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Synthesis and Polymerization of *N*-[[[*N'*-(α-Methylbenzyl)amino]carbonyl]methyl]maleimide

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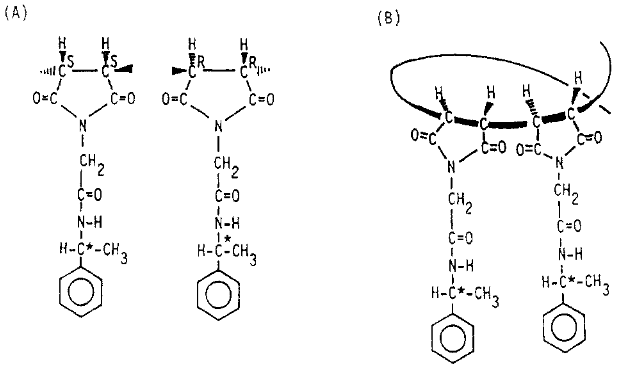
ABSTRACT: A novel type of optically active *N*-[[[*N'*-(α-methylbenzyl)amino]carbonyl]methyl]maleimide (MBCM) was synthesized from maleic anhydride, glycine, and (*R*)-(+)-α-methylbenzylamine. Radical homopolymerizations of MBCM were performed in several solvents at 70 and 150 °C for 22 h to give optically active polymers having $[\alpha]^{25}_{D} = 50.3 - 62.5°$. Radical copolymerizations of MBCM (M_1) were performed with styrene (ST, M_2) and methyl methacrylate (MMA, M_2) in dioxane at 70 °C. The monomer reactivity ratios (r_1 and r_2) and the Alfrey-Price *Q* and *e* values were determined to be as follows: $r_1 = 0.083$, $r_2 = 0.30$, $Q_1 = 0.72$, and $e_1 = 1.12$ in the MBCM/ST; $r_1 = 0.19$, $r_2 = 0.95$, $Q_1 = 1.32$ and $e_1 = 1.71$ in the MBCM/MMA system. Chiroptical properties of the polymers were also investigated.

Introduction

There have been many reports on polymerizations and copolymerizations of N-substituted maleimide (RMI).[1-9] However, only a few studies on the polymerization of optically active RMI have been made.[10,11] Since RMI has a five-membered ring structure containing a reacting double bond in itself, the polymerization of RMI resembles that of a cycloalkene derivative. Thus, RMI is particularly interesting. When a threo-diisotactic addition takes place in the polymerization of a cycloalkene, the polymerization can yield two types of trans additions, 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.[12] Okamoto et al. reported the asymmetric polymerization of *N*-phenylmaleimide.[2] We also reported that asymmetric polymerizations of 11 types of achiral RMI were performed with *n*-BuLi/(−)-sparteine (Sp) to obtain chiral poly(RMI) containing a relatively high specific rotation ($[\alpha]_D = -40°$, RMI = *N*-cyclohexylmaleimide).[3] The asymmetry could be attributed to a threo-diisotactic structure of RMI polymer main chains, i.e., a helix and/or excess of chiral centers of (*S*,*S*) or (*R*,*R*),[3] as shown in Chart I.

Recently, we reported on polymerization reactivities and chiroptical properties of chiral *N*-(α-methylbenzyl)maleimide (MBZMI),[13] *N*-[(menthoxycarbonyl)methyl]maleimide (MGMI)[14] and *N*-[[[*N'*-4-(α-methylbenzyl)amino]carbonyl]phenyl]maleimide (MBCP).[15] It was found that the specific rotation $[\alpha]_D$ and circular dichroism (CD) spectra for the copolymers could be attributed not only to chiral maleimide repeat units but also to comonomer units. It was suggested that asymmetric inductions into the homopolymer and copolymer main chain took place based on chiroptical properties for a model compound of the polymer and for the copolymers. The asymmetric induction was much influenced by optically active N-substituents, and the magnitude for the maleimide containing an optically active α-methylbenzyl group was the greatest in the values reported by the authors so far.[13-15] Thus, the selection of RMI bearing an optically active α-methylbenzyl group is thought to be better to study the effect on asymmetric induction in detail. It is not clear what kind of N-substituent structure having an optically active α-methylbenzyl group can best influence asymmetric induction. In addition, effects of the distance (the number of methylene or phenylene units) from the maleimide ring to a chiral carbon on asymmetric induction are not investigated.

Chart I



In this paper, a novel, optically active *N*-[[[*N'*-(α-methylbenzyl)amino]carbonyl]methyl]maleimide (MBCM) is prepared from maleic anhydride, glycine, and (*R*)-(+)-α-methylbenzylamine. MBCM is polymerized and copolymerized with styrene (ST) and methyl methacrylate (MMA) in the presence of radical initiators. The monomer reactivity ratios and *Q*-*e* values are determined. From the specific rotation and molecular ellipticity of the copolymers, optical activities for the copolymers contributed to both the chiral RMI residue and the comonomer unit are discussed, compared with that of MBCP including a phenyl group in the N-substituent.

Experimental Section

MBCM Monomer. MBCM monomer was synthesized from maleic anhydride, glycine, and (*R*)-(+)-α-methylbenzylamine, as shown in Scheme I.

***N*-Glycinylmaleamic acid (GMA).**[14] Maleic anhydride (47.1 g, 1.5 mol) and glycine (112.6 g, 1.5 mol) were dissolved in acetic acid (1600 mL), and then the mixture was stirred at room temperature for 5 h. The resulting crude GMA was filtered, dried, and then recrystallized from methanol to obtain pure GMA (95%). Mp: 197 °C (lit.[16] mp 187-188.5 °C). ^{1}H NMR [chemical shift, δ, in ppm from tetramethylsilane (TMS) in deuterium dimethyl sulfoxide (DMSO-d_6)]: 9.12 (m, 1 H, NH), 6.32 (d, J = 3.1 Hz, 2 H, CH=CH), 5.91 (d, J = 6.2 Hz, 2 H, CH$_2$). Elem anal. Calcd for $C_6H_7NO_5$: C, 41.63; H, 4.08; N, 8.09. Found: C, 41.51; H, 4.11; N, 8.15.

***N*-Glycinylmaleimide (GMI).** GMI was synthesized from GMA with dehydration using toluene and triethylamine.[14] GMI was purified by recrystallization from chloroform. Yield: 42%. Mp: 116 °C (lit.[16] mp 113.5 °C). ^{1}H NMR (δ in ppm from TMS in DMSO-d_6): 12.65-11.75 (s, 1 H, COOH), 6.78 (s, 2 H, CH=CH), 4.01 (s, 2 H, CH$_2$). Elem anal. Calcd for $C_6H_5NO_4$: C, 46.26; H, 3.21; N, 8.96. Found: C, 46.19; H, 3.32; N, 8.66.

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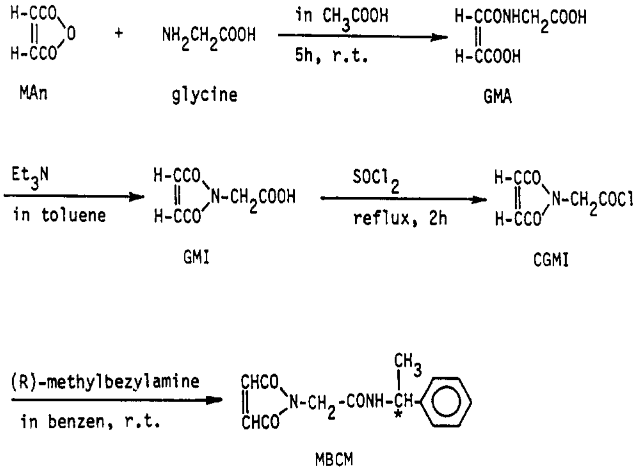
Scheme I



***N*-[(Chlorocarbonyl)methyl]maleimide (CGMI).** A mixture of GMI (35.5 g, 0.16 mol), thionyl chloride (400 g, 4.02 mol), and *tert*-butylcathecol (0.01 g) was refluxed for 2 h. Unreacted thionyl chloride was removed by evaporation, and then the residual product was distilled under reduced pressure to obtain pure CGMI (28.2 g). Yield: 73.3%. Bp: 82–84 °C (5.2×10^{-3} mmHg). ^{1}H NMR (δ in ppm from TMS in $CDCl_3$): 6.81 (s, 2 H, CH=CH), 4.64 (s, 2H, CH_2).

***N*-[[*N'*-((*R*)-α-Methylbenzyl)amino]carbonyl]methyl]maleimide (MBCM).** A benzene (250 mL) solution of CGMI (9.0 g, 0.10 mol) was added dropwise to a solution of (*R*)-α-methylbenzylamine (13.1 g, 0.10 mol) in benzene (250 mL) at 0–5 °C, and the mixture was stirred at room temperature for 2 h. The precipitated product was filtered, washed with water, dried, and then recrystallized twice from methanol/water (1/3) to obtain pure MBCM (3.4 g). Yield: 27%. Mp 145–146 °C. $[\alpha]^{25}_D$: 116.5° (c = 1 g/dL, l = 10 cm, THF). IR (KBr disk, cm^{-1}): 3250 (NH), 1710 (C=O), 1690 (COHN), 1645 (C=C), 1535 and 1490 (CONH), 1380 (CH_3), 810 (CH), 690 (cis HC=CH). ^{1}H NMR (δ in ppm from TMS in acetone-d_6): 7.88 (d, J = 11.2 Hz, 1 H, CONH), 7.35–6.97 (m, 5 H in phenyl groups), 6.90 (s, 2 H, CH=CH), 5.20–4.75 (m, 1 H, NCH); 1.45 (d, J = 6.1 Hz, 3 H, $NCCH_3$). Elem anal. Calcd for $C_{13}H_{14}O_3N_2$: C, 65.11; H, 5.46; N, 10.85. Found: C, 64.27; H, 5.57; N, 10.84.

Model Compound of Poly(MBCM): *N*-[[*N'*-((*R*)-α-Methylbenzyl)amino]carbonyl]methyl]succinimide (MBGSI). MBGSI was prepared from succinic anhydride, glycine, and (*R*)-α-methylbenzylamine, according to a method similar to that of MBCM. Yields and melting points of some precursors for MBGSI are as follows. *N*-Glycinylsuccinamic acid (GSA): yield 98%; mp 150–153 °C. *N*-Glycinylsuccinimide (GSI) recrystallized from methanol/water (1/1): yield 63%; mp 111–116 °C. *N*-[(Chlorocarbonyl)methyl]succinimide distilled under reduced pressure: yield 86%; bp 108–109 °C (5×10^{-3} mmHg).

MBGSI. Yield: 17%. Mp: 193–194 °C. $[\alpha]^{25}_D$: 115.5° (c = 1.0 g/dL, l = 10 cm, THF). IR (cm^{-1}): 3250 (NH), 1695 (C=O), 1640 (CH=CH in phenyl), 1385 (CH), 695 (phenyl). ^{1}H NMR (δ in ppm from TMS in acetone-d_6): 7.70 (d, J = 6.2 Hz, 1 H, NH), 7.48–6.98 (m, 5 H in phenyl groups), 5.32–4.78 (m, 1 H, CONCH), 2.70 (s, 4 H, CH_2CH_2), 1.46 (d, J = 6.2 Hz, 3 H, CH_3). Elem anal. Calcd for $C_{14}H_{16}O_3N_2$: C, 64.60; H, 6.20; H, 10.76. Found: C, 63.89; H, 6.15; N, 10.71.

Other Material. ST and MMA were purified by ordinary methods.[17] THF and dioxane (DOX) were purified by distillation after being refluxed in the presence of sodium. Methanol and other solvents were purified by the usual methods.[18] 2,2'-Azobis(isobutyronitrile) (AIBN) was recrystallized twice from methanol.

Homopolymerization and Copolymerization. Radical homopolymerization and copolymerization were carried out with AIBN as an initiator in THF in a sealed tube at 70 °C. After polymerization, the polymer solution was poured into a large amount of methanol. To remove unreacted optically active monomer, reprecipitation was repeated three times from acetone/methanol. The homopolymers insoluble in organic solvents were thoroughly washed with methanol. The compositions of the copolymer obtained were determined by nitrogen analysis.

Measurements. D-Line specific rotations were measured in THF at 25 °C with a Jasco DIP-140 (Japan Spectroscopic Co.). Optical rotatory dispersion (ORD) and circular dichroism (CD) spectra were obtained by a Jasco J-20C (Japan Spectroscopic Co.), equipped with a xenon source and a computing data processor. Molecular weights of polymers were measured by gel permeation chromatographic (GPC) analysis using the same technique as described in an earlier paper.[19] IR and NMR spectra were obtained and elemental analysis was achieved, using the same instruments as reported previously.[20]

Results and Discussion

Radical Homopolymerization of MBCM. Radical polymerizations of MBCM were performed under several conditions. The results are summarized in Table I. All polymerizations proceeded homogeneously throughout except in chloroform. In the polymerization in chloroform, a part of the polymer was insoluble and precipitated. The resulting polymers were white powders and had positive optical activity. The specific rotations $[\alpha]_D$ of the polymers were 59.9–62.9° except in chloroform. The specific rotation of the polymer obtained in chloroform was about 50° and was 20% less than the values for the polymers obtained in other solvents. It is difficult to explain the reason clearly. The fact may be associated with the heterogeneous polymerization process, as just described above. However, the IR and NMR spectra for the polymer obtained in chloroform were the same as those for other polymers. The resulting polymers were soluble in organic solvents such as THF, dioxane, dichloromethane, acetone, and cyclohexanone.

There was no difference in the ^{1}H NMR and IR spectra for the polymers obtained in different solvents. No olefinic proton resonance was evident in the ^{1}H-NMR spectra for the polymers, which suggests that an ordinary addition polymerization took place.

The number-average molecular weights ($\bar{M}_n$) were 2.1×10^3–3.8×10^4, and the polydispersities [weight-average molecular weight $(\bar{M}_w)/\bar{M}_n$] were 1.08–1.7 for the polymers. These values were similar to those for the poly(MBCP)s.[15]

The CD and UV spectra for the polymers are shown in Figures 1 and 2. In the CD spectra for the poly(MBCM), a large positive and some negative peaks were observed at about 228 and 255–270 nm, respectively. The former was attributable to the n → π* transition of the carbonyl groups in the imide ring and the amide group and the latter to the π → π* transition of the phenyl group. The CD pattern for the poly(MBCM) was similar to that of a model compound for the poly(MBCM), i.e., *N*-[[[*N'*-((*R*)-α-methylbenzyl)amino]carbonyl]methyl]succinimide (MBGSI), as shown in Figure 1, but the magnitude of molecular ellipicity (θ) at about 230 nm was different from that of the homopolymer. The reason for this may be that asymmetry was induced in the polymer main chain because of threo-diisotactic structure, as described later in detail. This can also be supported by the fact that the optical rotations of the MBCM monomer and the polymer were 116.5° and 115°, respectively. That is, if the optical activity was attributed to only an optically active α-methylbenzyl group, the resulting polymer may indicate about 115° of $[\alpha]_D$.

Cubbon[1] reported that eight N-substituted maleimide monomers (RMI) were polymerized using free-radical and *n*-BuLi initiators and that both types of initiator gave rise to polymers which have predominantly threo-diisotactic structure. RMI polymers may not be completely stereoregular and predominantly threo-diisotactic with occasional threo-disyndiotactic placements which disrupt the crystallinity to some extent.[1] In addition, the stereospec-

Table I
Radical Polymerizations of MBCM

run	MBCM $\times 10^3$ (mol)	initiator $\times 10^2$ (mol/L)	polym solvent[a] (mL)	polym temp (°C)	polym time (h)	convn (%)	$\bar{M}_n$[b] $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$[b]	$[\alpha]^{25}_D$[c] (deg)
1-1	1.90	AIBN (1.0)	THF (3)	70	22	trace	*d*		
1-2	1.95	AIBN (2.0)	DOX (5)	70	22	20.9	3.9	1.62	61.6
1-3	1.90	AIBN (1.0)	DMSO (1)	70	22	trace			
1-4	1.96	AIBN (2.0)	DMF (1)	70	22	4.79	*d*		
1-5	1.95	AIBN (2.0)	MC (2)	70	22	60.0	16.5	1.16	59.9
1-6	1.97	PH25[e] (2.2)	XY (5)	150	20	28.9	37.8	1.08	61.2
1-7	1.95	PH25[e] (2.1)	CB (5)	150	20	48.3	*d*		62.9
1-8	1.94	AIBN (2.0)	CF (3)	70	22	36.8	5.2	1.70	50.3
1-9	1.94	AIBN (2.0)	AC (3)	70	22	66.6	*d*		62.0

[a] THF, tetrahydrofuran; DOX, dioxane; DMSO, dimethyl sulfoxide; DMF, dimethylformamide; MC, methylene chloride; XY, *o*-xylene; CB, chlorobenzene; CF, chloroform; AC, acetone. [b] By GPC. [c] c = 1.0 g/dL, THF, l = 10 cm. [d] No measurement. [e] 2,5-Dimethyl-2,5-bis(*tert*-butylperoxy)hexyne-3.

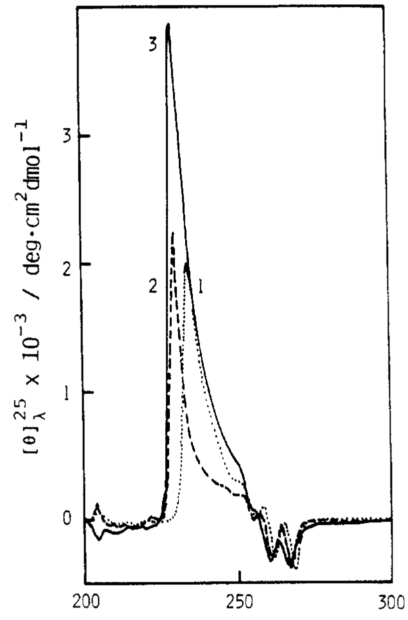


Figure 1. CD scans for (1) poly(MBCM) obtained with AIBN (run 1-2), (2) MBCM monomer, and (3) MBGSI (a model compound of poly(MBCM)).

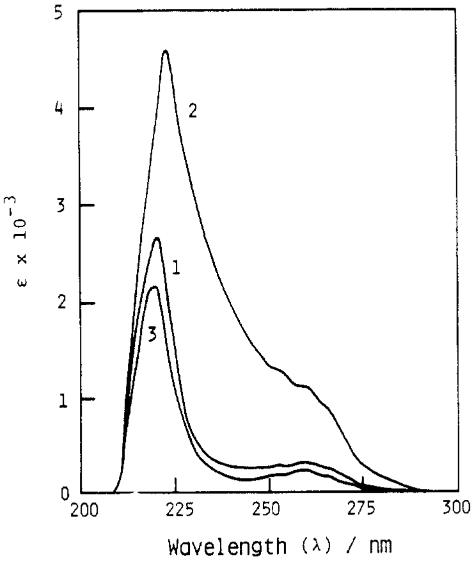


Figure 2. UV spectra for (1) poly(MBCM) obtained with AIBN (run 1-2), (2) MBCM monomer, and (3) MBGSI (a model compound of poly(MBCM)).

ificity 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.[1]

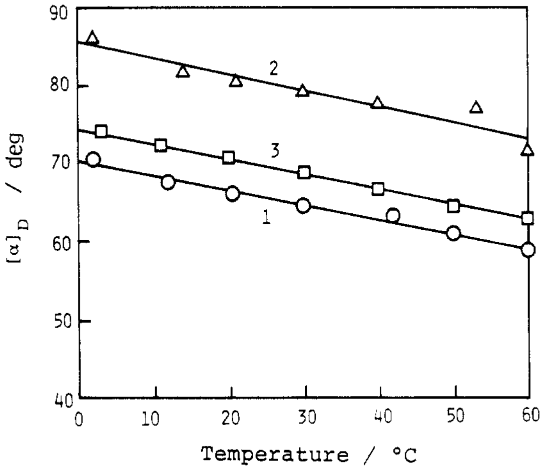


Figure 3. Temperature dependence on specific rotation of the polymer and the copolymers: (1) poly(MBCM) (run 1-2), (2) poly(MBCM-*co*-ST) (run 2-5), and (3) poly(MBCM-*co*-MMA) (run 3-5).

Our poly(MBCM)s obtained from the radical initiator were not crystalline but amorphous, as judged from the X-ray diffraction diagrams. Temperature dependence on the specific rotation for the polymers indicated a linear relation, and the slope was very small (temperature coefficient: $\Delta[\alpha]_D/\Delta T = -0.19$), as shown in Figure 3. These suggest that the main chain of poly(MBCM)s scarcely contains a helical structure and/or that there are not competing conformation states contributing to the optical activity.

Radical Copolymerization of MBCM with ST and MMA. The results of radical copolymerizations of MBCM (M_1) with ST (M_2) and MMA (M_2) in dioxane (DOX; 6 mL) at 70 °C in the presence of AIBN (2.0×10^{-2} mol/L) are summarized in Tables II and III, respectively. The copolymerization proceeded homogeneously throughout. The resulting copolymers were white powders and were optically active. Copolymer composition curves in the polymerizations of MBCM with ST and MMA are shown in Figure 4. Monomer reactivity ratios, r_1 and r_2, were determined as $r_1 = 0.083$ and $r_2 = 0.30$ in the MBCM/ST system and $r_1 = 0.19$ and $r_2 = 0.95$ in the MBCM/MMA system, according to the high-conversion method reported by Tüdös and co-workers[21] and to the integration method by Mayo and Lewis.[22] The Alfrey–Price[23] Q–e values for MBCM were calculated as $Q_1 = 0.72$ and $e_1 = 1.12$ in the MBCM/ST and $Q_1 = 1.32$ and $e_1 = 1.71$ in the MBCM/MMA system. These copolymerization parameters were similar to those for other RMI's reported previously.[24]

Chiroptical Properties of Copolymers. The CD and UV spectra for poly(MBCM-*co*-ST)s and poly(MBCM-*co*-MMA)s are shown in Figures 5 and 6, respectively. The

Table II
Radical Copolymerizations of MBCM (M_1) with ST (M_2) in DOX (6 mL) at 70 °C[a]

run	M_1 in monomer (mol %)	polym time (h)	convn (%)	N anal. (%)	M_1 in copolymer (mol %)	$\bar{M}_n{}^b \times 10^{-3}$	$\bar{M}_w/\bar{M}_n{}^b$	$[\alpha]^{25}{}_D{}^c$ (deg)
2-1	4.48	11	26.5	1.88	7.82			20.1
2-2	8.82	11	19.9	3.20	14.4			31.6
2-3	18.0	11	37.2	4.89	24.8	7.6	1.83	49.1
2-4	34.9	11	40.4	6.75	40.0			73.5
2-5	46.2	11	43.8	7.10	43.3	3.0	5.43	79.2
2-6	56.4	11	44.6	7.65	49.1	15.9	1.94	71.2
2-7	76.1	11	26.7	8.02	53.3	8.3	1.28	67.5
2-8	86.1	11	16.7	8.65	61.4	1.3	3.67	68.1
2-9	86.4	11	18.9	9.37	71.9			66.1

[a] [AIBN] = 2.0×10^{-3} mol/L; $M_1 + M_2 = 1.0$ g. [b] By GPC. [c] $c = 1.0$ g/dL, THF, $l = 10$ cm.

Table III
Radical Copolymerization of MBCM (M_1) with MMA (M_2) in DOX (6 mL) at 70 °C[a]

run	M_1 in monomer (mol %)	polym time (h)	convn (%)	N anal. (%)	M_1 in copolymer (mol %)	$\bar{M}_n{}^b \times 10^{-3}$	$\bar{M}_w/\bar{M}_n{}^b$	$[\alpha]^{25}{}_D{}^c$ (deg)
3-1	4.98	11	27.7	1.39	5.38	19.2	1.62	12.4
3-2	10.1	11	30.1	2.41	9.99	8.4	2.60	23.2
3-3	20.2	11	32.5	2.79	17.2	3.3	4.99	39.9
3-4	40.1	11	23.4	6.49	36.6	2.2	4.63	58.4
3-5	49.0	11	25.8	6.67	38.2	34.0	1.42	62.9
3-6	58.7	11	27.5	7.43	45.8	24.1	1.35	70.7
3-7	78.4	11	18.6	8.82	62.8			68.1
3-8	89.3	11	16.9	9.89	79.9			65.9
3-9	94.5	11	8.9	9.94	81.0	1.6	9.47	65.1

[a] [AIBN] = 1.0×10^{-2} mol/L; $M_1 + M_2 = 1.0$ g. [b] By GPC. [c] $c = 1.0$ g/dL, THF, $l = 10$ cm.

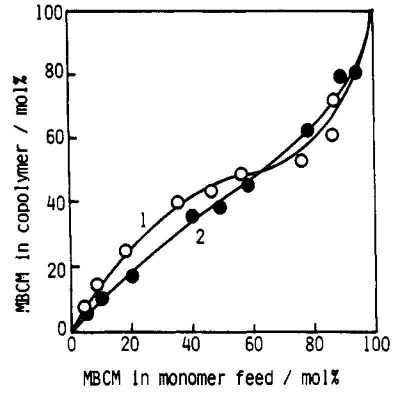


Figure 4. Copolymer composition curves for (1) MBCM/ST and (2) MBCM/MMA systems.

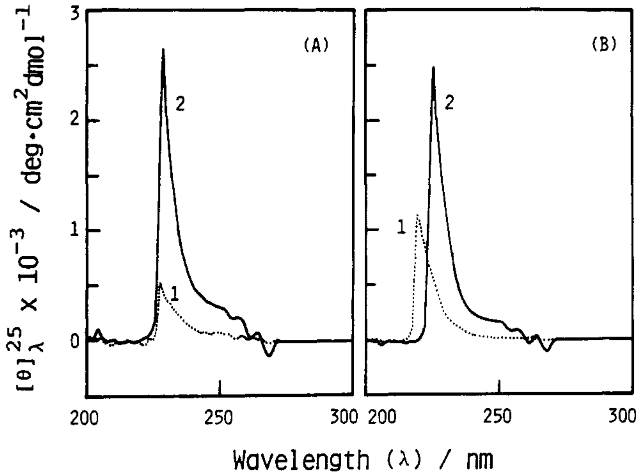


Figure 5. CD spectra for (A) poly(MBCM-*co*-ST) and (B) poly(MBCM-*co*-MMA): (1) ca. 5 mol % of MBCM in monomer feed (runs 2-1 and 3-1) and (2) 60 mol % of MBCM in monomer feed (runs 2-6 and 3-6).

patterns were almost similar to those for the homopolymer. The negative Cotton effect around 265 nm was observed and ascribed to the $\pi \rightarrow \pi^*$ transition of phenyl groups of the ST and MBCM monomer units. The positive Cotton effect was observed at about 225 nm, which attributed to the $n \rightarrow \pi^*$ transition of the carbonyl groups.

The relationship between the specific rotation of the copolymers and the measurement temperature gave linearity, and the slopes were very small (temperature coefficient: $\Delta[\alpha]_D/\Delta T = -0.19$ to -0.21), as shown in Figure 3. This suggests that there was little helical conformation in the copolymers, as well as the homopolymer.

Figure 7 shows the dependence of specific rotations $[\alpha]^{25}{}_D$ and molecular ellipticities (θ) (calculated from the average molecular weight of the monomeric units) on the composition (wt %) of poly(MBCM-*co*-ST)s. Both absolute values of specific rotations and molecular ellipticities of poly(MBCM-*co*-ST)s indicated the curves having a maximum. That is, a considerable deviation from linearity was observed. On the other hand, the absolute values of specific rotations of a mixture of poly(MBCM) and poly(ST) gave a good linear relationship, as shown in Figure 7. In the poly(MBCM-*co*-MMA)s, the same tendency could be observed, as shown in Figure 8. This suggests that the optical activity can be influenced by the comonomer: ST or MMA. It is interesting to note that the effect was observed even though an asymmetric carbon in MBCM was not favorably located in the immediate neighborhood of a maleimide ring. In this case the N-substituent of MBCM is a [[(α-methylbenzyl)amino]carbonyl]*methyl* group. This was detected in the MBCP/ST and MBCP/MMA systems.[15] That is, an asymmetric carbon in MBCP is also not located in the immediate neighborhood of a maleimide ring, and the N-substituent of MBCP is [[(α-methylbenzyl)amino]carbonyl]*phenyl* group. In the case of MBCP, however, the deviation existed *under* the linear line. That is, the chromophores, i.e., methylene or phenyl, connecting the optically active α-methylbenzyl group can affect optical activities of the copolymers.

The fact that deviation from the linear line was observed suggests that asymmetric induction copolymerization took place. In order to confirm asymmetric induction co-

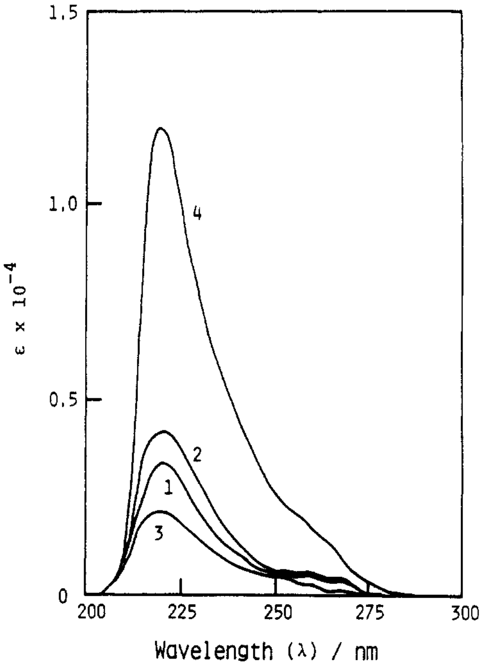


Figure 6. UV spectra for poly(MBCM-*co*-ST): (1) run 2-1 and (2) run 2-6. UV spectra for poly(MBCM-*co*-MMA): (3) run 3-1 and (4) run 3-6.

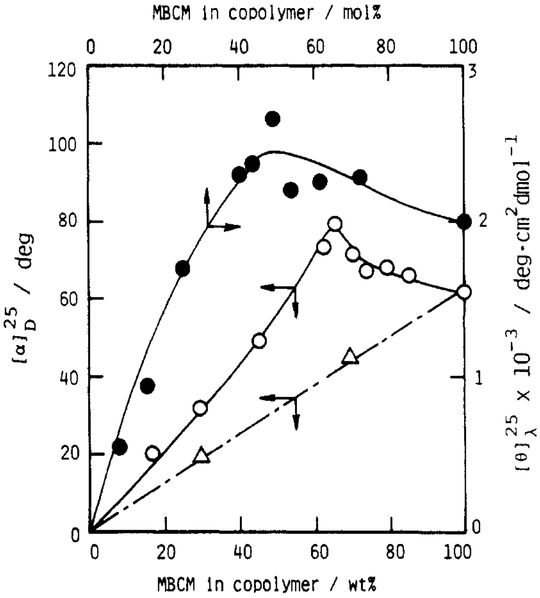


Figure 7. Dependence of (○) specific rotations $[\alpha]^{25}_{D}$ and (●) molecular ellipticities (θ) (λ = 227 ± 2 nm) on the composition (wt % and mol %) of poly(MBCM-*co*-ST)s and (△) a mixture of poly(MBCM) and poly(ST).

poymerization, removal of the optically active α-methylbenzyl group was attempted using acid and base catalysts, such as HCl, H_2SO_4, HBr, NaOH, KOH, and hydrazine monohydrate, and phenylhydrazine under several conditions. But the attempts were unsuccessful. Thus, the dependence of a diad sequence on the specific rotation and on the molecular ellipticities of the copolymers was investigated in order to clarify the possibility of the occurrence of asymmetric induction copolymerizations.

Figures 9 and 10 reveal the dependence of a diad sequence,[25,26] $P_2[m_1m_2]$, on specific rotations and on molecular ellipticities of poly(MBCM-*co*-ST)s and poly(MBCM-*co*-MMA)s, respectively. The $P_2[m_1m_2]$ value depicts the probability of a MBCM/ST or a MBCM/MMA diad sequence. $P_2[m_1m_2]$ was derived as follows:

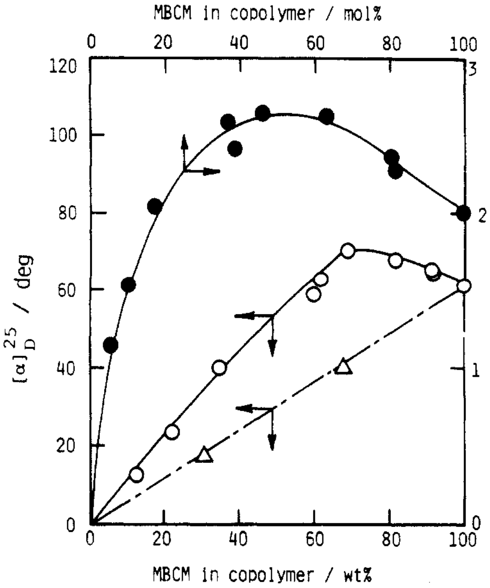


Figure 8. Dependence of (○) specific rotations $[\alpha]^{25}_{D}$ and (●) molecular ellipticities (θ) (λ = 223 ± 2 nm) on the composition (wt % and mol %) of poly(MBCM-*co*-MMA)s and (△) a mixture of poly(MBCM) and poly(MMA).

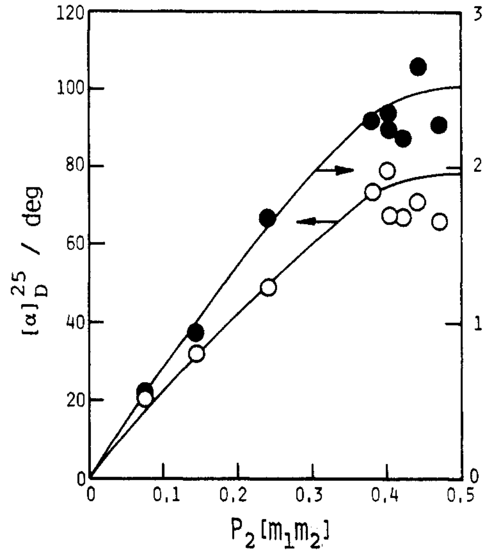


Figure 9. Relationships between (○) specific rotations $[\alpha]^{25}_{D}$, (●) molecular ellipticities (θ) (λ = 227 ± 2 nm), and a MBCM/ST diad sequence ($P_2[m_1m_2]$) in the copolymer.

where $P_1[m_1]$ and $P_1[m_2]$ are molar fractions of the copolymer, $P(m_1m_2)$ is given by the monomer molar ratio in the feed ($X = [M_1]/[M_2]$), and r_1 in the monomer reactivity ratio of MBCM. $1 + r_1X$ indicates an average sequence length ($\bar{l}_1$) of M_1. In the MBCM/ST system, both specific rotations and molecular ellipticities almost linearly increased with the diad sequence ($P_2[m_1m_2]$). In the MBCM/MMA system, a similar tendency was observed. These suggest that a new asymmetric center appeared in the MBCM/ST and the MBCM/MMA diad sequences, as illustrated in Chart II; C* is a chiral carbon. In this case, the chiral side chain might sterically control the attack of a ST or a MMA monomer on the growing chain end during the propagation reaction.[27]

It is thought that the contribution to ellipticity by ST and MMA counits is of conformational nature, i.e., a conformational dissymmetry of the macromolecules with a prevailing chirality. However, the specific rotations shown in Figures 9 and 10 contain the conformational dissymmetry of the macromolecules with a prevailing chirality.

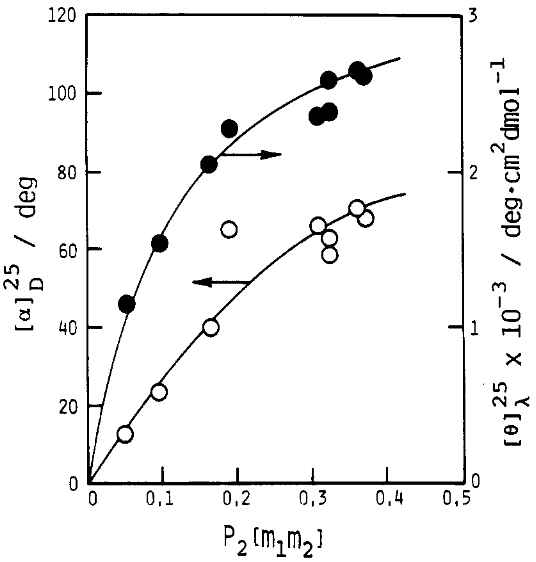
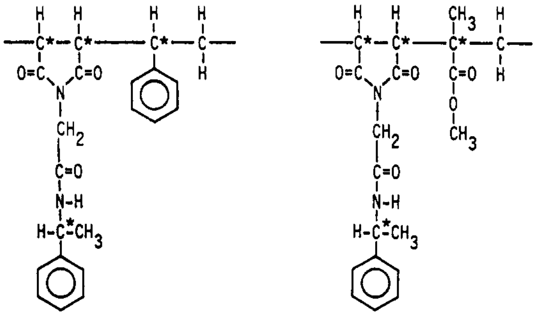


Figure 10. Relationships between (○) specific rotations $[\alpha]^{25}_{D}$, (●) molecular ellipticities (θ) (λ = 223 ± 2 nm), and a MBCM/MMA diad sequence ($P_2[m_1m_2]$) in the copolymer.

Chart II



$$P_1[m_1] + P_1[m_2] = 1$$

$$P_2[m_1m_2] = P_1[m_1]P(m_1m_2)$$

$$P(m_1m_2) = 1/(1 + r_1X)$$

Conclusion

(1) A novel type of optically active *N*-[[[*N*′-(α-methylbenzyl)amino]carbonyl]methyl]maleimide (MBCM) was synthesized and polymerized with AIBN to obtain chiral polymers.

(2) From the results of radical copolymerizations of MBCM (M_1) with ST(M_2) or MMA (M_2), the monomer reactivity ratios (r_1, r_2) and the *Q*–*e* values were determined as follows: r_1 = 0.19, r_2 = 0.47, Q_1 = 0.61, and e_1 = 0.76 in the MBCM/ST system r_1 = 0.30, r_2 = 0.93, Q_1 = 1.26, and e_1 = 1.53 in the MBCM/MMA system.

(3) The specific rotations and molecular ellipticities for the copolymers were influenced by the comonomers.

(4) Attempts to remove the optically active α-methylbenzyl group were unsuccessful, but, judging from the relationships between optical activities and a diad sequence, asymmetric induction copolymerization may take place in the MBCM/ST and MBCM/MMA systems. A new asymmetric center may appear in the MBCM/ST and MBCM/MMA diad sequences.

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References and Notes

(1) Cubbon, R. C. B. *Polymer* **1966**, *6*, 419.
(2) Okamoto, Y.; Nakano, T.; Kobayashi, H.; Hatada, K. *Polym. Bull. (Berlin)* **1991**, *25*, 5.
(3) Oishi, T.; Yamasaki, H.; Fujimoto, M. *Polym. J.* **1991**, *23*, 795.
(4) Oishi, T.; Kimura, T. *Kobunshi Ronbunshu* **1975**, *32*, 380; **1976**, *33*, 141; **1976**, *33*, 685.
(5) Yamada, M.; Takase, I.; Mishima, T. *Kobunshi* 1969, 26, 393. Yamada, M.; Takase, I.; Tsukano, T.; Ueda, Y. *Kobunshi* **1969**, *26*, 401.
(6) Mohamed, A. A.; Jebrael, F. H. *Macromolecules* **1986**, *19*, 32.
(7) Matsumoto, A.; Kubota, T.; Otsu, T. *Macromolecules* **1991**, *23*, 4508. Otsu, T.; Matsumoto, A.; Tatsumi, A. *Polym. Bull. (Berlin)* **1990**, *24*, 459. Matsumoto, A.; Oki, A.; Otsu, T. *Polym. J.* **1991**, *23*, 201.
(8) Hagiwara, T.; Shimizu, T.; Uda, T.; Hamana, H.; Narita, T. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 185. Hagiwara, T.; Someno, T.; Hamana, H.; Narita, T. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1011. Hagiwara, T.; Shimizu, T.; Someno, T.; Yamagishi, T.; Hamana, H.; Narita, H. *Macromolecules* **1988**, *21*, 3324.
(9) Iwatsuki, S.; Kubo, M.; Wakita, M.; Matsui, Y.; Kanoh, H. *Macromolecules* **1991**, *24*, 5009.
(10) Yamaguchi, H.; Minoura, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 929. Yamaguchi, H.; Minoura, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1970**, *8*, 1467.
(11) Sakota, N.; Kishiue, K.; Shimada, S.; Minoura, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 1787.
(12) Farina, M. The Stereochemistry of Linear Macromolecules. *Topics in Stereochemistry*; Eliel, L. E., Wilen, S. H., Eds.; John Wiley & Sons, Inc.: New York, 1987; Vol. 17.
(13) Oishi, T.; Fujimoto, M. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2789.
(14) Oishi, T.; Kamori, A., Fujimoto, M. *J. Macromol. Sci., Pure Appl. Chem.* **1992**, *A29*, 231.
(15) Oishi, T.; Fujimoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 1821.
(16) Rich, D. H.; Gesellchen, P. D.; Al Cheung, A. T.; Buckner, C. K. *Macromolecules* **1975**, *18*, 1004.
(17) Otsu, T.; Kinoshita, M. *Kobunshigousei no Jikkenhou*; Kagakudoujin: Kyoto, Japan, 1972; pp 69–91.
(18) Riddick, J. A.; Bunger, W. B.; Sakano, T. K. *Organic Solvent*; John Wiley & Sons, Inc.: New York, 1986.
(19) Oishi, T.; Morioka, Y.; Fujimoto, M. *Polym. J.* **1989**, *21*, 287.
(20) Oishi, T.; Fujimoto, M. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 2727.
(21) Tüdös, F.; Kelen, T.; Foldes-Berezsnich, T.; Turcsanyi, B. *J. Macromol. Sci., Chem.* **1976**, *A10*, 1513. The monomer reactivity ratios were determined by the *method 6* described in this paper.
(22) Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944**, *66*, 1594.
(23) Alfrey, T., Jr.; Price, C. C. *J. Polym. Sci.* **1947**, *2*, 101.
(24) Young, L. J. Tabulation of *Q*–*e* Values. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; p II-387.
(25) Harwood, H. J.; Ritchey, W. M. *J. Polym. Sci., Polym. Lett. Ed.* **1964**, *2*, 601.
(26) Kurokawa, M.; Yamaguchi, H.; Minoura, Y. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2241.
(27) Oishi, T.; Fujimoto, M. *J. Macromol. Sci., Chem.* **1988**, *A25*, 1039.

Registry No. MBCM (homopolymer), 144634-82-2; (MBCM)(St) (copolymer), 144634-83-3; (MBCM)(MMA) (copolymer), 144667-09-4; MBCM, 144634-80-0; GMA, 54930-24-4; GMI, 25021-08-3; CGMI, 17686-36-1; MBGSI, 144634-81-1; GSA, 5694-33-7; GSI, 5626-41-5; St, 100-42-5; MMA, 80-62-6; MAn, 108-31-6; $H_2NCH_2CO_2H$, 56-40-6; (*R*)-methylbenzylamine, 3886-69-9; succinic anhydride, 108-30-5; *N*-[(chlorocarbonyl)methyl]succinimide, 58142-32-8.