

Rodlike mesogenic molecules consisting of two diacetylenic groups: mesomorphic behavior and photoimaging

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A series of mesogenic compounds with two diacetylenic groups were synthesized. The diacetylene groups were connected to a benzene ring *via* ester linkages, becoming a part of a rigid rod. The thermal behavior of the compounds and their polymerization were investigated. Compounds **7**, **8**, **9** and **10** having long alkyl tails showed nematic mesophases. They were thermally polymerized in the isotropic state above 200 °C. Partial polymerization occurred by annealing in the liquid crystalline state. When the compounds were exposed to UV light in the liquid crystalline state, the polymerization was completed within 30 min to give amorphous polydiacetylenes. In the UV-Vis spectra, absorption of the polymers occurred up to about 600 nm, attributable to the short conjugated polydiacetylene backbones. Compound **9** with an octyl tail was fabricated into a thin film and the photopolymerization was carried out through a photomask in the liquid crystalline state resulting in a patterned image.

Introduction

Photoreaction of diacetylenes has been extensively studied due to their unique reactivity and the interesting properties of the resulting polymers.^{1,2} The reaction is known to proceed topochemically *via* 1,4-addition by irradiation and thus has been widely used for preparing ordered macromolecules. The topochemical polymerization of diacetylenes can be carried out in the solid state. A diacetylene single crystal is polymerized to give a single crystal of a polymer when a crystal structure satisfies the requirements for the topochemical polymerization. Such structural requirements can be also met in Langmuir–Blodgett films,^{3–5} self-assembling monolayers,^{6,7} and vesicles.⁸ The 1,4-polymerization of diacetylenes in liquid crystalline states was also reported to give highly ordered polymers.^{9–13} Liquid crystalline state polymerization is of great interest because of its application to the fabrication of stable, optically anisotropic films. In addition, it has potential imaging applications since LC molecules can be oriented macroscopically under electric or magnetic fields and photopolymerization will change their optical properties.

In our previous communication,¹⁴ we reported a photopolymerizable liquid crystal molecule with two photoreactive chalcone units. Photopolymerization by UV irradiation through a photomask resulted in an excellent patterned image, which resulted from the [2 + 2] addition reaction of chalcones in the irradiated area. These results prompted us to investigate further on photopolymerizable liquid crystals suitable for photoimaging. The photopolymerizable groups can be introduced either to the end of flexible spacers or into a mesogen, becoming a part of the rigid rod. The latter will be a better approach to obtain a high contrast in an image, resulting from the significant changes of the aligned structures by the polymerization and thereby the optical property changes of the irradiated area.

In this work, we prepared rodlike mesogenic molecules mainly consisting of two diacetylenic groups. Unlike the polymerization of diacetylenic compounds with one polymerizable group to yield polymers with ordered structures, the polymerization of these compounds was expected to occur at two

sites and thereby disrupt aligned molecules in a microdomain. We report here the polymerization of mesogenic diacetylenes and their application to photoimaging.

Experimental

Materials and instrumentation

4-Iodophenol, trimethylsilylacetylene, dichlorobis(triphenylphosphine)palladium(II), copper(I) iodide, bromine, terephthaloyl dichloride, and isophthaloyl dichloride were purchased from Aldrich and used as received. Reagent grade solvents were dried and purified as follows. Pyridine was distilled over calcium hydride. Tetrahydrofuran (THF) and 1,4-dioxane were dried over sodium metal and distilled. Methanol was dried over molecular sieves 4 Å and distilled. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-LA 300 (300 MHz) spectrometer or Bruker Avance DPX-300 (300 MHz) at room temperature. IR spectra were obtained with the use of a Perkin Elmer Spectrum GX I spectrometer. UV-Vis spectra were obtained with the use of a Hewlett-Packard HP8452A. Thermal analyses were performed using a TGA 2050 thermalgravimetric analyzer and a TA modulated DSC 2920. Optical microscopy study was performed with a Nikon 264445 equipped with a Linkam heating stage and Linkam TP 92 controller. Elemental analyses were performed at the National Center for Inter-University Research Facilities of Seoul National University, Seoul, Korea.

1-Bromoheptyne

4-Trimethylsilylethynylphenol and 4-ethynylphenol were prepared according to our previous report.¹⁵ Bromine (39.9 g, 0.25 mol) was added to a vigorously stirred solution of potassium hydroxide (37.5 g) in water (100 ml) at 0 °C.¹⁶ 1-Heptyne (0.15 mol) in 1,4-dioxane (80 ml) was added dropwise to the above mixture over 2 h. The reaction mixture was stirred for 40 h at room temperature and the reaction mixture was extracted with chloroform. The organic layer was dried with anhydrous MgSO₄. Upon filtration and evaporation the

product was isolated and used for reaction without further purification.

^1H NMR (CDCl_3 , 300 MHz): δ 2.20 (t, 2H, CCH_2), 1.54–0.91 (m, 9H, alkyl chain protons).

1-Bromooctyne, 1-bromononyne and 1-bromodecyne were prepared using the same method as described above.

1-(4-Hydroxyphenyl)-4-pentylbutadiyne (1)

Methanol (35 ml), a solution of hydroxylamine-HCl (0.75 g) in water (10 ml), a 70% aqueous solution of ethylamine (4.75 g), and copper(I) chloride (0.11 g) were placed in a flask.¹⁷ To the mixture, 4-ethynylphenol (14.9 mmol) was added in one portion. Then 1-bromoheptyne (14 mmol) was added over about 1 h, while keeping the temperature at 35 °C. After stirring for 6 h at the same temperature, a solution of KCN (0.37 g) and NH_4Cl (1.50 g) in water (50 ml) was added with vigorous stirring. The mixture was extracted with chloroform, dried with anhydrous MgSO_4 , and filtered. After evaporation of the solvent, the product was isolated by column chromatography on silica gel (25% ethyl acetate in hexane) as an oil (yield 52%).

^1H NMR (CDCl_3 , 300 MHz): δ 7.38, 6.77 (dd, 4H, C_6H_4), 5.30 (s, 1H, OH), 2.37 (t, 2H, CCH_2), 1.73–0.88 (m, 9H, alkyl chain protons).

1-(4-Hydroxyphenyl)-4-hexylbutadiyne (2)

This compound was prepared from 4-ethynylphenol and 1-bromooctyne as described for compound 1 as an oil (yield 56%).

^1H NMR (CDCl_3 , 300 MHz): δ 7.38, 6.77 (dd, 4H, C_6H_4), 5.28 (s, 1H, OH), 2.35 (t, 2H, CCH_2), 1.59–0.87 (m, 11H, alkyl chain protons).

1-(4-Hydroxyphenyl)-4-heptylbutadiyne (3)

This compound was prepared from 4-ethynylphenol and 1-bromononyne as described for compound 1 as an oil (yield 57%).

^1H NMR (CDCl_3 , 300 MHz): δ 7.38, 6.78 (dd, 4H, C_6H_4), 5.66 (s, 1H, OH), 2.35 (t, 2H, CCH_2), 1.59–0.86 (m, 13H, alkyl chain protons).

1-(4-Hydroxyphenyl)-4-octylbutadiyne (4)

This compound was prepared from 4-ethynylphenol and 1-bromodecyne as described for compound 1 as an oil (yield 66%).

^1H NMR (CDCl_3 , 300 MHz): δ 7.38, 6.77 (dd, 4H, C_6H_4), 5.56 (s, 1H, OH), 2.34 (t, 2H, CCH_2), 1.58–0.86 (m, 15H, alkyl chain protons).

1-(4-Hydroxyphenyl)-4-decylbutadiyne (5)

To a solution of 4-ethynylphenol (2.88 g, 24.4 mmol) and 1-dodecyne (10 ml, 46.8 mmol) in pyridine-methanol (1:1 v/v, 200 ml) was added copper(II) acetate (8.85 g, 48.8 mmol), and the reaction mixture was refluxed for 6 h under nitrogen. Insoluble solids were removed by filtration. After evaporation of the solvent, the product was isolated by column chromatography on silica gel (ethyl acetate-hexane = 1/3 v/v, yield 40%).

^1H NMR (CDCl_3 , 300 MHz): δ 7.38, 6.77 (dd, 4H, C_6H_4), 5.07 (s, 1H, OH), 2.34 (t, 2H, CCH_2), 1.58–0.85 (m, 19H, alkyl chain protons).

Bis(4-pentylbutadiynylphenyl) terephthalate (6)

To a solution of compound 1 (0.52 g, 2.5 mmol) in THF (100 ml) was added NaH (72 mg, 3.0 mmol). After the mixture was stirred for 1 h at room temperature, a solution of

terephthaloyl dichloride (0.27 g, 1.23 mmol) in THF (50 ml) was added. The solution was stirred for 6 h. After evaporation, the product was isolated by column chromatography on silica gel (methylene chloride-hexane = 5/1 v/v) and further purified by recrystallization from methylene chloride-hexane (yield 65%).

Elemental analysis. Calc. for $\text{C}_{38}\text{H}_{34}\text{O}_4$: C, 82.28; H, 6.18. Found: C, 82.24; H, 6.21%. ^1H NMR (CDCl_3 , 300 MHz): δ 8.32 (s, 4H, C_6H_4), 7.57, 7.22 (dd, 8H, C_6H_4), 2.37 (t, 4H, CCH_2), 1.57–0.90 (m, 18H, alkyl chain protons). ^{13}C NMR (CDCl_3 , 300 MHz): δ 163.8, 150.8, 133.8, 133.7, 130.3, 121.7, 120.2, 85.2, 74.8, 73.7, 64.9, 31.0, 27.9, 22.1, 19.5, 13.9. IR (KBr pellet, cm^{-1}): 2933, 2866, 2241, 2142, 1739, 1595, 1501, 1249, 1194.

Bis(4-hexylbutadiynylphenyl) terephthalate (7)

This compound was prepared from terephthaloyl dichloride (0.97 g, 4.4 mmol) and 1-(4-hydroxyphenyl)-4-hexylbutadiyne (2 g, 8.83 mmol) as described for compound 6 (yield 75%).

Elemental analysis. Calc. for $\text{C}_{40}\text{H}_{38}\text{O}_4$: C, 82.44; H, 6.5. Found: C, 82.40; H, 6.66%. ^1H NMR (CDCl_3 , 300 MHz): δ 8.31 (s, 4H, C_6H_4), 7.57, 7.22 (dd, 8H, C_6H_4), 2.37 (t, 4H, CCH_2), 1.57–0.88 (m, 22H, alkyl chain protons). ^{13}C NMR (CDCl_3 , 300 MHz): δ 163.8, 150.8, 133.8, 133.7, 130.3, 121.7, 120.2, 85.2, 74.8, 73.7, 64.9, 31.3, 28.5, 28.2, 22.5, 19.6, 14.0. IR (KBr pellet, cm^{-1}): 2930, 2855, 2240, 2144, 1740, 1597, 1499, 1257, 1192.

Bis(4-heptylbutadiynylphenyl) terephthalate (8)

This compound was prepared from terephthaloyl dichloride (0.74 g, 3.4 mmol) and 1-(4-hydroxyphenyl)-4-heptylbutadiyne (1.64 g, 6.8 mmol) as described for compound 6 (yield 64%).

Elemental analysis. Calc. for $\text{C}_{42}\text{H}_{40}\text{O}_4$: C, 82.59; H, 6.93. Found: C, 82.33; H, 7.05%. ^1H NMR (CDCl_3 , 300 MHz): δ 8.31 (s, 4H, C_6H_4), 7.57, 7.22 (dd, 8H, C_6H_4), 2.37 (t, 4H, CCH_2), 1.54–0.89 (m, 26H, alkyl chain protons). ^{13}C NMR (CDCl_3 , 300 MHz): δ 163.8, 150.8, 133.8, 133.7, 130.3, 121.7, 120.2, 85.2, 74.8, 73.7, 64.9, 31.7, 28.8, 28.7, 28.2, 22.6, 19.6, 14.0. IR (KBr pellet, cm^{-1}): 2926, 2853, 2242, 2145, 1740, 1595, 1503, 1266, 1198.

Bis(4-octylbutadiynylphenyl) terephthalate (9)

This compound was prepared from terephthaloyl dichloride (0.36 g, 1.6 mmol) and 1-(4-hydroxyphenyl)-4-octylbutadiyne (0.9 g, 3.5 mmol) as described for compound 6 (yield 45%).

Elemental analysis. Calc. for $\text{C}_{44}\text{H}_{46}\text{O}_4$: C, 82.72; H, 7.26. Found: C, 82.10; H, 7.40%. ^1H NMR (CDCl_3 , 300 MHz): δ 8.31 (s, 4H, C_6H_4), 7.57, 7.22 (dd, 8H, C_6H_4), 2.36 (t, 4H, CCH_2), 1.58–0.86 (m, 30H, alkyl chain protons). ^{13}C NMR (CDCl_3 , 300 MHz): δ 163.8, 150.8, 133.8, 133.7, 130.3, 121.7, 120.2, 85.2, 74.8, 73.7, 64.9, 31.8, 29.1, 29.0, 28.9, 28.2, 22.6, 19.6, 14.1. IR (KBr pellet, cm^{-1}): 2923, 2853, 2242, 2145, 1740, 1596, 1501, 1266, 1199.

Bis(4-decylbutadiynylphenyl) terephthalate (10)

This compound was prepared from terephthaloyl dichloride (1.0 g, 4.92 mmol) and 1-(4-hydroxyphenyl)-4-decylbutadiyne (2.78 g, 9.84 mmol) as described for compound 6 (yield 48%).

Elemental analysis. Calc. for $\text{C}_{48}\text{H}_{54}\text{O}_4$: C, 82.96; H, 7.83. Found: C, 82.84; H, 7.85%. ^1H NMR (CDCl_3 , 300 MHz): δ 8.31 (s, 4H, C_6H_4), 7.57, 7.22 (dd, 8H, C_6H_4), 2.38 (t, 4H, CCH_2), 1.58–0.86 (m, 38H, alkyl chain protons). ^{13}C NMR (CDCl_3 , 300 MHz): δ 163.7, 150.8, 133.8, 133.7, 130.3, 121.7, 120.2, 85.2, 74.8, 73.7, 64.9, 31.8, 29.5, 29.4, 29.3, 29.0, 28.8, 28.2, 22.6, 19.6, 14.0. IR (KBr pellet, cm^{-1}): 2918, 2850, 2243, 2152, 1737, 1595, 1501, 1279, 1204.

Bis(4-octylbutadiynylphenyl) isophthalate (11)

This compound was prepared from isophthaloyl dichloride (0.29 g, 1.4 mmol) and 1-(4-hydroxyphenyl)-4-octylbutadiyne (0.72 g, 2.8 mmol) as described for compound **6** (yield 35%).

Elemental analysis. Calc. for $C_{44}H_{46}O_4$: C, 82.72; H, 7.26. Found: C, 82.74; H, 7.47%. 1H NMR ($CDCl_3$, 300 MHz): δ 8.97 (t, 1H, C_6H_4), 8.46 (q, 2H, C_6H_4), 7.69 (t, 1H, C_6H_4), 7.56, 7.21 (dd, 8H, C_6H_4), 2.36 (t, 4H, CCH_2), 1.60–0.86 (m, 30H, alkyl chain protons). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 163.7, 150.8, 135.1, 133.8, 131.8, 130.0, 129.2, 121.8, 120.2, 85.2, 74.7, 73.7, 64.9, 31.8, 29.1, 29.0, 28.9, 28.2, 22.6, 19.6, 14.0. IR (KBr pellet, cm^{-1}): 2923, 2853, 2246, 1749, 1606, 1504, 1299, 1237.

UV irradiation

Thin films of the compounds prepared on glass plates by melt casting were placed on a Linkam heating stage equipped with a Linkam TP 92 controller under an UV lamp (100 W short-arc mercury lamp). Photopolymerization was carried out under nitrogen at desired temperatures.

Results and discussion

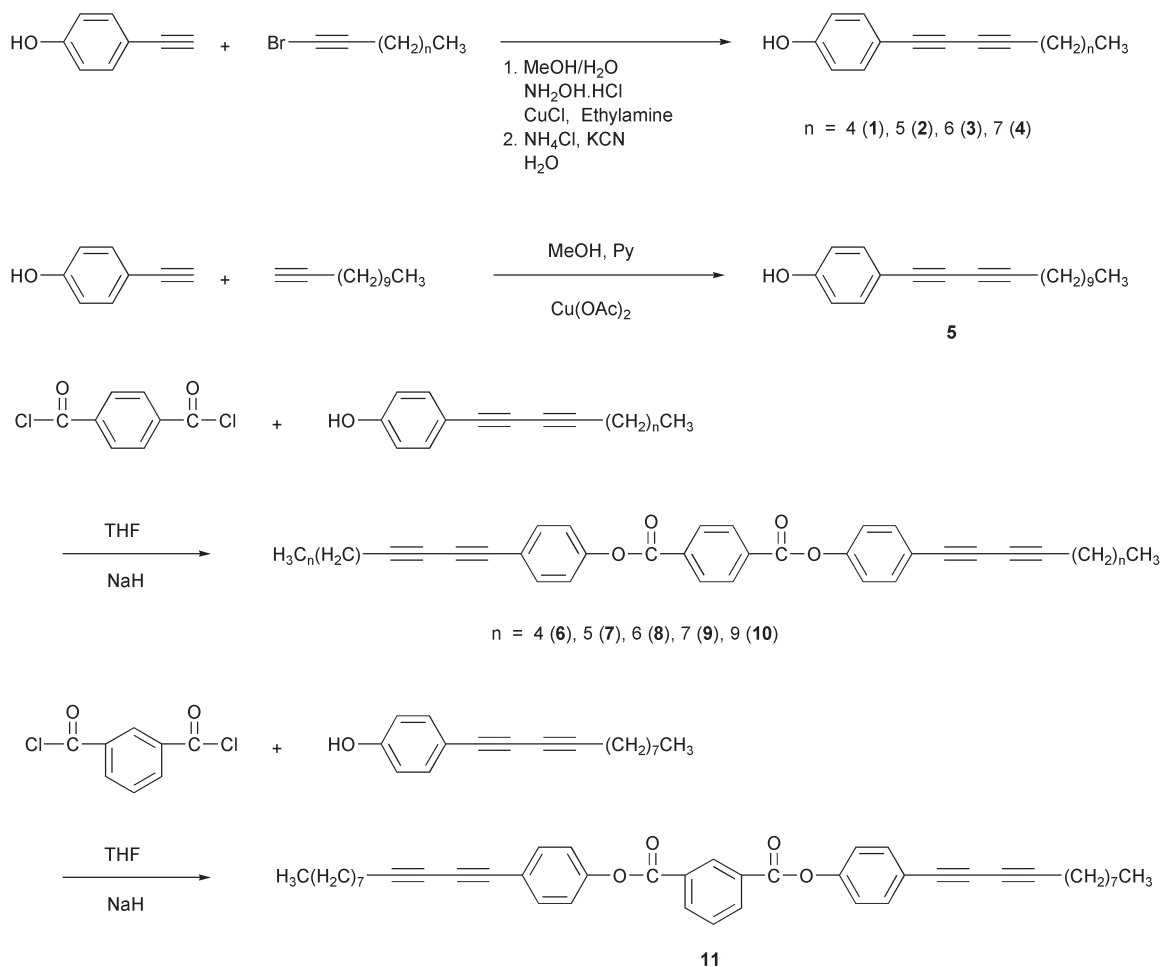
Monomer synthesis

Linear diacetylenic side groups were synthesized according to Scheme 1. 4-Trimethylsilylethynylphenol was prepared by the coupling reaction of 4-iodophenol with trimethylsilylacetylene in the presence of a palladium catalyst.^{15,18–22} The trimethylsilyl group was removed easily under basic conditions to give 4-ethynylphenol. The unsymmetric diacetylene side groups (**1–4**) were prepared by the Cadiot–Chodkiewicz coupling

reaction^{23–25} of 1-bromoalkynes with 4-ethynylphenol, whereas compound **5** was prepared by oxidative coupling reaction of 1-dodecyne with 4-ethynylphenol in the presence of copper(II) acetate in a solution of pyridine and methanol (1 : 1).²⁶ The oxidative reaction yielded three different diacetylene products, and the desired unsymmetric diacetylene was isolated by column chromatography on silica gel. Linear diacetylenes **6–10** were obtained by an esterification reaction of the side groups with terephthaloyl dichloride in THF and bent-shaped compound **11** by an esterification reaction of **4** with isophthaloyl dichloride. The structures of the products were confirmed by 1H and ^{13}C NMR spectroscopy, and elemental analysis.

Mesomorphic behaviors

We examined morphological changes of the linear ester compounds by differential scanning calorimetry (DSC) and polarizing optical microscopy. The transition temperatures and corresponding enthalpy values of the compounds are summarized in Table 1 and their DSC thermograms are depicted in Fig. 1. Compound **6** with a pentyl tail showed no mesophase. Only the melt transition on heating and crystallization on cooling were observed in DSC and polarizing microscopy analysis. By lengthening an alkyl tail to a hexyl, a liquid crystalline phase began to form. Compound **7** showed a monotropic transition. In DSC analysis, on heating, the peak for the crystal to isotropic liquid transition appeared at 135.4 °C and a strong exotherm was observed above 200 °C, indicating that thermal polymerization took place. When this compound was cooled from the isotropic liquid state to room temperature, only the peak for crystallization occurred at 107.5 °C. Nevertheless, we could observe a mesophase between 119 and 107 °C by polarizing microscopy. This compound



Scheme 1

Table 1 Phase transition temperatures and corresponding enthalpy values of the diacetylenic compounds

Compound	$T/^\circ\text{C}$ ($\Delta H/\text{kJ mol}^{-1}$) ^a	
	Heating	Cooling
6	K 145.2 (27) I	I 128.4 (27) K
7	K 135.4 (25) I	I 119 ^b N 107.5 (26) K
8	K 120.9 (27) N 196 ^b I	I 196 ^b N 105.5 (26) K
9	K 105.0 (26) N 210 ^b I	I 210 ^b N 95.5 (25) K
10	K 103.7 (28) N 214 ^b I	I 204 ^b N 87.3 (27) K
11	K 106.2 (35) I	I 94.4 (35) K

^aK = crystalline; N = nematic; I = isotropic. ^bDetermined by polarizing optical microscopy.

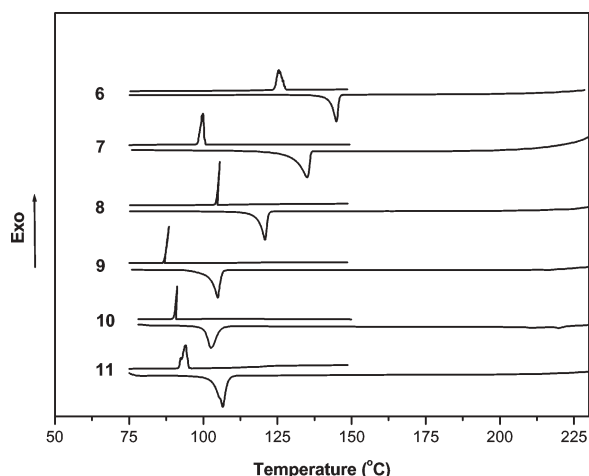


Fig. 1 DSC thermograms of the diacetylenic compounds obtained with a heating rate of $10^\circ\text{C min}^{-1}$ and a cooling rate of 5°C min^{-1} under nitrogen. For all compounds the second cooling and third heating traces are shown.

exhibited a *Schlieren* texture that was characteristic of a nematic phase. Compound **8** with a heptyl tail showed an enantiotropic transition. DSC analysis showed the peak for the crystal to liquid crystal transition at 120.9°C on heating and in the cooling scan, the peak for crystallization appeared at 105.5°C . We could also detect a broad mesophase range by polarizing optical microscopy. A *Schlieren* texture corresponding to a nematic phase was observed from 120.9 to 196°C on heating. Upon cooling from the isotropic state, the same texture emerged at 196°C . On further cooling to 105°C crystals began to form. Although the transition of the liquid crystal to the isotropic liquid was observed by polarizing optical microscopy, interestingly the peak for the corresponding transition did not appear in the DSC thermogram. This was ascribed to the fact that the thermal polymerization began to take place immediately after the isotropization. Compounds **9** and **10** also showed enantiotropic transitions and the temperature ranges of the liquid crystalline phases were broader than that of compound **8**. This shows that the mesophase became more stable as the flexible alkyl chain length was increased. Isophthalate **11**, a bent-shaped molecule with an octyl tail showed the melt transition at almost the same temperature as the corresponding terephthalate derivative (**9**), but did not form any mesophases.

Polymerization

All compounds were thermally polymerized in their isotropic states. DSC showed strong exotherms corresponding to the polymerization around 260°C . For compound **9** the polymerization was completed on heating on a glass plate under nitrogen at 220°C for 20 min, as determined by the

disappearance of the peaks for diacetylenic groups in the IR spectrum. The resulting polymer was dark red and insoluble in common organic solvents such as chloroform, which is a good solvent for the monomer.

Thermal polymerization also occurred in the liquid crystalline state. When compound **9** was annealed in the liquid crystalline state (170°C) for 16 h, it was partially polymerized. With a polarizing microscope, liquid crystalline phases were still observed on heating and cooling along with the amorphous polymer domains. About 30% of diacetylenic groups of the compound were found to be consumed when compared the absorbances of the diacetylene peaks in the IR spectra obtained before and after polymerization.

When exposed to UV light in the liquid crystalline state polymerization proceeded rapidly. Compound **9** was fabricated into a film on a glass plate by melt casting and then polymerized with UV light (100 W short-arc mercury lamp) for 30 min at 170°C . After polymerization, compound **9** turned into an amorphous dark red polymer which was not soluble in common organic solvents. In the IR spectrum (Fig. 2), two bands at 2145 and 2242 cm^{-1} corresponding to the diacetylenic groups decreased by more than 90% and a weak band at 2203 cm^{-1} emerged. In addition, the band around 1600 cm^{-1} became broader and stronger due to the formation of C=C double bonds. In the UV-Vis spectra (Fig. 3), the monomer had an absorption limit of about 400 nm , whereas the absorption of the polymer occurred up to about 600 nm , arising from the short conjugated polydiacetylene backbones.

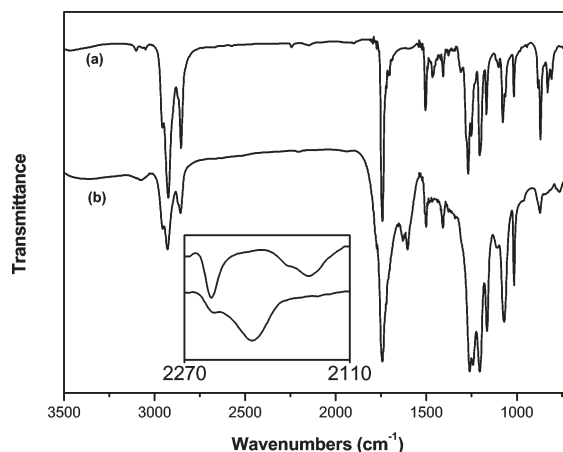


Fig. 2 IR spectra of (a) compound **9** (KBr) and (b) the polymer obtained upon liquid crystalline state polymerization. Inset: IR spectra of the diacetylene vibration range.

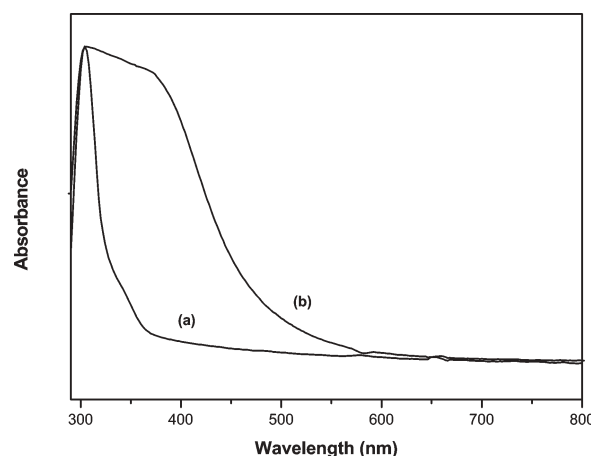


Fig. 3 UV spectra of (a) compound **9** and (b) the polymer as a film cast on a glass plate.

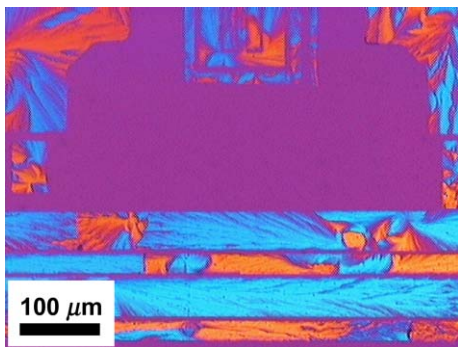


Fig. 4 Image patterns observed under polarizing optical microscopy. The patterns were obtained with compound **9** by UV irradiation through a photomask at 170 °C for 30 min.

Photoimaging

After a film (thickness *ca.* 2 μm) was prepared by casting compound **9** on a glass plate in its liquid crystalline state (170 °C), photopolymerization with a UV lamp (100 W short-arc mercury lamp) was carried out for 30 min through a photomask under nitrogen. Fig. 4 shows an image observed under polarizing optical microscopy. The image was obtained where the irradiated region appeared isotropic and the masked part remained birefringent under polarizing optical microscopy. This result is ascribed to the fact that the photopolymerization occurred at two sites on the molecule, resulting in a crosslinked polymer. Since two diacetylenic units comprised a rigid part of the molecule, the photoreaction disrupts aligned molecules in a microdomain rendering it isotropic.

In summary, rodlike mesogenic compounds mainly consisting of two diacetylenic units were synthesized as potential photoimaging materials. These compounds were thermally polymerized in the liquid crystalline state as well as in the isotropic state. They were also photopolymerized with UV light in the liquid crystalline state. Since the compounds had two diacetylenic units as a part of a rod, the polymerization in the liquid crystalline states occurred at two reactive sites, resulting in the disruption of the aligned structures of the liquid crystals and thereby resulting in optical property changes. We demonstrated that the liquid crystalline state photopolymerization of the compounds with two diacetylenic groups could be used for photoimaging.

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