Asymmetric induction copolymerization of chiral *N*-(*R*-α-methylbenzyl)maleimide with achiral *N*-(substituted)maleimide

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Radical and anionic copolymerizations of optically active *N*-(*R*-α-methylbenzyl)maleimide (MBZMI, M_1) with *N*-(phenyl)maleimide (PhMI, M_2) or *N*-(cyclohexyl) maleimide (CHMI, M_2) were performed in benzene at 60°C and toluene at 0°C, respectively. The monomer reactivity ratios (r_1, r_2) were determined. From these values, the m_1m_2 diad sequence content was evaluated. In the radical systems, the relationship between the specific rotations and the MBZMI content (wt%) in the copolymers showed a deviation from linearity. In the anionic systems, however, the relationship was almost linear. This suggests that the main polymer chains have different conformational structures and that asymmetry was induced into the polymer main chain.

(Keywords: radical copolymerization; anionic copolymerization; *N*-substituted maleimide; monomer reactivity ratio; optically active polymer)

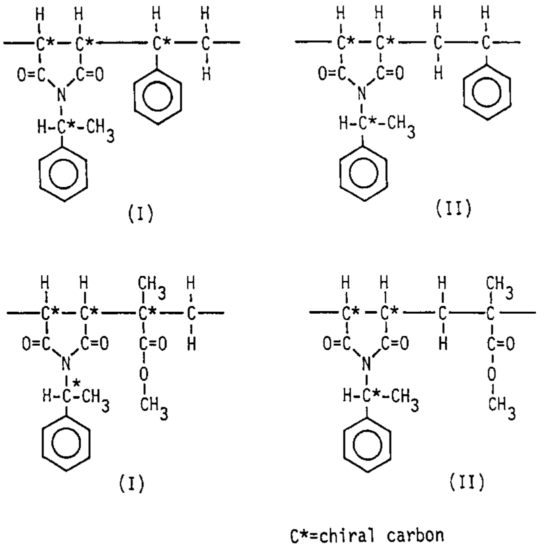
INTRODUCTION

Polymerization and copolymerization of optically active *N*-(*R*-α-methylbenzyl)maleimide (MBZMI or R-MBZMI) have been reported[1]. In the polymerization of MBZMI, the specific rotations ($[\alpha]_D$) were very different in the polymers obtained with a different initiator (radical or anionic) and a different polymerization solvent. In the radical copolymerization of MBZMI with styrene (ST) or methyl methacrylate (MMA), the relationship between the MBZMI content (wt%) in the copolymers and the specific rotation showed a considerable deviation from linearity. This suggests that asymmetry was introduced into the copolymer main chain, as shown in *Scheme 1* (type I).

Recently, we reported on polymerizations and copolymerizations of optically active *N*-(L-menthoxycarbonylmethyl)maleimide (MGMI)[2], *N*-(4-*N'*-(*R*-α-methylbenzyl)aminocarbonylphenyl)maleimide (MBPM)[3,4], *N*-(4-*N'*-(*R*-α-methylbenzyl)aminocarbonylmethyl)maleimide (MBCM)[5] and *N*-(cholesteroxycarbonylmethyl)maleimide (ChMI)[6]. In these reports, there was the possibility that a new asymmetric centre appeared in the repeating units of optically active *N*-(substituted)maleimide (RMI) because of the *threo*-diisotactic structure of the RMI polymer main chain, as illustrated in *Scheme 1* (type II).

Polymerizations of *cis*-cyclic alkene derivatives can yield two *trans* openings of the double bond, i.e. chiral centres of (*S,S*) and (*R,R*) as shown in *Scheme 2* (type I). If one is produced more than the other, the polymer obtained can be optically active[7].

In this paper, not a vinyl type monomer such as ST or MMA but a 1,2-disubstituted cyclic ethylene type monomer, i.e. a *cis*-cyclic alkene, was used as a comonomer of MBZMI. The aim of this paper is to explore the reactivities and chiroptical properties of the resulting copolymers in the copolymerization of a chiral *cis*-cyclic alkene with an achiral *cis*-cyclic alkene. Radical and anionic copolymerizations of an optically active MBZMI with *N*-(phenyl)maleimide (PhMI) or *N*-(cyclohexyl)maleimide (CHMI) were performed in benzene at 60°C and in toluene at 0°C, respectively. From the results, monomer reactivity ratios were determined. Asymmetric induction into the copolymer main chain is discussed based on the specific rotations and molecular ellipticities of the copolymers. The polymerization



Scheme 1

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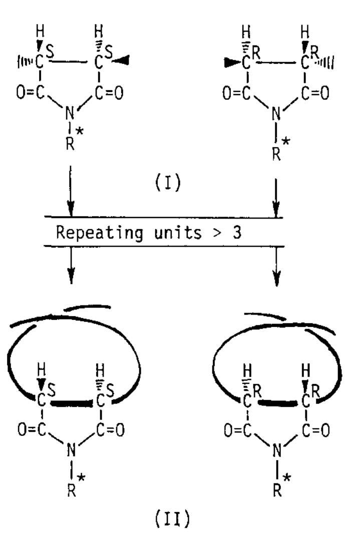


Scheme 2

reactivities and the chiroptical properties are discussed, and compared with those for poly(MBZMI-*co*-ST) and poly(MBZMI-*co*-MMA) reported previously[1].

There have been many reports[8–18] including patents[19–21] on the polymerization and copolymerization of RMI. However, except for our work, only a few investigations on the polymerization of optically active RMI have been carried out[22,23]. Consequently, the polymerization reactivities and chiroptical properties of chiral RMIs have not been extensively investigated.

EXPERIMENTAL

Monomers and model compounds

MBZMI (R-MBZMI) was synthesized from maleic anhydride and optically active *R*-α-methylbenzylamine, according to a procedure reported previously[1]; yield 45.6%; b.p. 137°C/2.1 × 10^{-2} mmHg; $[\alpha]_D = 72.1°$ ($c = 1.0$ g dl^{-1}; $l = 10$ cm; tetrahydrofuran, THF).

PhMI and CHMI were synthesized from maleic anhydride and the corresponding amine, according to the usual synthesis method of RMI[24]; PhMI: m.p. 91.0°C and CHMI: m.p. 89.0°C.

A model compound of poly(R-MBZMI)[1], i.e. *N*-(*R*-α-methylbenzyl)succinimide (R-MBZCI) was prepared from succinic anhydride and *R*-α-methylbenzylamine; b.p. 123–125°C/2.6 × 10^{-2} mmHg; $[\alpha]_D = 73.0°$ ($c = 1.0$ g dl^{-1}; $l = 10$ cm; THF).

A model compound of poly(S-MBZMI)[1], i.e. *N*-(*S*-α-methylbenzyl)succinimide (S-MBZCI) was prepared from succinic anhydride and *S*-α-methylbenzylamine; b.p. 123–124°C/2.5 × 10^{-2} mmHg; $[\alpha]_D = -75.1°$ ($c = 1.0$ g dl^{-1}; $l = 10$ cm; THF).

Other materials

Benzene, THF, toluene and other solvents were purified by the usual methods. 2,2′-Azobisisobutyronitrile (AIBN) was purified by recrystallization from chloroform twice, but commercially available n-butyllithium (n-BuLi) hexane solution was used without further purification.

Radical and anionic copolymerization

Radical copolymerization was performed with AIBN as an initiator in benzene in a sealed tube at 60°C. After polymerization, the solution was poured into excess methanol to precipitate the polymer. The polymer obtained was purified by reprecipitation from the THF solution into methanol three times. The polymer was filtered and dried *in vacuo* for 3 days at 40°C. The composition of the resulting copolymer was determined from ^{1}H n.m.r. spectra.

Anionic copolymerization was achieved in toluene at 0°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 excess methanol. The obtained polymer was purified by reprecipitation three times from the THF solution into methanol, and then filtered and dried *in vacuo* at 40°C.

Measurements

D-line specific rotations were measured with a Jasco DIP-140 (Japan Spectroscopic Co.) at 25°C. Optical rotatory dispersion (o.r.d.) and circular dichroism (c.d.) spectra were obtained at 25°C by a Jasco J-20C (Japan Spectroscopic Co.), equipped with a xenon source and a computing data processor. Molecular weights of copolymers were measured by g.p.c. on a Shimadzu LC 3A equipped with a data processor, using THF as the eluent and Shimadzu polystyrene gel HGS-10-15-20-40. N.m.r. spectra were obtained with a JEOL JNM-MH-100.

RESULTS AND DISCUSSION

Radical copolymerization of MBZMI with PhMI and CHMI

Radical copolymerizations of MBZMI (M_1) with PhMI (M_2) and CHMI (M_2) were performed with AIBN in benzene at 60°C. The results are summarized in *Table 1*. Copolymerization proceeded homogeneously throughout. The resulting copolymers were white powders and optically active. The rates of copolymerization for MBZMI with PhMI or CHMI were much smaller than those for MBZMI with ST or MMA. The $\overline{M_n}$ values of the poly(MBZMI-*co*-PhMI)s were similar to those of poly(MBZMI-*co*-CHMI)s, and smaller than those for poly(MBZMI-*co*-ST) and poly(MBZMI-*co*-MMA)[1].

Copolymer–composition curves of both systems, as shown in *Figure 1*, indicated a type of copolymerization along an azeotropic line. Monomer reactivity ratios, r_1 and r_2, determined by the Integration method[25] and the High Conversion method[26] were as follows: $r_1 = 0.79$, $r_2 = 0.69$ in the MBZMI–PhMI system and $r_1 = 0.40$, $r_2 = 1.06$ in the MBZMI–CHMI system.

Anionic copolymerization of MBZMI with PhMI and CHMI

Anionic copolymerizations of MBZMI (M_1) with PhMI (M_2) and CHMI (M_2) were performed with n-BuLi in toluene at 0°C. The results are summarized in *Table 2*. Copolymerization proceeded homogeneously throughout. The obtained copolymers were white powders and optically active. The $\overline{M_n}$ values of the poly(MBZMI-*co*-PhMI)s were 1.4×10^3–3.3×10^3, which were smaller than those of the copolymers obtained with AIBN.

Copolymer–composition curves of the MBZMI–PhMI and MBZMI–CHMI systems are shown in *Figure 2*. Each composition curve of the MBZMI–PhMI or MBZMI–CHMI system was almost the same as that of

Table 1 Radical copolymerization of MBZMI (M_1) with PhMI (M_2) or CHMI (M_2) in benzene (6 ml) at 60°C[a]

Run	M_2	M_1 in monomer (mol%)	Polym. time (h)	Conversion (%)	M_1 in copolymer (mol%)	$\overline{M}_n$[b] ($\times 10^{-3}$)	$\overline{M}_w/\overline{M}_n$[b]	$[\alpha]_D$[c] (deg)
1-1	PhMI	9.9	9.0	28.8	13.5	15.3	2.58	2.1
1-2	PhMI	20.1	9.0	22.5	18.1	10.0	2.65	3.8
1-3	PhMI	29.9	12.0	31.1	38.5	8.9	2.71	5.1
1-4	PhMI	52.1	12.0	22.7	53.6	7.1	2.54	5.5
1-5	PhMI	70.0	12.0	13.4	70.1	6.5	2.05	6.1
1-6	PhMI	90.0	12.0	8.8	88.2	5.3	1.67	8.9
2-1	CHMI	10.0	10.0	36.1	10.0	11.2	1.60	2.2
2-2	CHMI	30.8	10.0	28.1	24.0	9.3	1.78	5.4
2-3	CHMI	50.3	14.0	28.8	40.2	7.7	1.92	9.3
2-4	CHMI	70.0	14.0	13.9	58.8	6.5	1.59	14.1
2-5	CHMI	89.8	20.0	11.7	81.8	5.6	1.38	15.3

[a] $[AIBN] = 1.0 \times 10^{-2}\ mol\ l^{-1}$; $M_1 + M_2 = 2.0\ g$
[b] By g.p.c.
[c] $c = 1.0\ g\ dl^{-1}$, THF, $l = 10\ cm$

Table 2 Anionic copolymerization of MBZMI (M_1) with PhMI (M_2) or CHMI (M_2) in toluene (6 ml) at 0°C[a]

Run	M_2	M_1 in monomer (mol%)	Polym. time (h)	Conversion (%)	M_1 in copolymer (mol%)	$\overline{M}_n$[b] ($\times 10^{-3}$)	$\overline{M}_w/\overline{M}_n$[b]	$[\alpha]_D$[c] (deg)
3-1	PhMI	10.2	18.0	37.7	15.6	2.2	2.21	3.9
3-2	PhMI	30.4	18.0	46.0	31.9	2.6	2.09	13.2
3-3	PhMI	50.5	18.0	44.3	48.4	1.4	1.06	20.7
3-4	PhMI	70.1	18.0	26.5	71.7	1.9	1.57	30.5
3-5	PhMI	90.0	18.0	30.1	83.1	3.3	1.70	31.8
4-1	CHMI	9.9	18.0	52.8	8.1	2.9	1.82	4.6
4-2	CHMI	30.1	18.0	36.7	23.2	3.2	2.08	12.4
4-3	CHMI	51.2	18.0	32.4	38.3	2.9	2.35	21.3
4-4	CHMI	70.0	18.0	19.2	53.1	2.5	1.94	24.0
4-5	CHMI	89.8	18.0	24.1	65.8	3.0	1.36	27.7

[a] $[n\text{-}BuLi] = 1.0 \times 10^{-2}\ mol\ l^{-1}$; $M_1 + M_2 = 2.0\ g$
[b] By g.p.c.
[c] $c = 1.0\ g\ dl^{-1}$, THF, $l = 10\ cm$

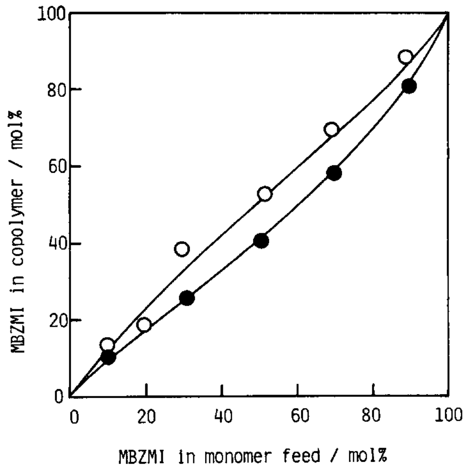


Figure 1 Copolymer composition curves for the MBZMI–PhMI system initiated with (○) AIBN and (●) n-BuLi

the radical copolymerization. In both the radical and anionic systems, the CHMI content in the polymer was lower than that of PhMI. The monomer reactivity ratios, r_1 and r_2, were calculated to be as follows: $r_1 = 0.50$, $r_2 = 0.49$ in the MBZMI–PhMI system and $r_1 = 0.11$, $r_2 = 1.09$ in the MBZMI–CHMI system.

Optical behaviour of the copolymers

Figure 3 shows the relationship between the specific rotation and the MBZMI content (wt%) in both radical copolymerization systems. The specific rotations of a mixture of poly(MBZMI) and poly(PhMI) showed a good linear relationship, as shown in *Figure 3*. The absolute values of the specific rotations of poly(MBZMI-*co*-PhMI)s increased with the MBZMI content (wt%). However, a significant deviation from linearity was observed, which suggests that asymmetric induction occurred in the main chain of the copolymers. In poly(MBZMI-*co*-CHMI)s, the same tendency could be observed, as shown in *Figure 3*. The deviations in the poly(MBZMI-*co*-PhMI) and poly(MBZMI-*co*-CHMI) were much smaller than those in the poly(MBZMI-*co*-ST) and poly(MBZMI-*co*-MMA) reported previously[1], as shown in *Figure 3*. It is difficult to explain why the deviation in the copolymerization of MBZMI with the vinyl type monomer is greater than that of MBZMI with RMI. However, in the radical copolymerization of MBCM[5] with ST, MMA or RMI, similar tendencies were

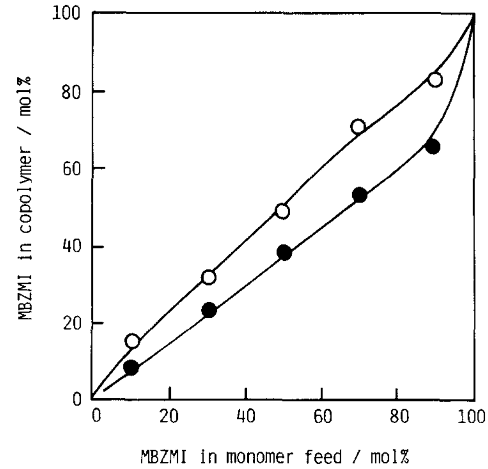


Figure 2 Copolymer composition curves for the MBZMI–CHMI system initiated with (○) AIBN and (●) n-BuLi

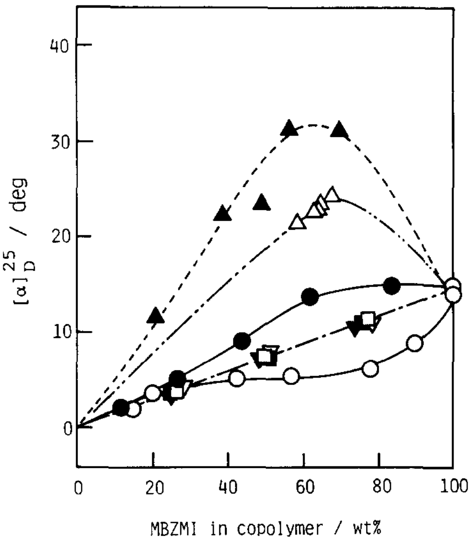


Figure 3 Dependence of specific rotations $[\alpha]_D^{25}$ on the composition (wt%) of: (○) poly(MBZMI-*co*-PhMI)s; (●) poly(MBZMI-*co*-CHMI)s; (△) poly(MBZMI-*co*-ST)s; (▲) poly(MBZMI-*co*-MMA)s; (□) a mixture of poly(MBZMI) and poly(PhMI); (■) a mixture of poly(MBZMI) and poly(CHMI); (▽) a mixture of poly(MBZMI) and poly(ST); (▼) a mixture of poly(MBZMI) and poly(MMA) obtained with AIBN in benzene

recognized. The reason may be attributed to the characteristic conformation of the RMI polymers. The polymers resulting from radical initiators may contain not only *threo*-diisotactic but syndiotactic structures, as reported by Cubbon[27].

The relationship between the specific rotation and the MBZMI content (wt%) for both anionic copolymerization systems is shown in *Figure 4*. The absolute values of the specific rotations of the poly(MBZMI-*co*-PhMI)s almost linearly increased with the MBZMI content (wt%). In the MBZMI–CHMI system, the absolute values of the specific rotations showed a little deviation from linearity. These results were very different from those of the radical copolymerizations. The reason why the deviation was different may result from an excess of chiral centres of (*R*,*R*) or (*S*,*S*) in the main chain, as illustrated in *Scheme 2* (type I). The repeating units of (*R*,*R*) or (*S*,*S*), which can be formed by the *threo*-diisotactic addition of RMI, can make a helix [*Scheme 2* (type II)].

The specific rotation ($[\alpha]_D = \sim 40°$) of the polymer obtained using n-BuLi is much larger than that of the polymer obtained radically ($[\alpha]_D = 14°$). However, the specific rotations of the R-MBZMI monomer, R-MBZCI [model compound of poly(R-MBZMI)] and S-MBZCI [model compound of poly(S-MBZMI)] are +72.1, +73.0 and −75.1°. If asymmetry into the polymer main chain is not induced, the resulting polymer may show a specific rotation ($[\alpha]_D$) of ~ +73°. The difference (~59°) of the specific rotation between the polymer obtained radically and R-MBZCI (the model of poly(MBZMI)) is much greater than that (~33°) of the specific rotation between the polymer obtained anionically and R-MBZCI. This suggests that the asymmetric induction in the radical homopolymerization was significantly greater than that in the anionic one.

In the copolymerizations, similar tendencies were observed. In the radical copolymerization, as shown in *Figure 3*, the M_2 monomer unit (PhMI or CHMI) greatly contributes to the optical rotation of the copolymer. In the anionic copolymerizations, however, the M_2 monomer unit only slightly contributes to it, as shown in *Figure 4*.

In both the MBZMI–PhMI and the MBZMI–CHMI systems, the relationship between the specific rotations of the copolymers and the temperature was linear, and the slopes were very small [the temperature coefficients ($\Delta[\alpha]_D/\Delta T$) = 0.11–0.14]. Thus, there may scarcely be a complete helix in poly(MBZMI-*co*-PhMI) and poly(MBZMI-*co*-CHMI) or in the homopolymers[1]. The polymer and copolymer may have an almost linear structure as illustrated in *Scheme 3*. That is, more than four successive units of (*S*,*S*) or (*R*,*R*) cannot exist, because more than a four-unit sequence would produce a helix, as shown in *Scheme 2* (type II). This can be confirmed by inspection of a poly(MBZMI).

As shown in *Figure 5*, the polymers obtained with both n-BuLi and AIBN gave a negative c.d. peak at ~250 nm. This also suggests that the polymer and copolymer contain the *threo*-diisotactic structure.

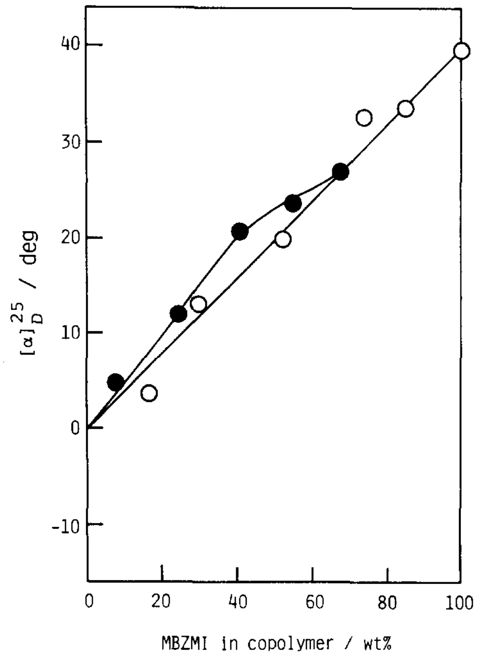
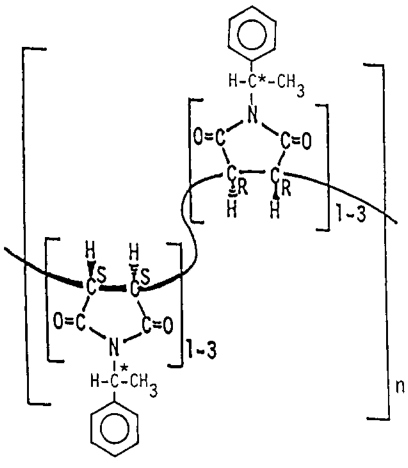


Figure 4 Dependence of specific rotations $[\alpha]_D^{25}$ on the composition (wt%) of (○) poly(MBZMI-*co*-PhMI)s and (●) poly(MBZMI-*co*-CHMI)s obtained with n-BuLi in toluene



Scheme 3

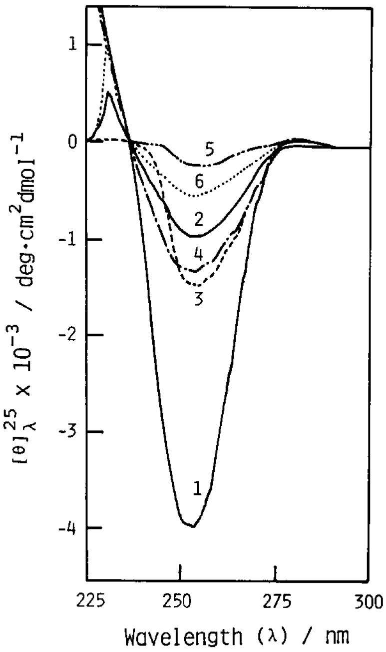


Figure 5 C.d. spectra for: (1) poly(MBZMI) obtained with n-BuLi in THF; (2) poly(MBZMI) obtained with n-BuLi in toluene; (3) poly(MBZMI-*co*-PhMI) (run 1-4); (4) poly(MBZMI-*co*-CHMI) (run 2-3); (5) poly(MBZMI-*co*-PhMI) (run 3-3); (6) poly(MBZMI-*co*-CHMI) (run 4-3)

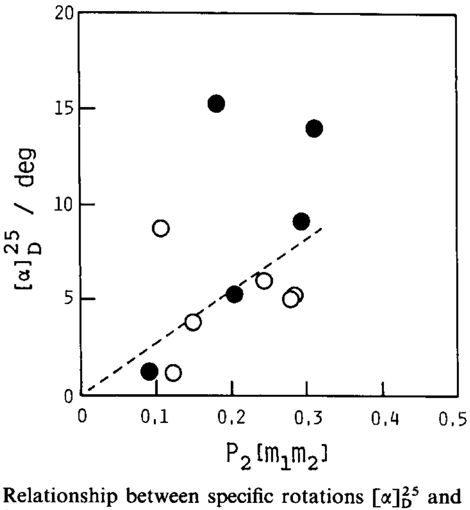
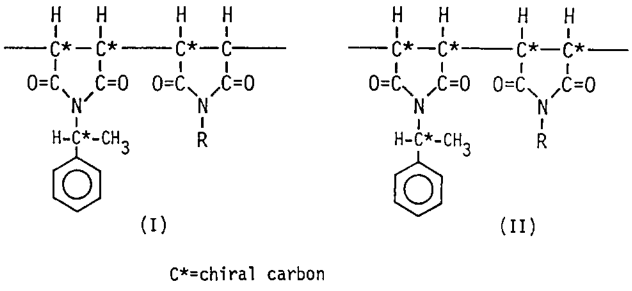


Figure 6 Relationship between specific rotations $[\alpha]_D^{25}$ and the diad sequence of the copolymer obtained with AIBN: (○) poly(MBZMI-*co*-PhMI); (●) poly(MBZMI-*co*-CHMI)



Scheme 4

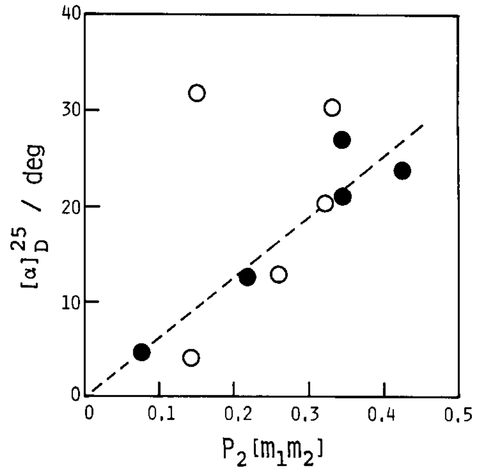


Figure 7 Relationship between specific rotations $[\alpha]_D^{25}$ and the diad sequence of the copolymer obtained with n-BuLi: (○) poly(MBZMI-*co*-PhMI); (●) poly(MBZMI-*co*-CHMI)

Asymmetric polymerization of achiral RMI gave optically active RMI polymers having relatively high specific rotation (*N*-cyclohexylmaleimide: $[\alpha]_D = \sim -40°$)[28,29]. It seemed that this asymmetry was attributed to the *threo*-diisotactic structure. The c.d. pattern of the resulting RMI polymers indicated a large negative or positive Cotton effect at ~250 nm[28,29].

In the c.d. spectra for poly(MBZMI-*co*-PhMI)s, as shown in *Figure 5*, one negative peak at ~250 nm was observed. The peak was ascribed both to the $\pi \rightarrow \pi^*$ transition of phenyl groups in the MBZMI and PhMI units and to the $n \rightarrow \pi^*$ transition of carbonyl groups in the MBZMI unit. In the c.d. spectra for poly(MBZMI-*co*-CHMI)s, a similar pattern was observed.

Figure 6 shows the dependence of a diad sequence[30,31] ($P_2[m_1m_2]$) on the specific rotations. The $P_2[m_1m_2]$ values, which were determined from the monomer reactivity ratios, indicate the probability of a MBZMI–PhMI or a MBZMI–CHMI diad sequence. In both radical copolymerization systems, the specific rotations generally increased with an increase of the diad sequence. This suggests that a new asymmetric centre appeared in the copolymer main chain by addition of a PhMI or a CHMI monomer to the growing chain end of MBZMI, as shown in *Scheme 4* (type I). This asymmetric induction was smaller than that of the copolymerization of MBZMI with ST or MMA, as described above.

In both anionic copolymerization systems, as shown in *Figure 7*, a similar tendency was observed to that of the radical copolymerization. That is, asymmetric induction, which is very little as described above, may take place as well as the radical copolymerization. In this case, the asymmetry may be attributed to the *threo*-diisotactic addition of MBZMI to a PhMI or a CHMI monomer, as illustrated in *Scheme 4* (type II).

CONCLUSIONS

1. In both radical copolymerizations of MBZMI with PhMI and CHMI, the relationship between the specific rotation of the resulting copolymers and the MBZMI content indicated considerable deviation from linearity. The deviations were smaller compared with those of poly(MBZMI-*co*-ST) and poly(MBZMI-*co*-MMA). The optical activity may be attributable to both the chiral α-methylbenzyl moiety and asymmetric induction into the copolymer main chain.
2. In the anionic copolymerizations, the deviation from linearity was very small. This suggests that there may be a little asymmetric induction.
3. From the results of the radical copolymerizations of MBZMI (M_1) with PhMI (M_2) or CHMI (M_2), monomer reactivity ratios (r_1, r_2) were determined as follows: $r_1 = 0.79$, $r_2 = 0.69$ in the MBZMI–PhMI system and $r_1 = 0.40$, $r_2 = 1.06$ in the MBZMI–CHMI system.
4. From the results of the anionic copolymerizations of MBZMI (M_1) with PhMI (M_2) or CHMI (M_2), monomer reactivity ratios (r_1, r_2) were determined as follows: $r_1 = 0.50$, $r_2 = 0.49$ in the MBZMI–PhMI system and $r_1 = 0.11$, $r_2 = 1.09$ in the MBZMI–CHMI system.
5. From the monomer reactivity ratios, the m_1m_2 diad sequences were evaluated. In both the radical and anionic systems, the specific rotations of the copolymers increased with an increase of the m_1m_2 diad sequence. This suggests that *threo*-diisotactic addition occurred in the copolymerization of MBZMI with PhMI or CHMI.

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