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Synthesis of a polymerizable discotic liquid crystalline compound with a 1,3,5-triazine core

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Abstract—Polymerizable 1,3,5-triazine derivatives were prepared, where diphenyldiacetylenic groups were connected to a triazine ring via secondary amino or ether linkages. The compound with secondary amino linkages and pheripheral octyloxy tails exhibited a hexagonal columnar mesophase, showing that intermolecular hydrogen bonding played a key role in molecular ordering. It was polymerized in the hexagonal columnar phase by UV irradiation, yielding the polymer with an ordered structure. © 2002 Elsevier Science Ltd. All rights reserved.

Polymerizable liquid crystal (LC) molecules are very useful in the preparation of anisotropic materials. The ordered arrays of mesogenic monomers in the LC state can be fixed by polymerization, which results in stable polymeric materials with a two or three dimensional long-range order.[1–4] We have been interested in polymerizable discotic liquid crystals because their polymerization can yield polymeric columns (Fig. 1).[5–7] Discotic mesophases are generally generated by the compounds having a disk-like core and flexible alkyl tails. There have been reported central cores such as benzene, polyaromatic, and macrocyclic rings. More recently a 1,3,5-triazine ring has been used as a core.[8–10] From the synthetic viewpoint, the mesogenic 1,3,5-triazine compounds have an advantage. Various nucleophilic side groups have been easily incorporated with the triazine ring by their reaction with cyanuric chloride, showing discotic as well as calamitic morphological behaviors depending on their structures.

In this work, we prepared polymerizable 1,3,5-triazine derivatives (**5**–**8**), where diphenyldiacetylenic groups were connected to a triazine ring via secondary amino or ether linkages. Compounds **7** and **8** had peripheral alkyloxy tails, while compounds **5** and **6** did not. We examined the effects of such structural variation on a morphological behavior and polymerization reactivity. Intermolecular hydrogen bondings of secondary amino groups and π–π interactions between aromatic rings were expected to play an important role in molecular ordering. Aliphatic tails would provide the mobility necessary to molecular arrangement into an ordered structure. We used a diacetylenic group as a part of the rigid mesogenic unit, as well as a polymerizable group. It is known that a diacetylene can be polymerized, topochemically by irradiation or thermal annealing, in the solid-state and the liquid-crystalline state.[11–29]

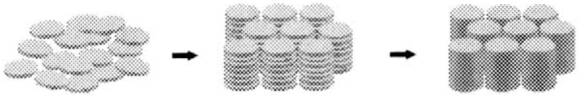

Figure 1. Schematic illustration of molecular ordering and polymerization of discotic mesogenes.

Scheme 1 illustrates the synthetic routes to the 1,3,5-triazine compounds. Compounds **1**–**4** were prepared according to our previous reports.[5–7] 4-Trimethylsilylethynylphenol and 4-trimethylsilylethynylaniline were prepared by coupling reaction of 4-iodophenol and 4-iodoaniline, respectively, with trimethylsilylacetylene in the presence of a palladium catalyst. The trimethylsilyl group was removed under basic conditions to give 4-ethynylphenol or 4-ethynylaniline. 1-Iodo-4-octyloxybenzene was prepared by the reaction of sodium 4-iodophenoxide with octyl bromide, and then acetylation reaction with trimethylsilylacetylene in the presence of a palladium catalyst was carried out, resulting in 4-octyloxyphenylacetylene. 4-Ethynylaniline and 4-ethynylphenol were coupled with 1-octyloxy-4-ethynylbenzene or phenylacetylene in the presence of copper(II) acetate to give compounds **1**–**4**.[30] 1,3,5-Tria-

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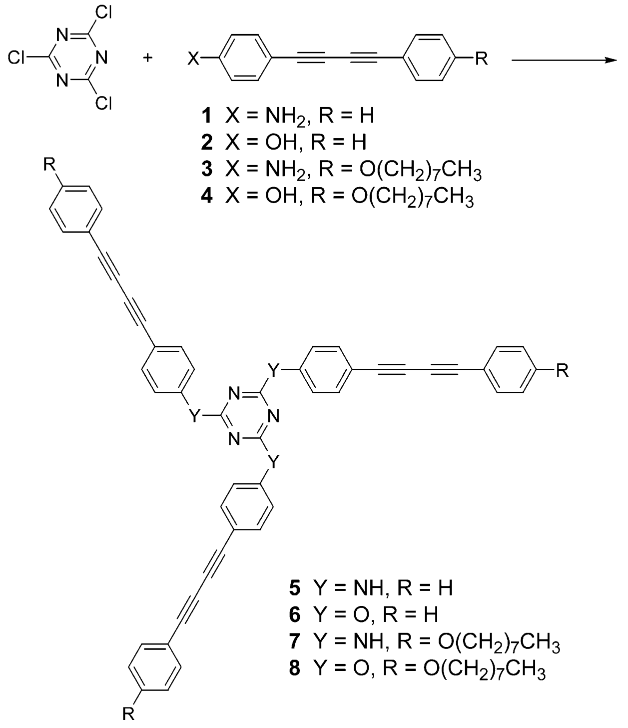

Scheme 1.

zine derivatives **5**–**8** were prepared by the reaction of compound **1**–**4** with cyanuric chloride under basic conditions, respectively.[31]

Thermal properties of compounds **5**–**8** were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (Table 1). Compounds **5** and **6** without flexible long alkyl chains were thermally polymerized in the solid state. DSC analysis showed very strong and sharp exothermic peaks at 250°C for compound **5** and 280°C for compound **6**, corresponding to thermal polymerization. No melt transitions were observed before polymerization. In the IR spectrum of compound **5**, two triple bond stretching peaks of diacetylenic groups at 2213 and 2146 cm^{-1} disappeared at the same time and the peak at 2220 cm^{-1} corresponding to new carbon–carbon triple bonds showed up after polymerization. The peak for the double bonds resulted from 1,4-polymerization, appeared at 1630 cm^{-1}.

Table 1. Phase transition temperatures of 1,3,5-triazine compounds

Compound	Phase transition temperature (°C)[a]	
	Heating	Cooling
5	K 250 P[b]	–
6	K 280 P[b]	–
7	K1 189 K2 197 LC 250 P	210[c] LC 187 K
8	K 228 I[d]	–

[a] K, K1, K2: crystal; LC: liquid crystal; I: isotropic liquid; P: polymer.

[b] Solid state polymerization occurred.

[c] The compound was cooled from 210°C.

[d] Isotropization was followed immediately by thermal polymerization.

Compound **7** showed a liquid crystalline phase. On the first heating, two endothermic peaks at 189 and 197°C appeared, corresponding to crystal to crystal and crystal to liquid crystal transition (45.7 KJ/mol), respectively. A broad and strong exothermic peak around 280°C was associated with thermal polymerization. In the polarizing optical microscopy study, it was observed that a birefringent phase began to form on heating above 197°C and thermal polymerization proceeded slowly without clearing transition. Above 250°C, the phase was solidified by rapid thermal polymerization. When the compound was cooled from 210°C at a rate of 5°C/min, it exhibited a mesophase until 187°C. The texture shown in Fig. 2 was observed by shearing the compound at 199°C. The texture was maintained when the compound was quenched from the LC state to room temperature. X-Ray analysis showed that compound **7** had a hexagonal columnar structure in the LC state.[32] The compound was polymerized by UV irradiation in the LC state, resulting in the polymer with an ordered structure.[33]

On the contrary, compound **8** with ether linkages, showed no mesophases. Only crystal to liquid transition occurred at 228°C, followed immediately by thermal polymerization. The only structural difference between compounds **7** and **8** is the nature of linking bonds between a 1,3,5-triazine core and a diacetylenic side group. Secondary amino groups of compound **7** are capable of hydrogen bonding and likely facilitated the aggregation of the molecules.

In summary, polymerizable 1,3,5-triazine derivatives (**5**–**8**) were prepared, where diphenyldiacetylenic groups were connected to a triazine ring via secondary amino or ether linkages. Only the compound with secondary amino linkages and peripheral octyloxy tails exhibited a hexagonal columnar mesophase, showing that intermolecular hydrogen bonding played a key role in molecular ordering. Compound **7** with a hexagonal columnar phase was polymerized in the LC state by UV irradiation to give the polymer with an ordered structure.

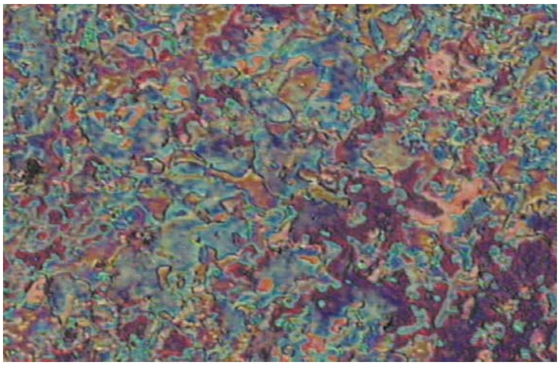

Figure 2. Optical polarized micrograph of compound **7** at 199°C obtained on heating (200 magnification).

Acknowledgements

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31. Compound **5**: To a solution of compound **1** (0.34 g, 1.56 mmol) in butanone/tetrahydrofuran (50 mL, 1:1 v/v) were added cyanuric chloride (0.072 g, 0.39 mmol) and potassium carbonate (0.21 g, 1.52 mmol) under nitrogen. The reaction mixture was refluxed for 20 h. After removal of precipitates by filtration, the filtrates were concentrated to dryness by evaporation under reduced pressure. The product was, cm^{-1}): 3392, 2213, 2146, 1562, 1515, 1478, 1408, 1177, 688, 528. ^{13}C NMR (CDCl$_3$, 200 MHz): δ 164.1, 139.2, 133.3, 132.5, 129.1, 128.4, 121.9, 120.1, 116.4, 81.6, 77.9, 74.1, 73.7. **6**: This compound was prepared according to the literature method.[7] ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.56–7.10 (m, 27H, aromatic ring protons). IR (KBr, cm^{-1}): 3454, 3072, 2934, 2855, 2230, 2151, 1570, 1506, 1366, 1216. ^{13}C NMR (CDCl$_3$, 200 MHz): δ 173.0, 151.8, 133.8, 132.5, 132.4, 129.2, 128.4, 121.7, 120.1, 81.9, 80.4, 74.5, 73.8. **7**: This compound was prepared by similar procedure to that described for compound **5** using compound **3** instead of compound **1**. The product was isolated by column chromatography on silica gel (tetrahydrofuran/hexane = 3/5) and further purified by recrystallization from tetrahydrofuran and hexane; yield 0.38 g (78%). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.57, 7.50 (dd, 12H, aromatic ring protons), 7.44, 6.85 (dd, 12H, aromatic ring protons), 7.04 (s, 3H, NH), 3.96 (t, 6H, OCH$_2$,), 1.9–0.8 (m, 45H, alkyl protons). IR (KBr, cm^{-1}): 3402, 2926, 2861, 2213, 2143, 1477, 1250, 831, 600. ^{13}C NMR (CDCl$_3$, 200 MHz) δ 164.1, 159.9, 150.4, 134.1, 133.2, 120.1, 114.7, 113.5, 81.9, 81.0, 74.0, 72.8, 68.2, 31.8, 29.3, 29.2, 29.1, 26.0, 22.7, 14.1. Anal. calcd for $C_{75}H_{78}N_6O_3$: C, 81.05; H, 7.07; N, 7.56. Found: C, 80.32; H, 7.09; N 7.40. **8**: To a solution of compound **4** (0.2 g, 0.58 mmol) in pyridine/ethyl acetate (150 mL, 1:1 v/v) were added cyanuric chloride (0.036 g, 0.19 mmol) and triethylamine (0.16 mL, 1.15 mmol). The reaction mixture was refluxed for 10 h. After removal of precipitates by filtration, the filtrates were concentrated to dryness by evaporation under reduced pressure. The product was purified by recrystallization from chloroform and hexane; yield 0.085 g (33.7%). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.52, 7.09 (dd, 12H, aromatic ring protons), 7.43, 6.81 (dd, 12H, aromatic ring protons), 3.95 (t, 6H, OCH$_2$), 1.85–0.7 (m, 51H, alkyl protons). IR (KBr, cm^{-1}): 2933, 2856, 2217, 2147, 1607, 1572, 1509. ^{13}C NMR (CDCl$_3$, 200 MHz): δ 173.4, 160.0, 152.0, 134.1, 133.9, 122.0, 120.5, 115.0, 113.5, 82.7, 80.0, 73.0, 68.0, 32.0, 29.0, 26.0, 22.5, 14.0. Anal. calcd for $C_{75}H_{75}N_3O_2$: C, 80.83; H, 6.78; N, 3.77. Found: C, 80.50; H, 7.09; N, 3.50.
32. Compound **7** was quenched to room temperature from its LC state at 199°C and subjected to X-ray analysis. In the small angle region, two peaks corresponding to *d* spacings of 44.8 and 25.9 Å appeared. They are in the ratio of $1:1/\sqrt{3}$, which is in good agreement with a hexagonal lattice.

33. Polymerization of compound **7** was performed by irradiation with UV light (a high-pressure mercury arc lamp, 100 W) for 10 h in the LC state (205°C). In compound **7**, each 1,3,5-triazine ring had three diacetylenic groups and about 41% of them were found to participate in the polymerization, when measured by IR spectroscopy. In the X-ray analysis, the polymer showed two peaks corresponding to *d* spacings of 39.8 and 27.5 Å, indicating that polymerization accompanied slight change of the monomeric alignments. One of likely arrangements of the polymer chains is a rectangular columnar phase when two reflections in X-ray diffractogram could be indexed as (100) and (010).