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SYNTHESIS AND CHIROPTICAL PROPERTIES OF POLY[*N*-(4-*N'*-(α -METHYLBENZYL)- AMINOCARBONYLPHENYL)MALEIMIDE]

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ABSTRACT

Radical homopolymerization of *N*-[4-*N'*-(α -methylbenzyl)-aminocarbonylphenyl]maleimide ((*S*)-MBCP) was carried out at 50 and 70°C for 24 h to give optically active polymers ($[\alpha]_D^{25} = 159.8$ to 163.4°). Radical copolymerizations of (*S*)-MBCP (M_1) were performed with styrene (ST, M_2), methyl methacrylate (MMA, M_2) in THF at 50°C. The monomer reactivity ratios (r_1 , r_2) and the Alfrey–Price Q , e values were determined as follows: $r_1 = 0.32$, $r_2 = 0.14$, $Q_1 = 1.74$, $e_1 = 0.96$ in the (*S*)-MBCP-ST system; $r_1 = 0.54$, $r_2 = 0.93$, $Q_1 = 1.11$, $e_1 = 1.23$ in the (*S*)-MBCP-MMA system. Chiroptical properties of the polymers and the copolymers were also investigated, and asymmetric induction into the copolymer main chain is discussed.

INTRODUCTION

When a threo-diisotactic addition takes place in polymerization of a cycloalkene, the polymerization can yield two types of trans-addition, i.e., chiral centers of (*S,S*) and (*R,R*). If one is produced more than the other, the resulting polymer can be optically active [1]. There have been many reports on the polymerization and copolymerization of *N*-substituted maleimide (RMI) [2–6]. However, only a few studies of the polymerization of optically active RMI have been made [7, 8].

Polymerization reactivity and chiroptical properties of RMI including a chiral group have not been sufficiently investigated. We reported that asymmetric polymerization of nonchiral RMI was performed with *n*-butyllithium (*n*-BuLi)/(-)-sparteine (Sp) to obtain chiral poly(RMI) containing relatively high specific rotation ($[\alpha]_D = -40^\circ$, RMI = *N*-cyclohexylmaleimide) [9]. The asymmetry could be attributable to a three-diisotactic structure of the RMI polymer main chain; i.e., excess chiral center of (*S,S*) or (*R,R*) [9]. We also reported on the polymerization reactivity and the chiroptical property of chiral *N*-(α -methylbenzyl)maleimide (MBZMI) [10].

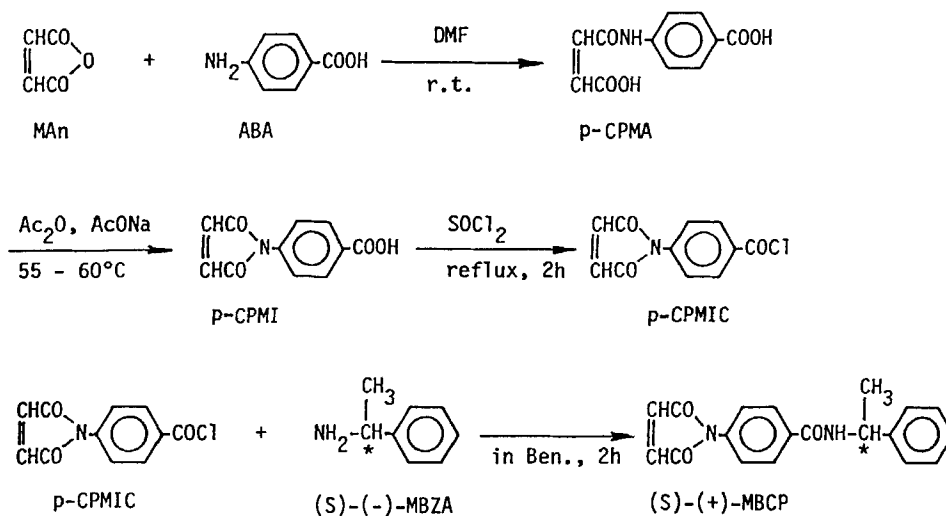
In this paper, an optically active *N*-[4-*N'*-(α -methylbenzyl)aminocarbonylphenyl]maleimide [(*S*)-MBCP], in which an asymmetric carbon is far removed from the maleimide ring, is polymerized and copolymerized with styrene (ST) and methyl methacrylate (MMA) using radical initiators. From the results, monomer reactivity ratios and *Q*-*e* values were determined. Asymmetric induction into the copolymer main chain is discussed and compared with that of MBZMI which had an asymmetric carbon located in close proximity to the maleimide ring.

EXPERIMENTAL

(*S*)-MBCP Monomer

(*S*)-MBCP monomer was synthesized from maleic anhydride, *p*-aminobenzoic acid, and (*S*)-(-)- α -methylbenzylamine, as shown in Scheme 1; this method is similar to that used for the synthesis of *R*-(-)-MBCP [11].

N-(4-Carboxyphenyl)maleamic acid (*p*-CPMA): yield 97%, mp 225–226°C. IR (KBr disk; wavenumber (cm⁻¹)): 3280 (NH); 2850–2200 (COOH); 1685 (CONH); 1620 (CH=CH); 1570 and 1520 (CONH); 1400 (CH); 1280 (C–O); 840 (*p*-substituent phenyl); 720 (*cis*-CH=CH). ¹H NMR (chemical shift; δ , ppm from TMS in deuterium dimethylsulfoxide (DMSO-*d*₆): 10.85–10.64 (m, 1H, NH); 7.80 and 7.61 (2d, *J* = 9.1 Hz, 4H, phenyl); 6.44 and 6.22 (2d, *J* = 11.9 Hz, 2H, CH=CH).



SCHEME 1.

N-(4-Carboxyphenyl)maleimide (p-CPMI): yield 85%, mp 244°C. IR (KBr disk; cm^{-1}): 3150 (OH); 2980 (CH); 2300 (COOH); 1770 and 1700 (C=O); 1640 and 1600 (C=C); 1390 (CH); 1200 (C-O); 820 (CH=CH); 690 (*cis*-CH=CH). ^1H NMR (chemical shift; δ , ppm from TMS in DMSO- d_6): 13.45–12.78 (m, 1H, COOH); 8.03 and 7.49 (2d, $J = 8.24$ Hz, 4H in phenyl); 7.22 (s, 2H, CO-CH=CH-CO).

N-[4-(Chlorocarbonyl)phenyl]maleimide (p-CPMIC): yield 73%, mp 168–169°C. IR (cm^{-1}): 1770 (COCl); 1715 (CONCO); 1595 (C=C); 1370 (CH); 720 (*cis*-CH=CH). ^1H NMR (δ , ppm from TMS in DMSO- d_6): 7.90 (d, $J = 9.1$ Hz, 2H in phenyl group); 7.38 (d, $J = 9.1$ Hz, 2H in phenyl); 7.06 (s, 2H, CH=CH in maleimide).

(*S*)-MBCP: A benzene (800 mL) solution of (*S*)- α -methylbenzylamine (28.4 g, 0.24 mol) was added dropwise to a solution of p-CPMIC (60 g, 0.24 mol) in benzene (300 mL) under nitrogen atmosphere, and the mixture was stirred at room temperature for 3 h. The precipitated product was filtered, dried, and then recrystallized from ethanol three times to obtain pure (*S*)-MBCP; 54 g, 70%, mp 201–202°C, $[\alpha]_{\text{D}}^{25} = 69.3^\circ$ ($c = 1$ g/dL, $l = 10$ cm, THF). IR (cm^{-1}): 3279 (NH); 1711 (C=O), 1688 (CONH); 1620 (C=C); 1519 and 1490 (CONH), 1380 (CH_3), 810 (CH), 690 (*cis*-H-C=C-H). ^1H NMR (δ , ppm from TMS in DMSO- d_6): 8.81 (d, $J = 11.1$ Hz, 1H, CONH); 7.96–7.28 (m, 9H, phenyl groups), 7.13 (s, 2H, CH=CH), 5.47–4.96 (m, 1H, N-CH); 1.48 (d, $J = 6.2$ Hz, 3H, N-C- CH_3). Elemental analysis (%): Found, C = 71.01, H = 5.06, N = 8.61; Calculated for $\text{C}_{19}\text{H}_{16}\text{O}_3\text{N}_2$, C = 71.23, H = 5.03, N = 8.74.

Model compound of poly(*S*)-MBCP: *N*-[4-(*N'*-(*S*)- α -methylbenzyl)-aminocarbonylphenyl]succinimide ((*S*)-MBSI): (*S*)-MBSI was prepared from succinic anhydride, *p*-aminobenzoic acid, and (*S*)- α -methylbenzylamine, and is similar to the method used for (*S*)-MBCP. Yields and mp of some precursors for (*S*)-MBSI are as follows: *N*-(4-carboxyphenyl)succinamic acid (CPSA): yield 98%; mp 250–253°C; *N*-(4-carboxyphenyl)succinimide (CPSI) recrystallized from methanol/water (1/1): yield 93%, mp 239–241°C. *N*-[4-(Chlorocarbonyl)phenyl]succinimide recrystallized from benzene: yield 86%; mp 188–189°C.

(*S*)-MBSI: Yield 75%; mp 197–198°C; $[\alpha]_{\text{D}}^{25} = 28.9^\circ$ ($c = 1.0$ g/dL, $l = 10$ cm, THF). IR (cm^{-1}): 3340 (NH); 1710 (C=O), 1630 (CH=CH in phenyl); 1385 (CH). ^1H NMR (δ , ppm from TMS in CDCl_3): 8.68 (d, $J = 8.2$ Hz, 1H, NH); 7.83 (d, $J = 8.2$ Hz, 2H in phenyl group); 7.35–6.98 (m, 7H in phenyl groups); 3.11 (q, $J = 9.1$ Hz, 1H, N-CH); 2.77 (s, 4H, CH_2 - CH_2); 1.49 (d, $J = 6.1$ Hz, 3H, CH_3). Elemental analysis (%): Found, C = 70.68, H = 5.51, N = 8.68; Calculated for $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_2$, C = 70.79, H = 5.62, N = 8.69.

Other Material

Styrene (ST) [12a], methyl methacrylate (MMA) [12b], tetrahydrofuran (THF), toluene, methanol, and other solvents were purified by the usual methods [12c]. 2,2'-Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) were purified by recrystallization from methanol and chloroform, respectively. Commercially available *n*-butyllithium (*n*-BuLi) hexane solution was used without further purification.

Homopolymerization and Copolymerization

Radical homopolymerization and copolymerization were carried out with AIBN or BPO as an initiator in solvent (see Table 1) in a sealed tube at constant temperature (50–100°C). After polymerization, the polymer solution was poured into a large amount of methanol. To remove any unreacted optically active monomer, reprecipitation was repeated three times from THF–methanol. The homopolymers, which were insoluble in organic solvents, were thoroughly washed with methanol. The composition of the copolymer obtained was determined by nitrogen analysis.

Measurements

D-line specific rotations were measured in THF ($c = 0.5$ g/dL; cell length = 5 cm) at 25°C with a Jasco DIP-140 (Japan Spectroscopic Co.). Optical rotatory dispersion (ORD) and circular dichroism (CD) spectra ($c = 0.5$ to 1.0 g/dL, $l = 1$ mm, THF) were obtained at 25°C by a Jasco J-20C (Japan Spectroscopic Co.) equipped with a xenon source and a computing data processor. Gel permeation chromatographic (GPC) analysis was achieved with a Shimadzu LC-3A instrument [UV (254 nm) detector; eluent: THF, 1.2 mL/min; 50°C; column system: Shimadzu HGS-40-20-15-10] equipped with a data processor. UV spectra were obtained with a Shimadzu 200A Spectrophotometer, using THF as a solvent and a concentration of 4.7×10^{-5} to 6.8×10^{-5} mol/L. The calibration curve was made from poly(ST) standards (Toyo Soda Manufacturing Co. Ltd.). Vapor pressure osmometer (VPO) analysis was done at 30°C with a Corona 114, using THF as solvent. IR and NMR spectra and elemental analysis data were obtained using the same instruments as reported previously [13].

RESULTS AND DISCUSSION

Radical and Anionic Homopolymerization of (S)-MBCP

Radical and anionic polymerizations of (S)-MBCP were performed under several conditions. The results are summarized in Table 1. In all systems a part of the polymer formed was insoluble in the solvent and precipitated. The polymers obtained were white powder and had positive optical activity. In radical homopolymerization, specific rotations $[\alpha]_D$ of the polymers were about 161°. The polymer (~0.1 g) obtained with AIBN in THF was soluble in 10 mL THF; the others were almost insoluble in organic solvents such as acetone, chloroform, DMSO, *N,N*-dimethylformamide (DMF), chlorobenzene, and dioxane. Amounts of insoluble polymers in THF are indicated in Table 1. The IR patterns for the polymers soluble in THF were different from those for the polymers insoluble in THF. That is, the different peak patterns assigned to amide groups (CONH) at 3250–3400 cm^{-1} and 1700–1600 cm^{-1} were observed as shown in Fig. 1. The A, B, and C peaks in Fig. 1 were all assigned to amide (CONH) groups. The C peak in the IR of the polymer insoluble in THF (2 in Fig. 1) was sharper than that of the polymer soluble in THF (B in Fig. 1), and shifted to a lower wavenumber than B. This suggests that the C peak of the amide group is associated with insolubility of the polymer. It is

TABLE 1. Radical Polymerizations of (S)-MBCP

Run	(S)-MBCP, mol/L	Initiator $\times 10^2$ mol/L	Polymer solvent, ^a mL	Polymerization temperature, $^{\circ}\text{C}$	Polymerization time, h	Yield, $\%$	Yield, $\%$	THF-soluble polymer				THF-insoluble polymer, yield, $\%$
								$\bar{M}_n \times 10^{-3b}$	\bar{M}_w/\bar{M}_n^b	$\bar{M}_n \times 10^{-3c}$	$[\alpha]_D^{25}$, degree ^d	
1-1	0.25	AIBN (1.0)	THF (6)	50	24	45.9	100	2.4	1.60	2.2	163.4	0
1-2	0.24	AIBN (1.0)	THF (6)	70	24	68.8	95	3.2	1.91	2.8	159.8	5
1-3	0.63	AIBN (1.0)	DMF (3)	70	15	13.5	1	—	—	—	—	99
1-4	0.26	BPO (1.0)	CB (10)	100	15	91.8	3	—	—	—	—	97
1-5	0.27	BPO (1.0)	DCB (10)	100	15	71.9	2	—	—	—	—	98
1-6	0.26	AIBN (1.0)	DOX (5)	70	24	76.4	6	2.1	1.58	1.2	162.2	94
1-7	0.28	AIBN (1.0)	CF (5)	70	24	77.7	6	2.5	1.82	1.8	160.5	94
1-8	0.26	AIBN (1.0)	EA (5)	70	24	93.0	2	—	—	—	—	98

^aTHF = tetrahydrofuran; DMF = dimethylformamide; CB = chlorobenzene; DCB = dichlorobenzene; DOX = dioxane; DCB = chloroform; EA = ethyl acetate.

^bBy GPC.

^cBy VPO.

^d $c = 1.0 \text{ g/dL}$; THF, $l = 10 \text{ cm}$.

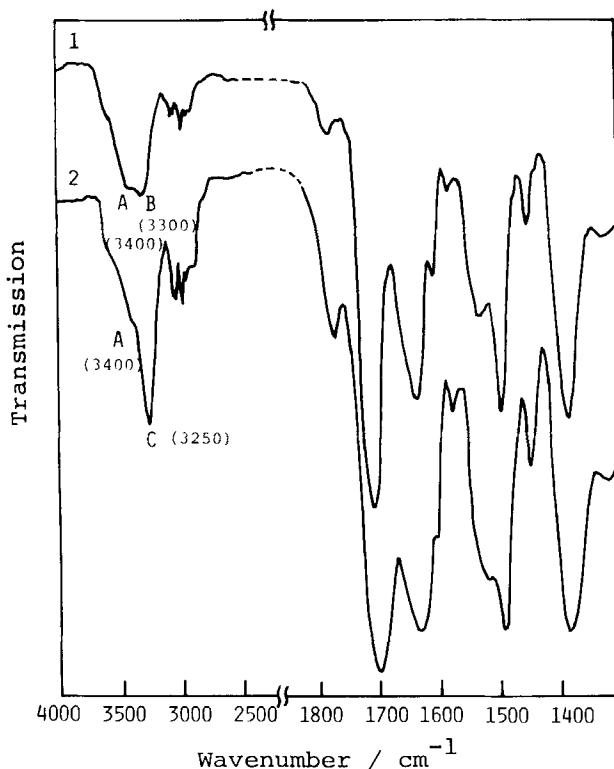


FIG. 1. IR spectra for the poly(*S*)-MBCP: 1) the polymer soluble in THF (Run 1-1) and 2) the polymer insoluble in THF (Run 1-5).

difficult to determine the structure of the polymer, but it seems that the polymers indicated by the C peak at 3250 cm^{-1} have a characteristic conformation and/or configuration; i.e., a threo-diisotactic and/or rigid polymer which is insoluble in organic solvents.

On the other hand, it can be thought that the insolubility is attributable to the molecular weight (\bar{M}_n) of the polymer. The NMR spectrum for poly(*S*)-MBCP (Run 1-1), as shown in Fig. 2, was the same as that for poly(*R*)-MBCP [11]. There were no significant signals assignable to products formed by side reactions. The $^1\text{H-NMR}$ spectrum of the polymer soluble in THF suggests that ordinary addition polymerization took place. In addition, \bar{M}_n for the part of polymer soluble in THF (Runs 1-6 and 1-7 in Table 1) was very small and was similar to those of the polymers obtained in THF (Run 1). The polymers having an \bar{M}_n of more than about 3000 may be insoluble in THF and other solvents. But the copolymers of (*S*)-MBCP and ST or MMA were soluble in THF, as described later. This tendency was also observed for (*R*)-MBCP polymers. The GPC curve for poly(*S*)-MBCP (Run 1-1) is shown in Fig. 3. The polydispersity (the weight-average molecular weight of \bar{M}_w/\bar{M}_n) was small: 1.6–1.9, and a GPC peak for an oligomer originating in a side reaction could not be detected. The \bar{M}_n 's for polymers were as follows: 2.1×10^3 to 3.2×10^3 by GPC; 1.2×10^3 to 2.8×10^3 by VPO.

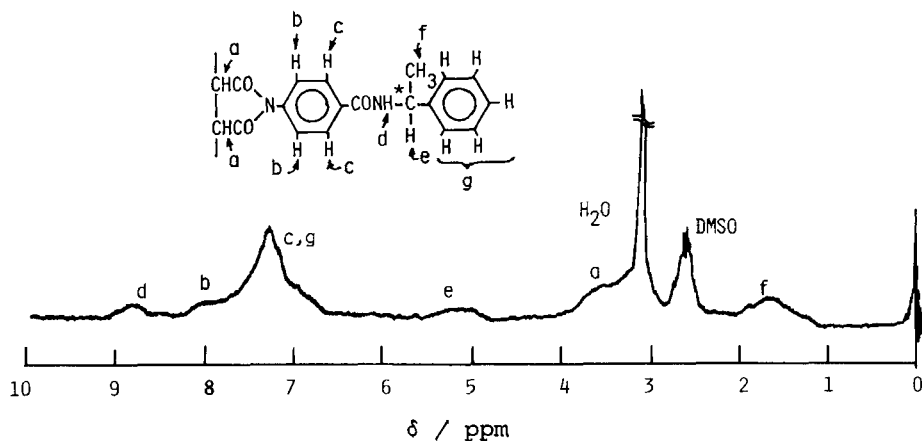


FIG. 2. ¹H-NMR spectrum for the poly((*S*)-MBCP) (Run 1-1).

CD and UV spectra for (*S*)-MBCP and poly((*S*)-MBCP) are shown in Figs. 4 and 5, respectively. In the CD spectrum for poly((*S*)-MBCP), only a large positive peak was observed at about 264 nm. The peak is attributable to the $n \rightarrow \pi^*$ transition of two carbonyl groups in the imide ring and the $\pi \rightarrow \pi^*$ transition of phenyl groups. The magnitudes of molecular ellipticity $[\theta]$ were much greater than that of the model compound for poly((*S*)-MBCP), i.e., *N*-[4-(*N'*-(*S*)- α -methylbenzyl)amino-carbonylphenyl]succinimide ((*S*)-MBSI), as shown in Fig. 4. This suggests that the

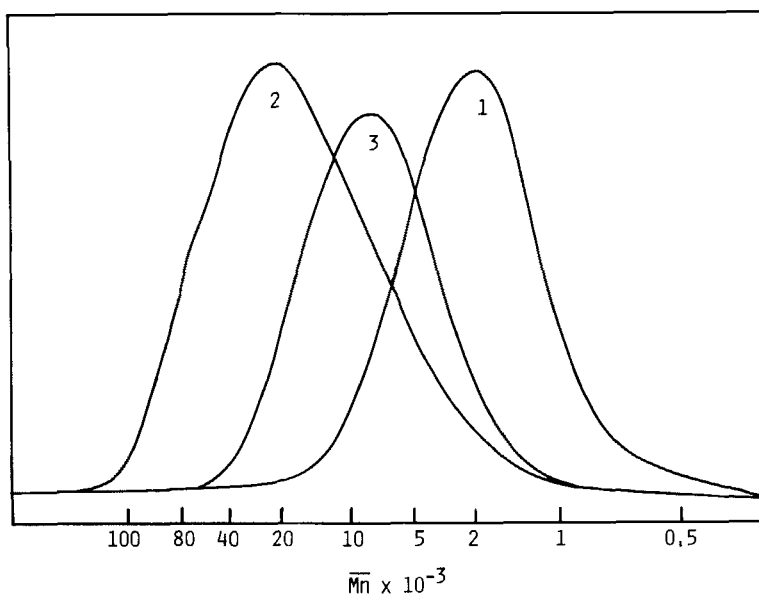


FIG. 3. GPC curves for the poly((*S*)-MBCP)s: 1) poly((*S*)-MBCP (Run 1-1), 2) poly((*S*)-MBCP-co-ST) (Run 2-3), and 3) poly((*S*)-MBCP-co-MMA) (Run 3-3).

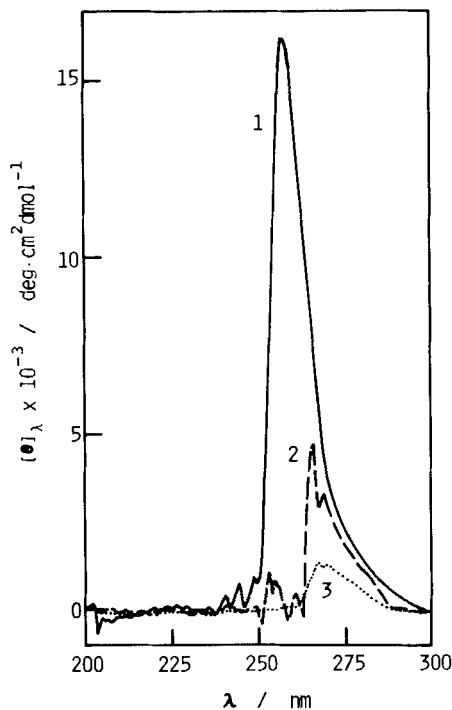


FIG. 4. CD scans for 1) poly(*S*)-MBCP) obtained with AIBN (Run 1-1), 2) (*S*)-MBCP monomer, and 3) (*S*)-MBSI [a model compound of poly(*S*)-MBCP)].

asymmetrical stereocenters of the side chain may influence the stereochemistry developed along the main chain. A possible structure may be the helical conformation of a threo-diisotactic polymer main chain as illustrated in Scheme 2(A).

Cubbon [2] reported the polymerization of eight *N*-substituted maleimide monomers (RMI) by free radical and *n*-BuLi initiators, and that both types of initiator gave rise to polymers which contain a predominantly threo-diisotactic polymer (interpretation) based on x-ray analysis only. RMI polymers may not be completely stereoregular but rather predominantly threo-diisotactic with occasional threo-disyndiotactic placements which disrupt the crystallinity to some extent [2]. The stereospecificity of RMI polymers results from the geometry of the monomer unit. This requires a trans opening of the double bonds and leads to the formation of a helix [2]. This can be supported by inspection of the poly(RMI). That is, a poly(RMI) model implies that threo-diisotactic polymers can form the 3_1 helix having a repeat distance of about 4.5 Å and a helix diameter of about 10 Å. Asymmetric polymerization of nonchiral RMI was carried out with *n*-BuLi/(-)-Sp to obtain chiral polymers. This chirality can be explained as arising from a helix and/or an excess of a chiral center of (*S,S*) or (*R,R*) [9]. These factors can only result from a predominantly threo-diisotactic addition (trans-addition).

The specific rotation of the polymer (Run 1-1) was independent of temperature. The relationship between the specific rotation of the polymer (Run 1-1) and the temperature (3 to 60°C) was linear with a very low slope; the temperature

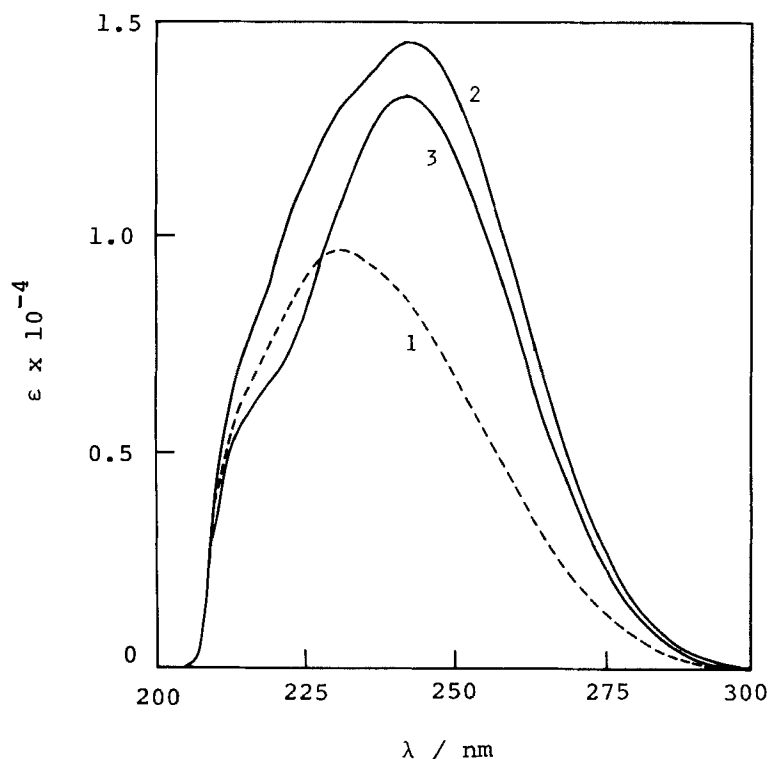


FIG. 5. UV spectra for 1) poly(*S*)-MBCP obtained with AIBN (Run 1-1), 2) (*S*)-MBCP monomer, and 3) (*S*)-MBSI [a model compound of poly(*S*)-MBCP].

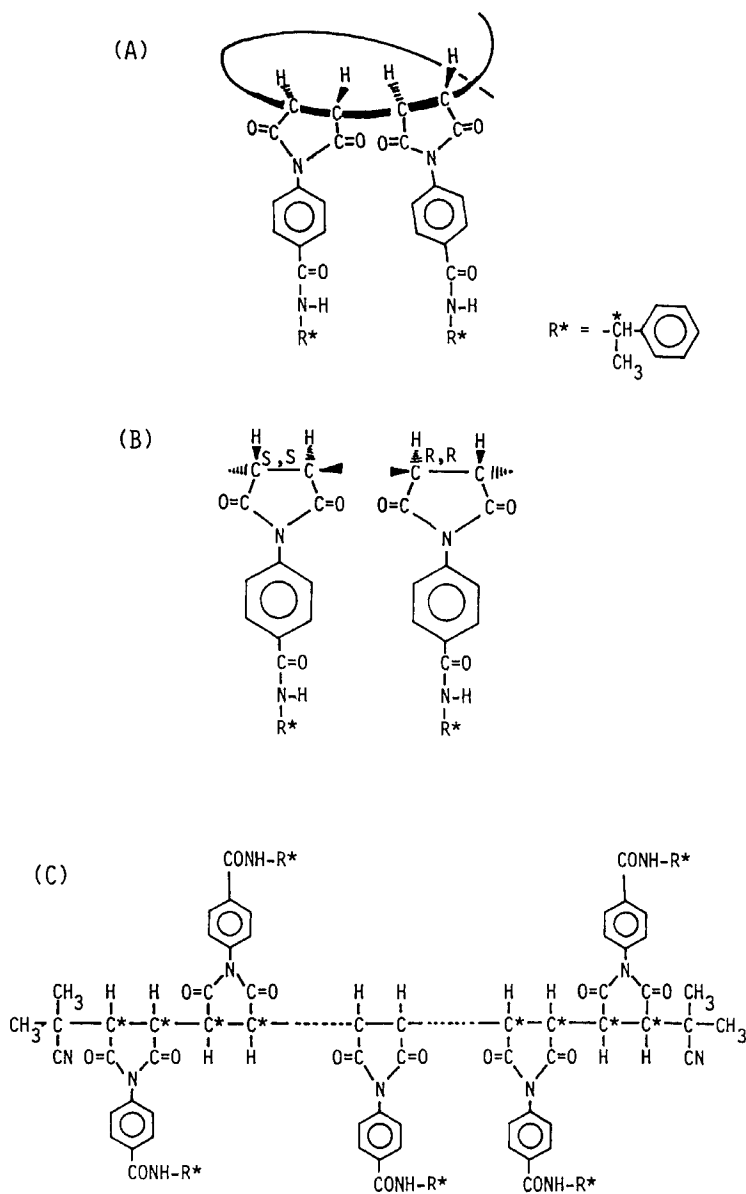
coefficient is $(\Delta[\alpha]_D/\Delta T) = 0.08$. This suggests that the main chain of poly(*S*)-MBCP contains very little helical structure and that there are no competing conformational states contributing to the optical activity.

Another contribution to the chirality of the polymers may be attributable to an excess of either (*S,S*) or (*R,R*) chiral centers, as shown in Scheme 2(B). In this case, more than four successive units of (*S,S*) or (*R,R*); i.e., a continuous threo-diisotactic structure would be required to produce a helix, which is not very likely.

The influence of asymmetric induction around both terminal (*S*)-MBCP units of the polymers cannot be ignored, as illustrated in Scheme 2(C), since the degree of polymerization for the polymers is very small.

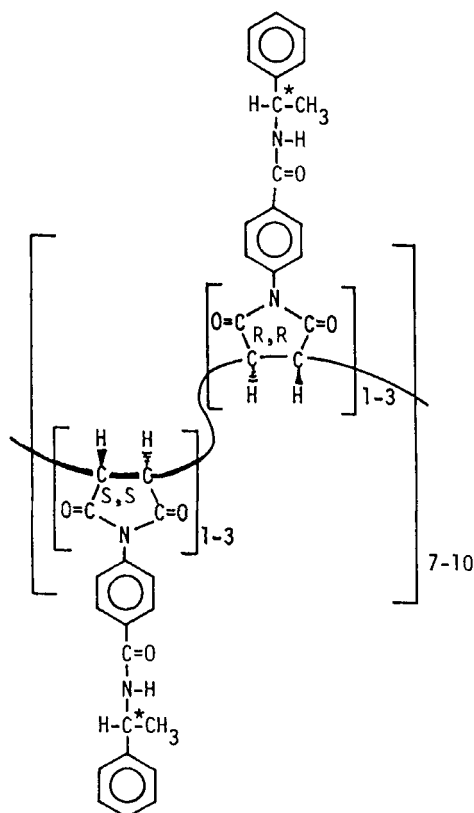
Radical Copolymerizations of (*S*)-MBCP with ST and MMA

The results of radical copolymerizations of (*S*)-MBCP (M_1) with ST (M_2) or MMA (M_2) in THF (16 mL) at 50°C in the presence of AIBN (1.0×10^{-2} mol/L) are summarized in Table 2. A fraction of the copolymer formed in all systems was insoluble in THF, but the soluble fraction of the copolymer was soluble to approximately 0.1 g/10 mL THF. Typical GPC curves for the copolymers are shown in Fig. 3; $\overline{M}_w/\overline{M}_n$ is relatively small. The copolymers are white powders and



SCHEME 2.

optically active in solution. Copolymer-composition curves in the polymerizations of (*S*)-MBCP with ST and MMA are shown in Fig. 6. The monomer reactivity ratios r_1 and r_2 were determined as $r_1 = 0.32$, $r_2 = 0.14$ in the (*S*)-MBCP-ST system and $r_1 = 0.54$, $r_2 = 0.93$ in the (*S*)-MBCP-MMA system according to the integration method by Mayo and Lewis [14]. The Alfrey-Price [15] Q - e values for (*S*)-MBCP were calculated as $Q_1 = 1.74$, $e_1 = 0.96$ in the (*S*)-MBCP-ST system and $Q_1 = 1.11$, $e_1 = 1.23$ in the (*S*)-MBCP-MMA system. The average Q , e values are



SCHEME 3.

1.43 and 1.10, respectively, and are significantly different from those ($Q = 0.96$, $e = 1.18$) for (*R*)-MBCP. This may result from the diastereoisomeric difference arising from a difference in optical purity and steric hindrance based on the cyclic 1,2-disubstituted ethylene type of the maleimide. However, the tendency for large Q and e values was similar to that for other RMIs reported previously [16].

Optical Behavior of Copolymers

In both CD and UV spectra for poly(*S*)-MBCP-*co*-STs and poly(*S*)-MBCP-*co*-MMA)s, as shown in Figs. 7 and 8, a positive Cotton effect around 264 nm was observed. It was 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 (*S*)-MBCP and MMA units.

Figure 9 shows the dependence of specific rotations $[\alpha]_D^{25}$ and molecular ellipticities $[\theta]_{25}^{264}$ on the composition (wt% and mol%) of poly(*S*)-MBCP-*co*-STs. The specific rotation $[\alpha]_D$ of a mixture of poly(*S*)-MBCP and poly(ST) shows a linear relationship (going through the origin) with the weight percent values of poly(*S*)-MBCP (5 in Fig. 9). The absolute values of specific rotations of poly(*S*)-MBCP-*co*-STs increased with the (*S*)-MBCP unit content. However, a little deviation from linearity was observed. This suggests that asymmetric induction took place in the

TABLE 2. Radical Copolymerization of (S)-MBCP (M_1) with ST (M_2) or MMA (M_2) in the THF (16 mL) at 50°C^a

Run	M_2	M_1 in monomer, mol%	Polymerization time, h	Conversion, %	N, %	M_1 in copolymer, mol%	$\bar{M}_n \times 10^{-3b}$	\bar{M}_w/\bar{M}_n^b	$[\alpha]_D^{25}$, degree ^c
2-1	ST	19.9	12	23.7	6.04	42.1	16.3	2.67	53.1
2-2	ST	39.4	12	43.7	6.60	50.0	19.3	1.83	58.7
2-3	ST	50.3	12	45.1	6.82	53.5	8.7	2.54	60.3
2-4	ST	60.6	12	38.6	6.88	54.5	6.2	2.45	63.4
2-5	ST	78.4	12	39.1	7.71	70.8	4.1	2.14	90.0
3-1	MMA	20.1	12	21.3	3.50	17.3	11.0	2.07	32.2
3-2	MMA	39.2	12	21.6	5.68	36.8	6.8	1.78	50.4
3-3	MMA	48.2	12	18.2	6.52	47.8	6.7	1.38	60.3
3-4	MMA	61.5	12	28.9	6.85	53.0	3.1	1.89	89.9
3-5	MMA	78.6	12	28.2	7.67	69.0	3.4	1.85	93.5

^a[AIBN] = 1.0×10^{-2} mol/L; $M_1 + M_2 = 2.0$ g.^bBy GPC.^c $c = 1.0$; THF, $l = 10$ cm.

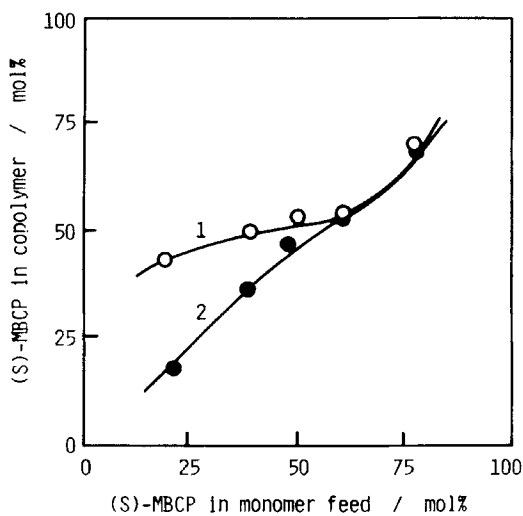


FIG. 6. Copolymer composition curves for 1) (S)-MBCP-ST and 2) (S)-MBCP-MMA system.

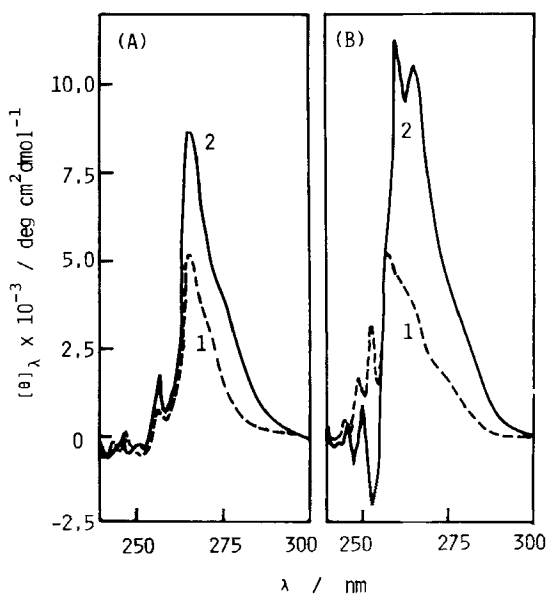


FIG. 7. CD spectra for (A) poly((S)-MBCP-co-ST) and (B) poly((S)-MBCP-co-MMA): 1) 20 mol% of (S)-MBCP in monomer feed (Runs 2-1 and 3-1), and 2) 80 mol% of (S)-MBCP in monomer feed (Runs 2-5 and 3-5).

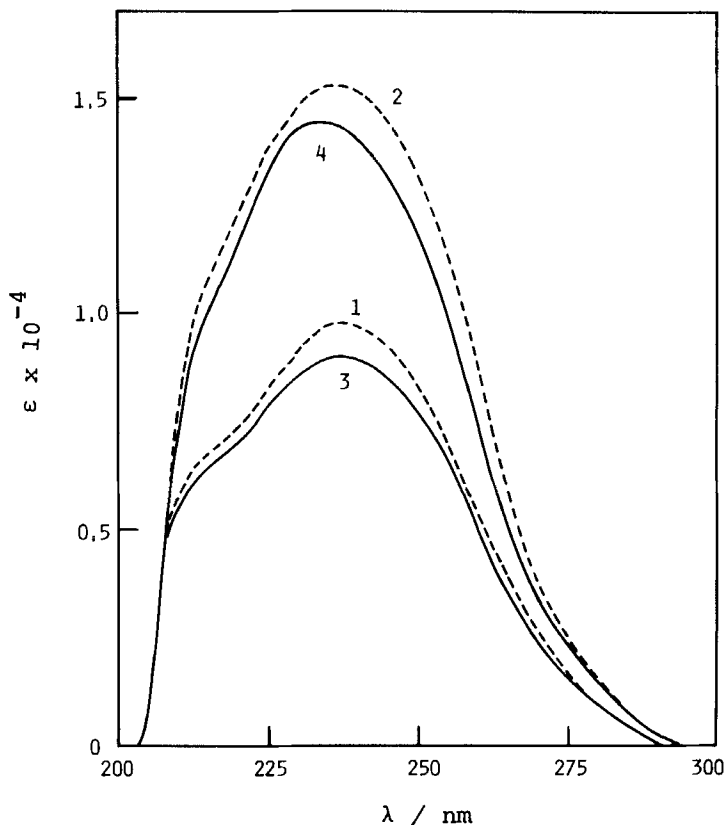


FIG. 8. UV spectra for the copolymers poly(*S*)-MBCP-*co*-ST): 1) Run 2-1, 2) Run 2-5, and poly(*S*)-MBCP-*co*-MMA): 3) Run 3-1, 4) Run 3-5.

main chain of the copolymers. The same tendency could be observed in poly(*S*)-MBCP-*co*-MMA)s, as shown in Fig. 10. It is interesting to note that asymmetric induction copolymerization occurred even though an asymmetric carbon was not favorably located in the vicinity of a maleimide ring. All the specific rotations for the (*S*)-MBCP copolymers were smaller than those for the mixture of poly(*S*)-MBCP) and poly(ST) or poly(MMA). This tendency was recognized in the (*R*)-MBCP copolymers. In the copolymerization of MBZMI with ST or MMA, a similar asymmetric induction into the copolymer main chain took place [10]. However, all the specific rotations for the MBZMI copolymers were greater than those for the mixture. The opposite chiral character may be associated with the *N*-substituent. Further details of this cannot be argued since only MBZMI and MBCP have been investigated so far.

The relationship between specific rotation of the copolymers (Runs 2-3 and 3-3) and the experimental temperature is linear, and the slopes are very small (the temperature coefficient: $\Delta[\alpha]_D/\Delta T = 0.08\text{--}0.11$). This suggests that a helical conformation may be absent in the copolymers as well as poly(*S*)-MBCP).

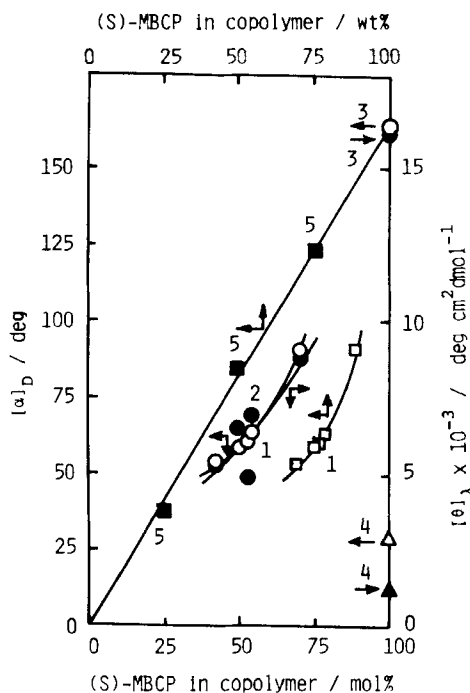


FIG. 9. Dependence of 1) specific rotations $[\alpha]_D^{25}$ and 2) molecular ellipticities $[\theta]_{262}^{25}$ on the composition (wt% and mol%) of poly((S)-MBCP-co-ST)s, 3) poly((S)-MBCP), 4) (S)-MBSI, and 5) a mixture of poly((S)-MBCP) and poly(ST).

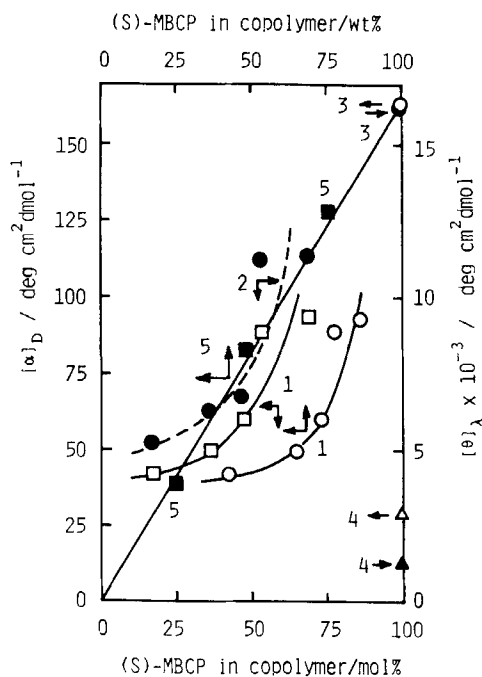


FIG. 10. Dependence of 1) specific rotations $[\alpha]_D^{25}$ and 2) molecular ellipticities $[\theta]_{262}^{25}$ on the composition (wt% and mol%) of poly((S)-MBCP-co-MMA)s, 3) poly((S)-MBCP), 4) (S)-MBSI, and 5) a mixture of poly((S)-MBCP) and poly(MMA).

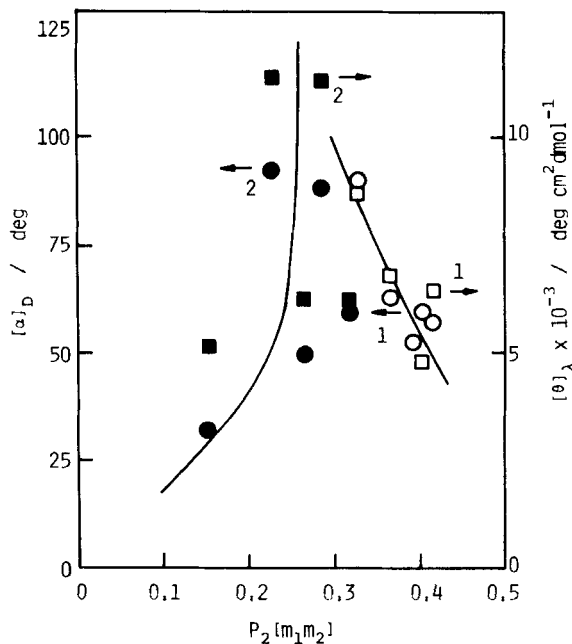


FIG. 11. Relationships between specific rotations $[\alpha]_D^{25}$, molecular ellipticities $[\theta]_{262}^{25}$ and 1) (*S*)-MBCP-ST, 2) (*S*)-MBCP-MMA diad sequence ($P_2[m_1m_2]$) in the copolymer.

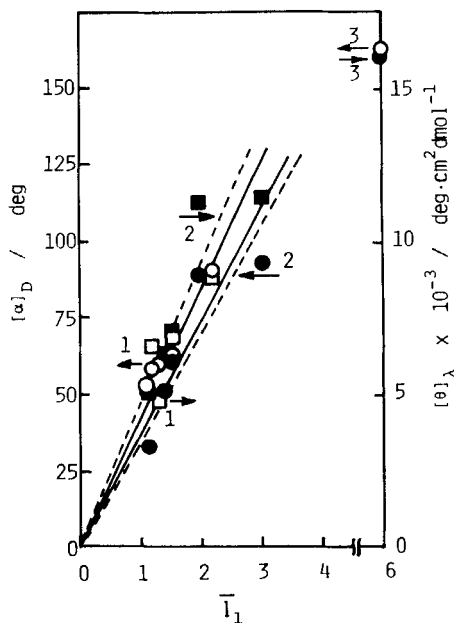


FIG. 12. Relationships between specific rotation $[\alpha]_D$ and average sequence length of (*S*)-MBCP unit (\bar{l}_1) in 1) poly((*S*)-MBCP-co-ST)s, 2) poly((*S*)-MBCP-co-MMA)s, and 3) poly((*S*)-MBCP).

Figure 11 indicates the dependence of a diad sequence [17, 18], $P_2[m_1m_2]$, on specific rotations of the copolymers. The $P_2[m_1m_2]$ value indicates the probability of a (S)-MBCP-ST or a (S)-MBCP-MMA diad sequence. $P_2[m_1m_2]$ was derived as follows:

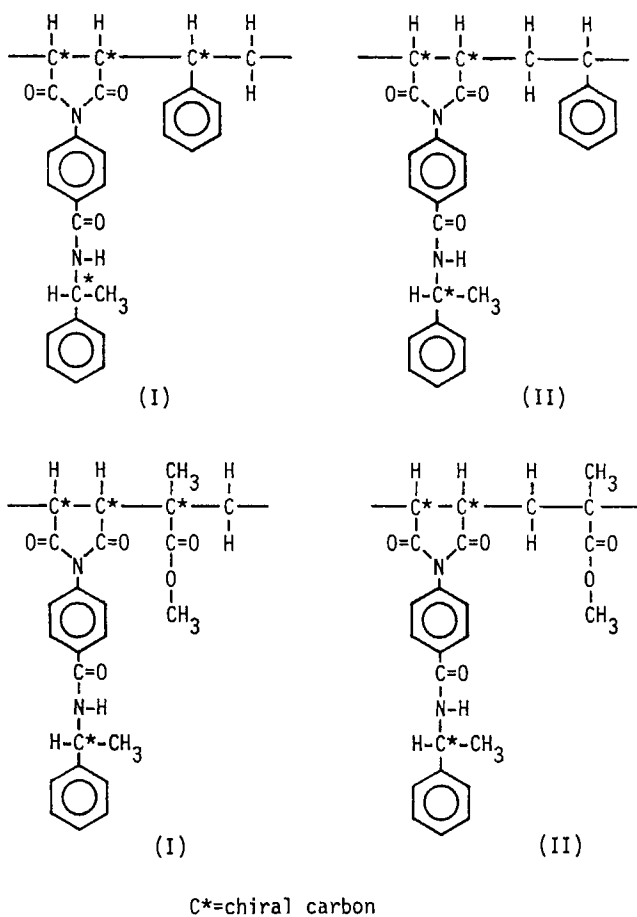
$$P_1[m_1] + P_1[m_2] = 1$$

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

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

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 (S)-MBCP. $1 + r_1X$ indicates an average sequence length (\bar{l}_1).

In both the (S)-MBCP-ST and (S)-MBCP-MMA systems, specific rotations and molecular ellipticities increased with the diad sequence ($P_2[m_1m_2]$). However, the relationship was not linear, which suggests that a new asymmetric center appeared not only in the (S)-MBCP-ST or (S)-MBCP-MMA diad sequences but also in other sequences. Figure 12 shows the relationship between specific rotation and



SCHEME 4.

average sequence length [19] (\bar{l}_1) of (*S*)-MBCP units in poly((*S*)-MBCP-*co*-ST)s and poly((*S*)-MBCP-*co*-MMA)s. An average (mean) sequence length (\bar{l}_1) is given by $1 + r_1 X$ in derivation equations of the $P_2[m_1, m_2]$, as described above. The specific rotation and the molecular ellipticities increase almost linearly with the average sequence length. This indicates that a new asymmetric center might be introduced into (*S*)-MBCP unit sequence. In this case, as described in the Homopolymerization Section, the occurrence of threo-diisotactic polymerization was required, and the chirality is attributable to excessive chiral center of (*R,R*) or (*S,S*) in the polymer main chain. It may be concluded that asymmetric induction took place in both (*S*)-MBCP-ST or (*S*)-MBCP-MMA and (*S*)-MBCP unit sequences, as illustrated in Scheme 4 (C* is a chiral carbon).

CONCLUSIONS

(1) A novel type of optically active *N*-[4-*N'*-(α -methylbenzyl)amino-carbonylphenyl]maleimide [(*S*)-MBCP] was synthesized and polymerized with radical initiators to obtain chiral polymers.

(2) The CD pattern of (*S*)-MBCP polymers was different from that of the polymer model compound. This indicates that a new chiral center may appear in the polymer main chain, and asymmetry may be ascribed to excessive chiral centers of (*R,R*) or (*S,S*) of (*S*)-MBCP unit sequence.

(3) From the results of radical copolymerizations of (*S*)-MBCP (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: $r_1 = 0.32, r_2 = 0.14; Q_1 = 1.74, e_1 = 0.96$ in the (*S*)-MBCP-ST system, and $r_1 = 0.54, r_2 = 0.93, Q_1 = 1.11, e_1 = 1.23$ in the (*S*)-MBCP-MMA system.

(4) Asymmetric induction copolymerization took place in both the (*S*)-MBCP-ST and (*S*)-MBCP-MMA systems. A new asymmetric center appeared not only in the (*S*)-MBCP-ST and (*S*)-MBCP-MMA diad sequences, but also in the (*S*)-MBCP unit sequence.

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