Thermal Properties of Liquid-Crystalline Polyitaconates with Paired Mesogens

Kazuo SUGIYAMA* and Kohei SHIRAISHI
Department of Industrial Chemistry, Faculty of Engineering, Kinki University, Hirokoshinkai, Kure, Hiroshima 737-01
(Received December 20, 1990)

Synopsis. 2-Methylenesuccinates (Itaconates) (**2**) having two 4-methoxyazobenzene moieties as paired mesogenic groups were prepared. The monomer **2** was radically homopolymerized and copolymerized with non-mesogenic monomer, dioctadecyl itaconate (DOI). Paired mesogenic homopolyitaconate exhibits a nematic phase and the copolymers of the monomer **2** with DOI also show a mesomorphic phase up to 25 mol% of DOI content. The enhancement of mesophase formation by paired mesogens is discussed.

In order to obtain comprehensive knowledge concerning the structure–property relation of thermotropic liquid crystalline side-group polymers (TLCPs), numerous polymers have been prepared and their mesomorphic properties investigated with a variation of the type of mesogen and the spacer in polyacrylates,[1,2] polymethacrylates,[3] polyesters[4,5] and polysiloxanes.[6] The properties of TLCPs are varied by the mesogenic structure and how mesogens are incorporated into the backbones. TLCPs with accentuated liquid-crystalline properties were prepared with paired mesogenic units fixed to a polysiloxane main chain.[7,8]

The concentration of mesogens along the polymer chain could also be achieved by making use of polymethylenesuccinates (polyitaconates).[9] The polymerization reactivity of itaconate monomers with paired mesogens and the mesomorphic properties of the polymers are, however, not obvious concerning detail. In recent papers, the syntheses and thermal behaviors of non-vinyl TLCPs were reported. The polymers considered were polyfumarate[10] or polyitaconate[11] backbones, a methylene spacer and 4-(4-methoxyphenylazo)-phenoxy and 4-(4-cyanophenoxycarbonyl)phenoxy mesogenic groups. In this brief note, we described the enhancement of mesophase formation by pairing the mesogens in polyitaconates, poly[bis[6-[4-(4-methoxyphenylazo)phenoxy]hexyl]itaconate].

Experimental

Preparation of Monomers: Bis[6-[4-(4-methoxyphenylazo)phenoxy]hexyl] itaconate **2** was prepared as follows: a benzene solution of 0.05 mol of itaconic anhydride and a 0.11 mol of 6-[4-(4-methoxyphenylazo)phenoxy]-1-hexanol was refluxed in the presence of a catalytic amount of *p*-toluenesulfonic acid for 3 d. After removing the solvent, the crude product was recrystallized twice from benzene. 83.9% yield; mp 121—122.4 °C; ^{1}H NMR ($CDCl_3$) δ=1.12—1.86 (m, 16H, $-CH_2(CH_2)_4CH_2-$), 3.36 (s, 2H, $-CH_2-$), 3.84—4.33 (m, 8H, $-CH_2(CH_2)_4CH_2-$), 3.91 (s, 6H, $-OCH_3$), 5.72—5.80 (m, 1H, H–CH=), 6.30—6.45 (m, 1H, H–CH=), 6.89—7.93 (m, 16H, Aromatic). Found: C, 68.78; H, 7.01; N, 7.44%. Calcd for $C_{43}H_{50}O_8N_4$ (M, 750.900): C, 68.78; H, 6.71; N, 7.46%.

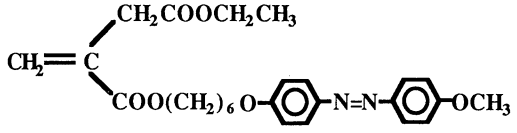
Dioctadecyl itaconate (DOI) was prepared from the reaction of 0.18 mol of itaconic anhydride and 0.40 mol of 1-octadecanol according to the preparation method of **2**. 83.6% yield; mp 59.4—59.8 °C; ^{1}H NMR ($CDCl_3$) δ=0.77—1.74 (m, 70H, $-CH_2(CH_2)_{16}CH_3$), 3.26 (s, 2H, $-CH_2-$), 3.88—4.18 (m, 4H, $-CH_2(CH_2)_{16}CH_3$), 5.48—5.62 (m, 1H, H–CH=), 6.12—6.24 (s, 1H, H–CH=). Found: C, 77.66; H, 12.25%. Calcd for $C_{41}H_{78}O_4$ (M, 635.076): C, 77.54; H, 12.38%.

6-[4-(4-methoxyphenylazo)phenoxy]hexyl methacrylate was prepared by adding dropwise a slight excess of methacryloyl chloride to 6-[4-(4-methoxyphenylazo)phenoxy]-1-hexanol dissolved in anhydrous THF at 0 °C and in the presence of triethylamine. 66.3% yield; mp 81.2—82 °C; ^{1}H NMR ($CDCl_3$) δ=1.43—2.00 (m, 8H, $-CH_2(CH_2)_4CH_2-$), 2.08 (s, 3H, $-CH_3$), 4.14 (s, 3H, $-OCH_3$), 3.56—4.52 (m, 4H, $-CH_2-(CH_2)_4CH_2-$), 5.76—5.93 (m, 1H, H–CH=), 6.32—6.49 (s, 1H, H–CH=), 7.20—8.41 (m, 8H, Aromatic). Found: C, 69.68; H, 7.12; N, 16.14%, Calcd for $C_{23}H_{28}O_4N_2$ (M, 396.491): C, 69.66; H, 7.08; N, 16.33%.

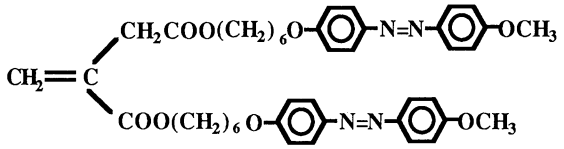
Polymerization: The polymerization procedure was the same as that described by Sugiyama.[12] Polymers were reprecipitated twice from benzene and methanol. The intrinsic viscosities [η] of the polymer were determined in benzene at 30 °C with an Ubbelohde viscometer. The composition ratios of the copolymers were calculated from the nitrogen content as obtained by elemental analysis.

Results and Discussion

Itaconates with mono- and paired mesogenic units, the monomers **1** and **2**, are shown in Scheme 1. The polymerization of the monomer **2** was carried out using a free-radical initiator. The results given in Table 1 show that monomer **2** polymerizes to give mesomorphic polyitaconates with moderate conversion. As far as the viscosity behavior in benzene is concerned, their intrinsic viscosities are relatively small. The weight-averaged molecular weight was estimated to be 3430 for the polymer of [η]=0.027 dL g^{-1} by means of GPC measure-



Monomer 1



Monomer 2

Scheme 1. Structure of monomers **1** and **2**.

Table 1. Radical Polymerization and Phase Transition Temperature of **2**[a]

2	[ACN]×10²	Yield	$[\eta]$[b]	Phase transition temp/°C	
mmol	mmol	%	dL g^{-1}	T_m	T_i
0.67	1.34	8.3	0.059	101	136
0.67	2.68	10.4	0.052	100	130
0.67	4.02	18.2	0.044	98	137
0.67	5.36	25.0	0.042	97	131
0.67	6.70	58.0	0.027	97	122

a) Polymerized with 1,1′-Azobis(cyclohexanecarbonitrile) (ACN) in benzene (2 mL) at 100 °C for 7 d. b) Measured in benzene at 30 °C. c) Measured by DSC on heating cycle.

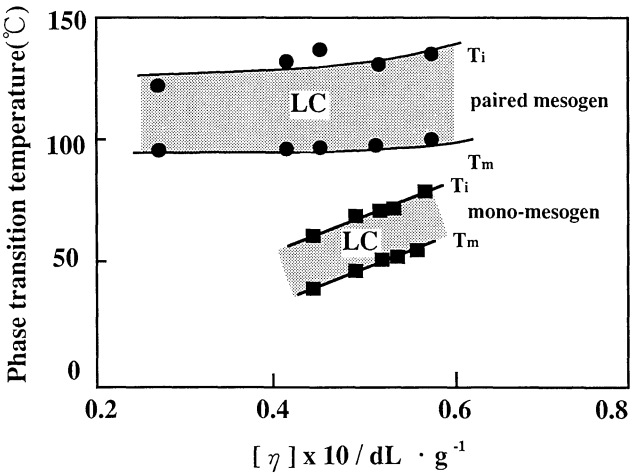


Fig. 1. Relationship between phase transition temperature and $[\eta]$ for the mono-mesogenic (■) and the paired mesogenic (●) polyitaconates.

ment.[13]

The molecular weight of polyitaconates seems to high sufficient to discuss the liquid crystalline properties. A DSC study showed that all of the paired mesogenic polyitaconates as well as mono-mesogenic polymers[11] turned into mesophase, since they showed two endothermic peaks and an exothermic peak upon heating and cooling cycles, respecctively. The mono-mesogenic polyitaconates showed rather broad melting and clearing peaks,[11] while the paired mesogenic polyitaconates showed sharp transition peaks at higher temperatures than the mono- would be favorable for liquid crystalline alignment and give sharp peaks in thermal analysis. According to polarized optical microscopy (POM), the mesophase of polyitaconates showed a schlieren texture and was confirmed to be nematic phase. The schlieren texture of polyitaconates was retained unchanged up to room temperature. It is suggested from a DSC trace on cooling cycles and POM that the polyitaconates are frozen in the mesophase at room temperature. The phase-transition temperatures determined by means of DSC measurements are tabulated in Table 1. Figure 1

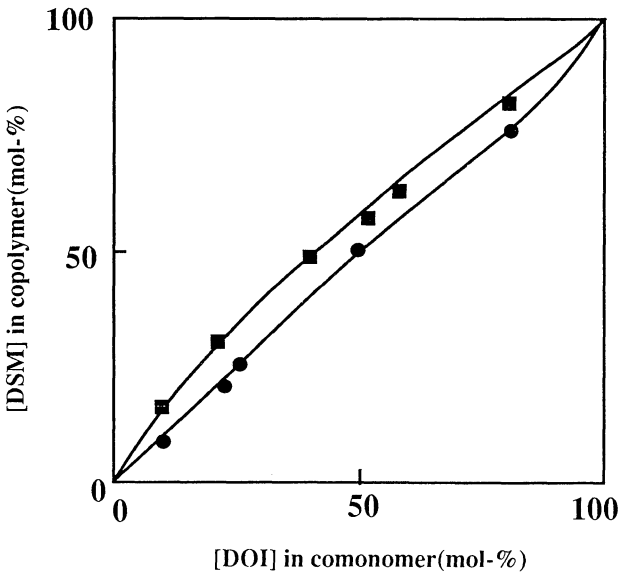


Fig. 2. Composition curve for the polymerization of monomers **1** (■) and **2** (●) with DOI (M_1) initiated with 1,1′-azobis(cyclohexanecarbonitrile) in benzene at 100 °C.

shows the relationships between the phase-transition temperature and the intrinsic viscosity for the polyitaconates. The clearing temperature (T_i) of polyitaconates gradually increases with an increase in the intrinsic viscosity values, as observed in liquid crystalline polyacryrates with $[\eta]$ below 0.1 dL g^{-1}.[14] Comparing the two kind of polymers, paired mesogenic polyitaconates show a higher T_i and a wider range of nematic states than do the mono-mesogenic ones. This is explained by concentrating the mesogenic groups along the main chain: paired mesogenic groups favor a lateral interaction between successive pendant groups. It is known that the distance between successive pendent mesogenic groups along the polymer backbone plays an important role for mesophase formation in alternating mesogenic copolymers.[15]

In order to reinforce the enhancement of mesophase formation by paired mesogens, the copolymerization of itaconates (M_2) with non-mesogenic DOI monomer (M_1) was carried out radically with 1 mol% for monomer amounts of ACN in bulk at 100 °C. The obtained copolymers were 30—50% in yield with 0.041—0.045 dL g^{-1} intrinsic viscosities. Figure 2 shows the composition curves for copolymerization. Applying the data in Fig. 2 to a curve-fitting method, the monomer reactivity ratios were calculated to be r_1=0.45 and r_2=0.95 for monomer **1** and r_1=1.02 and r_2=0.81 for monomer **2**, respectively. It is suggested that two kinds of polyitaconates radicals are nearly equal in reactivity for the DOI monomer, while the DOI radical decreases reactivity for itaconate with a paired mesogenic group, as is known from the steric effect of the bulky nature of the pendant groups. Thermal analyses of these random copolymers provided information concerning the

Table 2. Comparison of Phase Transition Temperature of Various Mesomorphic Side Chain Polymers[a)]

R	$[\eta]$/dL g^{-1}	T_m/°C	T_i/°C
-H[18)]	0.060	97	130
$-CH_3$[b)]	0.072	85	121
$-CH_2COOC_2H_5$[11)]	0.056	45	78
$-CH_2COO-(CH_2)_6-O-\langle\bigcirc\rangle-N=N-\langle\bigcirc\rangle-OCH_3$	0.059	101	136

a) $-[-CH_2-C(R)-]_n-$ with R = $COO-(CH_2)_6-O-\langle\bigcirc\rangle-N=N-\langle\bigcirc\rangle-OCH_3$.

b) Polymethacrylate was obtained from the polymerization of 6-[4-(4-methoxyphenylazo)phenoxy]hexyl methacrylate initiated by 1 mol% of 1,1′-azobisisobutyronitrile in the presence of 3.5 mol% of mercaptoacetic acid in benzene at 60°C for 24 h.

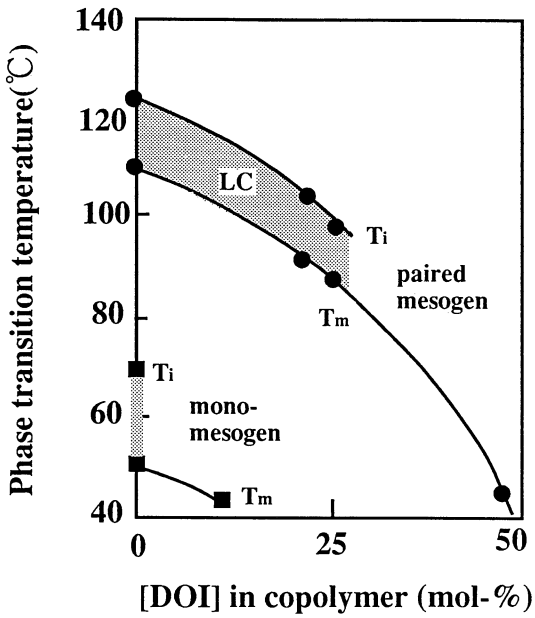


Fig. 3. Relationship between phase transition temperature and DOI content in copolymer of monomers **1** (■) and **2** (●) with DOI.

enhancement of the mesophase by introducing a pairing of the mesogens. Figure 3 exhibits the effect of nonmesogenic component on mesophase formation in a random copolymer. Paired mesogenic polyitaconates showed a nematic phase up to 25 mol% of DOI content, although the dilution lowered the phase-transition temperatures. On the other hand, copolymers of monomesogenic itaconates with nonmesogenic DOI showed no mesophase, even when the polyitaconates were diluted with 10 mol% of DOI content; it showed only the melting point. It is concluded that paired mesogens enhance the interaction of successive pendants in the liquid crystalline state and that the mesophase of copolymers with nonmesogenic DOI can be retained.

It is well known that the variation of substituents at the α-position of mesomorphic vinyl polymers causes a change in the kind of mesophase and transition temperature.[16,17)] Table 2 shows the transition temperature of various polymers bearing methoxyazobenzene moieties as a mesogenic group. In the case of monomesogenic liquid-crystalline polymers, large substituents at the α-position lower the transition temperature, since it accounts for the prevention of the mesogenic units from a liquid crystalline aligning due to their bulky nature. On the other hand, a paired mesogenic polymer shows a higher transition temperature based on a close packing of the mesogenic groups.

References

1) F. Hessel, R-P. Herr, and H. Finkelmann, *Makromol. Chem.*, **188**, 1597 (1987).
2) J. J. Mallon and S. W. Kantor, *Macromolecules*, **23**, 1249 (1990).
3) M. L. Tsai and S. H. Chen, *Macromolecules*, **23**, 1908 (1990).
4) S. Bualek and R. Zentel, *Makroml. Chem.*, **189**, 797 (1988).
5) I. G. Voigt-Martin, H. Durst, B. Reck, and H. Ringsdorf, *Macromolecules*, **21**, 1620 (1988).
6) C. H. Hsu, J. M. Rodriguez-Parada, and V. Percec, *J. Polym. Sci., Part A, Polym. Chem.*, **25**, 2425 (1987).
7) S. Diele, B. Hisgen, B. Reck, and H. Ringsdorf, *Makromol. Chem., Rapid Commun.*, **7**, 267 (1986).
8) S. Diele, S. Oelsner, F. Kuschel, B. Hisgen, H. Ringsdrof, and R. Zentel, *Makromol. Chem.*, **188**, 1993 (1987).
9) P. Keller, *Macromolecules*, **18**, 2337 (1985).
10) K. Shiraishi and K. Sugiyama, *Chem. Lett.*, **1990**, 1697.
11) K. Shiraishi, K. Sugiyama, and T. Otsu, *Bull. Chem. Soc. Jpn.*, **62**, 4083 (1989).
12) K. Sugiyama, *J. Macromol. Sci., -Chem.*, **A23**, 1155 (1986).
13) GPC measurements was carried out in THF with TSKgel G1000H, TSKgel G2000H, and TSKgel G3000H columns based on polystyrene as standard with an HLC-8020.
14) S. G. Kostromin, R. V. Talrose, V. P. Shibaev, and N. A. Platé, *Macromol. Chem., Rapid Commun.*, **3**, 803 (1982).
15) Y. Frere, F. Yang, P. Gramain, D. Guillon, and A. Skoulios, *Makromol. Chem.*, **189**, 419 (1988).
16) M. Portugall, H. Ringsdorf, and R. Zentel, *Makromol. Chem.*, **183**, 2311 (1982).
17) R. Zentel and H. Ringsdorf, *Makromol. Chem., Rapid Commun.*, **5**, 393 (1984).
18) A. S. Angeloni, D. Caretti, C. Carlini, E. Chiellini, G. Galli, A. Altomare, R. Salaro, and M. Laus, *Liq. Cryst.*, **4**, 513 (1989).