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Liquid Crystalline Polymers from Fumarates Containing Mesogenic Methoxyphenylazophenoxy Groups

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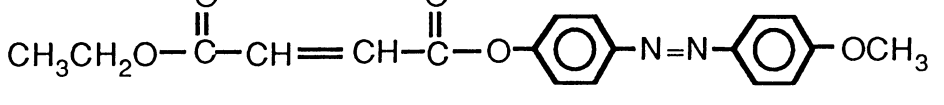
Radical polymerization of three fumarates, ethyl 4-(4-methoxyphenylazo)phenyl fumarate (**1**), ethyl 6-[4-(4-methoxyphenylazo)phenoxy]hexyl fumarate (**2**), and ethyl 11-[4-(4-cyanophenoxycarbonyl)phenoxy]undecyl fumarate (**3**) was carried out in benzene. Monomers **2** and **3** polymerize to give nematic polyfumarates [poly(**2**), poly(**3**)], while monomer **1** gives no polymer. From the copolymerization of monomer **2** (M_2) with styrene (M_1) the monomer reactivity ratios r_1 and r_2 were found to be 0.60 and 0.06, respectively. The copolymerization of monomers **2** and **3** was also carried out in an attempt to obtain a guest-host system [poly(**2**/**3**)]. The rate of isomerization from trans- to cis-azobenzene was found to be 0.038 min^{-1} for poly(**2**/**3**).

During the last decade, the side chain type of liquid crystalline polymers (LCPs) has been widely investigated with respect to their chemical and physical properties as well as their potential applications. In these polymers, the mesogenic groups are linked to flexible polysiloxanes$^{1)}$ or to polyethylene chains, e.g. in polyacrylates,$^{2,3)}$ polymethacrylates,$^{2,4)}$ and polyitaconates.$^{5,6)}$ Few polyfumarates exhibiting mesogenic behavior have so far been prepared. On the other hand, it has been established that dialkyl fumarates polymerize radically to produce non- or semi-flexible rodlike polymers with a high molecular weight.$^{7,8)}$ Our effort has been directed toward the synthesis of liquid crystalline fumarates,$^{9-11)}$ in an attempt to obtain a novel type of LCPs. In this letter, we report the polymerization of ethyl 4-(4-methoxyphenylazo)phenyl fumarate (**1**),$^{9)}$ ethyl 6-[4-(4-methoxyphenylazo)phenoxy]hexyl fumarate (**2**),$^{12)}$ and ethyl 11-[4-(4-cyanophenoxycarbonyl)phenoxy]undecyl fumarate (**3**).$^{13)}$ The polymerization of the monomers



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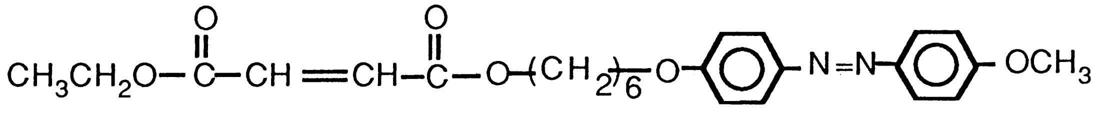

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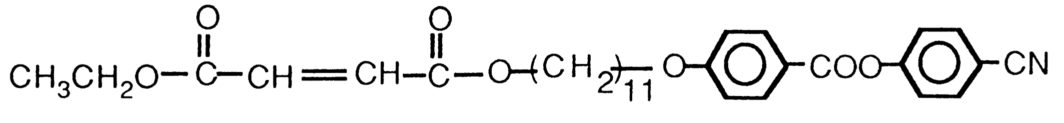

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1 -**3** was carried out using a free radical initiator by the method described.[14] The results in Table 1 shows that monomers **2** and **3** polymerize to give poly(**2**) and poly(**3**) with fairly low intrinsic viscosity, while monomer **1** gives only trace of polymer. We believe that the propagation of monomer **1** radical is hindered by the steric effect of the bulky mesogenic group directly fixed to the vinylene group. As the reactivity of monomer **2** is rather low monomer **2** (M_2) was copolymerized radically with styrene (M_1) in order to determine the monomer reactivity ratio. Figure 1 shows the composition curve of the copolymers of monomer **2** with styrene.[15] From Fig.1, using the curve-fitting method,[16] the values of styrene (r_1) and monomer **2** (r_2) were calculated to be 0.60 and 0.06, respectively. Otsu et al. clarified that generally, dialkyl fumarates have a tendency to copolymerize alternatively with styrene. For instance, r_1 and r_2 were found to be 0.29 and 0.02 respectively, for the copolymerization of styrene (M_1) with diethyl fumarate (M_2).[17]

Table 1. Radical polymerization[a] and thermal properties of **2**

Monomer (mmol)	Comonomer (mmol)	ACN[b] (mol%)	Yield %	[η][c] dL · g^{-1}	Tm ℃	Ti ℃	Abbr.
1 2.00	--	10.0	Trace	--	--	--	poly(**1**)
2 2.00	--	10.0	19.5	0.05	53.8	87.1	poly(**2**)
3 3.00	--	5.0	68.7	0.08	57.2	78.0	poly(**3**)
2 2.00	**3** 2.00	5.0	15.1	0.09	49.1	86.3	poly(**2**/**3**)

a) Polymerized in bulk at 100 ℃ for 7 days. b) ACN; 1,1'-Azobis(cyclohexanecarbonitrile).
c) Measured in benzene at 30 ℃.

The copolymer of monomer **2** with styrene seems to be an alternating one as well. These facts describe that the reactivity of monomer **2** is identical with that of dialkyl fumarates.

Monomer **1** in which the mesogenic group is bound directly to the polymerizable group exhibits an enantiotropical nematic phase (K 53 N 160.6 I).[9] On the other hand, it was found that if the mesogenic group is bound to the vinylene group via a spacer group the monomers show no mesophase. This suggests that the spacer group decreases the attractive interaction between the molecules; the spacer might prevent the molecules from aligning in a liquid-crystalline state. A DSC study showed that poly(**2**), poly(**3**), and poly(**2**/**3**) exhibit mesophases (Fig.2). Optical microscopy of the homopolymers reveals a schlieren texture identified as nematic phase. Though the copolymers of monomer **2** with styrene did not exhibit any liquid crystalline phases, poly(**2**/**3**) was found to be nematic with a wider temperature range of the mesophase than those of the homopolymers. Poly(**2**/**3**) is then taken as polymer guest-host (GH) system for GH mode.[18-20] A progressive spectral change, due to the isomerization from trans- to cis- azobenzene was found for poly(**2**) and poly(**2**/**3**) during irradiation (λ =253.7 nm). From the disappearance of the absorption of the trans- azobenzene chromophore (λ max=365 nm) in THF, the observed first order rate constants were estimated to be 0.019 and 0.038 min^{-1} for poly(**2**) and the guest-host system respectively, according to the method described in a previous paper.[21] These nematic LCPs are believed to be the first representative

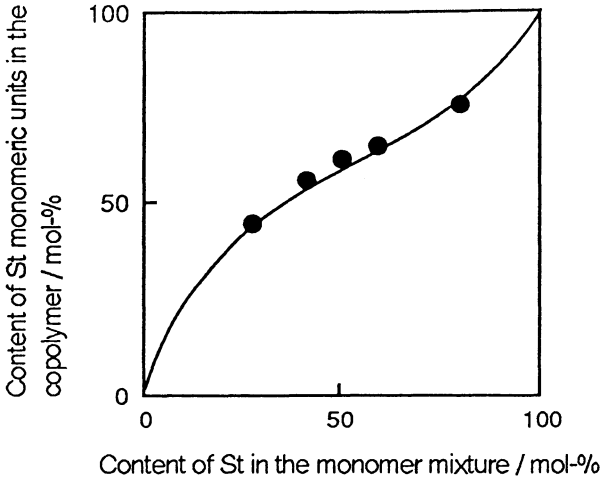

Fig. 1. Composition cruve for the copolymerization of **2** (M_2) and styrene(St) (M_1) initiated by Azobisisobutyronitrile in benzene at 60 ℃.

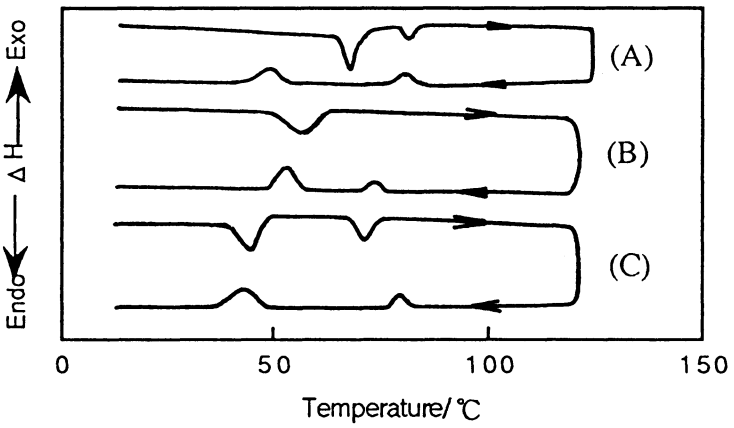

Fig. 2. DSC thermograms of poly(**2**), (A); poly(**3**), (B); and guest-host system, (C); heating and cooling rate; 5 ℃/min.

examples obtained from 1,2-disubstituted ethylenic monomers and may find application as photoresponsive membrane materials.

References

1) H. J. Coles and R. Simon, *Polymer*, 26, 1801(1985).

2) R. V. Talrose, S. G. Kostromin, V. P. Shibaev, N. A. Platé, H. Kresse, K. Sauer, and D. Demus, *Makromol. Chem., Rapid Commun.*, 2, 305(1981).

3) H. Ringsdorf and R. Zentel, *Makromol. Chem.*, 183, 1245(1982).

4) H. Ringsdorf and H.-W. Schmidt, *Makromol. Chem.*, 185, 1327(1984).

5) M. Eich and J. H. Wendorff, *Makromol. Chem., Rapid Commun.*, 8, 467(1987).

6) K. Shiraishi, K. Sugiyama, and T. Otsu, *Bull. Chem. Soc. Jpn.*, 62, 4083(1989).

7) T. Otsu and K. Shiraishi, *Macromolecules*, 18, 1975(1985).

8) T. Otsu, A. Tatumi, and A. Matsumoto, *J. Polym. Sci., Polym. Lett. Ed.*, 24, 113(1986).

9) K. Shiraishi, K. Sugiyama, A. Sakamoto, and T. Otsu, *Bull. Chem. Soc. Jpn.*, 61, 783(1988).

10) K. Sugiyama, A. Sakamoto, Y. Murata, K. Shiraishi, and T. Otsu, *Nippon Kagaku Kaishi*, 1987, 1064.

11) K. Shiraishi, A. Sakamoto, and K. Sugiyama, *Nippon Kagaku Kaishi*, 1988, 946.

12) Monomer **2** was obtained from the reaction of 6-[4-(4-methoxyphenylazo)phenoxy]-1-hexanol with ethyl (E)-3-(chloroformyl)acrylate; mp 99.3 ℃, yield 63%, ^{1}H NMR(CDCl$_3$) δ =0.83-1.12(t, J=4 Hz, 3H, -CH$_2$CH$_3$), 1.32-2.18(m, 8H, -OCH$_2$(CH$_2$)$_4$CH$_2$O-), 3.85(s, 3H, -OCH$_3$), 3.91-4.36(m, 6H, -OCH$_2$(CH$_2$)$_4$CH$_2$O-, -OCH$_2$CH$_3$), 6.79(s, 2H, -CH=CH-), 6.81-8.01(m, J=4 Hz, 8H, aromatic): Found: C, 65.92; H, 6.60; N, 6.18%. Calcd for $C_{25}H_{30}N_2O_6$(454.528); C, 66.06; H, 6.65; N, 6.16%.

13) Monomer **3** was obtained from the reaction of 11-[4-(4-cyanophenoxycarbonyl)phenoxy]-1-undecanol with ethyl (E)-3-(chloroformyl)acrylate; mp 82 ℃, yield 53%, ^{1}H NMR(CDCl$_3$) δ =1.14-2.18 (m, 21H, -OCH$_2$(CH$_2$)$_9$CH$_2$O-, -CH$_2$CH$_3$), 4.08-4.76(m, 6H, -OCH$_2$(CH$_2$)$_9$CH$_2$O-, -CH$_2$CH$_3$), 7.23(s, 2H, -CH=CH-), 7.12-8.72(m, 8H, phenyl): Found: C, 69.61; H, 6.87; N, 2.39%. Calcd for $C_{31}H_{37}NO_7$(535.643); C,69.51; H, 6.96, N, 2.61%.

14) K. Sugiyama, *J. Macromol. Sci., Chem.*, A23, 1155(1986).

15) The copolymerization products from monomer **2** and styrene were analyzed by ^{1}H NMR for the phenyl protons of monomer **2** and styrene.

16) R. W. Tidwell and G. A. Mortimer, *J. Polym. Sci., Part A*, 3, 369(1965).

17) N. Toyoda, M. Yoshida, and T. Otsu, *Polym. J.*, 15, 255(1983).

18) G. H. Heilmeier, J. A. Castellano, and L. A. Zanoni, *Mol. Cryst. Liq. Cryst.*, 8, 293(1984).

19) H. Ringsdrof and H-W. Schmidt, *Makromol. Chem.*, 188, 1327(1984).

20) M. Eich and J. H. Wendorff, *Makromol. Chem., Rapid Commun.*, 8, 467(1987).

21) K. Okuyama, H. Watanabe, M. Shimomura, K. Hirabayashi, T. Kunitake, T. Kajiyama, and N. Yasuoka, *Bull. Chem. Soc. Jpn.*, 59, 3351(1986).

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