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Synthesis and Polymerization of *N*-(*L*-Menthylcarboxylatomethyl)maleimide

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SYNTHESIS AND POLYMERIZATION OF *N*-(L-MENTHYLCARBOXYLATOMETHYL)MALEIMIDE

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ABSTRACT

A new type of optically active *N*-(L-menthylcarboxylatomethyl)maleimide (MGMI) was synthesized from maleic anhydride, glycine, and L-menthol. Radical homopolymerization of MGMI was performed at 50°C for 24 h to give optically active polymer having $[\alpha]_D = -57^\circ$. Radical copolymerizations of MGMI (M_1) were performed with styrene (ST, M_2), methyl methacrylate (MMA, M_2) in benzene at 50°C. From the results, the monomer reactivity ratios (r_1 , r_2) and the Alfrey-Price Q , e values were determined as follows: $r_1 = 0.16$, $r_2 = 0.006$ for the MGMI-ST system; $r_1 = 0.15$, $r_2 = 1.65$ for the MGMI-MMA system, and $Q_1 = 0.72$, $e_1 = 1.59$ calculated from the MGMI-MMA system. Anionic homopolymerizations of MGMI were also carried out. Chiroptical properties of the polymers were investigated.

INTRODUCTION

There have been many reports including patents on polymerization and copolymerization of *N*-substituted maleimide (RMI) [1–5]. However, only a few investigations have been made on polymerization of optically active RMI [6, 7]. We also reported on the polymerization reactivity and chiroptical properties of chiral *N*-(α -methylbenzyl)maleimide (MBZMI) [8]. Polymerizations of cycloalkene derivatives can yield two *trans*-addition, i.e., chiral centers of (S,S) and (R,R). If one is produced more than the other, the obtained polymer can be optically active [9]. We

reported that asymmetric polymerizations of nonchiral RMI were performed with *n*-BuLi/(-)-Sparteine(Sp) to obtain chiral poly(RMI) containing relatively high specific rotation ($[\alpha]_D = -40^\circ$, RMI = *N*-cyclohexylmaleimide) [10]. The asymmetry could be attributable to a three-diisotactic structure of RMI polymer main chain, i.e., the helical structure and/or the excessive chiral center of (S,S) or (R,R) [10].

In this paper, a novel, optically active *N*-(L-menthylcarboxylatomethyl)maleimide, i.e., *N*-(L-menthyl glycinyl) maleimide (MGMI), is prepared from maleic anhydride, glycine, and L-menthol. MGMI is polymerized and copolymerized with styrene (ST) and methyl methacrylate (MMA) in the presence of radical initiator. From the results, monomer reactivity ratios and *Q-e* values are determined. From specific rotation and molecular ellipticity measurements of the copolymers, asymmetric induction into the copolymer main chain is discussed. MGMI is polymerized with anionic initiator, *n*-BuLi, to obtain chiral polymer. The structural difference of the MGMI polymer obtained with radical or anionic initiator is described. In addition, attempts to resolve racemic compounds are made, by using the obtained polymers as chiral stationary phases in high-performance liquid chromatography (HPLC).

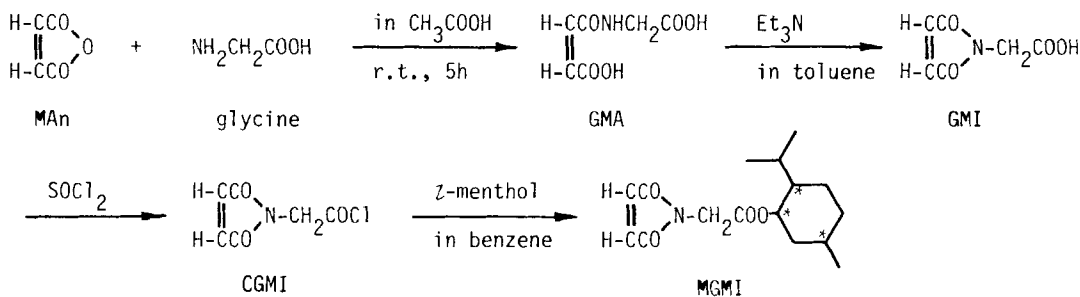
EXPERIMENTAL

MGMI Monomer

MGMI monomer was synthesized from maleic anhydride, glycine, and L-menthol, as shown in Scheme 1.

N-Glycinyl Maleamic Acid (GMA)

A mixture of 47.1 g (1.5 mol) of maleic anhydride (MAN) and 112.6 g (1.5 mol) of glycine in 1600 mL of acetic acid was stirred for 5 h at r.t. The product was filtered and dried. Crude GMA was recrystallized from methanol to obtain pure GMA: yield 95%; mp. 197°C. IR (cm^{-1}): 3450 (OH), 3290 (NH), 2500–2700 (COOH), 1715 (C=O), 1670 (CONH), 1610 (HC=CH), 1550–1450 (CONH), 1220 (C–O), 695 (*cis*-CH=CH). ^1H NMR (chemical shift: δ , ppm from tetramethylsilane (TMS) in d_6 -DMSO): 9.13 (*m*, 1H, NH), 6.33 (*d*, $J = 3.1$ Hz, 2H, CH=CH), 5.91 (*d*, $J = 6.2$ Hz, 2H, CH₂).



SCHEME 1.

N-Glycinyll Maleimide (GMI)

A mixture of 125.1 g (0.72 mol) of GMA and 152.9 g (1.5 mol) of triethylamine in 3500 mL of toluene was mechanically stirred until the theoretical amount of water was removed. After the reaction, the toluene layer was decanted and the solvent was evaporated to give the *N*-glycinylltriethylammonium salt. Hydrochloric acid was added to the salt to adjust the solution to pH 1. The product was extracted with ethyl acetate, and the organic layer was separated and dried with magnesium sulfate. The ethyl acetate was evaporated out to obtain crude GMI, which was recrystallized from chloroform; yield 31%. After the decantation, the residue, i.e., dark brown oil, was also treated with hydrochloric acid to make it pH 1. The treatment was the same procedure as described above to obtain crude GMI. Total yield: 42%; mp. 118°C (lit. [11] 113.5°C). IR (KBr disk), wave number (cm^{-1}): 3100 (COOH), 3000 (CH), 2700–2300 COOH, 1775, 1745, 1690 (C=O), 1620 (HC=CH), 1440 (CH_2), 1190 (C–O–), 690 (*cis*-CH=CH–). ^1H NMR (δ , in ppm from TMS in d_6 -DMSO): 12.65–11.75 (*s*, 1H, COOH); 6.78 (*s*, 2H, CH=CH); 4.01 (*s*, 2H, CH_2). Results of elemental analysis (%): Found, C = 46.19, H = 3.32, N = 8.66; Calcd. for $\text{C}_6\text{H}_5\text{NO}_4$; C = 46.46, H = 3.25, N = 9.03.

N-[(Chloroformyl)methyl]maleimide (CGMI)

A solution of 20 g (0.13 mol) of GMI in 70 mL of thionyl chloride was refluxed for 2 h. After the reaction was completed, thionyl chloride was removed, and the residue was distilled under reduced pressure to give CGMI bp. 85–87°C/ 1.6×10^{-2} mmHg; 17.2 g (76%). IR (neat), (cm^{-1}): 1790 (COCl), 1715 (C=O), 1415 (CH_2), 1145 (C–O–), 695 (*cis*-CH=CH–). ^1H NMR (δ , ppm from TMS in CDCl_3): 6.80 (*s*, 2H, CH=CH), 4.65 (*s*, 2H, CH_2).

N-(*L*-Menthyl Glycinyll)maleimide (MGMI)

A mixture of CGMI (17.2 g: 0.098 mol) and *L*-menthol (15.4 g: 0.099 mol) in benzene was refluxed for 2 h to obtain crude MGMI. After the benzene solution of MGMI was treated with column chromatography packing of activated alumina, crude MGMI was distilled under reduced pressure three times to obtain pure MGMI (58% yield based on CGMI; bp. 154–155°C/ 8.5×10^{-2} mmHg); $[\alpha]_D = -48.1^\circ$ ($C = 1.0$; $l = 10$ cm; THF). IR (cm^{-1}): 1750 and 1730 (C=O); 1640 (C=C); 1200 and 1170 (OC=O). ^1H NMR (δ , ppm from TMS in CDCl_3): 6.68 (*s*, 2H) CH=CH; 4.70 (*m*, 1H) O–CH–; 4.20 (*s*, 2H) N– CH_2 CO; 2.18–0.70 (*m*, 18H) protons in menthyl. Elemental analysis (%): Found, C = 68.30, H = 8.24, N = 4.98; Calcd. for $\text{C}_{16}\text{H}_{23}\text{O}_4\text{N}$, C = 68.57, H = 8.28, N = 5.09.

Model Compound of Poly (MGMI):

N-(*L*-Menthylcarboxylatomethyl)succinimide (MGSI)

MGSI was prepared from succinic anhydride, glycine, and *L*-menthol, according to a method similar to that of MGMI. Yields and mp. or bp. are as follows: *N*-(*L*-glycinyll)succinamic acid (GSA): yield 98%; mp. 150–153°C; *N*-(*L*-glycinyll)succinimide (GSI): yield 63%, mp. 111–116°C, *N*-(*L*-chloroformylmethyl)succinimide (CGSI) recrystallized from benzene (50)/cyclohexane (50): yield 93%, mp. 81–84°C.

MGSI: yield 42%; bp. $145^{\circ}\text{C}/2 \times 10^{-2}$ mmHg; $[\alpha]_{\text{D}} = -47.6^{\circ}$ ($c = 1.0$ g/dL, $l = 5$ cm, THF). IR (cm^{-1}): 1753 and 1732 (C=O); 1200 and 1170 (OC=O). ^1H NMR (δ , ppm from TMS in CDCl_3): 4.45–4.98 (m , 1H) O—CH— in menthyl group; 4.15 (s , 2H) $N\text{-CH}_2\text{CO}$; 2.72 (s , 4H) $\text{CH}_2\text{-CH}_2$; 2.41–0.65 (m , 18H) protons in menthyl.

Other Materials

Styrene (ST), methyl methacrylate (MMA), tetrahydrofuran (THF), toluene, and methanol were purified by the usual methods. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. Commercially available *n*-butyllithium (*n*-BuLi) hexane solution was used without further purification.

Homopolymerization and Copolymerization

Radical homopolymerization and copolymerization were carried out with 2,2'-azobisisobutyronitrile (AIBN, mp. 102°C) as an initiator in benzene or THF in a sealed tube at 50°C . After polymerization, the polymer solution was poured into a large amount of methanol. To remove an unreacted optically active monomer, reprecipitation was repeated three times from THF-methanol. Composition of the copolymer obtained was determined by nitrogen analysis.

Anionic homopolymerization and copolymerization were achieved in toluene at 0° and -78°C by using *n*-BuLi as a catalyst under a nitrogen atmosphere. The polymerization was terminated with a few drops of methanol by using a syringe. The solution was poured into a large amount of methanol to precipitate the polymer, which was filtered and dried. The obtained polymers were purified with reprecipitation from the THF solution into methanol three times.

Measurements

D-line specific rotations were measured with a Jasco DIP-140 (Japan Spectroscopic Co.) at room temperature. Optical rotatory dispersion (ORD) and circular dichroism (CD) spectra were obtained at room temperature by a Jasco J-20C (Japan Spectroscopic Co.), equipped with a xenon source and a computing data processor. Molecular weight of polymers was measured by gel permeation chromatographic (GPC) analysis using the technique described in an earlier paper [12]. IR and NMR spectra were obtained and elemental analysis was carried out, using the same instruments as reported previously [13].

RESULTS AND DISCUSSION

Radical and Anionic Homopolymerization of MGMI

Radical and anionic polymerizations of MGMI were performed under several conditions. The results are summarized in Table 1. The polymerizations proceeded homogeneously throughout. The obtained polymers were white powders and had negative optical activity. In radical homopolymerization, specific rotations $[\alpha]_{\text{D}}$ of polymers were about -57° , whose absolute values were larger than those (-41 to

TABLE 1. Radical and Anionic Polymerization of MGMI

Run	MGMI (mol/L)	AIBN (<i>n</i> -BuLi) $\times 10^2$ (mol/L)	Polym. solvent ^a (mL)	Polym. temp. (°C)	Polym. time (h)	Conversion (%)	<i>N</i> -analysis (%)	\bar{M}_n^b $\times 10^{-4}$	\bar{M}_w/\bar{M}_n^b	$[\alpha]_D^c$ (deg)
1-1	0.81	1.0	Ben(2)	50	24	48.6	4.46	2.9	1.4	-56.1
1-2	0.82	3.0	Ben(2)	50	24	76.4	4.46	2.5	1.4	-57.0
1-3	0.81	1.0	THF(2)	50	20	89.1	4.38	3.1	1.5	-58.1
1-4	1.5	3.0	THF(2)	50	20	90.1	4.39	3.0	1.7	-57.8
1-5	0.81	(3.0) ^d	Tol(6)	0	24	71.0	4.98	3.2	1.3	-41.1
1-6	1.2	(3.0) ^d	Tol(6)	-78	24	46.3	4.96	1.4	1.6	-43.7
1-7	0.82	(3.0) ^d	THF(6)	0	24	59.4	4.84	2.4	1.4	-44.0
1-8	0.83	(3.0) ^d	THF(6)	-78	24	95.0	4.29	1.9	1.5	-44.8

^aBen: benzene; THF: tetrahydrofuran; Tol: Toluene.^bBy GPC.^c $c = 1.0$, THF, $l = 10$ cm, r.t.^d*n*-BuLi.

-44.8°) obtained from anionic polymerizations. The higher the concentration of AIBN, the better were the yields of the polymers. But specific rotations and number-average molecular weight (M_n) were almost similar. In anionic polymerization, the yields were influenced by the solvents and the temperatures. M_n for the polymer obtained at low temperature (-78°C) was lower than that at high temperature (0°C). The M_n and polydispersity [weight-average molecular weight (M_w)/ M_n] were as follows: 2.5×10^4 to 3.1×10^4 and 1.4–1.7 for the polymers obtained by the radical initiator and 1.4×10^4 to 3.2×10^4 and 1.3–1.6 for the polymers obtained by the anionic initiator.

ORD spectra for the homopolymers obtained with radical and anionic initiators were found to fit the simple Drude equation. CD spectra for the polymers are shown in Fig. 1. In the polymer obtained with radical initiator, a large positive and a small negative CD peak were observed at about 220 nm and 250 nm, respectively. Both peaks were thought to be attributable to $n \rightarrow \pi^*$ transition of the two carbonyl groups in the imide ring. In the CD spectrum for the polymer obtained with *n*-BuLi, the CD pattern was quite different from that for the polymer obtained with AIBN. That is, the CD peak for the polymers obtained with anionic initiator at about 250 nm was not negative but was clearly positive. The CD pattern for the polymer obtained with AIBN was almost the same as that for a model compound of poly-

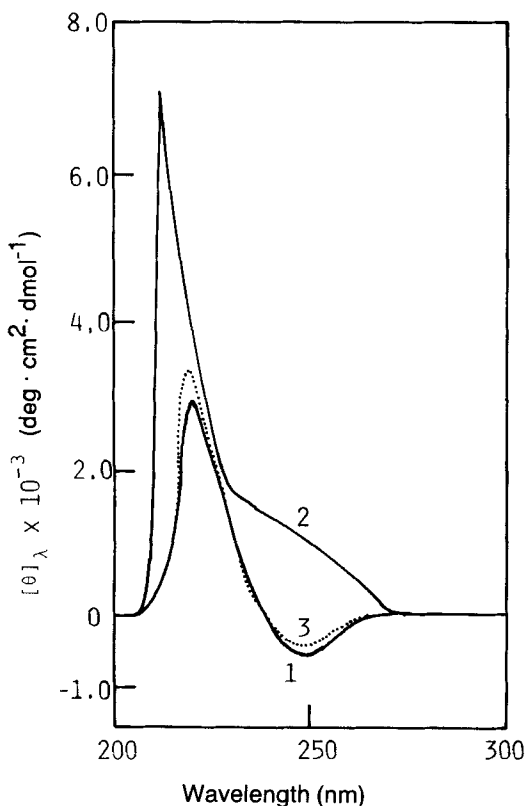
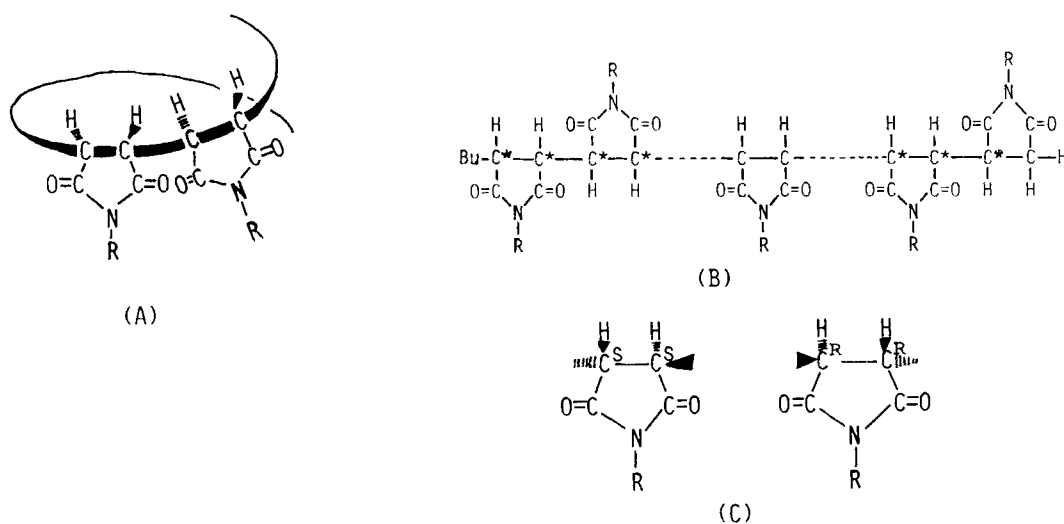


FIG. 1. CD scans for (1) poly(MGMI) obtained with AIBN (run 1-1), (2) poly(MGMI) obtained with *n*-BuLi (run 1-5), and (3) model compound of poly(MGMI); MGSI.

(MGMI), i.e., *N*-(*L*-menthylcarboxylatomethyl)succinimide (MGSI), as shown in Fig. 1. This suggests that asymmetry of the polymer obtained with AIBN can be ascribed to the *N*-substituent, a chiral menthyl group. The reason may be that the polymer obtained with radical initiator contains almost atactic polymers. It seems that the chirality of the polymer obtained with *n*-BuLi can be attributed both to the chiral menthyl group and to other chiral factors. There are thought to be three types, as illustrated in Scheme 2. In type A, chirality of the polymer may be attributable to a helical conformation of the three-diisotactic polymer main chain. Type B is asymmetric induction around both the terminal MGMI units of the polymer. In type C, chirality is attributable to excessive chiral centers of (*R,R*) or (*S,S*) in the polymer main chain.

Cubbon reported [2] that eight *N*-substituted maleimide monomers (RMI) were polymerized by free radical and *n*-BuLi, and that both types of initiator gave rise to polymers that contain a predominantly three-diisotactic polymer based only on X-ray analysis. According to his paper [2], RMI polymers may not be completely stereoregular and predominantly three-diisotactic with occasional three-disyndiotactic placements that disrupt the crystallinity to some extent. In addition, he reported [2] that the stereospecificity of RMI polymers arises as a result of the geometry of the monomer unit, which requires *trans* opening of the double bonds and leads to the formation of a helix. Our MGMI polymers obtained from radical and anionic initiators were not crystalline but amorphous, as judged from X-ray diffraction diagrams shown in Fig. 2. The temperature dependence and solvent effect on the specific rotation for the polymers are shown in Fig. 3. In the poly(MGMI) obtained with AIBN (1 in Fig. 3), linear relation was observed and the slopes were very small. In the poly(MGMI) obtained with *n*-BuLi (2 in Fig. 3), similar trends were observed. These suggest that the main chains of poly(MGMI) scarcely contain a helical structure, i.e., type A in Scheme 2.

¹H NMR spectra for polymers obtained with AIBN or *n*-BuLi, as shown in



SCHEME 2.

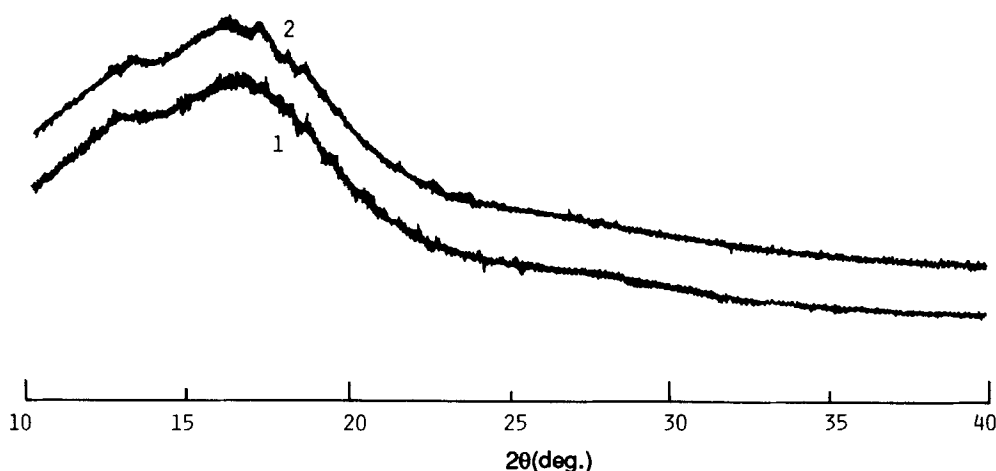


FIG. 2. X-ray diffraction diagrams for (1) poly(MGMI) obtained with AIBN (run 1-1) and (2) Poly(MGMI) obtained with *n*-BuLi (run 1-5).

Fig. 4, were in general similar. But peaks at about 3.5 ppm assigned to main-chain protons (a in Fig. 4) and peaks at about 4.2 ppm due to methylene protons (b in Fig. 4) in NMR for the polymers obtained with *n*-BuLi were broader than those for the polymer obtained with AIBN. This suggests that the protons exist in the region of complicated structure, that is, three-diisotactic structure. ^{13}C NMR spectrum for the polymer obtained with *n*-BuLi is shown in Fig. 5. The spectrum was similar to that obtained with AIBN. But the peaks for carbons (3 and 4 in Fig. 5) in poly-(MGMI) obtained with *n*-BuLi were more complicated than those obtained with AIBN. IR spectra for both polymers were almost the same. Thus, it may be concluded that the chirality for the polymer obtained with *n*-BuLi was attributable to excessive chiral center of (S,S) or (R,R) (type C in Scheme 2). In this case, more than four successive units of (S,S) or (R,R) may not exist, since more than a four-unit sequence of (S,S) or (R,R), i.e., a continuous three-diisotactic structure, must produce a helix. This can be confirmed by inspection of the poly(MGMI) model. Cubbon [2] also reported that inspection of the RMI polymer model indicates that three-diisotactic polymers can form the 3_1 helix in which the repeat distance is 4.7 Å, and that the diameter of the helix with no substituents on the nitrogen is about 10 Å. However, there is scarcely helical structure in our poly-(MGMI), as described above. Consequently, poly(MGMI) obtained with *n*-BuLi may take an almost linear structure, as illustrated in Scheme 3. Asymmetric induction around both the terminal MGMI units of the polymers (type B in Scheme 2) may not be ignored.

Radical Copolymerizations of MGMI with ST and MMA

The results of radical copolymerizations of MGMI (M_1) with ST (M_2), MMA (M_2) in benzene (6 mL) at 50°C in the presence of AIBN (1.0×10^{-2} mol/L) are summarized in Table 2. Copolymerization proceeded homogeneously throughout. The obtained copolymers were white powders and optically active. Copolymer-

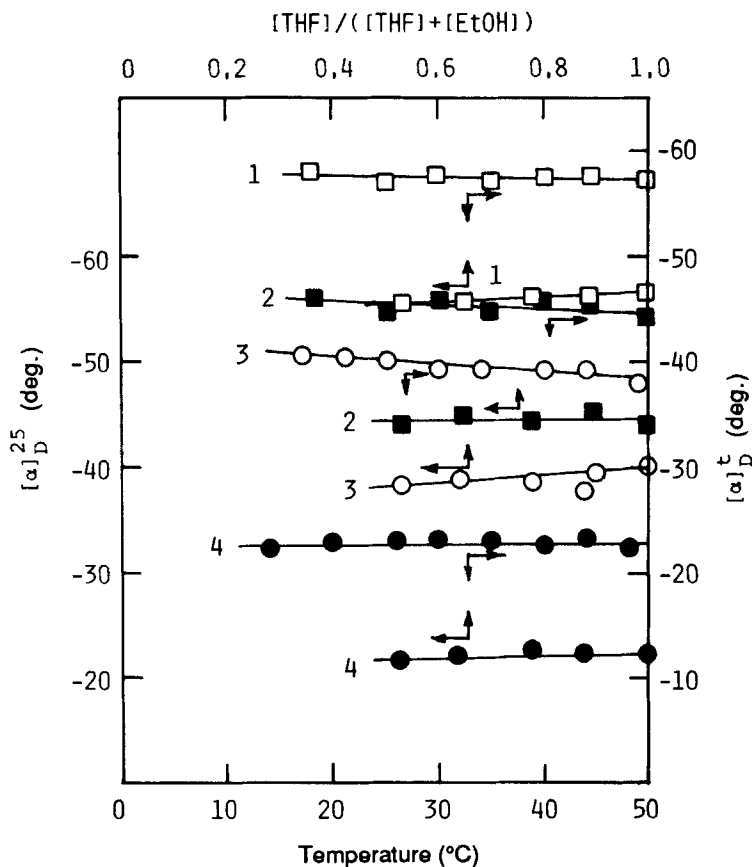


FIG. 3. Temperature dependence and solvent effect on the specific rotation $[\alpha]_D$: (1) poly(MGMI) obtained with AIBN (run 1-1), (2) poly(MGMI) obtained with *n*-BuLi (run 1-5), (3) poly(MGMI-*co*-ST) (run 2-3), and (4) poly(MGMI-*co*-MMA) (run 3-3).

composition curves of poly(MGMI-*co*-ST)s and poly(MGMI-*co*-MMA)s are shown in Fig. 6. Monomer reactivity ratios, r_1 and r_2 , were determined as $r_1 = 0.12$, $r_2 = 0.006$ in the MGMI-ST system and $r_1 = 0.15$, $r_2 = 1.65$ in the MGMI-MMA system, according to the Mayo-Lewis [14] method. The Alfrey-Price [15] Q - e values for MGMI were calculated from the MGMI-MMA system as $Q_1 = 0.72$, $e_1 = 1.59$. These copolymerization parameters were similar to those for other RMI reported previously [16].

Optical Behavior of Copolymers

Figure 7 shows the relationship between the specific rotation and content (wt%) of the monomeric unit of MGMI in both copolymer systems. The absolute values of specific rotations of poly(MGMI-*co*-ST)s increased with the content of MGMI unit. However, a little deviation from the linearity was observed, which suggests that asymmetrical induction occurred in the main chain of the copolymers. In poly(MGMI-*co*-MMA)s, the same tendency could be observed. In CD spectra

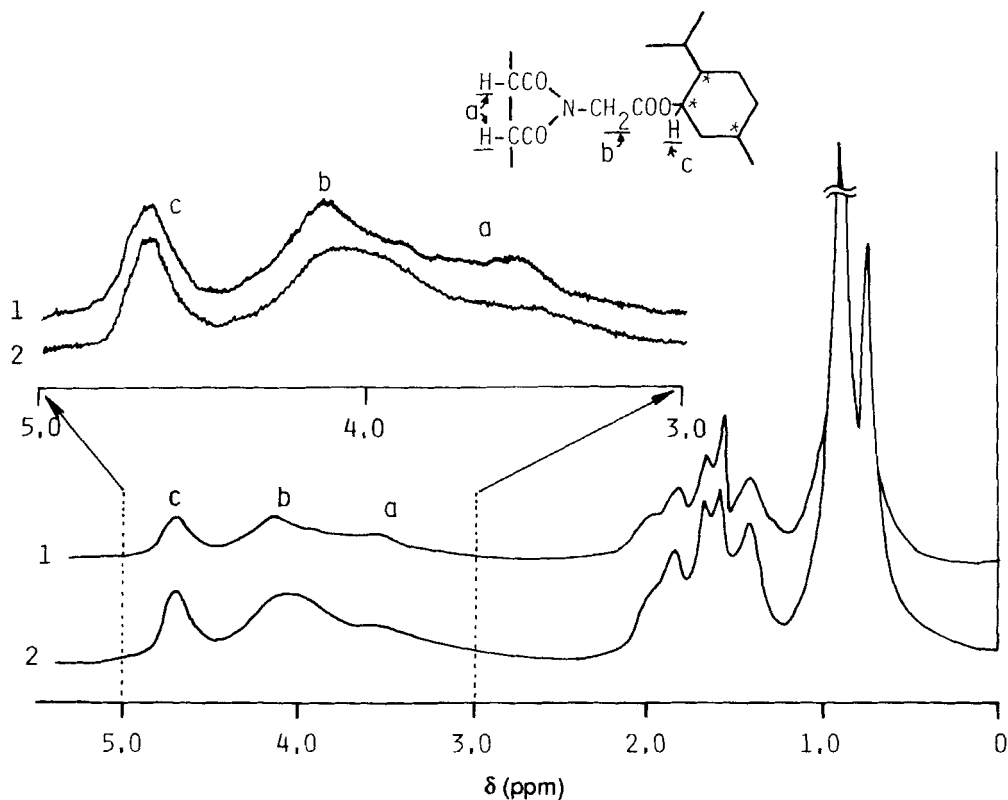


FIG. 4. ^1H NMR spectra for: (1) poly(MGMI) obtained with AIBN (run 1-1) and (2) poly(MGMI) obtained with *n*-BuLi (run 1-5).

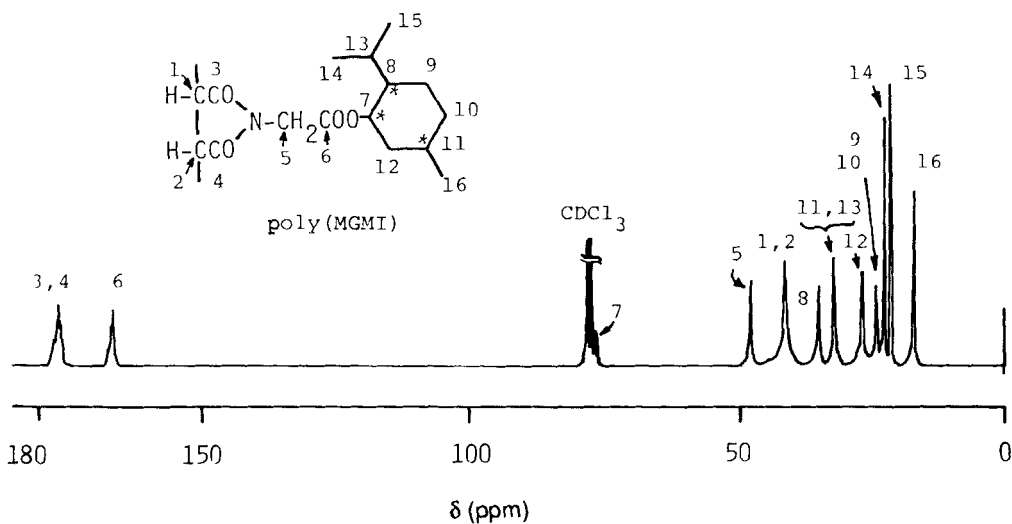
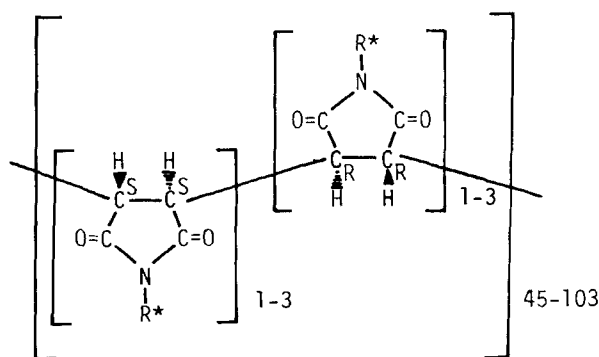


FIG. 5. ^{13}C NMR spectrum for poly(MGMI) obtained with *n*-BuLi (run 1-5).



SCHEME 3.

for poly(MGMI-*co*-ST)s, as shown in Fig. 8, a negative and a positive peak around 250 and 225 nm are ascribed to the $\pi \rightarrow \pi^*$ transition of phenyl groups of the ST unit and to the $n \rightarrow \pi^*$ transition of carbonyl groups of the MGMI unit, respectively. In poly(MGMI-*co*-MMA)s, both peaks at about 215 and 250 nm also contain the contribution to the $n \rightarrow \pi^*$ transition of carbonyl groups of the MMA unit. Figure 9 shows the relationships between molecular ellipticity $[\theta]$ and content of the monomeric unit of MGMI in the copolymers. All the relationships gave rise to deviations from linearity, which suggests that asymmetry was introduced into the copolymer main chain. As shown in Fig. 3 (3 and 4), the relationship between optical rotation of copolymers and temperature gave linearity, and the same tendency was recognized in the relationship between optical rotation and the solvent. Judged from the temperature and solvent dependence on the specific rotations, it seemed that there was no helical conformation in the copolymers. Figure 10 illustrates the dependence of a diad sequence [17, 18], $P_2 [m_1 m_2]$, on the specific rotations. The $P_2 [m_1 m_2]$ values indicate the probability of a MGMI-ST or a MGMI-MMA dyad sequence. In the MGMI-ST system, linear relationship was not clear because of the alternating copolymer. But in the MGMI-MMA system, a linear relationship was clearly observed. This suggests that a new asymmetric center appeared in the copolymer main chain by addition of a ST or a MMA monomer to a growing chain end of MGMI, as shown in Scheme 4 (C^* is a chiral carbon).

Attempts to Resolve Racemic Compounds

A macroporous spherical silica gel particles, Lichrospher SI 1000 (Merck), was silicized from a large amount of dichlorodiphenylsilane [19]. The silicized gel (2.5 g) was coated with the obtained polymer (run 1-4, 0.5 g), by using THF as solvent, according to the method reported previously [20]. Attempts were made to resolve several racemic compounds, DL-menthol, DL- α -methyl ethyl alcohol, DL-mandelic acid, DL-phenylalanine, DL- α -methylbenzylamine, and 1,1-bi-2-naphthol, with the column (theoretical plate numbers for benzene of 3200, flow rate of 0.5 mL/min) by using methanol as eluent at 20°C. Resolution of the racemic compounds was unsuccessful under these conditions. We still try to resolve many racemic compounds with the column prepared from other poly(MGMI)s and the copolymers under several conditions.

TABLE 2. Radical Copolymerization of MGMI (M_1) with ST (M_2) or MMA (M_2) in Benzene (6 mL) at 50°C^a

Run ^b	M_2	M_1 in monomer (mol%)	Polym. time (h)	Conversion (%)	N-analysis (%)	M_1 in copolymer (mol%)	$\bar{M}_n^b \times 10^{-4}$	\bar{M}_w/\bar{M}_n^b	$[\alpha]_D^c$ (deg)
2-1	ST	23.3	0.5	11.3	3.35	48.9	7.0	1.01	-39.1
2-2	ST	40.2	0.5	10.5	3.49	53.1	7.1	1.01	-39.8
2-3	ST	51.7	0.5	9.6	3.58	56.0	6.8	1.01	-41.1
2-4	ST	60.2	0.5	7.1	3.52	54.0	6.6	1.01	-41.1
2-5	ST	78.5	2.0	5.8	3.61	57.0	6.3	1.01	-41.7
3-1	MMA	20.2	2.5	6.8	1.43	13.0	5.8	1.01	-14.6
3-2	MMA	39.7	2.5	7.3	1.56	14.5	5.8	1.01	-14.3
3-3	MMA	51.8	4.0	8.1	2.14	22.5	4.5	1.13	-23.4
3-4	MMA	59.1	4.0	7.7	2.53	29.1	4.5	1.11	-27.7
3-5	MMA	78.0	4.0	7.5	3.64	57.0	3.3	1.33	-38.4

^a[AIBN] = 1.0×10^{-2} mol/L; $M_1 + M_2 = 3.0$ g.^bBy GPC.^c $c = 1.0$, THF, $l = 10$ cm, at r.t.

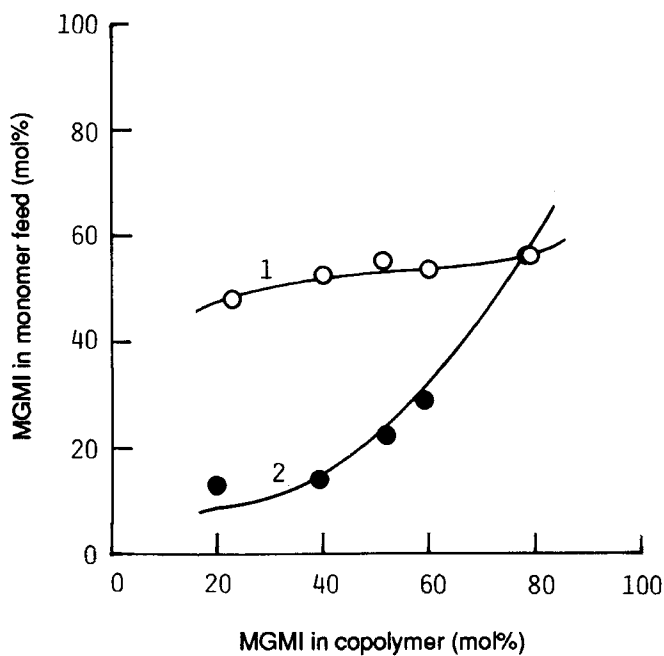


FIG. 6. Copolymer composition curves for (1) MGMI-ST and (2) MGMI-MMA system.

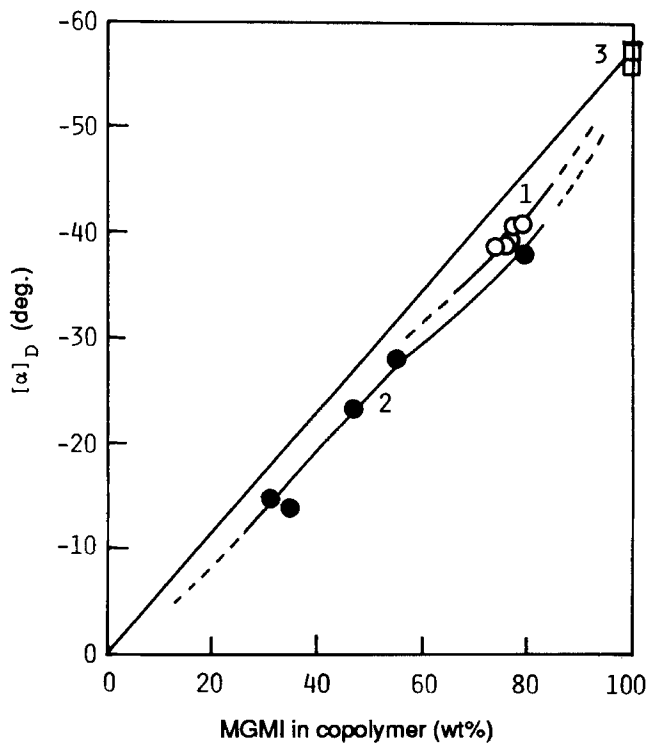


FIG. 7. Relationships between specific rotation $[\alpha]_D$ and content of the monomeric unit MGMI in copolymers: (1) poly(MGMI-co-ST), (2) poly(MGMI-co-MMA), and (3) poly(MGMI) obtained from AIBN (runs 1-1 to 1-4).

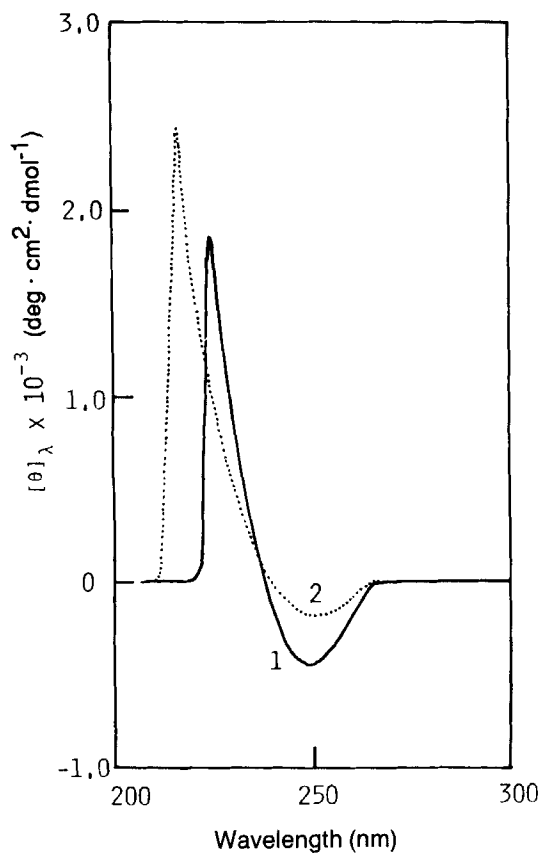


FIG. 8. CD scans for (1) poly(MGMI-co-ST) (runs 2-3) and (2) poly(MGMI-co-MMA) (run 3-3).

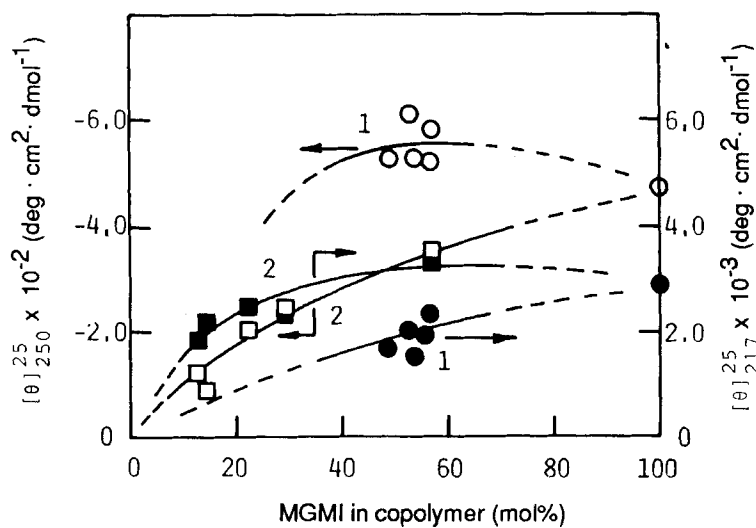


FIG. 9. Relationships between molecular ellipticities $[\theta]$ and content of the monomeric unit MGMI in copolymers: (1) poly(MGMI-co-ST) and (2) poly(MGMI-co-MMA).

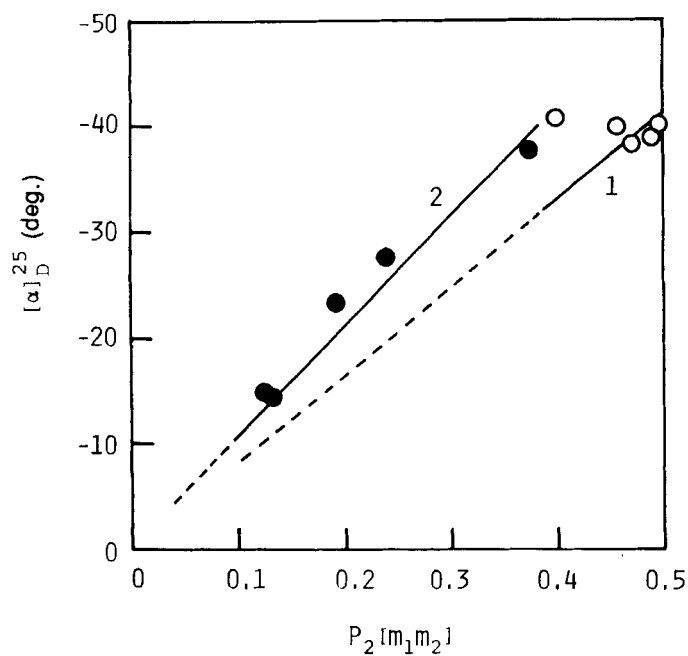
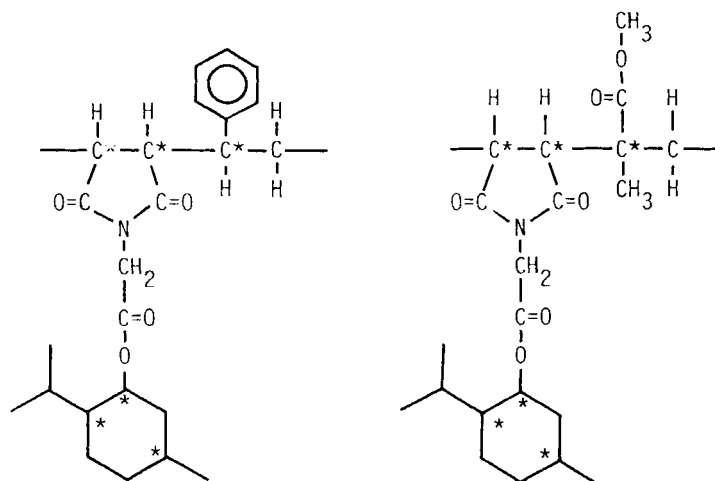


FIG. 10. Relationships between specific rotation $[\alpha]_D$ of the copolymer and $P_2 [m_1 m_2]$: (1) poly(MGMI-co-ST) and (2) poly(MGMI-co-MMA).



SCHEME 4.

CONCLUSIONS

1. A novel type of optically active *N*-(*L*-menthylcarboxylatomethyl)-maleimide (MGMI) was synthesized and polymerized with radical and anionic initiator to obtain chiral polymers.

2. Conformation of MGMI polymer obtained with anionic initiator was different from that of the polymer obtained with radical initiator.

3. From the results of radical copolymerizations of MGMI (M_1) with ST (M_2) or MMA (M_2), monomer reactivity ratios (r_1 , r_2) and Q - e values were determined as follows: $r_1 = 0.16$, $r_2 = 0.006$ in the MGMI-ST system, $r_1 = 0.15$, $r_2 = 1.65$, $Q_1 = 0.72$, $e_1 = 1.59$ in the MGMI-MMA system.

4. Asymmetric induction copolymerization took place in the MGMI-ST and MGMI-MMA systems.

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