Control of Phase-transition Behavior and Polymerization Capability by Methyl Addition to Dialkyl Fumarates Bearing Cyanobiphenyl Mesogens

Nozomu Fujii,[1] Tsuyoshi Michinobu,[1,2] and Kiyotaka Shigehara*[1,2]
[1]*Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588*
[2]*Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588*

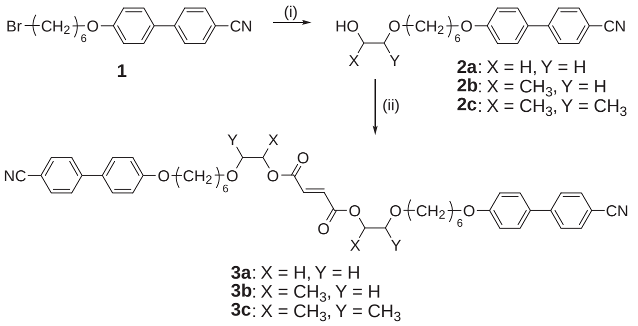
(Received June 11, 2007; CL-070631; E-mail: jun@cc.tuat.ac.jp)

Addition of methyl groups to dialkyl fumarates bearing two cyanobiphenyl mesogens dramatically changed the phase-transition behavior and polymerization capability. No mesophase appeared and radical polymerization did not proceed in the absence of the branched methyl groups, whereas well-defined liquid-crystal phases were observed in the ambient temperature range and high molecular weight polymers were obtained in the presence of the branched methyl groups. An increase in the number of the attached methyl groups decreases the liquid crystalline temperature width as well as the molecular weight of the resulting polymers.

Increasing attention has been paid to dimeric liquid crystalline compounds, in which two mesogenic groups are typically linked through a flexible spacer, for understanding and tuning of phase behavior.[1] Symmetry breaking by means of variation of flexible alkyl chain spacer lengths or selection of mesogenic groups is known to affect the phase-transition temperatures and the resulting mesophases. For example, the odd–even effect of alkyl chain carbon numbers on the thermal and optical properties was clearly observed.[2] Nonsymmetric dimers bearing different mesogenic groups tended to display higher-order liquid-crystalline phases due to the facile formation of segmented layers.[3] Recently, a new approach to control of phase behaviors of liquid-crystalline compounds, that is, methyl addition to alkyl moieties, was proposed and verified for an antiferroelectric compound by Thisayukta and Samulski.[4] After methyl additions, an anticlinic smectic C_A phase newly appeared below the smectic A phase.

Following our work on potent functionalities of poly(dialkyl fumarate)s revealed by the electronic properties of the Langmuir–Blodgett ultrathin films,[5] we are recently trying to give liquid-crystalline properties to poly(dialkyl fumarate)s. One of the most significant features of poly(dialkyl fumarate)s, in addition to the high thermal stability originating from the rigid backbone, is the doubled side-chain density with respect to common vinyl polymers. Since high molecular weight poly(dialkyl fumarate)s are usually prepared by radical polymerization of branched dialkyl fumarates in bulk,[6] the fumarate monomers bearing two mesogenic groups become liquid-crystalline dimers, and the branched moiety can serve as a methyl addition part controlling the phase behavior. Here, we report for the first time the remarkable change in both the phase behavior and the polymerization capability by simple addition of methyl groups to the dialkyl fumarates.

Cyanobiphenyl group was employed as a mesogen for a comparison to other reported dimeric liquid-crystalline compounds, especially of fumarates.[2,7,8] Starting from 4′-(6-bromohexyloxy)-4-cyanobiphenyl (**1**), prepared from 4-cyano-4′-hydroxybiphenyl and dibromohexane, ether synthesis with an excess amount of the diols (or the monoprotected propanediol followed by deprotection) furnished **2a**–**2c** in 44–67% yield (Scheme 1). Here, addition of ammonium salts was found to significantly improve the reaction yield owing to the inhibition of Na^+ ion chelation with the alkoxide moieties.[9] The subsequent reaction with maleic anhydride in the presence of *p*-toluenesulfonic acid (*p*-TsOH) followed by cis–trans isomerization, catalyzed by morpholine,[10] afforded the dialkyl fumarates bearing two cyanobiphenyl mesogens **3a**–**3c** in a satisfactory yield. The compounds were unambiguously characterized by ^{1}H NMR and FT-IR measurements (see Supporting Information).[12]



Scheme 1. Synthesis of dialkyl fumarates **3a**–**3c**. (i) NaH, ethylene glycol or 2-(tetrahydro-2-pyranyloxy)-1-propanediol or 2,3-butanediol, benzyltriethylammonium chloride, THF, 24 h; then pyridinium *p*-toluenesulfonate (for **2b**). **2a**: 44%, **2b**: 53%, **2c**: 67%. (ii) maleic anhydride, *p*-TsOH, C_6H_6, 80 °C, 12 h; then, morpholine, C_6H_6, 80 °C, 4 h. **3a**: 69%, **3b**: 71%, **3c**: 70%.

The fumarates **3a**–**3c** were thermally stable. Decomposition temperatures of **3a**–**3c** determined by thermogravimetric analysis exceed 270 °C. The phase-transition temperatures and the phases determined by the differential scanning calorimetry (DSC) measurements and polarized optical microscopy (POM) images, respectively, are summarized in Table 1. The fumarate **3a** without branched methyl groups did not show any mesophas-

Table 1. Phase behaviors of dialkyl fumarates **3a**–**3c**

	Phase-transition behavior[a]						
3a	Cr			63.1 104.8			Iso
3b	G	−4.7 −2.5	S_A	22.4 25.1	N	34.4 35.9	Iso
3c	G	−2.5 −0.7	S_A	22.3 24.4	N	24.2 26.4	Iso

[a]Transition temperatures (°C) and phases determined by DSC (at a rate of 10 °C min^{-1} upon cooling: top, upon heating: bottom) and POM. Iso: isotropic liquid; S_A: smectic A; G: glass; Cr: crystal.

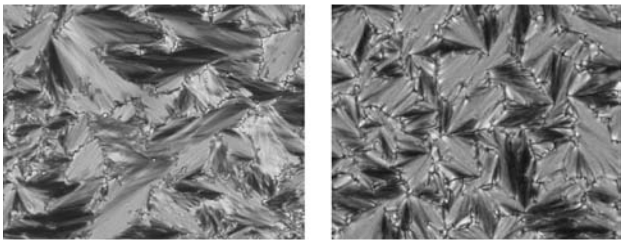


Figure 1. Polarized optical micrographs of **3b** (left) and **3c** (right) at 20 °C during the cooling cycle (×40).

es, whereas the branched dialkyl fumarates **3b** and **3c** displayed well-defined transitions to mesophases in the ambient temperature range upon both heating and cooling cycles, indicating the enatiotropic liquid crystals. Both **3b** and **3c** possess two mesophases, of which lower temperature phases were determined to be a smectic A phase by the observed focal conic fan textures of POM images as well as the shearing experiments (Figure 1). Accordingly, the higher temperature mesophases were a nematic phase. Interestingly, the introduction of an excess amount of methyl groups, on the contrary, destabilizes the liquid-crystalline phases. The temperature range of the nematic phase decreased by ca. 10 °C from **3b** to **3c**. These results were also substantiated by the temperature dependent X-ray diffraction (XRD) measurements. For example, the mesophases of **3b** and **3c** at 20 °C exhibit a very broad peak at 2 theta (θ) $\approx 20°$ ($d = 4.4$ Å), characteristic of a smectic A phase (Figure 2). The peak positions are supposed to represent the mesogen intervals in the smectic A phases.[11] However, the crystalline phase of **3a** shows many diffraction patterns associated with the random orientation of the solid molecules.

Furthermore, a dramatic change in the polymerization capability after methyl addition to the dialkyl fumarate was observed. The fumarates **3a**–**3c** were heated in bulk at 80 °C in the presence of 10 mol % benzoyl peroxide (BPO) for 10 days (Scheme 2). Polymerization of **3a** did not proceed at all, whereas **3b** and **3c** furnished the corresponding poly(dialkyl fumarate)s with a molecular weight (M_n) of 9000 and 7400, respectively, and an exceptionally narrow polydispersity (M_w/M_n) of 1.1, measured by GPC ($CHCl_3$ eluent, calibrated by polystyrene standards). These results are consistent with the previous report by Otsu that only branched dialkyl fumarates can afford high molecular weight polymers.[6] A decrease in the molecular weight of the polymers from **3b** to **3c** might be derived from the increased steric hindrance in the propagation process.

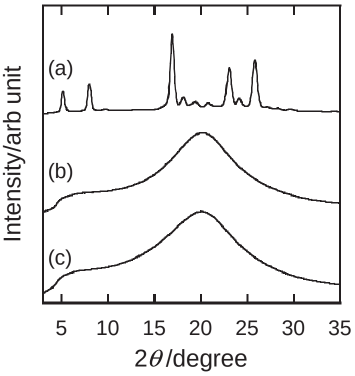
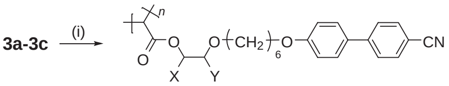


Figure 2. X-ray diffraction patterns of (a) **3a** in the crystalline phase at 40 °C, (b) **3b** in the smectic A phase at 20 °C, and (c) **3c** in the smectic A phase at 20 °C.



poly3a-3c

Scheme 2. Radical polymerization of **3a**–**3c**. (i) BPO, 80 °C, 10 days.

In conclusion, we have shown the effect of methyl groups in the dialkyl fumarates bearing cyanobiphenyl mesogens on the phase behavior and the polymerization capability. Taking together into account the mesophase temperature widths as well as the molecular weights of the polymers, the efficiency of both liquid crystallinity and polymerization capability increases in the series **3a** < **3c** < **3b**. As for the phase tuning, this novel approach of methyl addition is, in sharp contrast to the conventional methods, capable of inducing a dramatic change in the properties, as represented by the great differences between **3a** and **3b**. Further elucidation of chirality effects at the branched position will be worthwhile for future work.

We thank Prof. K. Noguchi (Tokyo University of Agriculture and Technology) for the assistance in the XRD measurements and Drs. K. Ariga and T. Nakanishi (National Institute for Materials Science) for the use of recycling HPLC.

References and Notes

1 a) *Handbook of Liquid Crystals*, ed. by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill, Wiley-VCH, Weinheim, **1998**, Vol. 2A and 2B. b) C. Tschierske, *J. Mater. Chem.* **2001**, *11*, 2647. c) I. M. Saez, J. W. Goodby, *J. Mater. Chem.* **2005**, *15*, 26. d) S.-W. Choi, T. Izumi, Y. Hoshino, Y. Takahashi, K. Ishikawa, J. Watanabe, H. Takezoe, *Angew. Chem., Int. Ed.* **2006**, *45*, 1382.

2 a) H. Furuya, K. Asahi, A. Abe, *Polym. J.* **1986**, *18*, 779. b) N. V. Tsvetkov, V. V. Zuev, V. N. Tsvetkov, *Liq. Cryst.* **1997**, *22*, 245. c) C. T. Imrie, G. R. Luckhurst, *J. Mater. Chem.* **1998**, *8*, 1339.

3 C. V. Yelamaggad, I. S. Shashikala, D. S. S. Rao, G. G. Nair, S. K. Prasad, *J. Mater. Chem.* **2006**, *16*, 4099.

4 J. Thisayukta, E. T. Samulski, *J. Mater. Chem.* **2004**, *14*, 1554.

5 a) K. Shigehara, M. Hara, H. Nakahama, S. Miyata, Y. Murata, A. Yamada, *J. Am. Chem. Soc.* **1987**, *109*, 1237. b) K. Shigehara, Y. Murata, N. Amaya, A. Yamada, *Thin Solid Films* **1989**, *179*, 287.

6 a) T. Otsu, O. Ito, N. Toyoda, S. Mori, *Makromol. Chem., Rapid Commun.* **1981**, *2*, 725. b) T. Otsu, M. Yoshioka, *Macromolecules* **1992**, *25*, 1615. c) K. Shiraishi, K. Sugiyama, *Chem. Lett.* **1990**, 1697.

7 a) K. Jähnichen, L. Häußler, M. Rätzsch, *Mol. Cryst. Liq. Cryst.* **1996**, *287*, 57. b) Y. K. Han, K. M. Kim, *Bull. Korean Chem. Soc.* **1999**, *20*, 1421.

8 a) J. W. Emsley, G. R. Luckhurst, G. N. Shilstone, I. Sage, *Mol. Cryst. Liq. Cryst.* **1984**, *102*, 223. b) C. T. Imrie, G. R. Luckhurst, *J. Mater. Chem.* **1998**, *8*, 1339. c) A. Ferrarini, C. Greco, G. R. Luckhurst, *J. Mater. Chem.* **2007**, *17*, 1039.

9 H. C. Aspinall, N. Greeves, W.-M. Lee, E. G. Mclver, P. M. Smith, *Tetrahedron Lett.* **1997**, *38*, 4679.

10 a) G. R. Clemo, S. B. Graham, *J. Chem. Soc.* **1930**, 213. b) A. G. Cook, A. B. Voges, A. E. Kammrath, *Tetrahedron Lett.* **2001**, *42*, 7349.

11 *Liquid Crystals and Plastic Crystals*, ed. by G. W. Gray, P. A. Winsor, Halsted, New York, **1974**.

12 Supporting information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) July 14, 2007; doi:10.1246/cl.2007.1052