a film cast on a glass plate. Compound **9** had an absorption limit of about 500 nm. After polymerization, absorption occurred up to about 700 nm, corresponding to the conjugated polydiacetylene chains.

Conclusion

We prepared polymerizable disklike compounds that had a benzene ring core and three rigid diacetylenic units. The diacetylenic units were attached to the benzene ring via ester linkages, thereby constructing a part of the rigid disks. On heating, the compounds showed interesting morphological changes, which were much dependent on the lengths of flexible alkoxy tails. The compounds with butyloxy, hexyloxy, and octyloxy tails had hexagonal columnar structures in their LC states. The disklike compounds were photopolymerized with UV in liquid crytalline states or solid states and the conversions of the monomers to the polymers were relatively high in the LC states.

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