

NOTES

**Asymmetric Induction Copolymerization of Chiral  
*N*-[*N'*-( $\alpha$ -Methylbenzyl)aminocarbonylmethyl]maleimide  
with Achiral *N*-(Substituted)maleimide**

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We reported the polymerization and copolymerizations of optically active *N*-(*L*-menthoxy carbonylmethyl)maleimide (MGMI),<sup>1</sup> *N*-(4-*N'*-( $\alpha$ -methylbenzyl)aminocarbonylphenyl) maleimide (MBCP),<sup>2,3</sup> and *N*-(cholesteroxy carbonylmethyl)maleimide (ChMI).<sup>4</sup> A new asymmetric center appeared in the repeating units of optically active *N*-(substituted)-maleimide (RMI) because of a three-diisotactic structure of the RMI polymer main chain. In radical copolymerizations of the optically active RMI with styrene (ST) or methyl methacrylate (MMA), the relationship between content (wt%) of the optically active RMI in copolymers and the specific rotation for the resulting copolymer caused considerable deviation from a linear line. This suggests that asymmetry is introduced into the copolymer main chain.<sup>1-4</sup>

Recently, the polymerization and copolymerization of optically active *N*-[*N'*-( $\alpha$ -methylbenzyl) aminocarbonylmethyl]maleimide (MBCM) were reported.<sup>5</sup> In the radical copolymerization of MBCM with ST or MMA, the relationship between the content (wt%) of MBCM in the copolymers and specific rotation caused great deviation from a linear line.

In this article, not a vinyl type monomer such as ST or MMA but a 1,2-disubstituted cyclic ethylene type monomer; *i.e.*, *cis*-cyclic alkene was used as a comonomer of MBCM. The objective of this paper was 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 copolymerizations of an optically active MBCM with *N*-phenylmaleimide (PhMI), *N*-cyclohexylmaleimide (CHMI), *N*-*n*-propylmaleimide (PMI) were performed in benzene at 60°C. Asymmetric induction into the copolymer main chain is discussed based on specific rotations and molecular ellipticities measurements of the copolymers. Copolymerization reactivities and chiroptical properties are discussed, as compared with those for poly(MBCM-*co*-ST) and poly(MBCM-*co*-MMA) reported previously.<sup>5</sup>

## EXPERIMENTAL

### *Materials*

**MBCM Monomer.** MBCM was synthesized from maleic anhydride, glycine and optically active *R*-(+)- $\alpha$ -methylbenzylamine, according to the method reported previously<sup>5</sup>;

*N*-(Glyciny)l)maleamic Acid (GMA).<sup>5</sup> GMA was synthesized from Maleic anhydride and glycine. Yield 95%; mp 196–197°C.

*N*-(Glyciny)l)maleimide (GMI).<sup>5</sup> GMI was synthesized from GMA with dehydration by using toluene and triethylamine; yield 46%, mp 115–116°C.

*N*-[(Chlorocarbonyl)methyl]maleimide (CGMI).<sup>5</sup> CGMI was prepared from GMI with thionyl chloride in the presence of *t*-butylcatechol: Yield 75.5%; bp 83–85°C/5.3 × 10<sup>-3</sup> mmHg.

MBCM.<sup>5</sup> MBCM was synthesized from CGMI and (*R*)- $\alpha$ -methylbenzylamine. Yield 31%, mp 144–146°C,  $[\alpha]_D^{25} = 116.5^\circ$  ( $c = 1 \text{ g dl}^{-1}$ ,  $l = 10 \text{ cm}$ , THF).

Model Compound of Poly(MBCM): *N*-[(*N*-(*R*)- $\alpha$ -Methylbenzyl)aminocarbonylmethyl]succinimide (MBGSI). MBGSI was prepared from succinic anhydride, glycine and (*R*)- $\alpha$ -methylbenzylamine, according to method similar to that of MBCM.

MBGSI. Total yield 17%; mp 193–194°C;  $[\alpha]_D^{25} = 115.5^\circ$  ( $c = 1.0 \text{ g dl}^{-1}$ ,  $l = 10 \text{ cm}$ , THF).

PhMI, CHMI, and PMI were synthesized from maleic anhydride and the corresponding amine, according to the ordinary synthesis method of RMI<sup>6</sup>: PhMI: mp 91.0°C, CHMI: mp 89.0°C, and PMI bp 100°C/24 mmHg.

Dioxane, tetrahydrofuran (THF), and other solvents were purified by the usual methods. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization twice from chloroform.

#### Radical Copolymerization

Radical copolymerizations were performed with AIBN as an initiator in dioxane in a sealed tube at 60°C. After polymerization, the polymer solution was poured into a large amount of methanol to precipitate the polymer. The resulting polymer was purified by reprecipitation twice from the THF solution to methanol. It was filtered and dried *in vacuo* for 2 days at 45°C. The composition of the copolymer was calculated by <sup>1</sup>H NMR spectra.

#### Measurements

D-line specific rotations and circular dichroism (CD) spectra were obtained at 25°C using the same instruments reported previously.<sup>5</sup> Molecular weights of copolymers were measured by gel permeation chromatography (GPC), according to the same procedure reported previously.<sup>5</sup>

## RESULTS AND DISCUSSION

#### Radical Copolymerization of MBCM with PhMI, CHMI, or PMI

Radical copolymerizations of MBCM (M<sub>1</sub>) with PhMI (M<sub>2</sub>), CHMI (M<sub>2</sub>), or PMI (M<sub>2</sub>) were performed with AIBN in dioxane at 60°C. The results are summarized in Table I.

Copolymerization proceeded homogeneously throughout. The copolymers were colorless powders and optically active. Their yields in the MBCM–PhMI, MBCM–CHMI, and MBCM–PMI systems were much smaller than those in the MBCM–ST and MBCM–MMA systems reported previously.<sup>5</sup> There were few differences among  $\bar{M}_n$  in the three copolymerization systems. When the content of MBCM in monomer feeds increased,  $\bar{M}_n$  of the resulting copolymer decreased, as shown in Figure 1 and Table I.

It seems that there were small side reactions and the copolymer main chains took almost polyvinylene type structures, judging from the IR and NMR spectra for the copolymers.

Copolymer–composition curves for the MBCM–PhMI, MBCM–CHMI, and MBCM–PMI systems are shown in Figure 2. The curves were different from those for MBCM–ST and MBCM–MMA systems.<sup>5</sup> Monomer reactivity ratios,  $r_1$  and  $r_2$ , were determined according to the Integration<sup>7</sup> and High Conversion methods.<sup>8</sup> The values were as follows:  $r_1 = 0.65$ ,  $r_2 = 0.65$  in the MBCM–PhMI system,  $r_1 = 4.26$ ,  $r_2 = 0.85$ , in the MBCM–CHMI system, and  $r_1 = 1.55$ ,  $r_2 = 0.48$  in the MBCM–PMI system.

## Asymmetric Induction Copolymerization

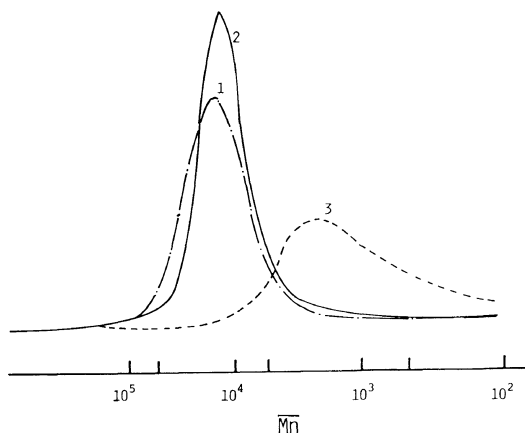
**Table I.** Radical copolymerization of MBCM ( $M_1$ ) with RMI ( $M_2$ ) in dioxane (6 ml) at 60°C<sup>a</sup>

Run	$M_2$	$M_1$	Polym. time	Conversion	$M_1$ in	$\bar{M}_n^b$	$\bar{M}_w/\bar{M}_n^b$	$[\alpha]_D^{25c}$
		in monomer			copolymer			
		mol%	h	%	mol%			
1	CHMI	10.0	12	34.3	10.1	5.2	1.82	13.2
2	CHMI	30.0	12	26.6	46.9	6.5	1.64	26.2
3	CHMI	50.0	22	25.9	66.8	7.0	1.45	41.3
4	CHMI	70.0	22	16.6	84.3	3.2	1.51	51.0
5	CHMI	90.0	22	9.9	97.8	1.4	1.44	55.4
6	PhMI	10.4	12	42.7	9.9	6.1	2.71	11.9
7	PhMI	29.0	12	37.2	33.5	5.5	2.01	25.3
8	PhMI	50.3	12	27.6	54.4	4.9	1.86	37.8
9	PhMI	70.0	12	18.7	70.2	3.8	1.79	48.8
10	PhMI	90.0	12	10.8	85.0	1.7	1.56	57.3
11	PMI	10.6	22	32.7	15.2	10.2	1.68	19.1
12	PMI	29.0	22	20.5	42.0	9.4	1.64	38.7
13	PMI	49.4	22	17.8	64.3	8.1	1.69	48.9
14	PMI	72.8	22	19.8	82.2	4.6	1.67	54.7
15	PMI	89.6	22	17.7	91.1	1.6	1.65	61.4

<sup>a</sup>  $[AIBN] = 1.0 \times 10^{-2} \text{ mol l}^{-1}$ ;  $M_1 + M_2 = 1.0 \text{ g}$ .

<sup>b</sup> By GPC.

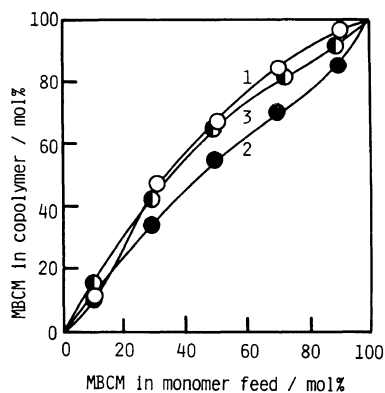
<sup>c</sup>  $c = 1.0 \text{ g dl}^{-1}$ ,  $l = 10 \text{ cm}$ , THF.



**Figure 1.** GPC curves for poly(MBCM-co-PMI) obtained from (1) 10 mol% [run 11], (2) 50 mol% [run 13], and (3) 90 mol% [run 15] of MBCM in the monomer feed.

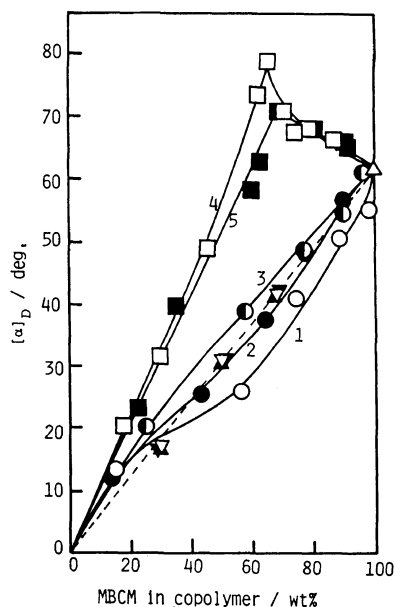
### Optical Behavior of the Copolymers

Figure 3 shows the relationship between specific rotation and content (wt%) of the MBCM monomeric unit in the three radical copolymerization systems. The relationship between the specific rotations of a mixture of



**Figure 2.** Copolymer composition curves for (1) MBCM-CHMI, (2) MBCM-PhMI, and (3) MBCM-PMI systems.

poly(MBCM) and poly(PhMI) and content (wt%) of poly(MBCM) was a good linear one, as shown in Figure 3 ( $\nabla$ ). The absolute values of specific rotations of poly(MBCM-co-PhMI)s increased with the content (wt%) of MBCM unit. However, small deviation from linearity was observed. This suggests that asymmetric induction occurred in the main

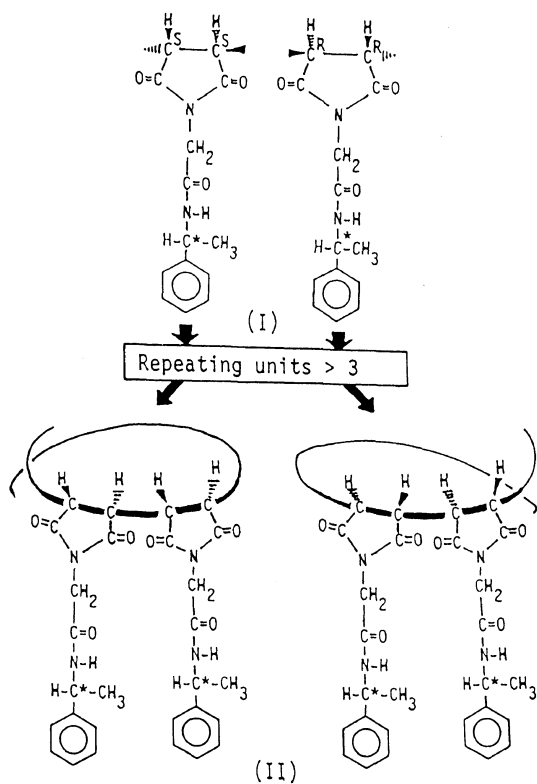


**Figure 3.** Dependence of specific rotations  $[\alpha]_D^{25}$  on the composition (wt%) of (1) poly(MBCM-*co*-CHMI), (2) poly(MBCM-*co*-PhMI), (3) poly(MBCM-*co*-PMI), (4) poly(MBCM-*co*-ST), and (5) poly(MBCM-*co*-MMA), ( $\nabla$ ) a mixture of poly(MBCM) and poly(PhMI), ( $\blacktriangledown$ ) a mixture of poly(MBCM) and poly(CHMI), ( $\blacktriangle$ ) a mixture of poly(MBCM) and poly(PMI), and ( $\triangle$ ) poly(MBCM) obtained with AIBN [ref 5].

chain of the copolymers. In poly(MBCM-*co*-CHMI)s and poly(MBCM-*co*-PMI)s, similar tendencies could be observed, as shown in Figure 3. However, deviations in these three systems were much less than those in the poly(MBCM-*co*-ST) and poly(MBCM-*co*-MMA) reported previously.<sup>5</sup>

Asymmetry in the three copolymerization systems may result from excess of chiral center of (*R,R*) or (*S,S*) in main chain, as illustrated in Scheme 1 (type I). The repeating units of (*R,R*) or (*S,S*), formed by the three-diisotactic additions of RMI, can make a helix [Scheme 1 (type II)].

In the three copolymerization systems, the relationship between the specific rotations of the copolymers and the temperature gave linearity and the slopes were very small [temperature coefficients ( $\Delta[\alpha]_D/\Delta T$ ) = 0.09 to

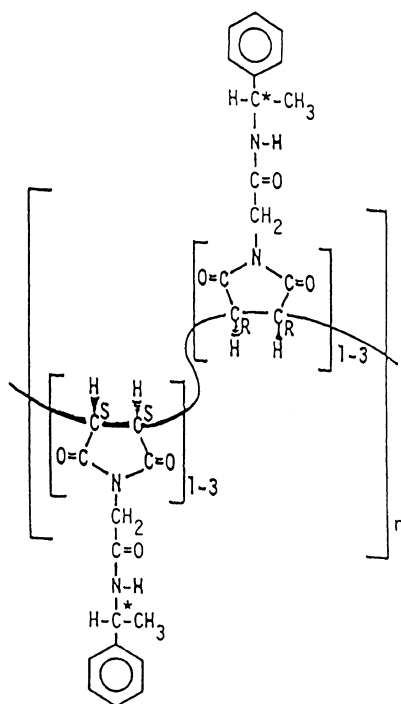


**Scheme 1.**

0.12] (the range of temperature from 0 to 60°C). This suggests that there may scarcely be complete helix in the poly(MBCM-*co*-PhMI), poly(MBCM-*co*-CHMI) and poly(MBCM-*co*-PMI) and/or there are not competing conformation states contributing to optical activity.

Therefore, the resulting copolymer may take an almost linear structure as illustrated in Scheme 2. That is, more than four successive units of (*S,S*) or (*R,R*) may not exist. This is because, more than a four-unit sequence of (*S,S*) or (*R,R*) would produce a helix,<sup>9</sup> as shown in Scheme 1 (type II). This can be confirmed by inspection of poly(MBCM).

In the CD and UV spectra for poly(MBCM-*co*-PhMI)s, as shown in Figure 4, some small negative and positive peaks at about 250–275 nm were observed. The peaks were ascribed to  $\pi \rightarrow \pi^*$  transition of phenyl groups in the



Scheme 2.

MBCM and PhMI units and to  $n \rightarrow \pi^*$  transition of carbonyl groups in the MBCM and PhMI units. Figure 5 depicts the CD and UV spectra for poly(MBCM-*co*-CHMI) and poly(MBCM-*co*-PMI). Three negative peaks were obvious in the range of 255 to 275 nm, and a strong positive peak was detected at about 230 nm. The former was attributed to  $\pi \rightarrow \pi^*$  transition of phenyl groups in MBCM and PhMI units and to  $n \rightarrow \pi^*$  transition of carbonyl groups in MBCM and RMI (*i.e.*, PhMI, CHMI, and PMI) units, and the latter to the  $n \rightarrow \pi^*$  transition of carbonyl groups in MBCM and RMI units.

As can be seen from Figures 4 and 5, CD patterns at 250 nm were different for the three copolymers and characteristic peaks were observed. This is consistent with the fact that optically active RMI homopolymers obtained from asymmetric polymerization of achiral RMI with *n*-butyllithium (*n*-BuLi)/(-)-sparteine indicated characteristic CD peaks at

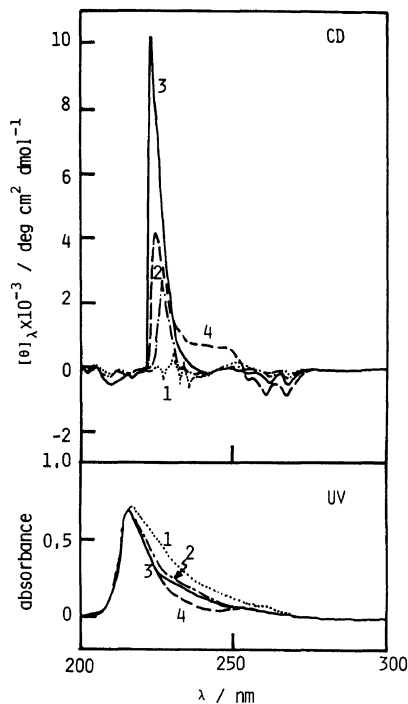
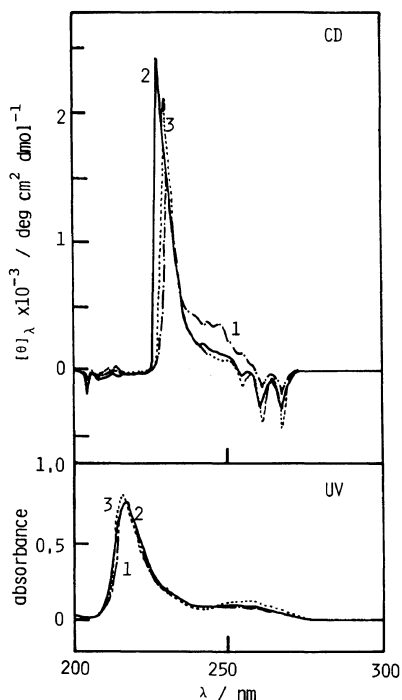


Figure 4. CD and UV spectra for poly(MBCM-*co*-PhMI) obtained from (1) 50 mol% [run 8], (2) 70 mol% [run 9], (3) 90 mol% [run 10] of MBCM in the monomer feed, and (4) MBGSI (model compound of poly(MBCM)).

250 nm.<sup>10</sup> Therefore, it is considered that CD peaks in the vicinity of 240 to 270 nm and for the MBCM copolymers may be associated with the threo-diisotactic structure of maleimide.

Asymmetric polymerizations of achiral RMI gave optically active RMI polymers having relatively high specific rotation (CHMI:  $[\alpha]_D = ca. -40^\circ$ ).<sup>10</sup> This asymmetry appeared due to the threo-diisotactic structure, as shown in Scheme 1 (type I and/or II; *N*-substituent = cyclohexyl).

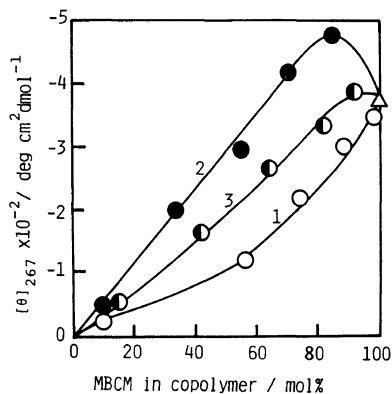
Figure 6 depicts the relationship between molecular ellipticities  $[\theta]$  at 267 nm and content of MBCM (mol%). In all systems, small deviation from linear line was observed, as well as in the relationship between the specific rotation  $[\alpha]_D$  and the content of MBCM in the copolymer described above. This suggests that asymmetric induction into the copolymer main chain may take place.



**Figure 5.** CD and UV spectra for (1) poly(MBCM-co-CHMI) [run 3], (2) poly(MBCM-co-PMI) [run 13], and (3) poly(MBCM) obtained with AIBN [ref 5].

To confirm asymmetric induction copolymerization, removal of the optically active  $\alpha$ -methylbenzyl group was attempted but without success using acid and base catalysts such as HCl, H<sub>2</sub>SO<sub>4</sub>, HBr, NaOH, KOH, hydrazine monohydrate, phenyl hydrazine under several conditions.

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**Figure 6.** Dependence of molecular ellipticities  $[\alpha]_{267}^{25}$  on the composition (mol%) of poly(MBCM-co-RMI): (1) poly(MBCM-co-CHMI)s, (2) poly(MBCM-co-PhMI)s, and (3) poly(MBCM-co-PMI)s.

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