Liquid-Crystalline Behavior and Configuration Change of Polyitaconates with Methoxyazobenzene as Mesogens

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Synopsis. Nematic polyitaconates having 4-methoxyazobenzene moieties as mesogen in the side chain were prepared. Thermal properties, polymer composition, and the photoinduced configuration change have been examined to suggest a possible use of the polymers for photosensitive liquid-crystalline materials.

During the last decade, the side chain type of liquid crystalline polymers (LCPs) have been widely investigated on their chemical and physical properties as well as potential application. In these polymers, the mesogenic groups examined were flexible polysiloxanes[1] and different types of vinyl backbone such as polyacrylates,[2,3] polymethacrylates,[2,4] and polyitaconates.[5] In the course of our study on thermotropic behavior and potential uses of LCPs,[6—8] nematic polyitaconates, poly[ethyl ω-[4-(4-methoxyphenylazo)phenoxy]alkyl itaconate]s, Poly**2**, were prepared and their configuration changes were photochemically studied.

Experimental

4-[4-(ω-Hydroxyalkoxy)phenylazo]anisole, **1**: 4-[4-(6-hydroxyhexyloxy)phenylazo]anisole, **1a**, and 4-[4-(11-hydroxyundecyloxy)phenylazo]anisole, **1b** were prepared from the *O*-alkylation of 4-(4-hydroxyphenylazo)anisole with ω-halo-1-alkanol in the presence of KOH and KI according to the method used in the preparation of 4-(ω-hydroxyalkoxy)benzoic acids.[9]

1a (n=6): 51.0% yield; mp 122—123 °C; ^{1}H NMR ($CDCl_3$) δ=1.13—1.30 (*t*, *J*=4 Hz, 3H, $-C\underline{H}_3$), 1.43—2.17 (m, 8H, $HOCH_2(C\underline{H}_2)_4CH_2O-$), 3.79 (s, 3H, $-OC\underline{H}_3$), 3.22—4.15 (m, 4H, $HOC\underline{H}_2(CH_2)_4C\underline{H}_2O-$), and 6.55—7.97,(m, 8H, aromatic).

1b (n=11): 65.1% yield; mp 86—87 °C; ^{1}H NMR ($CDCl_3$) δ=1.27—2.28 (m, 18H, $HOCH_2\ (C\underline{H}_2)_9CH_2O-$), 3.42 (s, 3H, $-OC\underline{H}_3$), 3.68—4.51 (m, 4H, $HOC\underline{H}_2\ (CH_2)_9C\underline{H}_2O-$), and 7.37—8.66 (m, 8H, aromatic).

Ethyl 3-chloroformyl-3-butenoate: Ethyl 3-chloroformyl-3-butenoate from ethyl 3-carboxy-3-butenoate and thionyl chloride. 85% yield; bp 86—86.5 °C/8 mmHg (1 mmHg≈133.322 Pa).

Ethyl ω-[4-(4-methoxyphenylazo)phenoxy]alkyl itaconate, **2**: 0.05 mol of **1** was dissolved in 300 mL of chloroform and 0.10 mol of triethylamine. Then a trace of 1,4-benzoquinone was added with stirring and cooling at 0 °C, and a 0.10 mol portion of ethyl 3-chloroformyl-3-butenoate was dropped into the solution. After stirring for 4 h at 60 °C, ca. 200 mL of water was added to the reaction mixture. The chloroform layer was then washed with water and evaporated to dryness, and the residual solid was recrystallized from ethanol.

4-Ethyl 1-[6-[4-(4-methoxyphenylazo)phenoxy]hexyl] 2-methylenesuccinate, **2a** (n=6): 60.2% yield; mp 82 °C; ^{1}H NMR ($CDCl_3$) δ=1.13—1.30 (t, 3H, *J*=4 Hz, $-C\underline{H}_3$), 1.43—2.17 (m, 8H, $-OCH_2(C\underline{H}_2)_4CH_2O-$), 4.00 (s, 3H, $-OC\underline{H}_3$), 4.10—4.28 (q, 2H, $-C\underline{H}_2-$), 4.28—4.64 (m, 4H, $-OC\underline{H}_2(CH_2)_4C\underline{H}_2O-$), 5.87—6.06 (m, 1H, $\underline{H}-CH=$), 6.55—6.74 (m, 1H, $\underline{H}-CH=$), and 7.16—8.52 (m, 8H, aromatic).

Found: C, 67.10; H, 6.23; N, 5.98%. Calcd for $C_{24}H_{30}O_6N_2$: C, 66.94; H, 6.48; N, 6.00%.

4-Ethyl 1-[6-[4-(4-methoxyphenylazo)phenoxy]undecyl] 2-methylenesuccinate, **2b** (n=11): 59.4% yield; mp 64 °C; ^{1}H NMR ($CDCl_3$) δ=0.94—2.11 (m, 18H, $-OCH_2(C\underline{H}_2)_9CH_2O-$), 3.25 (s, 2H, $-C\underline{H}_2-$), 3.78 (s, 3H, $-OC\underline{H}_3$), 3.79—4.34 (m, 6H, $-OC\underline{H}_2(CH_2)_9C\underline{H}_2-$, $-C\underline{H}_2-$), 5.46—5.61 (m, 1H, $\underline{H}-CH=$), 6.06—6.24 (m, 1H, $\underline{H}-CH=$), and 6.63—7.84 (m, 8H, aromatic).

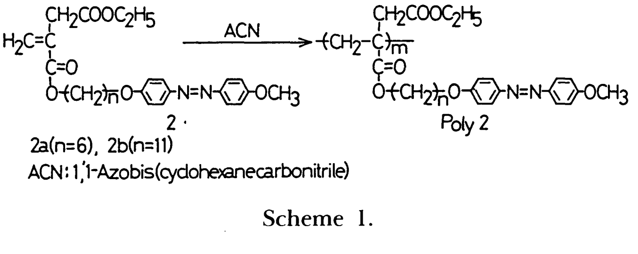
Found: C, 70.09; H, 6.35; N, 5.32%. Calcd for $C_{31}H_{40}O_6N_2$: C, 70.31; H, 6.28; N, 5.29%.

Polymerization: The polymerization procedure was the same as that described by Sugiyama.[10] Polymers were reprecipitated twice from benzene and methanol. The copolymerization products from monomer **2** and styrene were analyzed by ^{1}H NMR for the phenyl protons of monomer **2** and styrene. The intrinsic viscosity (dL·g^{-1}) of the polymer was determined in benzene at 30 °C by a Ubbelohde viscometer.

Measurements: The phase-transition temperature was determined by means of differential scanning calorimeter, using a Rigaku Thermoflex DSC 8230B. Microscopic observation was performed by an Olympus microscope with temperature controlling heating stage. The cis-trans isomerization of polymers was carried out as follows: a known amount of the polyitaconate in THF was put in a quartz tube, which was placed on a merry-go-round Rayonet photochemical reactor Model-RMA-400 equipped with 4 RPR-253.7 nm lamps. The distance between the tube and lamps was 10 cm. After irradiating the sample for a given time, an aliquot of the solution was taken for UV measurement by a Shimadzu UV 200S spectrophotometer.

Results and Discussion

Thermal Properites: Monomers **2** are yellow crystals and showed no mesophase. It was found that monomer **2** can polymerize by a free radical reaction to give homopolymers, [Poly**2**] with low intrinsic viscosity as shown in Scheme 1. Poly**2** with various intrinsic viscosity values were prepared by changing the polymerization conditions. All of Poly**2** turned into mesophase, which showed the Schlieren texture and were confirmed to be a nematic phase by observation and polarization microscopy of thin samples. The phase-



Scheme 1.

Table 1. Radical Polymerization of **2** and Characterization of Poly **2**

	2	Initiator×10²	Yield	$[\eta]^{c)}\times10^2$	Phase transition temp$^{d)}$/°C	
	mol	mmol	%	dL·g^{-1}	T_m	T_i
2a$^{a)}$	2.12	4.20	11.6	5.6	45	78
	2.12	6.78	13.5	5.3	48	76
	2.12	10.17	19.1	5.2	52	71
	2.12	13.56	22.2	4.9	50	68
	2.12	17.00	26.6	4.4	38	61
2b$^{b)}$	1.77	1.77	24.5	6.2	67	127
	0.23	1.15	31.1	6.0	54	120
	0.27	2.51	54.0	5.2	52	118

a) Polymerized with 2,2′-azobisisobutyronitorile (AIBN) in benzene (1g of **1a**/2 mL of benzene) at 60 °C for 24 h. b) Polymerized with 1,1′-azobis(cyclohexanecarbonitrile)(ACN) in bulk at 100 °C for 7 days. c) Measured in benzene at 30 °C. d) Determined by means of DSC thermogram on heating cycle (rate, 5 K·min^{-1}).

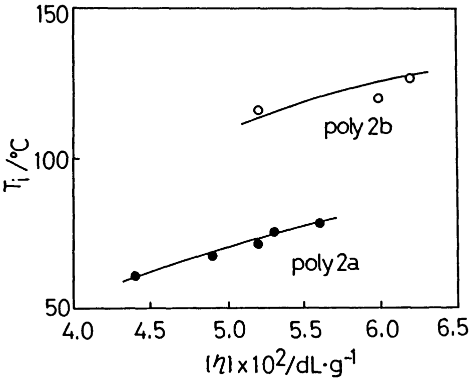


Fig. 1. Relationship between T_i and $[\eta]$ for Poly **2a**.

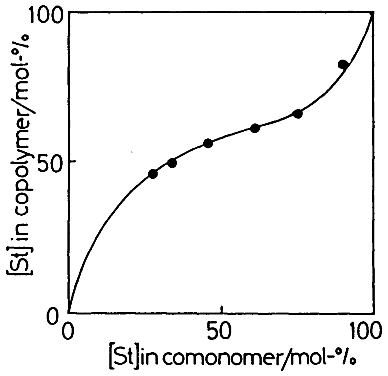


Fig. 2. Composition curve for the polymerization of the monomer **2a** (M_1) and styrene (M_2).

transition temperature determined by DSC was in good agreement with that obtained from the polarization microscopic measurement. The results are listed in Table 1. From the data in Table 1, it can be seen that the phase transition temperature of Poly**2** is influenced by the length of methylene spacer groups as well as intrinsic viscotiy of the polymer. Figure 1 shows the dependence of isotropization temperature (T_i) on intrinsic viscosity of Poly**2**. T_i values of both Poly**2a** and Poly**2b** increase gradually with the increase of intrinsic viscosity values. In general, the phase behavior of LCPs depends on their molecular weight and this influence is strong for low molecular weight,[9,11] for instance, T_i values of liquid crystalline polyacrylates increase with the increase in $[\eta]$ below 0.1.[12]

Copolymerization: Since monomer **2** showed low polymerization reactivity, monomer **2a** (M_1) was radically copolymerized with styrene (M_2) in order to know the monomer reactivity ratio of monomer **2**. Figure 2 shows the composition curves for the copolymerization of monomer **2a** with styrene initiated by AIBN in benzene at 60 °C. Applying the data in Fig. 2 to the curve-fitting method,[13] r_1 and r_2 were calculated to be 0.11 and 0.44, respectively. Monomer **2a** was then found to copolymerize alternatively with styrene. Sato et al.[14] reported that $r_1=0.36$ and $r_2=0.40$ for the copolymerization of methyl phenethyl itaconate (4-methyl 1-phenethyl 2-methylenesuccinate) (M_1) and styrene (M_2). The r_1 of monomer **2a** is smaller than that of methyl phenethyl itaconate. This is explained by the bulkiness of mesogenic group in monomer **2a**. From either DSC or polarization microscopic measurements, none of the copolymers exhibited liquid crystalline behavior.

Cis-Trans Isomerization: The photoinduced configuration change due to a cis-trans isomerization of the chromophore such as azobenzene is known to control the permeation of water, ion, etc. through the membrane.[15,16] The configuration change of Poly**2** was photochemically studied for the purpose of applying the polymer to practical separation. The progressive spectral change for Poly**2a** due to the isomerization from *trans*- to *cis*-azobenzene was observed during the irradiation of 253.7 nm light. From a decline of the absorption of trans-azobenzene chromophore ($\lambda_{max}=365$ nm) in THF, the first-order rate constant was, estimated to be 0.021 s^{-1} according to the method described by Sugiyama et al.[17] These nematic polyitaconates will have the possibility of use for a photoresponsive membrane material.

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