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SYNTHESIS AND POLYMERIZATION OF OPTICALLY ACTIVE DI-*L*-MENTHYL ITACONATE

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ABSTRACT

Optically active di-*L*-menthyl itaconate (DMI) was prepared from itaconic acid and *L*-menthol. DMI was polymerized in bulk at 80°C to give a chiral homopolymer having a specific rotation of -76.9°. DMI (M_1) was copolymerized with styrene (ST, M_2), *N*-cyclohexylmaleimide (CHMI, M_2), vinyl acetate (VAc, M_2) and methyl methacrylate (MMA, M_2) with azobisisobutyronitrile in benzene at 50°C. The monomer reactivity ratios (r_1 , r_2) and Alfrey-Price Q , e values were determined as $r_1 = 0.56$, $r_2 = 0.55$, $Q_1 = 0.76$, $e_1 = 0.29$ for DMI-ST; $r_1 = 0.0$, $r_2 = 5.6$ for DMI-MMA; $r_1 = 0.0$, $r_2 = 0.25$ for DMI-VAc; and $r_1 = 0.31$, $r_2 = 0.56$ for DMI-CHMI. The chiroptical properties of the polymers were investigated.

INTRODUCTION

There have been many reports on polymerizations and copolymerizations of mono- and dialkyl itaconates [1]. Lately there have been more than 20 reports containing patents on itaconic acid and its esters in 1 year. Cowie et al. reported on glass-transition points, heat capacity, and other physical properties of itaconic acid polymers [2-6]. Copolymerization of trifluoropropane with itaconic acid was carried out by using γ -rays [7]. Takane et al. studied polymerizable itaconate phospholipids and their polymeric lipo-

somes [8]. Bjorkquist et al. reported on cyclopolymerization and regioselective synthesis of vinyl itaconate [9]. Velickovic et al. investigated the solubility parameters of poly[bis(cyclohexyl-*n*-alkyl) itaconate] and poly[bis(phenyl-*n*-alkyl) itaconate] [10]. Asharov et al. reported on the polymerization of α - and β -monoalkyl esters of itaconic acid [11]. Bimendina et al. studied complex formation between poly(vinyl pyrrolidone) and poly(methyl itaconate) and its copolymers [12].

There have been many patents on lenses (e.g., Ref. 13), antioxidants (e.g., Ref. 14), coatings (e.g., Ref. 15), binders (e.g., Ref. 16), adhesives (e.g., Ref. 17), copy materials (e.g., Ref. 18), and films (e.g., Ref. 19). However, no investigations on polymerizations of optically active itaconate have been made. Particularly, there have been no reports on circular dichroism (CD) spectra for itaconate monomer, polymer, and copolymers. In the present paper a novel, optically active di-*L*-menthyl itaconate (DMI) was prepared and copolymerized with a number of monomers.

EXPERIMENTAL

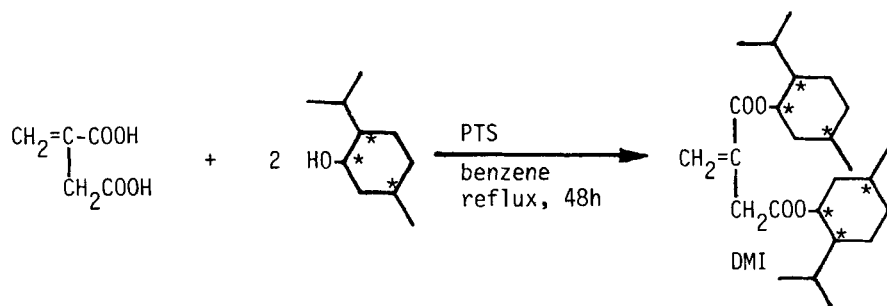
Materials

Styrene (ST), methyl methacrylate (MMA), and vinyl acetate (VAc) were purified by the usual methods. *N*-Cyclohexylmaleimide (CHMI) (mp 89°C) was prepared from maleic anhydride and cyclohexylamine [20].

DMI Monomer

Optically active DMI was prepared from itaconic acid and *L*-menthol, as shown in Scheme 1. A mixture of 80 g (0.61 mol) itaconic acid, 220 g (1.41 mol) *L*-menthol, and 20 g *p*-toluenesulfonic acid (PTS) in 750 mL benzene was refluxed for 48 h, using a Dean-Stark trap to remove the easily obtained water. After the reaction, the reaction mixture was neutralized with dilute NaOH and then washed with water. After drying with magnesium sulfate, the solution was evaporated under vacuum to remove benzene and unreacted *L*-menthol. The distillation was continued to obtain crude DMI (yield 76%). If the distillation temperature is above about 200°C, DMI isomerizes to di-*L*-menthyl citraconate. The crude DMI was carefully purified by distilling three times. Yield 51%, bp 160–162°C/0.06 torr, colorless oil, $[\alpha]_D^{20}$ -78.3 ($c = 1.0\%$, THF, $l = 10$ cm).

IR (cm^{-1}): 1720 (C=O), 1645 (C=C), 1190 (COOR). $^1\text{H-NMR}$ (δ , ppm in CDCl_3): 5.9 (d, $J = 39$ Hz, 2H) $\text{CH}_2=\text{C}$; 4.2–5.0 (m, 2H) $-\text{C}-\text{CH}$; 3.25



SCHEME 1.

(s, 2H) $-\text{CH}_2\text{COO}-$; 1.1-2.3 (m, 18H) CH_2 in menthyl; 0.9 (d, $J = 1.2$ Hz, 12H) $(\text{CH}_3)_2\text{C}$; 0.72 (s, 6H) CH_3-C .

Analysis. Calculated for $\text{C}_{25}\text{H}_{42}\text{O}_4$: C = 73.85, H = 10.41%. Found: C = 73.62, H = 10.43%.

Homopolymerization and Copolymerization

Radical homopolymerizations of DMI were carried out with α, α' -azobisisobutyronitrile (AIBN) (0.01, 0.03, 0.10 mol/L) as initiator in benzene and in bulk at 50–80°C. After the required amounts of DMI monomer and benzene or THF containing a constant amount of AIBN were placed in a polymerization tube, it was degassed under vacuum (2.5×10^{-3} torr) by the ordinary freezing and thawing technique, as described earlier [21]. After polymerization, the solution was poured into a large amount of petroleum ether. To remove any unreacted DMI thoroughly, reprecipitation was repeated three times from THF/petroleum ether. The polymer was filtered and dried under vacuum.

Radical copolymerizations of DMI with ST, MMA, VAc, or CHMI were accomplished with AIBN as initiator in benzene at 50°C by the same technique. The composition of the copolymer obtained was determined by elemental analysis (C, H, and N).

Measurements

60 MHz ^1H -NMR spectra were recorded in CDCl_3 with TMS as internal standard with a Hitachi R-24 NMR spectrometer. IR spectra were obtained

on a Jasco IR-G infrared spectrometer (Japan Spectroscopic Co.) with thin films on KBr disks. UV spectra were obtained in THF solutions on a Shimadzu UV 200 A spectrophotometer. Optical rotatory dispersion (ORD) and circular dichroism (CD) measurements of polymers in THF solution were performed on a Jasco J-20C spectropolarimeter equipped with a xenon source and a computing data processor. *D*-line specific rotations were measured in THF solution on a Jasco DIP-140 digital polarimeter. GPC measurements were performed at 50°C with a Shimadzu LC3A liquid chromatograph equipped with a data processor (THF as solvent and Shimadzu polystyrene gel HGS-40-20-15 columns).

RESULTS AND DISCUSSION

Homopolymerization of DMI

Radical homopolymerizations of DMI were performed in benzene, THF, or in bulk. The results are summarized in Table 1. In solution polymerization, yields were very low (Runs A-1 to A-4), possibly due to steric hindrance of the two bulky *L*-menthyl groups. Accordingly, chiroptical measurements could not be made. However, homopolymers could be obtained in bulk in about 25-30% yield, with $[\alpha]_D^{20} = -76.9$.

Copolymerizations of DMI with Vinyl Monomers

Copolymerizations of DMI (M_1) with ST (M_2), CHMI (M_2), VAc (M_2), or MMA (M_2) were performed in benzene at 50°C with AIBN (25.0 mmol/L). All copolymerizations proceeded homogeneously throughout. The results of the copolymerizations are summarized in Table 2. Four types of copolymer composition curves are shown in Fig. 1. They indicate that the DMI content in the copolymer tends to increase with the DMI content in the monomer feed. Monomer reactivity ratios were determined by the Fineman-Ross method [22] and were refined by the curve-fitting method. Alfrey-Price [23] Q_1 and e_1 values were then calculated by assuming that $Q_2 = 1.0$ and $e_2 = -0.8$ for ST [24] (Table 3). Compared to the parameters for dimethyl or dibutyl itaconates, the r_1 values are generally smaller, which indicates that the homopolymerizability of DMI is low. The reason for this may be due to the steric hindrance of two bulky *L*-menthyl groups in the side chain.

TABLE 1. Result of Solution and Bulk Polymerizations of DMI^a

Run	Solvent, mL	AIBN, mmol/L	Polymerization temperature, °C	Yield, %	$\bar{M}_n^b \times 10^{-3}$	$\bar{M}_w/\bar{M}_n^b \times 10^{-4}$	$[\alpha]_D^{20}$ degree ^c	$[\theta]_{214}^{20}$ d	λ_C , nm ^c
A-1	Benzene (4 mL)	10	50	Trace	—	—	—	—	—
A-2	THF (4 mL)	10	50	Trace	—	—	—	—	—
A-3	Benzene (4 mL)	30	80	Trace	—	—	—	—	—
A-4	THF (4 mL)	30	80	Trace	—	—	—	—	—
A-5	None	30	80	25.0	5.23	2.8	-76.9	5380	178
A-6	None	100	80	30.5	1.59	11.2	-76.7	6020	171

^aDMI 2 g; polymerization time 48 h.^bDetermined by GPC.^cC 1.0%, THF, l 10 cm.^ddeg·cm²/dmol; c 1.0%, THF, l 1 mm.

TABLE 2. Results of Radical Copolymerizations of DMI (M_1) with Other Monomers in Benzene at 50°C^a

M_1 in monomer, mol%	M_2	Polymerization time, h	Yield, wt%	M_1 in copolymer, ^b mol%	$\bar{M}_n^c \times 10^{-3}$	\bar{M}_w/\bar{M}_n^c	$[\alpha]_D^{20}$, degree	λ_c , nm ^e
20.1	ST	17	7.9	24.3	6.2	5.4	-39.4	161
40.1		17	7.2	41.4	5.9	3.5	-48.4	160
50.4		17	6.4	53.2	4.8	3.6	-49.8	163
59.8		17	5.5	61.2	4.0	2.8	-52.1	163
79.8		17	2.7	68.5	3.7	2.9	-55.6	160
20.0	CHMI	7	10.1	21.3	13.0	19.9	-28.0	181
40.1		7	9.4	41.4	6.8	7.2	-46.1	181
49.7		7	7.2	46.8	2.8	4.8	-51.7	165
60.7		7	7.0	53.6	2.7	4.1	-56.1	164
79.7		7	3.1	63.6	4.8	1.8	-61.5	157

20.1	VAc	12	10.1	32.1	3.0	7.5	-63.0	129
38.7		12	11.0	45.5	6.3	3.2	-69.7	142
49.6		12	8.9	47.0	9.8	1.5	-70.1	134
61.4		12	7.8	41.0	2.2	2.9	-69.7	125
76.4		12	3.4	19.4	2.0	2.3	-68.1	128
20.7	MMA	7	6.8	8.9	54.1	1.9	-28.3	166
40.4		7	4.2	13.5	23.4	1.8	-41.3	145
49.6		7	3.3	16.2	10.2	3.3	-44.8	142
59.3		7	2.2	18.3	11.0	2.1	-46.0	130
78.7		14	1.9	17.9	2.0	3.6	-68.3	152

^a[AIBN] = 25 mmol/L; $M_1 + M_2 = 3.0$ g; benzene 8 mL.

^bCalculated from C analysis or from N analysis (for DMI-CHMI systems).

^cEstimated by GPC.

^dIn THF; l 10 cm.

^eBy ORD curves; in THF; l 10 cm.

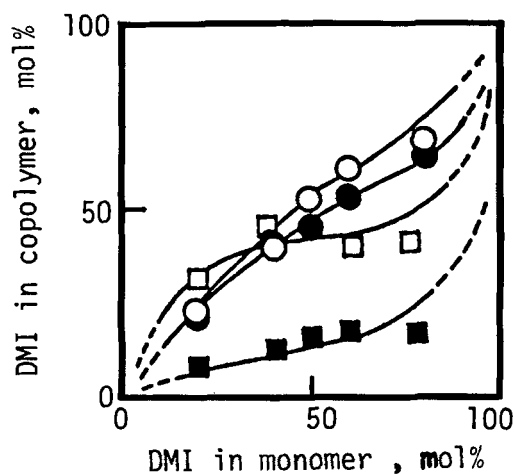


FIG. 1. Copolymer composition curves for (○) poly(DMI-co-ST), (●) poly(DMI-co-CHMI), (□) poly(DMI-co-VAc), and (■) poly(DMI-co-MMA).

TABLE 3. Copolymerization Parameters of Dialkyl Itaconates (DRI)

DRI, ^a M_1	M_2	Monomer reactivity ratios		Q_1	e_1
		r_1	r_2		
DMI	ST	0.56 ± 0.07	0.55 ± 0.08	0.76	0.29
DMI	MMA	0.0 ± 0.08	5.60 ± 0.1	—	—
DMI	VAc	0.0 ± 0.07	0.25 ± 0.08	—	—
DMI	CHMI	0.31 ± 0.08	0.56 ± 0.09	—	—
CH ₃ —	ST	0.14	0.48	0.56	0.84
CH ₃ —	MMA	0.3	1.3	—	—
C ₄ H ₉ —	ST	0.38	0.40	0.83	0.57
C ₄ H ₉ —	MMA	0.4	0.8	—	—
C ₄ H ₉ —	VAc	6.3	0.02	—	—

^aDMI = di-*l*-menthyl itaconate, CH₃— = dimethyl itaconate, C₄H₉— = di-*n*-butyl itaconate.

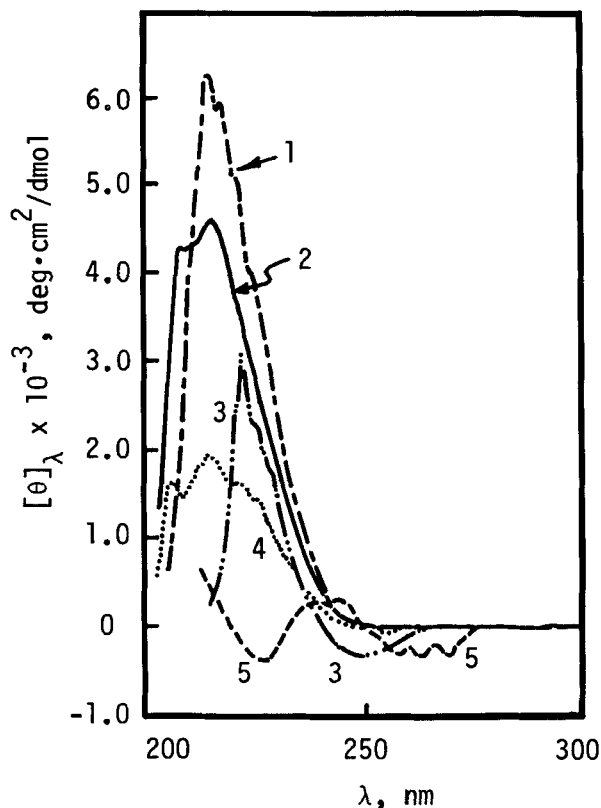


FIG. 2. CD curves for (1) poly(DMI), (2) poly(DMI-co-VAc), (3) poly(DMI-co-CHMI), (4) poly(DMI-co-MMA), and (5) poly(DMI-co-ST).

Chiroptical Properties of the Copolymers

The homopoly(DMI), poly(DMI-co-ST)s, poly(DMI-co-CHMI)s, poly(DMI-co-VAc)s, and poly(DMI-co-MMA)s had negative optical activity, as shown in Tables 1 and 2. The absolute values of the specific rotation for each copolymer system increased with increasing DMI content in the copolymer.

Circular dichroism (CD) curves for the polymers are shown in Fig. 2. The CD peaks of poly(DMI-co-ST) (50 mol% DMI in monomer feed) are in the range 250–275 nm. The molecular ellipticities $[\theta]$ were about -100 to -550 $\text{deg}\cdot\text{cm}^2/\text{dmol}$. This may be ascribed to the $\pi\rightarrow\pi^*$ transition based on the phenyl group of the monomeric unit of ST. That is, poly(DMI-co-ST)s showed

induced optical activity of the nonchiral co-unit (i.e., ST) owing to the preferential chirality of the main chain.

In the cases of poly(DMI), poly(DMI-co-VAc), and poly(DMI-co-MMA), very small and negative CD peaks ($[\theta]_{250} = -18$ to $-52 \text{ deg}\cdot\text{cm}^2/\text{dmol}$) owing to the $n \rightarrow \pi^*$ transition of carbonyl groups were observed at about 250 nm. In the poly(DMI-co-CHMI) samples, however, significant negative CD peaks due to the $n \rightarrow \pi^*$ transition of carbonyl groups were observed at about 250 nm, as shown in Fig. 2. The absolute ellipticities ($[\theta] = -150$ to $-486 \text{ deg}\cdot\text{cm}^2/\text{dmol}$) at 251 nm decreased with increasing DMI content of the copolymer. The results suggest that poly(DMI-co-CHMI) also displayed induced optical activity of the nonchiral co-unit (i.e., CHMI) owing to the preferential chirality of the main chain.

Poly(DMI), poly(DMI-co-VAc), and poly(DMI-co-MMA) had very large and positive CD peaks at $215 \pm 2 \text{ nm}$ (Fig. 2). These CD peaks and their magnitudes were reconfirmed by use of a 0.1-mm quartz cell for the measurements. The magnitude of the molecular ellipticities $[\theta]$ at $215 \pm 2 \text{ nm}$ tends to increase with increasing DMI content in each copolymer system.

CONCLUSIONS

(1) A novel type of optically active di-*L*-menthyl itaconate (DMI) was synthesized and polymerized in bulk with a radical initiator to obtain chiral polymers. The specific rotation, $[\alpha]_D$, and the molecular ellipticities $[\theta]_{214}^{20}$ of the homopolymers obtained were -76.9 and 5400 to $6000 \text{ deg}\cdot\text{cm}^2/\text{dmol}$, respectively. The number-average molecular weights were 5400 to 6000 .

(2) The monomer reactivity ratios r_1 , r_2 and the Alfrey-Price Q , e values were obtained (Table 3). The number-average molecular weights of the copolymers were 2000 – $54\,000$, and the specific rotations $[\alpha]_D$ of the copolymers were -28 to -70 .

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