Unexpected Phase Behaviors of Poly(fumarate)s Carrying Tolane-based Mesogenic Side Chains

Tsuyoshi Michinobu,[1,2] Hiroshi Noguchi,[1] Nozomu Fujii,[1] Masatoshi Tokita,[3] Junji Watanabe,[3] 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*
[3]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552*

(Received January 7, 2008; CL-080012; E-mail: jun@cc.tuat.ac.jp)

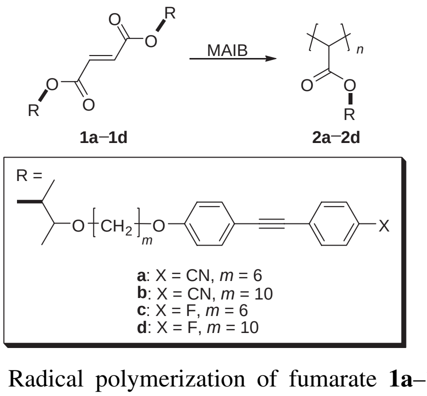
Poly(fumarate)s carrying tolane-based mesogenic side chains were for the first time prepared by radical polymerization. The phase behaviors characterized by differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD) analysis indicated that the liquid crystalline temperature ranges clearly decreased upon polymerization. This very rare behavior could be derived from the delicate balance between the mesogen structure and the rigid polyfumarate backbone.

Tolane derivatives, which are an expanded form of biphenyl analogues, are particularly attractive for optical applications because of their high birefringence, low viscosity, and good thermal stability.[1] Many monomeric or oligomeric liquid crystalline molecules containing tolane moieties have been synthesized for the use as, e.g., reflective displays owing to improved light-scattering efficiency, contrast ratio, and short response time.[2] However, there is still great room for improvement in the liquid crystallinity, that is, the tuning of the mesophases and the transition temperatures. Polymerization of the liquid crystalline monomers generally leads to expansion of the mesophase temperature range. For example, monodispersed poly(methyl methacrylate)s bearing cyanobiphenyl mesogens, prepared by anionic polymerization, are reported to show an increase in the clearing point and, on the contrary, a slight decrease in the transition temperature from mesophase to crystal phase with increase in molecular weight.[3] Poly(fumarate)s are an interesting class of polymers, which possesses a rigid backbone originating from bulky and dense side chains.[4] The recently reported poly(fumarate) bearing cyanobiphenyl mesogens displayed similar phase behavior to the side chain liquid crystalline poly(methyl methacrylate)s. As compared to the monomeric fumarate, the corresponding polymer exhibited a remarkably wide mesophase temperature range of 34.0–141.7 °C, although the molecular weight was not significantly high.[5] Moreover, the observed mesophase of the poly(fumarate) was a smectic phase, leading to a wide variety of electrooptic applications.

We very recently reported the efficient synthesis of the liquid crystalline fumarates **1a**–**1d** bearing two tolane-based mesogens without using acidic conditions.[6] They demonstrated the tunability of the liquid crystalline phases by derivatization of tolane moiety and variation of the alkyl chain spacer length between the fumarate and tolane mesogens. Thus, fluorotolane derivatives with a longer alkyl chain spacer tended to form higher-order liquid crystalline phases than cyanotolane ones with a shorter alkyl chain spacer. Considering the drastic change in the phase behavior of the fumarate monomer bearing two cyanobiphenyl mesogens upon polymerization,[5] this tendency of tolane derivatives was also expected to be amplified when they are polymerized. In this paper, we for the first time report the successful preparation of poly(fumarate)s **2a**–**2d** bearing tolane-based mesogens by radical polymerization of the corresponding fumarate monomers. However, we also describe their remarkable and unexpected phase behaviors including disappearance of the mesophases as well as the narrow mesophase temperature range, if any, that were in contrast to those observed for the poly(fumarate) bearing cyanobiphenyl mesogens.

The fumarate monomers **1a**–**1d** were heated in benzene at 60 °C in the presence of 10 mol % MAIB for 3 days (Scheme 1). After removal of the monomeric and oligomeric fractions by preparative HPLC, the resulting polymers showed almost the same molecular weight and an exceptionally narrow polydispersity as a reported polyfumarate bearing cyanobiphenyl mesogens,[5] indicating the living nature of the polymerization (Table 1 and Figure 1S).[7,8] The ^{1}H NMR and IR spectra substantiated the polymer structures (see Supporting Information[8]). The ^{1}H NMR spectra of the polymers were equivalent to the broadened spectra of the corresponding fumarate monomers. In the IR spectra, the C≡C stretching vibration peaks clearly exist, suggesting that the radical polymerization with MAIB proceeded without any side reactions with tolane moieties (Figure 2S).[8]

The tolane-containing poly(fumarate)s **2a**–**2d** were thermally stable. Decomposition temperatures determined by TGA exceed 300 °C. Phase-transition temperatures were carefully determined by DSC measurements and temperature-dependent POM observations, and the data are summarized in Table 1. Although all fumarate monomers **1a**–**1d** showed liquid crystalline phases, poly(fumarate)s **2a** and **2c** with a shorter alkyl chain spacer did not exhibit mesophases in both heating and cooling scans. On the other hand, **2b** and **2d** with a longer alkyl chain spacer displayed mesophase transitions (Figure 1). Combined with the Schlieren textures observed by POM (Figure 2a) as well as the broad XRD pattern (Figure 3a), the nematic phase was revealed for



Scheme 1. Radical polymerization of fumarate **1a**–**1d** in the presence of MAIB (dimethyl 2,2′-azobisisobutyrate).

Table 1. Summary of the molecular weight and phase-transition temperature of the poly(fumarate)s

	$M_n/10^{-4}$	M_w/M_n	Phase-transition temperature/°C	
2a	0.68	1.1	G 43.6 Iso.	heating
			Iso. 40.2 G	cooling
2b	1.1	1.1	G 21.0 N 34.3 Iso.	heating
			Iso. 29.5 N 16.9 G	cooling
2c	0.92	1.2	G 25.3 Iso.	heating
			Iso. 24.2 G	cooling
2d	1.2	1.2	G 23.9 Sm 48.6 Iso.	heating
			Iso. 39.9 Sm 19.7 G	cooling

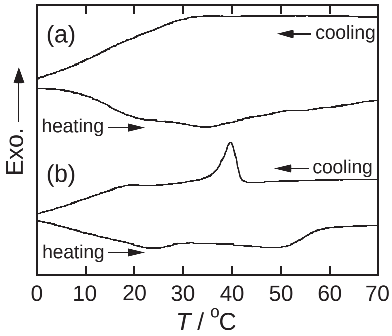


Figure 1. DSC thermograms of (a) **2b** and (b) **2d** at a scanning rate of 10 °C min^{-1}.

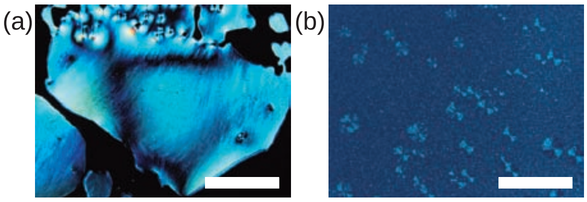


Figure 2. POM images of (a) **2b** and (b) **2d** at 20 °C in the cooling cycle. The bar represents 400 µm.

2b. Remarkably, the nematic phase temperature range (21.0–34.3 °C for heating cycle) significantly decreased as compared to that of the smectic phase of **1b** (−11.1–56.7 °C for heating scan).[6] Polymerization of a liquid crystalline monomer sometimes leads to a decrease in the liquid crystalline phase, but a decrease in the liquid crystalline temperature range is, to our knowledge, very rare. In contrast to the phase behaviors of **1d**, **2d** suggested an enantiotropic liquid crystal, but no noticeable expansion of the temperature range was observed. The POM image indicated a higher-order liquid crystalline phase (Figure 2b), and the XRD pattern provided evidence of the smectic phase (Figure 3b). A layer spacing value of 3.72 nm was estimated under the assumption that the peak at $2\theta = 4.75°$ is the second reflection. From the obvious reflection at 20.9°, a smectic B phase was suggested. The broad peak at ca. 5° is characteristic of the poly(fumarate)s, representing the diameter of the polymer backbone. That **2d** shows a higher-order liquid crystalline phase than **2b** is consistent with the phase behaviors of the corresponding fumarate monomers.

In conclusion, the liquid crystallinity as represented by the mesophase appearance and the temperature range was remarkably decreased upon polymerization of the fumarate monomers bearing tolane-based mesogens. This novel finding could originate from the delicate balance between the tolane-based mesogens and rigid polyfumarate backbone. Further studies on the backbone effects are at present underway.

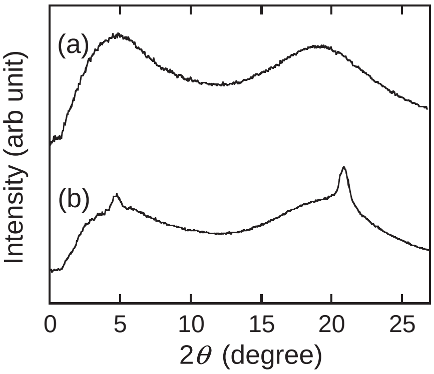


Figure 3. XRD patterns of (a) **2b** at 25 °C and (b) **2d** at 30 °C.

We thank Dr. K. Ariga and Dr. T. Nakanishi (National Institute for Materials Science) for the use of the recycling HPLC.

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