Liquid Crystals Obtained from Disclike Mesogenic Diacetylenes and Their Polymerization

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Since the topochemical polymerization of diacetylenes by irradiation or thermal annealing was first reported more than two decades ago,[1] it has become one of the favorite methods used to obtain the organized macromolecules.[2] Various types of diacetylenes have been prepared and used for Langmuir−Blodgett films,[3] self-assembling monolayers,[4] and vesicles.[5] The polymerization of diacetylenes occurs in liquid crystalline (LC) phases as well as in the solid state.[6] In an LC state, molecules are self-organized into ordered arrays comparable to those in Langmuir−Blodgett or self-assembling processes. Most diacetylenic mesogens found in the literatures consist of rigid and linear diacetylenic parts and flexible alkyl chains, which exhibit nematic or smetic phases.[6,7] Disclike mesogenic diacetylenes are of particular interest. They stack in columns, and zipping of diacetylenes along the column axis by polymerization will lead to supramolecules with columnar structures. In this paper, we report novel disclike mesogenic diacetylenes which are polymerizable in LC states.

Three disclike diacetylenes (**1**−**3**) were synthesized as potential mesogens (Figure 1). The linear diacetylenic side groups were prepared according to Scheme 1. Ethynylation with (trimethylsilyl)acetylene in the presence of bis(triphenylphosphine)palladium(II) chloride and CuI in triethylamine[8] and subsequent removal of the trimethylsilyl group in a solution of KOH/MeOH gave compound **4**. 4-Ethynylphenol and 4-ethynylaniline, prepared following literatures procedures[8a,d] were coupled with 4-(octyloxy)phenylacetylene or 1-octyne in the presence of copper(II) acetate[9] in a solution of pyridine and methanol (1:1). The unsymmetrical diacetylene products were isolated by column chromatography on silica gel (ethyl acetate/
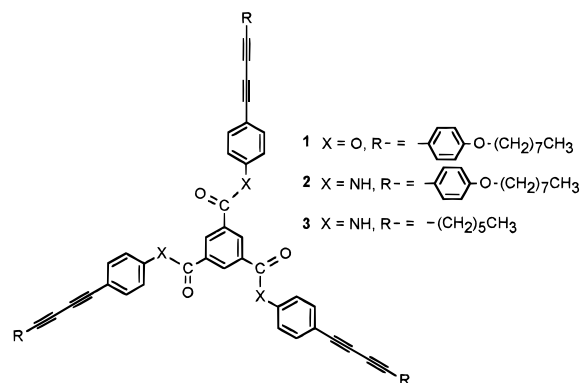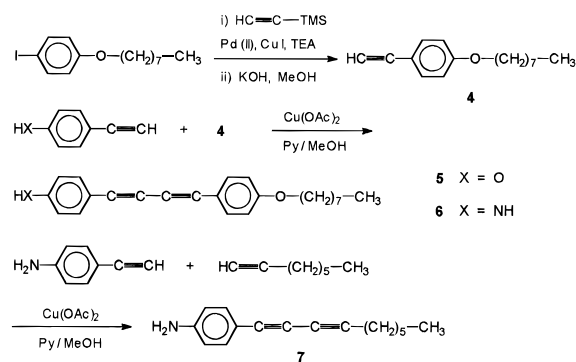

Figure 1. Structures of disclike diacetylenes.

Scheme 1

hexane) and further purified by recrystallization from ethyl acetate/methanol (**5**, mp 110 °C) or ethyl acetate/hexane (**6**, mp 103 °C; 7, mp 148 °C). The linear diacetylenes **5**−**7** were linked to benzene cores by esterification or amidation reactions. Compounds **1**−**3** were purified by column chromatography on silica gel (methylene chloride/hexane) and then recrystallization from ethyl acetate/methanol (**1** and **2**) or chloroform/hexane (**3**).[10]

Compound **1** showed a monotropic transition. In DSC analysis an endotherm at 132 °C appeared on the first heating but disappeared on reheating. A clearing transition was observed at 146 °C. On heating beyond 200 °C, a strong exotherm appeared, indicating thermal polymerization took place. When cooled from the isotropic liquid state to room temperature, the compound exhibited one exothermic transition at 137 °C ($\Delta H = -13.6$ kJ/mol). A birefringent phase with mosaic textures[11] began to form at 140 °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 (see Figure 2a) were fully developed at 137 °C, the compound was quenched to room temperature and subjected to XRD experiments. In the small-angle region, at least three peaks corresponding to *d* spacings of 30.3, 26.5, and 20.4 Å appeared. They are in the ratio of $1:\sqrt{3}/2:2/3$, which is in good agreement with a hexagonal lattice. The calculated diameter of the disc is 52 Å by simple molecular modeling, and the peak with a *d* spacing of 26.5 Å likely corresponds to the radius. Wide-angle XRD showed a peak with a *d* spacing of 3.5 Å atop a diffuse peak, which probably resulted from stacking of the discs.

Compound **2** exhibited a clearing transition at a much higher temperature than compound **1** because of hydrogen bondings

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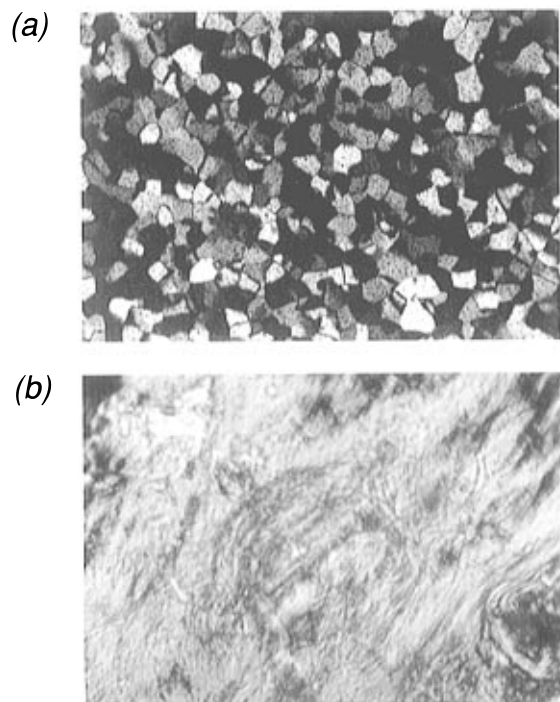
Figure 2. Optical polarized micrographs of compound **1** at 137 °C obtained on cooling from the isotropic liquid (a, 200 magnification) and of compound **2** obtained at 194 °C on heating (b, 500 magnification).

between amide groups. DSC analysis showed a endothermic clearing transition at 204 °C, followed by the strong exotherm corresponding to thermal polymerization. Although no peak other than the clearing transition peak appeared in DSC thermogram, an ordered fluid phase formed above 190 °C.[12] A highly viscous phase with a needle-like texture was first observed by polarizing optical microscopy and became thread-like by shearing (see Figure 2b). A wide-angle XRD diffractogram obtained after quenching from the LC state to room temperature showed only a broad peak around $2\theta = 24°$. In the small angle region, a peak with a d spacing of 34.6 Å was observed, and thus we believe that compound **2** was organized into discotic nematic phases. Since compound **2** was polymerized immediately after clearing, phase transitions on cooling could not be investigated.

The DSC thermogram of compound **3** showed only a second-order transition at 80 °C and a strong exotherm above 200 °C. The compound became shearable at approximately 120 °C and the birefringent texture began to form. We presume that compound **3** was either in glassy state or as very small crystals. Wide-angle XRD also showed a broad peak. The texture did not develop further, since the fluidity decreased rapidly due to thermal polymerization. The higher susceptibility of compound **3** to thermal polymerization compared with compounds **1** and **2** is ascribed to the absence of the second phenyl ring in the side group.[2]

When annealed in LC states at 197 °C under nitrogen, compound **2** turned to a dark reddish solid in 24 h. Optical microscopy showed the material was still birefringent. Although the IR spectroscopy showed only a 35% absorbance decrease for the acetylene stretching bands at 2149 and 2216 cm^{-1}, no unreacted monomer was extracted with chloroform[13] and the endothermic melt transition for the monomer was not seen in the DSC thermogram. The XRD diffractogram showed a peak with a d spacing of 35.0 Å, a broad peak at $2\theta = 24°$ as was observed for the monomer, and an additional broad peak at $2\theta = 12.0°$ ($d = 7.4$ Å). The IR and XRD results suggest that only one of three diacetylenic groups of each monomer participated in polymerization without much altering the liquid crystalline structure.

Heating of compound **1** in the LC state at 137 °C did not induce polymerization. When exposed to UV light (254 nm, 12 W) for 40 h at the same temperature under nitrogen, it turned deep yellow. The phase was still birefringent, and mosaic textures from unreacted monomers were seen. In the IR spectrum of compound **1**, two weak bands at 2149 and 2223 cm^{-1} from symmetric and asymmetric stretching vibrations of carbon−carbon triple bonds appeared. After polymerization, the absorbances of two bands decreased in the same proportion by 25% 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 suggests that the polymerization proceeded by 1,4-addition. In striking contrast to the polymerization of compound **2**, monomer conversion determined from the melt enthalpy decrease in the DSC thermogram was almost consistent with the IR result. The polymerized sample showed an XRD pattern similar to that of the monomer. Noticeable was that the peak with a d spacing of 26.5 Å shifted to 25.7 Å and of 18.5 Å shifted to 18.0 Å, and a broad peak appeared at 7.2 Å. No significant change was observed in the wide-angle region. Since the stacking distance of the discs was suitable for the to-pochemical polymerization in the hexagonal columnar structure, the polymerization likely proceeded in a vertical direction with respect to the disc plane, which would allow more than one diacetylenic group of the monomer to participate in polymerization. In fact, the IR spectrum of the insoluble polymer prepared by the monomer extraction with chloroform showed that about 85% of the diacetylenic groups were consumed.

Supporting Information Available: Experimental details (5 pages). See any current masthead page for ordering and Internet access instructions.

(10) For **1**: ^{1}H NMR (CDCl$_3$, 200 MHz) δ 9.25 (s, 3H, benzene ring protons), 7.65, 7.25 (dd, 12H, benzene ring protons), 7.50, 6.85 (dd, 12H, benzene ring protons), 3.95 (t, 3H, OCH$_2$), 1.90−0.80 (m, 45H, alkyl chain protons); ^{13}C NMR (CDCl$_3$) 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. Anal. Calcd for C$_{81}$H$_{78}$O$_9$: C, 81.37; H, 6.57. Found: C, 80.90; H, 6.71. For **2**: ^{1}H NMR (DMSO-d_6, 200 MHz) δ 10.90 (s, 3H, NH), 8.85 (s, 3H, benzene ring protons), 7.90, 7.65 (dd, 12H, benzene ring protons), 7.55, 7.00 (dd, 12H, benzene ring protons), 4.05 (t, 6H, OCH$_2$), 1.80−0.80 (m, 45H, alkyl chain protons); ^{13}C NMR (DMSO-d_6) δ 165.0, 160.1, 138.2, 135.6, 134.5, 133.5, 120.5, 120.4, 118.9, 114.8, 113.8, 82.5, 80.9, 75.1, 73.3, 68.4, 32.1, 30.0, 29.7, 29.5, 26.3, 22.9, 14.4; IR (KBr pellet, cm^{-1}) 3436, 2940, 2860, 2216, 2149, 1673. Anal. Calcd for C$_{81}$H$_{81}$N$_3$O$_6$: C, 81.58; H, 6.85; N, 3.52. Found: C, 81.98; H, 6.86; N, 3.69. For **3**: ^{1}H NMR (DMSO-d_6) δ 10.8 (s, 3H, NH), 8.70 (s, 3H, benzene ring protons), 7.90, 7.60 (dd, 12H, benzene ring protons), 2.41 (t, 6H, CCH$_2$), 1.71−0.92 (m, 33H, alkyl chain protons); ^{13}C NMR (DMSO-d_6) δ 164.2, 137.7, 135.6, 133.3, 129.5, 120.1, 118.8, 85.2, 81.5, 74.1, 65.1, 31.3, 28.6, 28.2, 22.5, 19.6, 14.0; IR (KBr pellet, cm^{-1}) 3292, 3103, 2935, 2864, 2243, 2156, 1667. Anal. Calcd for C$_{57}$H$_{57}$N$_3$O$_3$: C, 82.27; H, 6.91; N, 5.05. Found: C, 82.07; H, 6.90; N, 5.25.

(11) Mosaic textures were reported to appear in smetic phases of hexagonal structures. See: Demus, D. In *Liquid Crystals: Application and Uses*; Bahadur, B. Ed.; World Scientific: Singapore, 1990; Vol. 1, p 1.

(12) The reason for the absence of the transition peak at 190 °C in DSC thermogram is not clear at this point. One possible explanation is that molecules were ordered slowly into LC states from the disordered glassy state. In fact, wide-angle XRD of compound **2** before heating did not show any prominent peak indicating a crystal lattice.

(13) The polymerized sample was not soluble in chloroform, which dissolved the monomer easily. It was slightly soluble in *N,N*-dimethylformamide (DMF). In the UV-vis spectra obtained in DMF, the monomer showed λ_{max} and the absorption limit at 359 and 420 nm, respectively, while the polymer showed λ_{max} below 280 nm and some absorption above 550 nm.