

Fluorination Effect of the Peripheral Chains on the Mesomorphic Properties in Discotic Liquid Crystals of Hexasubstituted Triphenylene

Naohiro Terasawa, Hirosato Monobe, Kenji Kiyohara, and Yo Shimizu*
*Mesophase Technology Research Group, Special Division for Human Life Technology,
 National Institute of Advanced Industrial Science and Technology, AIST-KANSAI,
 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577*

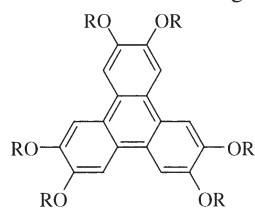
(Received October 29, 2002; CL-020923)

Two homologues of novel triphenylene mesogens possessing $-\text{O}(\text{CH}_2)_3\text{CF}_3$ (**F1**) and $-\text{O}(\text{CH}_2)_3(\text{CF}_2)_5\text{CF}_3$ (**F6**) were synthesized and investigated on the mesomorphic behavior to reveal that these show a hexagonal columnar (Col_h) mesophase. The mesomorphic behavior is obviously different from those of the corresponding hydrocarbon homologues, $-\text{O}(\text{CH}_2)_3\text{CH}_3$ (**C1**) and $-\text{O}(\text{CH}_2)_8\text{CH}_3$ (**C6**). Interestingly, it was found that **F1** shows a disordered Col_h phase, though **C1** forms only a plastic hexagonal columnar (Col_{hp}) mesophase.

Fluorinated materials have attracted much attention because of their unique properties. The substitution of hydrogen atom by fluorine one increases chemical and oxidative stability, weatherability and melting point, while it decreases flammability, adhesion, dielectric constant and refractive index.¹ It is thought that these characteristics of fluorinated compounds are derived from the property of fluorine atom and unique physical property of C–F bond. Especially, it is well known that the fluorinated alkanes are more rigid than the corresponding hydrogenated alkanes, and that fluorophilic interaction works among fluoroalkyl chains, whilst among fluoroalkyl and alkyl chains fluorophobic interaction acts.² These intermolecular interactions relating to fluoroalkyl chains are interesting in terms of not only mesophase formation but also its functionality.

As for a calamitic liquid crystal, it was shown that the fluorophilic and the fluorophobic interactions around the terminal fluoroalkylated chains enhance the mesophase thermal stability and facilitate the formation of smectic phase.³ On the other hand, for discotic liquid crystals, only one report has been so far, in which any clear effects of the fluoroalkyl chain on the discotic mesomorphism were not shown.⁴

In this work, two homologues of novel triphenylene mesogens with fluorinated parts in the chains (**F1** and **F6**) were synthesized and a new aspect of fluorination of the peripheral chains in a discotic mesogen was found.



F1 : $\text{R} = -(\text{CH}_2)_3\text{CF}_3$
F6 : $\text{R} = -(\text{CH}_2)_3(\text{CF}_2)_5\text{CF}_3$

C1 : $\text{R} = -(\text{CH}_2)_3\text{CH}_3$
C6 : $\text{R} = -(\text{CH}_2)_3(\text{CH}_2)_5\text{CH}_3$

Two homologues, 2,3,6,7,10,11-hexakis-(1H,1H,2H,2H,3H,3H-perfluorobutyl)triphenylene (**F1**) and 2,3,6,7,10,11-hexakis-(1H,1H,2H,2H,3H,3H-perfluorononyl)triphenylene (**F6**) were synthesized according to the literatures with some modifications.⁵ The identifications of compounds were

carried out by ^1H NMR, ^{19}F NMR, IR and TOF-MS spectra with elemental analyses.⁶

Figure 1 shows DSC curves of **F1** and **F6** on heating run and two endothermic peaks were observed, which correspond to the melting and clearing points. The textures of these mesophases were typical for columnar mesophases. The phase transition temperatures and enthalpies were summarized in Table 1 with the parameters for the corresponding hydrocarbon homologues (**C1** and **C6**). X-Ray diffraction measurements revealed that both of **F1** and **F6** exhibit hexagonal columnar (Col_h) mesophase with disordered columns (Figure 2). The observed reflections for the mesophase showed a spacing ratio of $1:1/\sqrt{3}:1/2$ which is an evidence of hexagonal arrangement of columns. A broad halo is also observed in the wide angle region (ca. 4.1 \AA) derived from the molten peripheral chains.⁷ Furthermore, one additional broad halo is seen at ca. 5.2 \AA for **F6** and this could be related to the averaged value of the interchain distance for the perfluoroalkylated parts, considering the estimated value ($5\text{--}6\text{ \AA}$) for the

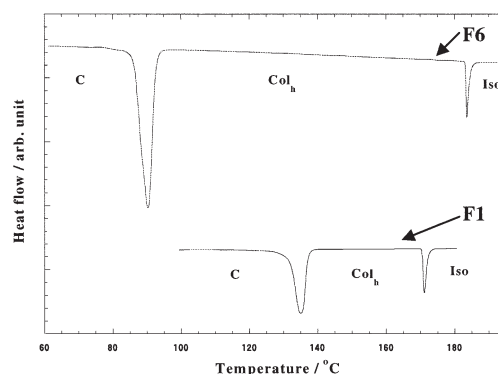


Figure 1. DSC traces of **F1** and **F6** (heating rate at 5°C min^{-1}). C: crystal, Col_h : hexagonal columnar mesophase, Iso: isotropic liquid.

Table 1. Phase transition parameters of **F1**, **F6** and the corresponding alkyloxyderivatives (**C1** and **C6**)

Compound	Transition	Temperature/ $^\circ\text{C}$	$\Delta H/\text{kJ mol}^{-1}$
F1	C \rightarrow Col_h	132	22.1
	$\text{Col}_h \rightarrow$ Iso	171	4.7
C1 ^a	C \rightarrow Col_{hp}	87	24.7
	$\text{Col}_{hp} \rightarrow$ Iso	144	20.5
F6	C \rightarrow Col_h	89	55.2
	$\text{Col}_h \rightarrow$ Iso	183	5.2
C6	C \rightarrow Col_h	56	72.9
	$\text{Col}_h \rightarrow$ Iso	77	2.7

^a Col_{hp} : plastic hexagonal columnar phase.

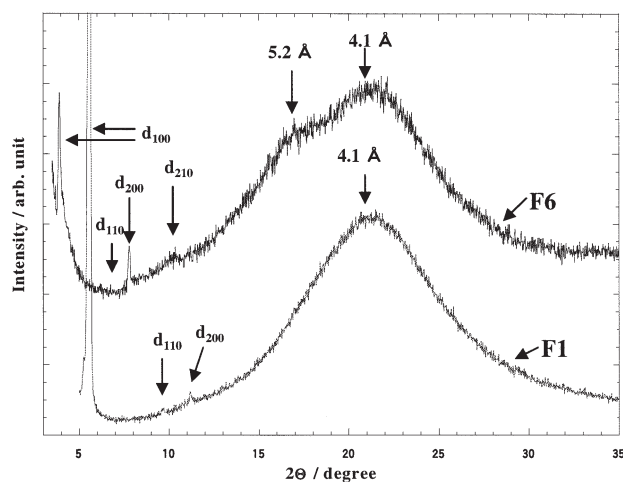


Figure 2. X-Ray diffraction patterns of Col_h mesophase for **F1** (125 °C) and **F6** (80 °C) on cooling.

diameter of perfluoroalkyl chain rod.⁸ The lattice constants a_{hex} of the Col_h phases show the similar values to those of **C1** and **C6** (19.2 Å and 25.2 Å, respectively). The X-ray diffraction parameters are summarized in Table 2.

Table 2. Observed parameters of X-ray diffractions for **F1** and **F6**

Compound	$a_{\text{hex}}/\text{\AA}$	hkl	$d_{hkl}/\text{\AA}$
F1 (125 °C)	18.2	100	15.8
		110	9.1
		200	7.9
			4.1 (broad)
F6 (80 °C)	26.1	100	22.6
		110	13.0
		200	11.4
		210	8.5
			5.2 (broad)
			4.1 (broad)

An enhancement of the thermal stability of Col_h mesophase was found for **F1** and **F6** in comparison with those of **C1** and **C6**. It was also observed that the fluoromethylene chain enlarges the transition enthalpy of the clearing point of Col_h phase. Furthermore, it is very interesting to see that, for both **F1** and **F6**, no reflection peaks derived from the intracolumnar order was detected in XRD patterns of Col_h mesophase. This means that **F1** forms a disordered Col_h mesophase, while **C1** shows so-called plastic hexagonal columnar (Col_{hp}) one.⁹ The disordered columnar phase even for the shorter chains is the first observation as the effect of fluorinated alkane on columnar mesomorphism of discotics. The strong interaction among the terminal trifluoro-

methyl groups might form a tube-like rigid structure in a column and the larger size of the fluorinated parts than the hydrocarbon alkanes might provide an enough space for the mobility of triphenylene cores within the columns. These results are interesting in terms of not only chemistry of liquid crystals, but also supramolecular chemistry.

References and Notes

- 1 "Organofluorine Chemistry. Principles and Commercial Applications," ed. by R. E. Banks, B. E. Smart, and J. C. Tatlow, Plenum, New York (1994).
- 2 a) A. E. Feiring, *J. Macromol. Sci., Pure Appl. Chem.*, **A31**, 1657 (1994). b) D. F. Eaton and B. E. Smart, *J. Am. Chem. Soc.*, **112**, 2821 (1990). c) C. W. Burn and E. R. Howells, *Nature*, **174**, 549 (1954).
- 3 a) B.-Q. Chen, Y.-G. Yang, and J.-X. Wen, *Liq. Cryst.*, **24**, 539 (1998). b) P. Kromm, M. Cotrait, J. C. Rouillon, P. Barois, and H. T. Nguyen, *Liq. Cryst.*, **21**, 121 (1996). c) T. Doi, Y. Sakurai, A. Tamatani, S. Takenaka, S. Kusabayashi, Y. Nishihata, and H. Terauchi, *J. Mater. Chem.*, **1**, 169 (1991). d) H. Liu and H. Nohira, *Liq. Cryst.*, **22**, 217 (1997). e) H. T. Nguyen, G. Sigaud, M. F. Achard, F. Hardouin, R. J. Twieg, and K. Betterton, *Liq. Cryst.*, **10**, 389 (1991). f) S. Takenaka, *J. Chem. Soc., Chem. Commun.*, **1992**, 1748.
- 4 U. Dahn, C. Erdelen, H. Ringsdorf, R. Festag, J. H. Wendorff, P. A. Heiney, and N. C. Maliszewskyj, *Liq. Cryst.*, **19**, 759 (1995).
- 5 a) H. Liu and H. Nohira, *Liq. Cryst.*, **20**, 581 (1996). b) N. Boden, R. C. Borner, R. J. Bushby, A. N. Cammidge, and M. V. Jesudason, *Liq. Cryst.*, **15**, 851 (1993).
- 6 a) **F1**: ¹H NMR (CDCl₃, TMS, 500.0 MHz) δ 2.17–2.24 (m, 12H), 2.38–2.50 (m, 12H), 4.29 (t, $J = 6.0$ Hz, 12H), 7.81 (s, 6H); ¹⁹F NMR (CDCl₃, CFCl₃, 376.1 MHz) δ –66.8 (t, $J = 10.7$ Hz, 18F); MS $m/z = 984.7$ (calcd 984.3 for C₄₂H₄₂F₁₈O₆); FTIR (KBr, cm^{–1}) 1520, 1439, 1386, 1341, 1255, 1231, 1175, 1154, 1133, 1062, 1030; Anal. Calcd for C₄₂H₄₂F₁₈O₆: C, 51.23; H, 4.30; F, 34.73. Found: C, 51.16; H, 4.28; F, 34.53. b) **F6**: ¹H NMR (CDCl₃, TMS, 500.0 MHz) δ 2.20–2.28 (m, 12H), 2.36–2.50 (m, 12H), 4.30 (t, $J = 5.8$ Hz, 12H), 7.81 (s, 6H); ¹⁹F NMR (CDCl₃, CFCl₃, 376.1 MHz) δ –81.4 (t, $J = 10.0$ Hz, 18F), –114.8–115.2 (m, 12F), –122.5 (s, 12F), –123.5 (s, 12F), –124.0 (s, 12F), –126.6–126.9 (m, 12F); MS $m/z = 2484.4$ (calcd 2484.2 for C₇₂H₄₂F₇₈O₆); FTIR (KBr, cm^{–1}) 1520, 1442, 1266, 1236, 1191, 1146, 1034, 698; Anal. Calcd for C₇₂H₄₂F₇₈O₆: C, 34.80; H, 1.70; F, 59.63. Found: C, 34.62; H, 1.53; F, 59.39.
- 7 A. M. Levelut, *J. Phys., Lett.*, **40**, 81 (1979).
- 8 G. Johansson, V. Percec, G. Ungar, and K. Smith, *Chem. Mater.*, **9**, 164 (1997).
- 9 J. Simmerer, B. Glösen, W. Paulus, A. Kettner, P. Schuhmacher, D. Adam, K. H. Etzbach, K. Siemensmeyer, J. H. Wendorff, H. Ringsdorf, and D. Haarer, *Adv. Mater.*, **8**, 815 (1996).