Synthesis and the Phase Behavior of Liquid-crystalline Fumarates Bearing Tolane-based Mesogens

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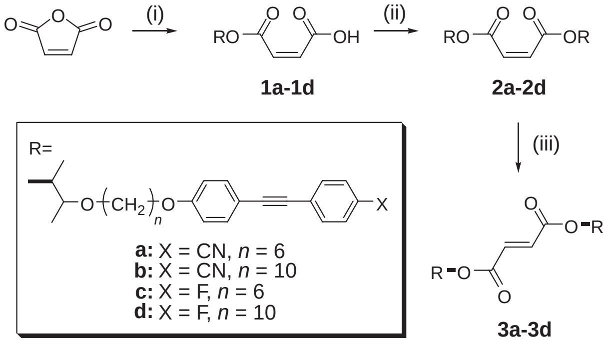
A new synthetic route to fumarates bearing tolane-based mesogens was developed without using acidic conditions. Effect of the tolane end group as well as alkyl chain spacer length on the liquid-crystal phases and the temperature range was comprehensively investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD) analysis.

Because of high birefringence, low viscosity, and good thermal stability, tolane structures are particularly attractive for optical applications.[1] Many liquid-crystalline tolane derivatives have been synthesized for the use as reflective displays, which suggested the improved light-scattering efficiency and contrast ratio as well as the short response time through the thinner cell gap.[2] However, a major problem of tolane compounds is the high melting points and, concomitantly, clearing points. To decrease these transition temperatures without decreasing the mesogen density for efficient appearance of liquid-crystal phases, a new molecular design is required.

We have been continuing the project on the synthesis of the difunctionalized fumarates and the polymerization by either radical initiators or methathesis catalysts.[3] It has been a general opinion that 1,2-disubstituted ethylenes do not homopolymerize with radical initiators because of the steric hindrance of the substituents in the propagation process until the pioneering work by Otsu, who revealed that dialkyl fumarates could be polymerized in bulk with radical initiators to furnish the corresponding polymers of a molecular weight of $>10^4$.[4] After that, fumarates disubstituted with bulkier alkyl groups such as isopropyl and *tert*-butyl groups were found to give much higher molecular weight polymers.[5] The resulting poly(fumarate)s feature high thermal stability originating from the rigid backbone as well as the doubled substituent density with respect to vinyl polymers, leading to exceptionally fascinating functional polymers. Therefore, we decided to attach tolane structures to the branched alkyl fumarates through the alkyl chain spacer, in view of the further extension to the liquid-crystalline polymers. The branched alkyl moiety and the flexible alkyl chain spacer are expected to efficiently decrease the transition temperatures to the liquid-crystal phases. Here, we report for the first time liquid-crystalline fumarates bearing tolane mesogens, of which phase behavior was investigated by the variation of the tolane end group and the alkyl chain spacer length.

Generally, reactions of alcohol with fumaric acid and maleic anhydride under acidic conditions readily afford disubstituted fumarate and maleate, respectively, in a reasonable yield.[6] However, the target fumarates bearing two tolane mesogens were synthesized under acid-free conditions, since the carbon–carbon triple bond of the tolane moiety is sensitive to acids (see Supporting Information[10]). Starting from maleic anhydride, the reaction with the tolane-bearing alcohols, prepared by the Sonogashira coupling followed by the sequential ether syntheses, under basic conditions provided the monosubstituted maleates **1a**–**1d** (Scheme 1). Gratifyingly, we found that extraction of the reaction mixtures with saturated aq $NaHCO_3$ solution followed by careful neutralization yields **1a**–**1d** in a quantitative yield. The subsequent esterification by the Mitsunobu reaction[7] proceeded in a satisfactory yield, furnishing disubstituted maleates **2a**–**2d**. Without the isolation, the maleates **2a**–**2d** were subjected to the cis–trans isomerization reaction. This reaction, catalyzed by morpholine, proceeds in a quantitative yield for disubstituted maleates but mainly produces undesired addition products for the monosubstituted maleates.[8] Hence, the disubstituted fumarates **3a**–**3d** could be obtained directly from the monosubstituted maleates **1a**–**1d** in a yield of 27–52%.



Scheme 1. Synthesis of dialkyl fumarates bearing tolane mesogens. (i) ROH, Et_3N, CH_2Cl_2, r.t., 5 h, 100%; (ii) ROH, diethyl azodicarboxylate, PPh_3, THF, rt, 24 h; (iii) morpholine, toluene, 90 °C, 4 h, **3a**: 34% (from **1a**), **3b**: 52% (from **1b**), **3c**: 33% (from **1c**), **3d**: 27% (from **1d**).

The tolane-containing fumarates **3a**–**3d** were thermally stable. Decomposition temperatures of **3a**–**3d** determined by thermogravimetric analysis exceed 300 °C. The phase-transition temperatures and the corresponding enthalpy changes (ΔH) were determined by the differential scanning calorimetry (DSC) measurements, and the data are summarized in Table 1. The liquid-crystal phases of **3a**–**3c** were observed upon both heating and cooling cycles, indicating the enantiotropic liquid crystals. Polarized optical microscopy (POM) images suggested the nematic phase for **3a** and the smectic phase for **3b** and **3c** (Figure 1). However, the liquid-crystal phase of **3d** appeared only in the cooling scan, and the phase was assigned to be higher-order in the smectic phase by the POM image and X-ray diffraction (XRD) pattern (vide infra). Another exceptional feature of **3d** is the crystal phase, rather than a glass state, which is probably caused by the delicate balance between the

Table 1. Phase-transition behaviors of the tolane-containig fumarates[a]

		Phase-transition temperature/°C (ΔH/kJ mol^{-1})
3a	heating	G −2.5 N 34.6 (−1.43) Iso.
	cooling	Iso. 32.2 (1.28) N 0.3 G
3b	heating	G −11.1 Sm 56.7 (−5.63) Iso.
	cooling	Iso. 56.7 (5.59) Sm −8.2 G
3c	heating	G −1.4 Sm 24.8 (−17.5) Iso.
	cooling	Iso. 19.0 (16.4) Sm 1.3 G
3d	heating	Cr 37.2 (−53.8) Iso.
	cooling	Iso. 35.9 (19.9) Sm 17.2 (19.5) Cr

[a] DSC measurements were carried out under nitrogen flow, at a scanning rate of 10 °C min^{-1}. G: Glass, N: Nematic, Iso.; Isotropic, Sm: Smectic, Cr: Crystal.

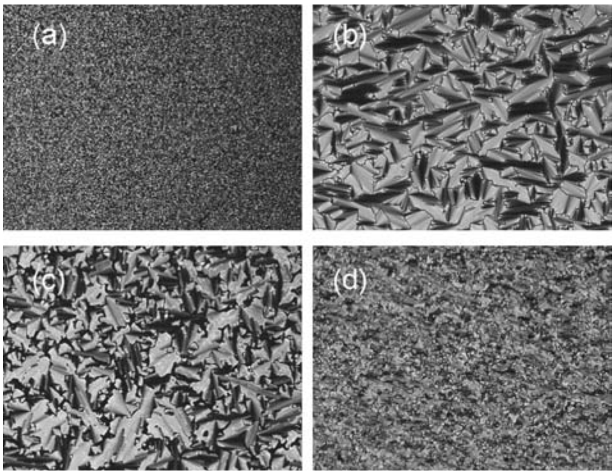


Figure 1. POM images in the cooling scan of (a) **3a** at 30 °C, (b) **3b** at 30 °C, (c) **3c** at 20 °C, and (d) **3d** at 30 °C.

longer crystalline alkyl chains and the weak mesogenic interactions. It should be noted that the liquid-crystal temperatures of **3a**–**3d** are remarkably low as compared to the previously reported liquid-crystalline fumarates, which possess the transition temperatures to the liquid-crystal phases of >80 °C.[9]

For the cyanotolane derivatives, an increase in the alkyl chain spacer length extremely expands the liquid-crystal temperature range, whereas the difference between the fluorotolane derivatives is not significant. The XRD analysis reveals a clear difference between the cyanotolane and the fluorotolane derivatives. The cyanotolane derivatives exhibit a very broad peak at $2\theta \approx 20°$, whereas the fluorotolane derivatives show a sharp peak at almost the same position ($2\theta = 20.0°$; $d = 4.4$ Å) together with some additional peaks (Figure 2). The *d*-spacing value is supposed to originate from the mesogen intervals in the smectic phases for both **3c** and **3d**. The fact that the peak of **3d** is sharper than that of **3c**, as well as the POM images of **3a** and **3b**, indicates a longer alkyl chain spacer leads to a higher-order phase. The XRD results also suggest that the fluorotolane derivatives tend to form higher-order phases. Comparison of the ΔH values in the DSC thermograms between the cyano- and fluorotolane derivatives supports this result. The values of the fluorotolane derivatives are much greater than those of the cyanotolane derivatives, indicating more strongly ordered state for the fluorotolane derivatives.

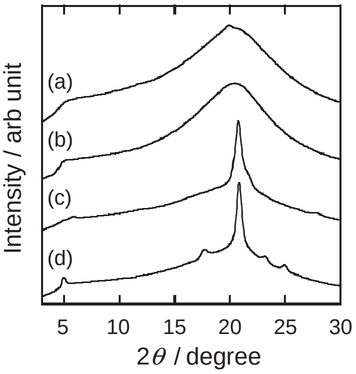


Figure 2. XRD patterns in the cooling scan of (a) **3a** at 20 °C, (b) **3b** at 25 °C, (c) **3c** at 15 °C, and (d) **3d** at 25 °C.

In conclusion, we have successfully developed an acid-free synthetic route to dialkyl fumarates bearing tolane mesogens. This new route will open the door to introduction of other acid-sensitive components into fumarates as well as synthesis of asymmetrically substituted fumarates. The synthesized tolane-containing fumarates display significantly lowered phase-transition temperatures. The further investigation of the phase behavior of the corresponding poly(fumarate)s is now pursued.

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