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ASYMMETRIC INDUCTION COPOLYMERIZATION OF OPTICALLY ACTIVE *N*-(1-MENTHYL CARBOXYLATOMETHYL) CITRACONIMIDE WITH METHYL METHACRYLATE

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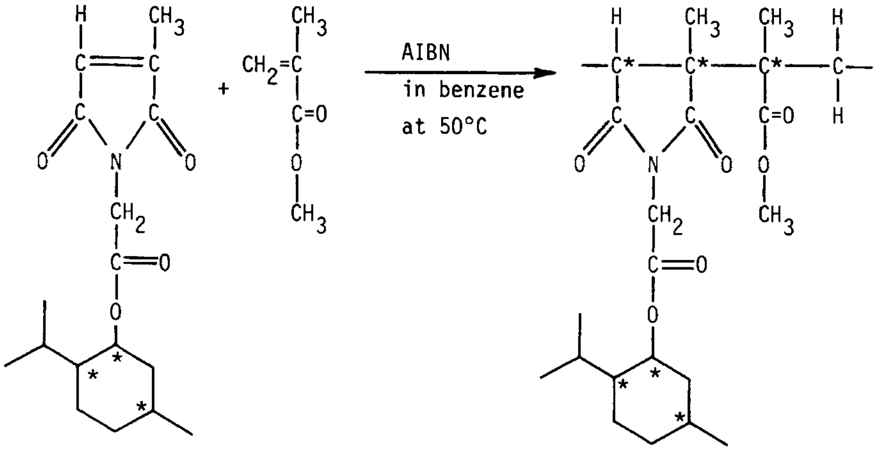
ABSTRACT

Copolymerization of an optically active *N*-(1-menthyl carboxylatomethyl)citraconimide (MCMCI) was carried out with methyl methacrylate (MMA) with azobisisobutyronitrile as the initiator in benzene at 50°C. All the copolymers obtained were optically active. After the removal of the optically active menthyl group, the hydrolyzed poly(MCMCI-*co*-MMA)'s still showed optical activity. The asymmetric induction to the copolymer main chain and the mechanism are discussed based on the measurements of optical rotatory dispersion and circular dichroism of the original and hydrolyzed copolymers.

INTRODUCTION

There have been a few investigations on asymmetric induction by radical copolymerizations of chiral α,β-disubstituted ethylene, especially of five-membered cyclic imide monomers with other achiral vinyl monomers [1-4]. We have reported on the synthesis and polymerization of optically active *N*-α-methylbenzylmaleimide [5] and *N*-α-methylbenzylcitraconimide [6]. In those studies, however, we could not always conclude that a new asym-



SCHEME 1.

metric center appeared in the copolymer main chains because we failed in our attempts to remove completely the optically active groups from each copolymer. Most recently, we reported the asymmetric induction radical copolymerization of optically active *N*-(1-menthyl carboxylatomethyl)citraconimide (MCMCI) with styrene (ST) [7]. We concluded that in the MCMCI-ST system, the asymmetric mechanism might be attributable to the steric effect of the 1-menthyl group in the propagation step rather than to the formation of a chiral charge-transfer (CT) complex between MCMCI and ST.

In this article we report on the radical copolymerization of *N*-(1-menthyl carboxylatomethyl)citraconimide (MCMCI) with methyl methacrylate (MMA) (Scheme 1) and the optically active copolymers obtained. The optical behaviors of the original and hydrolyzed copolymers were investigated. In the absence of the formation of a chiral CT complex, an asymmetric induction mechanism is discussed.

EXPERIMENTAL

Monomer

N-(1-Menthyl carboxylatomethyl)citraconimide (MCMCI) [7] was prepared from *N*-carboxymethylcitraconimide (CMCI) (30 g, 0.18 mol) and 1-menthol (30.5 g, 0.20 mol; mp 43°C; $[\alpha]_D^{19}$ -46.5 for a 1% solution in CH_3OH; $[\alpha]_D^{28}$

-48.7 for a 1.0% solution in THF) with *p*-toluenesulfonic acid (2 g) as a catalyst for 14 h at the boiling temperature of benzene (150 mL). Results: colorless oil, 40.3 g; yield 74.1%; bp 180°C/1.5 torr; $[\alpha]_D^{20}$ -44.1 (THF, *c* 1.0%, *l* 10 cm); $[\alpha]_D^{20}$ -44.3 (CH_3OH, *c* 1.0%, *l* 10 cm); n_D 1.4850. Elemental analysis: Calculated for $C_{17}H_{25}NO_4$: C, 66.43; H, 8.20; N, 4.56%. Found C, 66.46; H, 8.24; N, 4.52%. Methyl methacrylate (MMA) was purified by the usual methods.

Solvents and Catalyst

The solvents used, such as methanol, benzene, and tetrahydrofuran (THF), were purified by the usual methods. Azobisisobutyronitrile (AIBN) was recrystallized several times from methanol mp 102°C.

Copolymerization

Radical copolymerization was carried out in sealed tubes with AIBN as initiator in benzene and at 50°C. After copolymerization, the polymer solution was poured into a large amount of methanol. To remove the unreacted optically active monomer, the precipitation was repeated several times from THF-methanol. The composition of the copolymer was determined by elemental analysis (C, H, and N).

Hydrolysis of the Copolymers

The copolymers obtained were hydrolyzed by the same methods as reported previously [7]. The mixture of the copolymer (0.3-0.5 g) in 150 mL THF and a methanol solution (150 mL) of potassium hydroxide was refluxed for 48-52 h. The reaction mixture was concentrated under reduced pressure, and then about 300 mL water was added. The product was precipitated with dilute hydrochloric acid, filtered, and then dried. The crude product (about 0.3 g) obtained was again hydrolyzed according to the processes just described. This procedure was repeated three times. The hydrolyzed copolymers were purified three times by precipitating with methanol/ether.

RESULTS AND DISCUSSION

Copolymerization

The results of the radical copolymerization of MCMCI with MMA in benzene are summarized in Table 1. The copolymers obtained were optically

TABLE 1. Results of Radical Copolymerization of MCMCI (M_1) with MMA (M_2)

Run no.	M_1 in feed, mol%	Conversion, %	N analysis, %	M_1 in copolymer, mol%	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$[\alpha]_D^{25}$,[b] deg	λ_c,[b] nm
1	21.2	61.8	1.18	10.2	3.1	0.8	-10.1	153
2	40.8	46.6	1.84	18.1	12.0	3.3	-17.3	161
3	50.3	40.3	2.24	23.9	5.2	2.0	-20.9	158
4	60.3	32.9	2.68	31.8	4.9	2.1	-23.5	169
5	79.9	16.4	3.42	49.6	0.3	0.4	-30.4	160

[a] [AIBN] = 10 mmol/L; solvent, benzene (4 mL); time, 96 h; temperature, 50°C.
[b] In THF, *c* 1.0%, *l* 10 cm.

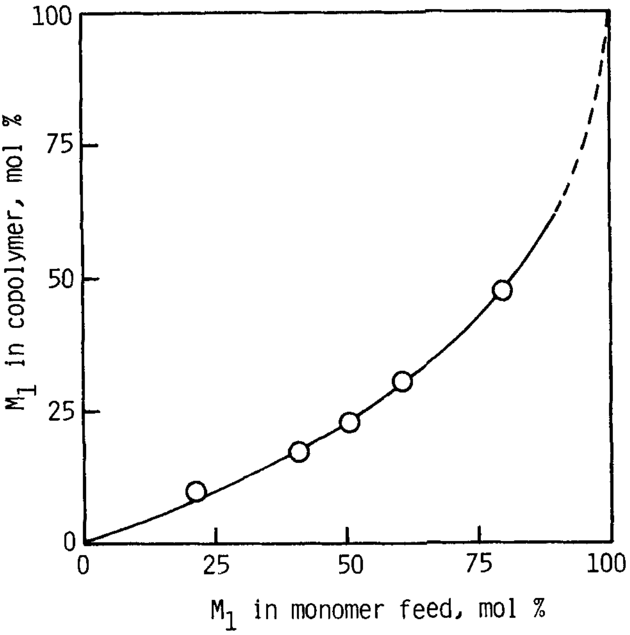


FIG. 1. Composition curve for MCMCI (M_1) and MMA (M_2) system

active white powders. The composition curve of poly(MCMCI-*co*-MMA)s is shown in Fig. 1. The monomer reactivity ratios, determined by the method of Mayo and Lewis [8], were $r_1 = 0.15$ and $r_2 = 2.60$. The Alfrey-Price [9] Q_1-e_1 values for MCMCI were determined as $Q_1 = 0.44$, $e_1 = 1.39$. These parameters indicate no formation of a chiral CT complex between MCMCI and MMA. The Q_1-e_1 values were similar to those of the other *N*-substituted citraconimides [6, 10, 11].

Optical Behavior of the Copolymers

Poly(MCMCI-*co*-MMA) showed negative optical activity. As shown in Fig. 2(A), the absolute value of the specific rotation of poly(MCMCI-*co*-MMA) increased with increasing MCMCI unit content. However, a large deviation from linearity was observed, which suggests that asymmetry is introduced into the copolymer main chain [2-4].

ORD curves for all the copolymers showed negative simple dispersion and

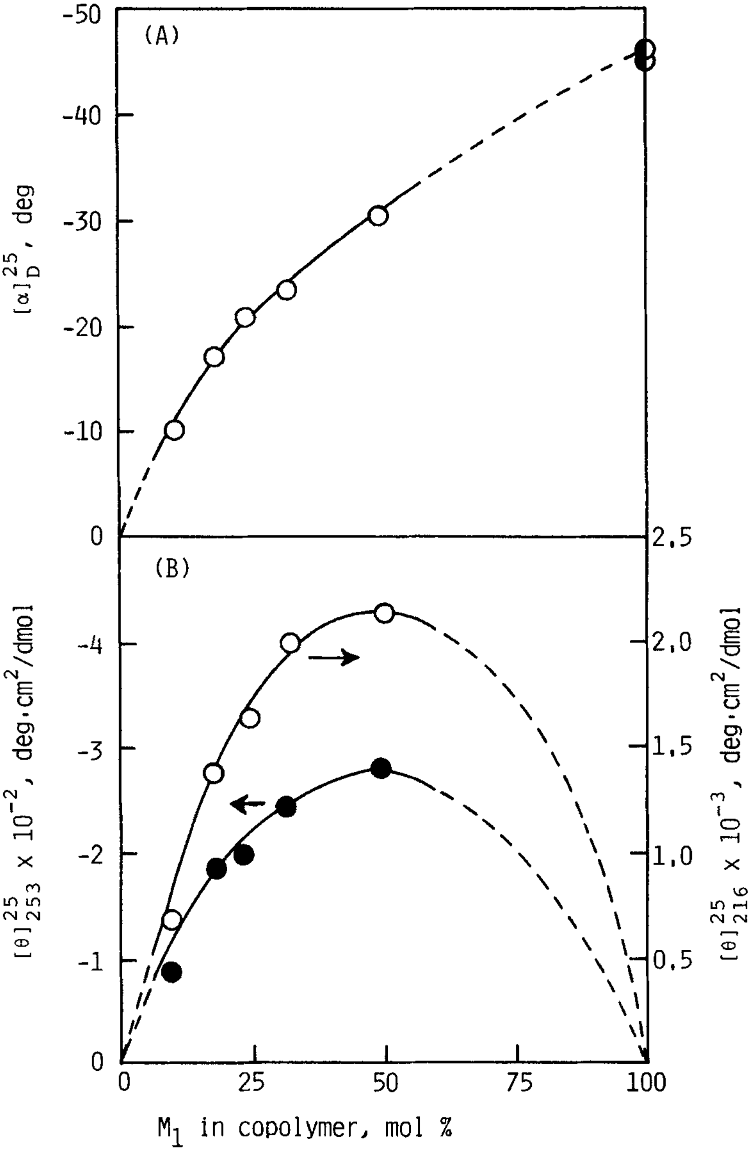


FIG. 2. Relationships between (A) specific rotation, $[\alpha]_D{}^{25}$, (B) molecular ellipticity, $[\theta]_{250}{}^{25}$, and content of the monomeric unit MCMCI (M_1) in the copolymer. (◐): MCMCI homopolymer (bulk polymerization 70°C; $\bar{M}_w$ 88 000) [7].

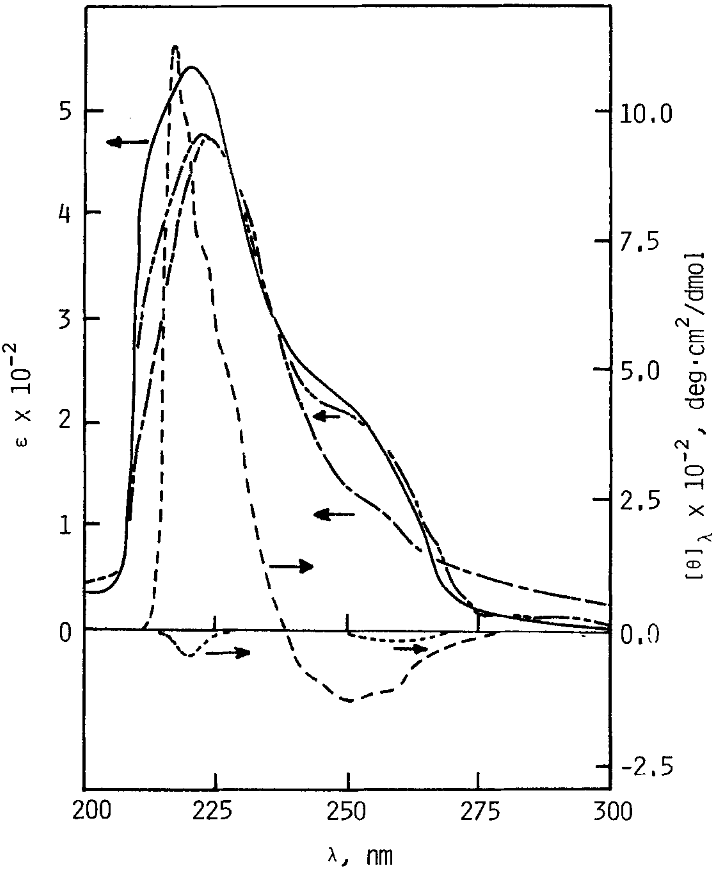


FIG. 3. UV and CD scans for original poly(MCMCI-*co*-MMA) (Run 5) [UV (—), CD (– –)] ; hydrolyzed poly(MCMCI-*co*-MMA) (Run 8) [UV (– - –), CD (- - -)] ; and UV scan for poly(CMCI-*co*-MMA) (— - - —).

fit the simple Drude equation between 350 and 600 nm. The λ_c values of poly(MCMCI-*co*-MMA) were from 153 to 169 nm (see Table 1). These values may be due to the n→π* transition of the ester groups of the MCMCI unit.

UV and CD curves of the original poly(MCMCI-*co*-MMA) are shown in Fig. 3. Two CD peaks of poly(MCMCI-*co*-MMA) (Run 5) lie at 253 and 216 nm; the mean residue ellipticities were -88 to -283 (253 nm) and 688 to 2150 (216 nm) deg·cm^2/dmol, respectively. These peaks may be due to the n→π* transition of carbonyl groups of monomeric units of MCMCI in the copoly-

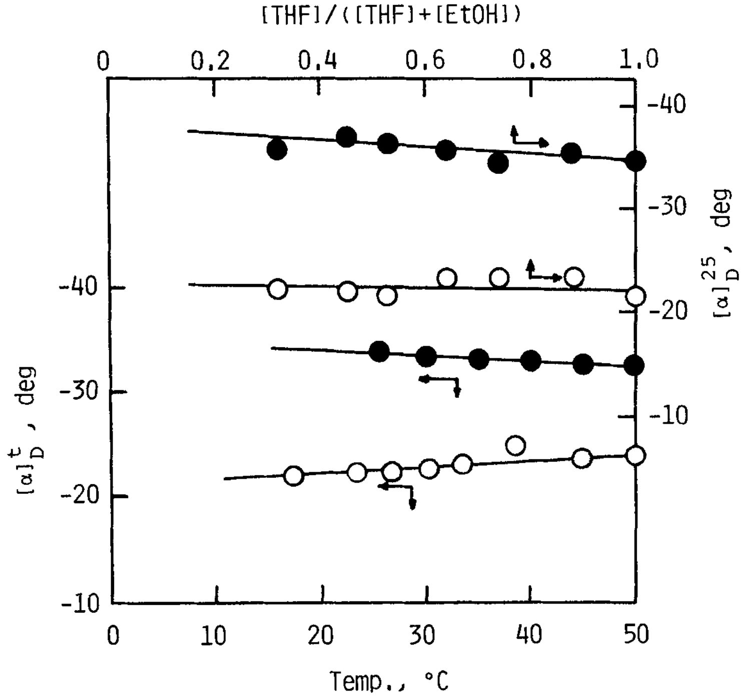


FIG. 4. Temperature dependence on the specific rotation ($[\alpha]_D$, $c \sim 1.0$, THF, l 10 cm) and effect of solvent on the specific rotation ($[\alpha]_D$, $c \sim 1.0$, THF and EtOH, l 10 cm of (○) poly(MCMCI-*co*-MMA) (Run 3) and (●) poly(MCMCI-*co*-ST) [7].

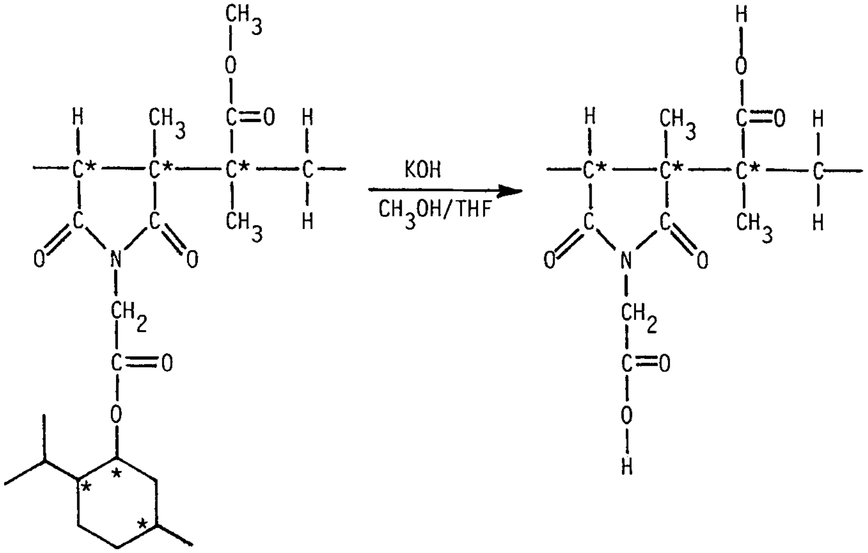
mer. The relationship between molecular ellipticity and the mole fraction of monomeric units of MCMCI in the copolymers is shown in Fig. 2(B). A large deviation from a linear relationship is present, as it was for the specific rotations. This result again suggests that an asymmetry has been introduced into the copolymer main chain.

The temperature and solvent effects on the specific rotation of poly(MCMCI-*co*-MMA) were investigated. As illustrated in Fig. 4, linear relationships were observed. The values of the temperature coefficient ($\Delta[\alpha]_D/\Delta T$) were between -0.05 and -0.08, indicating that a helical conformation of the copolymers may not be present [5]. The corresponding measurements for poly(MCMCI-*co*-ST) were not reported in the previous article [7] but are included in Fig. 4. Good linear relations were observed, and the temperature coefficients were between 0.03 and 0.07.

Optical Behavior of the Hydrolyzed Copolymers

In order to confirm asymmetric induction, poly(MCMCI-*co*-MMA)'s were hydrolyzed in a mixture of THF and CH_3OH (volume ratio 1:1) with potassium hydroxide (Scheme 2), according to the method described in the Experimental section. The hydrolyzed copolymers obtained were identified by comparing their infrared and ^1H-NMR spectra with those of the original copolymers. Infrared and ^1H-NMR spectra of the hydrolyzed copolymers indicate the same patterns as poly[*N*-carboxymethylcitraconimide (CMCI)-*co*-methacrylic acid] which had been radically copolymerized previously. The theoretical and found values of the elemental analysis of hydrolyzed copolymer are shown in Table 2.

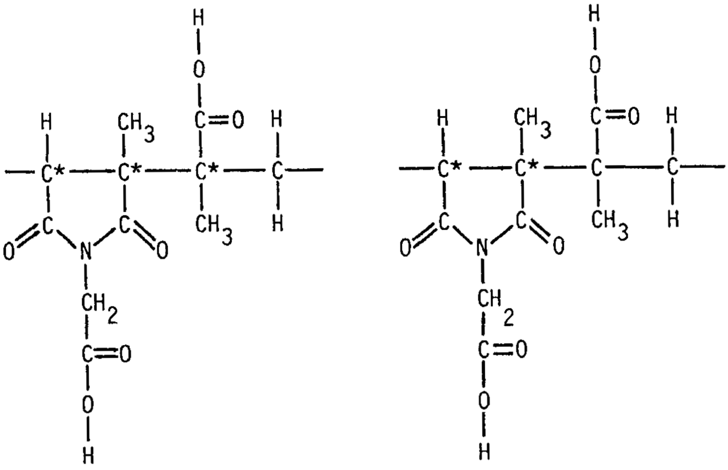
The hydrolyzed poly(MCMCI-*co*-MMA) still showed optical activity after hydrolysis (see Table 3), which confirmed the introduction of asymmetry into the copolymer main chain, as illustrated in Scheme 3(a).



SCHEME 2.

TABLE 2. Elemental Analysis of Hydrolyzed Copolymers

Hydrolysis run no.	Original copolymer run no.	Calculated C	Calculated H	Calculated N	Found C	Found H	Found N
6	1	54.69	6.50	1.51	55.08	6.55	1.81
7	2	53.96	6.16	2.51	54.72	6.22	2.39
8	3	53.48	5.94	3.16	54.21	6.09	3.30
9	4	52.89	5.66	3.96	53.22	5.92	3.82
10	5	51.78	5.14	5.46	52.58	5.09	5.11



(a) (b)

SCHEME 3.

TABLE 3. Optical Behavior of Hydrolyzed Copolymer from MCMCI (M_1) with MMA (M_2)

	Original copolymers					Hydrolyzed copolymers	
Run no.	Run no.	MCMCI, mol%	P_2 $[m_1 m_2] \times 100$	$[\alpha]_D^{25}$,[a] deg	λ_c,[a] nm	$[\alpha]_D^{25}$,[b] deg	λ_c,[b] nm
6	1	10.2	9.8	-10.1	153.2	-1.1	297.7
7	2	18.1	16.4	-17.3	161.1	-0.6	268.2
8	3	23.9	20.7	-20.9	158.0	-1.5	257.8
9	4	31.8	25.9	-23.5	169.9	-2.1	264.4
10	5	49.6	31.1	-30.4	160.9	-2.5	270.9

[a] *c* 1.0%, THF, *l* 10 cm.

[b] *c* 1.0%, THF, *l* 5 cm.

The ORD curve for the hydrolyzed copolymers satisfied a simple Drude equation. The λ_c values were between 258 and 298 nm, as shown in Table 3, and were red-shifted from the λ_c (153 to 170 nm) values of the original copolymers. This behavior, also recognized in the MCMCI-ST system, indicates that a new asymmetric center has appeared in the main chain and is quite different from that expected for a chiral side chain.

The UV and CD curves for the original and hydrolyzed poly(MCMCI-*co*-MMA), and a UV curve for the poly(*N*-carboxymethylcitraconimide (CMCI)-*co*-MMA) are shown in Fig. 3. The UV curve of poly(MCMCI-*co*-MMA) has a shape similar to that of poly(CMCI-*co*-MMA). The UV peaks of the hydrolyzed poly(MCMCI-*co*-MMA) appeared at about 260 and 220 nm. One seems to be due to the $n \rightarrow \pi^*$ transition of the carbonyl groups in both the MCMCI and MMA units. The other may be attributable to the $n \rightarrow \pi^*$ transition of the carbonyl groups in the MCMCI units. In these regions the negative and small CD peaks ($[\theta] = \sim-20$ (260 nm); $[\theta] = \sim-50$ deg·cm^2/dmol(220 nm)) were observed.

The $P_2[m_1m_2]$ [12, 13] values listed in Table 3 indicate the probability of a MCMCI-MMA diad sequence. $P_2[m_1m_2]$ was derived as follows:

$$P_1[m_1] + P_2[m_2] = 1$$

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

$$P(m_1m_2) = 1/(1 + r_2x)$$

where $P_1[m_1]$ and $P_1[m_2]$ are mole 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 is the monomer reactivity ratio of MCMCI.

The good linearity between the optical rotation of the hydrolyzed copolymer and the probability of diad sequences [12] in the copolymer (Fig. 5) indicates that a new asymmetric center has appeared in the copolymer main chain by addition of the MMA monomer to the growing chain end of MCMCI. The slopes, ($\Delta[\alpha]_D/\Delta P_2[m_1m_2]$), of the two straight lines for the original and hydrolyzed poly(MCMCI-*co*-MMA) were -96 and -8, respectively, compared to -82 and -11 for poly(MCMCI-*co*-ST). That the absolute value of this slope for the hydrolyzed poly(MCMCI-*co*-MMA) was smaller than that for the hydrolyzed poly(MCMCI-*co*-ST) may be attributable to differences in the alternating character [7] between the MCMCI-ST and MCMCI-MMA systems.

In the copolymerizations of MCMCI with MMA, there is little possibility of formation of a chiral CT complex, judging from the *Q*-*e* values and the

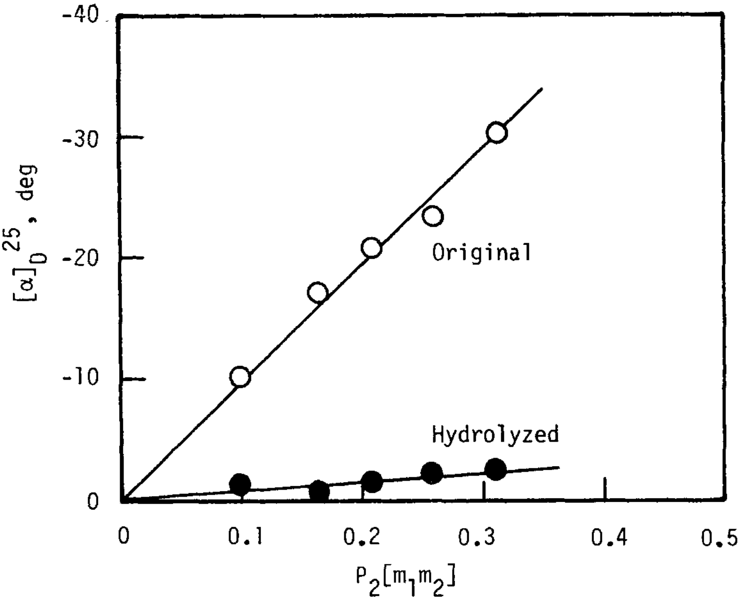
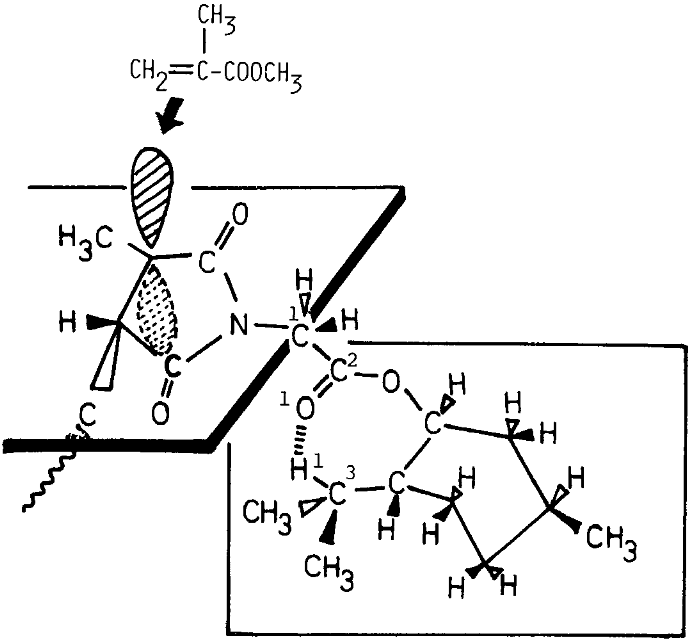


FIG. 5. Relationships between $[\alpha]_D^{25}$ of the original or hydrolyzed poly[MCMCI (M_1)-*co*-MMA (M_2)] and $P_2[m_1m_2]$.

copolymer composition curve (Fig. 1) of MCMCI (*Q* 0.44, *e* 1.39) and MMA (*Q* 0.74, *e* 0.40). Thus an asymmetric induction mechanism is thought to be due to the difference in steric hindrance for the approach of MMA monomer, as shown in Scheme 4. That is, it can be thought that the sp^2 of the growing chain end (i.e., five-membered imide ring) is a plane. The chiral side chain might sterically control the attack of MMA monomer on the growing chain end during the propagation reaction. The free rotation of the N–C^1 bond might be inhibited by steric hindrance. It is very difficult to explain the stability of the conformation. When H^1 is between O^1 and C^3, the l-menthyl residue may be in its preferred position because of the interaction (like a hydrogen bond) between H^1 and O^1. Rotation of the C^1–C^2 bond could hardly occur.

The MMA monomer can preferentially attack the growing chain end from the upper plane of the system. In this case a new asymmetric center could develop at the carbon atoms linked to the carbonyl groups of the MCMCI unit (see Scheme 3b), but not to the methyl or to the carbonyl groups of



SCHEME 4.

MMA unit. The specific rotation of the hydrolyzed homopoly(MCMCI) [7] was zero, which indicates that an asymmetric carbon atom had not been introduced into the main chain of the homopolymer. In addition, the specific rotation of the copolymers depends on the value of P_2 $[m_1 m_2]$, which suggests that the asymmetric carbon atoms are not introduced into the main chain of the $m_1 m_1$ diad sequence.

In order to obtain more detailed information on steric hindrance for the approach of a comonomer, we copolymerized MCMCI with α-methylstyrene under various conditions with a radical initiator, but no copolymers could be obtained.

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