Synthesis and Biaxial Nematic Properties of Novel Liquid Crystalline X-shaped Mesogens Containing Perfluoroalkyl Alkanes as a Side Chain

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Abstract

Novel X-shaped molecules containing perfluoroalkyl alkanes as a side chain have been synthesized and characterized. The properties of mesophases were investigated by a combination of differential scanning calorimetry (DSC), polarizing optical microscopy (POM), X-ray diffractometry (XRD) and electro-optical measurements.

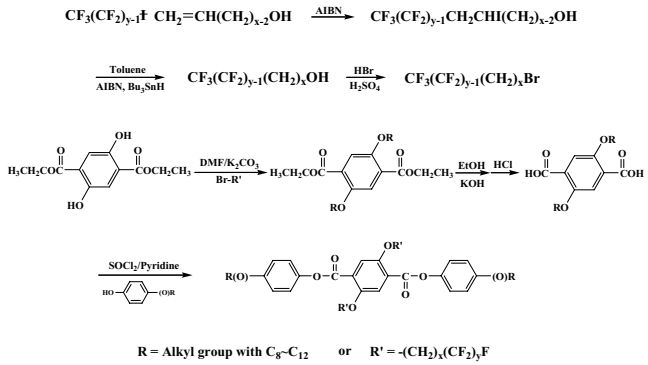
1. Introduction

Since Freiser's prediction for the existence of the biaxial nematic phase, this topic has attracted much attention due to its interesting electro-optical properties and potential device applications with the expectation of much faster response time than the uniaxial nematics. During the last decades, the most attempts to synthesize thermotropic mesogenic molecules to exhibit the biaxial nematic phase had not been successful. Also, there was so far only ambiguous and qualitative optical evidence for the existence of the thermotropic biaxial nematic phase. Recently, it was reported that bent-core molecules with oxadiazole core unambiguously exhibited the biaxial nematic phase. In the biaxial nematic phase, molecules are oriented along mutually perpendicular major and minor directors. The biaxial arrangement can be investigated by the following experimental techniques: (1) texture observation, (2) conoscopic observation, and (3) ^{2}H-NMR measurement. The structure with perfluoroalkyl alkanes has been accepted as another non-conventional liquid crystalline mesogens. The chains of such molecules consist of fluorocarbon and hydrocarbon segments whose miscibility is generally poor, and thus amphiphilic molecules with perfluoroalkyl alkanes could form thermotropic liquid crystal phase.

In this study, we have synthesized and characterized X-shaped molecules with perfluoroalkyl alkanes as a side chain, and their electro-optical properties and the existence of the biaxial nematic phase was investigated.

2. Experimental

Synthetic route to X-shaped molecules containing perfluoroalkyl alkanes as a side chain is shown in Scheme 1.



Scheme 1. Synthetic route to X-shaped compounds.

Synthesis. The fluorocarbon-hydrocarbon dibllock molecule was prepared by free-radical addition of perfluorooctyl iodide to the corresponding alkene, followed by reduction of the iodide. The diethyl 2,5-dialkoxyterephthalates was saponified with aqueous potassium hydroxide to yield the 2,5-dialkoxyterephthalic acids. Conversion into the acid chlorides was achieved by refluxing with excess of thionyl chloride. The final product was prepared by substitution reaction of the 2,5-dialkoxyterephthalic dichloride with alkoxyphenol in methylene chloride, which was purified by chromatography on silica gel by eluting with 10:1 $CHCl_3$/EtoAc. Compound with R = OC_8H_{17}: FT-IR (KBr pellet, cm^{-1}): 3062 (aromatic =C-H, st), 2935, 2861 (aliphatic C-H, st), 1747 (C=O, st), 1504, 1419 (aromatic C=C, st), 1218 (aliphatic CF_3, st), 1150 (aliphatic CF_2, st). ^{1}H NMR ($CDCl_3$, δ in ppm): 7.52 (2H, s, Ar-H), 7.12-7.08 (4H, d, Ar-H), 6.92-6.88 (4H, d, Ar-H), 3.93 (8H, t, OCH_2), 1.83-1.47 (12H, m, OCH_2CH_2), 1.26-1.13 (48H, m, $(CH_2)_7CF_2$, $(CH_2)_5CH_3$), 1.03-0.83 (6H, m, CH_2CH_3).

Characterization. IR and NMR spectra were obtained by Jasco 300E FT/IR and Bruker DPX 200 MHz NMR spectrometers, respectively. The phase transition temperatures were determined by DSC (NETZSCH DSC 200 F3) and polarizing optical microscope (Zeiss, Jenapol). DSC measurements were performed in a N_2 atmosphere, and the heating and cooling rates were 10°C/min. Optical textures were observed by the polarizing microscope equipped with a camera and a thermo-controller (Mettler FP82HT).

3. Results and discussion

The molecular structures of obtained compounds were identified by FT/IR and ^{1}H NMR spectrometry, and the resultant data were in accordance with the expected molecular formula. The purity of obtained compounds was confirmed by thin layer chromatography (TLC) and elementary analyses. The phase transition temperatures obtained by DSC and POM are summarized in Table 1. The melting temperature (T_m) of the compounds are in the range of 53-96℃ depending on the structure of therminal flexible groups (R). Using an optical microscope, on heating and cooling the sample we could identify their mesophases. The X-shaped compound with R = OC_8H_{17} shows a monotropic mesophase, but the other X-shaped compound with R = $C_{12}H_{25}$ could not form a liquid crystalline phase. According to electro-optical investigation, the compound with R = OC_8H_{17} could not show switching property indicating smectic A phase.

TABLE 1. Yield, transition temperature (℃), and enthalpy changes (in parenthesis, J/g) for X-shaped compounds.

R	Yield (wt%)	Heating[b]	Cooling [b]		
		Cr[a]-I	I-N	N-Cr	I-Cr
OC_8H_{17}	56	96 (47.1)	94 (4.2)	71 (36.0)	-
$C_{12}H_{25}$	63	53 (34.8)	-	-	4.2 (6.63)

[a]Cr = crystalline phase; N = nematic phase; I = isotropic phase. [b]DSC heating and cooling rates: 10℃/min

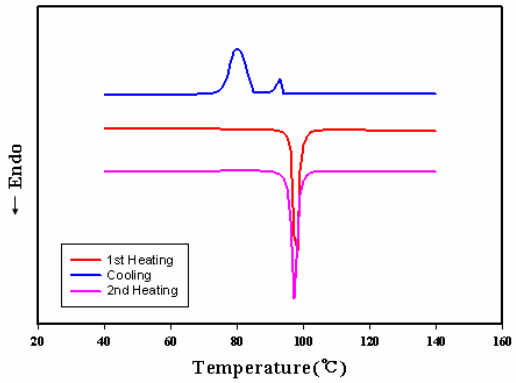


Fig. 1. DSC thermograms of compound with R=OC_8H_{17} (heating and cooling rates: 10℃/min).

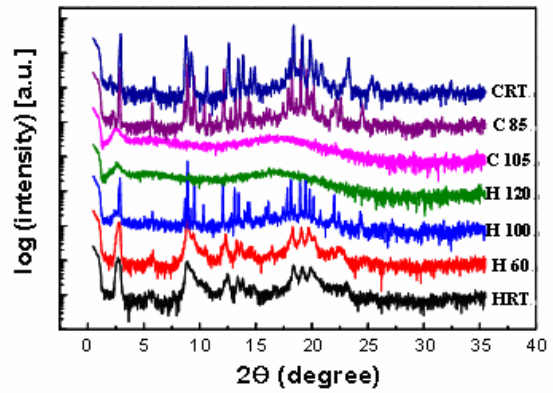


Fig. 2. X-ray diffraction patterns of compound with R = OC_8H_{17} at a given temperature (RT: room temperature; H: heating; C: cooling).

4. Summary

Novel X-shaped molecules containing perfluoroalkyl alkanes as a side chain have been synthesized and characterized. According to X-ray measurements, the compound with R = OC_8H_{17} can form nematic phase monotropically. Unexpectedly, the other compound with R = $C_{12}H_{25}$ could not form a liquid crystalline phase. According to electro-optical investigation, the compound with R = OC_8H_{17} could not show switching property indicating smectic A phase.

5. Acknowledgements

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6. References

1. M. J. Freiser, *Phys. Rev. Lett.* **24**, 1041 (1970).
2. G. R. Luckhurst, *Thin Solid Films* **393**, 40 (2001).
3. L. A. Madsen, T. J. Dingemans, M. Nakata, and E. T. Samulski, *Phys. Rev. Lett.* **92**, 145505 (2004).
4. B. R. Acharya, A. Primak, and S. Kumar, *Phys. Rev. Lett.* 2004, 92, 145506.
5. J. Hopken and M. Moller, *Macromolecules* **25**, 2482-2489 (1992).