Synthesis and polymerization of *N*-[4-(cholesteroxycarbonyl)phenyl]maleimide

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A new type of optically active *N*-[4-(cholesteroxycarbonyl)phenyl]maleimide (ChPMI) was synthesized from maleic anhydride, aminobenzoic acid and cholesterol. Radical homopolymerizations of ChPMI were performed in several solvents at 70°C to give optically active polymers having $[\alpha]_D = 2.3$ to 41.1°. Radical copolymerizations of ChPMI (M_1) were performed with styrene (ST, M_2) and methyl methacrylate (MMA, M_2) in toluene at 70°C. From the results, the monomer reactivity ratios (r_1, r_2) and the Alfrey–Price Q, e values were determined as follows: $r_1 = 0.080$, $r_2 = 0.020$, $Q_1 = 6.57$, $e_1 = 1.74$ for the ChPMI-ST system; $r_1 = 0.11$, $r_2 = 0.80$, $Q_1 = 1.73$, $e_1 = 1.96$ for the ChPMI-MMA system. Anionic homopolymerizations of ChPMI were also carried out. Chiroptical properties of the polymers and copolymers were investigated.

(Keywords: polymerization; *N*-[4-(cholesteroxycarbonyl)phenyl]maleimide; optically active polymer; monomer reactivity ratio; *Q*, *e* values; asymmetric induction copolymerization)

INTRODUCTION

There have been many reports[1–10] including patents (for examples, see refs 11–13) on the polymerization and copolymerization of *N*-substituted maleimide (RMI). However, only a few investigations on the polymerization of optically active RMI have been made[14,15]. The polymerization reactivities and chiroptical properties of chiral *N*-(α-methylbenzyl)maleimide (MBZMI)[16] and *N*-(L-methoxycarbonylmethyl)maleimide[17] were reported. 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*). If one is produced more than the other, the obtained polymer can be optically active[18]. Lately, asymmetric polymerizations of achiral RMI were performed with n-butyllithium (n-BuLi)/(−)-sparteine (Sp) to obtain chiral poly(RMI)s containing a relatively high specific rotation[19,20]. The asymmetry could be attributed to a *threo*-diisotactic structure arising from helical structure and/or from the excess of chiral stereogenicity (*S,S*) or (*R,R*)[19].

It was well known that many cholesterol derivatives are thermotropic liquid crystalline[21]. Cholesterol has been the most commonly encountered pendent chiral moiety; both homopolymers and copolymers with a pendent cholesteryl group have been reported[22–27]. These are all related to liquid-crystalline polymers. On the other hand, cholesterol is also interesting as an inclusion compound[28]. To the best of our knowledge, there have been no detailed reports on the polymerization reactivities of monomers including a cholesteryl moiety. No *N*-substituted maleimide (RMI) containing a cholesteryl moiety has been investigated. The mechanisms of the asymmetric polymerization and the asymmetric induction copolymerization of *cis*-cyclic olefin are not fully elucidated. Since the cholesteryl moiety is chiral and very bulky, it is interesting to study the polymerization reactivities of RMI having a cholesteryl moiety and the chiroptical properties from the viewpoint of asymmetric induction copolymerization of *cis*-cyclic olefin. Thus, *N*-(cholesteroxycarbonylmethyl)maleimide (ChMI) was investigated recently[29].

In this paper, a novel, optically active *N*-[4-(cholesteroxycarbonyl)phenyl]maleimide (ChPMI) is synthesized from maleic anhydride, *p*-aminobenzoic acid and cholesterol. ChPMI is polymerized and copolymerized with styrene (ST) and methyl methacrylate (MMA) in the presence of a radical initiator. From the results, monomer reactivity ratios and *Q*, *e* values are determined. Asymmetric induction into the copolymer main chain is discussed based on the specific rotations and molecular ellipticities of the copolymers. ChPMI is also polymerized with an anionic initiator, n-BuLi, to obtain an optically active polymer. The polymerization reactivities and the chiroptical properties are discussed, as compared with those for ChMI reported previously[29]. Thermotropic properties of the ChPMI monomer, polymers and copolymers are also briefly described.

EXPERIMENTAL

ChPMI monomer

ChPMI monomer was synthesized from maleic anhydride, *p*-aminobenzoic acid and cholesterol, as shown in *Scheme 1*.

N-(4-Carboxyphenyl)maleamic acid (*p*-CPMA)[30] was synthesized from maleic anhydride (MAn) and *p*-aminobenzoic acid (ABA) in *N,N*-dimethylformamide (DMF) at room temperature; yield 96%; m.p. 225–226°C.

N-(4-Carboxyphenyl)maleimide (*p*-CPMI)[30] was prepared by dehydration of *p*-CPMA in the presence of

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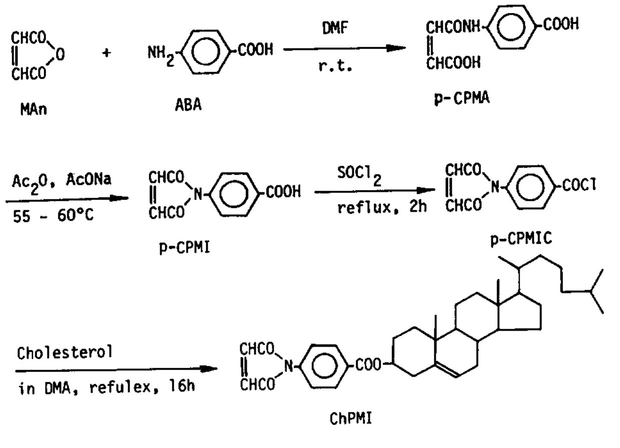


Scheme 1

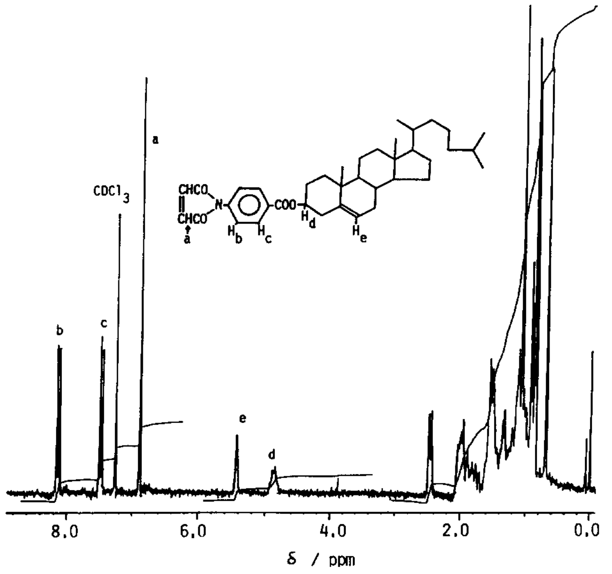


Figure 1 ^{1}H n.m.r. spectrum for ChPMI monomer

sodium acetate in acetic anhydride at 55–60°C; yield 85%; m.p. 244°C.

N-(4-Chlorocarbonyl)phenyl]maleimide (*p*-CPMIC) was prepared by treating *p*-CPMI with thionyl chloride to obtain crude *p*-CPMIC, which was recrystallized from benzene; yield 73%; m.p. 168–169°C.

N-[4-(Cholesteroxycarbonyl)phenyl]maleimide (ChPMI) was prepared by adding a solution of *p*-CPMIC (10.0 g, 0.04 mol) in 140 ml of *N*,*N*-dimethylaniline dropwise to 120 ml of benzene solution-dissolved cholesterol (15.5 g, 0.04 mol) and t-butyl catechol as an inhibitor at room temperature. After the addition, the solution was refluxed for 16 h. The reaction was performed under nitrogen atmosphere throughout. After the reaction was completed, the benzene was evaporated under reduced pressure. The residual mixture was poured into a large amount of ice–water containing 1% HCl to dissolve *N*,*N*-dimethylaniline completely. The residual yellow precipitate was filtered, thoroughly washed with water, and dried *in vacuo*. The crude ChPMI was purified by reprecipitation from the chloroform solution to a large amount of methanol. The precipitation was repeated five times to obtain pure ChPMI; yield 11.7 g, 50% pale yellow powder, m.p. 165–168°C; $[\alpha]_D = 3.3°$ ($c = 1.0$ g dl^{-1}; $l = 10$ cm; THF).

I.r. (KBr disc, cm^{-1}): 2850 (CH, CH$_2$, CH$_3$), 1760 and 1710 (CO-N-CO), 1680, 1640 and 1600 (C=C), 1450, 1420 and 1360 (CH, CH$_2$, CH$_3$), 1270 and 1140 (OC=O), 830 (CH in phenyl), 690 (*cis* CH=CH). ^{1}H nuclear magnetic resonance (n.m.r.) and ^{13}C n.m.r. spectra (δ, ppm from TMS in CDCl$_3$) are shown in *Figures 1* and *2*.

Elemental analysis (%): found, C = 77.03, H = 8.66, N = 2.52; calc. for $C_{38}H_{51}O_4N$, C = 77.91, H = 8.77, N = 2.39.

A model compound of poly(ChPMI), *N*-[4-(cholesteroxycarbonyl)phenyl]succinimide (ChPSI) was prepared from succinic anhydride, *p*-aminobenzoic acid and cholesterol, using a similar method to that for ChPMI. Yields and melting points of precursors are as follows: *N*-(4-carboxyphenyl)succinamic acid (*p*-CPSA): yield 98%; m.p. 150–153°C; *N*-(4-carboxyphenyl)succinimide (*p*-CPSI): yield 93%; m.p. 239–241; *N*-(4-chlorocarbonylphenyl)succinimide (*p*-CCPSI) recrystallized from benzene: yield 86%; m.p. 188–189°C.

ChPSI: total yield 10.5%, m.p. 215–217°C; $[\alpha]_D = 22.7°$ ($c = 1.0$ g dl^{-1}, $l = 10$ cm, THF). I.r. (KBr disc, cm^{-1}): 2855 (CH, CH$_2$, CH$_3$), 1755 and 1715 (CO–N–CO), 1645 (CH=CH in phenyl), 1450, 1420 and 1360 (CH, CH$_2$, CH$_3$), 1270 and 1140 (OC=O), 830 (CH in phenyl). ^{1}H n.m.r. (δ, ppm from TMS in CDCl$_3$): 8.38–8.12 (m, 2H in phenyl), 7.50–7.25 (m, 2H in phenyl), 5.43–5.42 (m, 1H, C=CH– in cholesteryl), 4.91–4.82 (m, 1H, O–CH– in cholesteryl), 2.74 (s, 4H, CH_2–CH_2 in maleimide), 2.48–0.69 (m, 43H, other protons of cholesteryl group).

Other materials

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

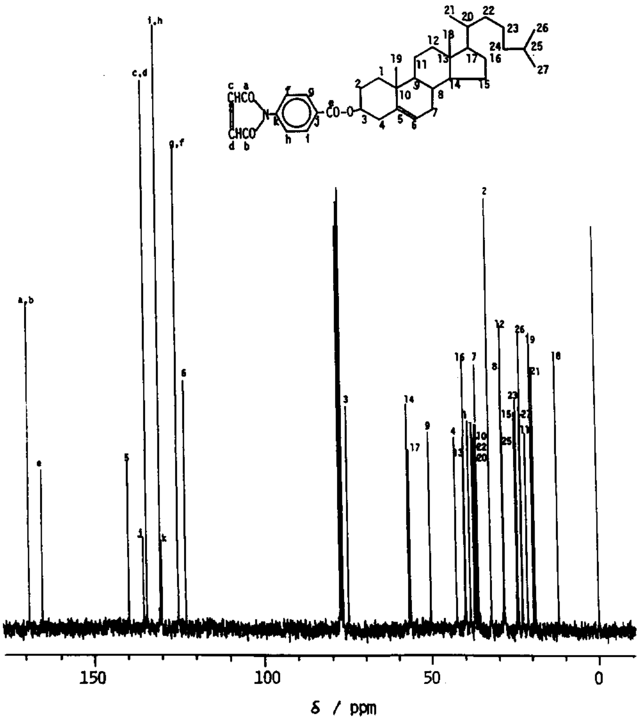


Figure 2 ^{13}C n.m.r. spectrum for ChPMI monomer

Homopolymerization and copolymerization

Radical homopolymerizations were performed with AIBN as an initiator in THF, chlorobenzene (CB), *o*-dichlorobenzene (DCB), toluene (TOL), chloroform (CHO) or dioxane (DOX) in a sealed tube at 70°C. After polymerization, the polymer solution was poured into a large amount of acetone to precipitate the polymer. The obtained polymer was purified by reprecipitation from the chloroform solution to acetone three times. The polymer was filtered and dried *in vacuo* for 3 days at 40°C.

Radical copolymerizations of ChPMI with ST or MMA were carried out in toluene at 70°C, according to similar procedure to the homopolymerizations. Composition of the copolymer obtained was calculated by ^1H n.m.r. spectra.

Anionic homopolymerization was achieved in toluene or THF 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 a large amount of acetone. The obtained polymer was purified by reprecipitation three times from the chloroform solution to acetone, and then filtered and dried *in vacuo* at 40°C.

Hydrolysis of the polymers and copolymers

The mixture of the polymer (or copolymer) (0.2–0.5 g) in THF (150 ml) and methanol (150 ml) with potassium hydroxide was refluxed for 60–72 h. The solvents in the reaction mixture were completely evaporated out, and 300 ml of water was added to the residue. Hydrochloric acid was added to the solution to give a pH value of 4–5. The precipitate was filtered, washed with water and dried. To remove the cholesterol formed, the product was reprecipitated from the THF solution into a large amount of diethyl ether. The obtained product (a mixture of the original and hydrolysed polymers) was hydrolysed again under the same conditions as described above, to obtain the completely hydrolysed polymer. The resultant product was reprecipitated three times from the THF solution into a large amount of methanol, and then filtered and dried. The hydrolysed polymers were identified by the n.m.r. spectra.

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 using 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 (g.p.c.) analysis, using the same technique as described in an earlier paper[31]. I.r. and n.m.r. spectra were obtained and elemental analysis was carried out, using the same instruments as reported previously[32].

RESULTS AND DISCUSSION

Radical and anionic homopolymerization of ChPMI

Radical and anionic polymerizations of ChPMI were performed under several conditions. The results are summarized in *Tables 1* and *2*. The radical polymerizations proceeded homogeneously throughout, except for the polymerization in THF. In the polymerization in THF, part of the polymer produced was insoluble in THF, and precipitated. The obtained polymers were white powders and had positive optical activities. The number-average molecular weights ($\overline{M}_n$) of poly(ChPMI)s obtained with the radical initiator were 5.2×10^4 to 4.1×10^3, and were extremely affected by the solvent. The $\overline{M}_n$ for the polymers obtained in the solvent having a phenyl group were greater than those for others. G.p.c. curves for the polymers are shown in *Figure 3*. In the g.p.c. curves of the polymers obtained in CB and DCB, two peaks were observed at $\overline{M}_n$ values of about 7×10^5 and 2×10^5. In the g.p.c. curves of the polymers obtained in THF, DOX and TOL, the peak was also observed at an $\overline{M}_n$ of about 4×10^3. In a previous study[29], homopolymerization of ChMI was performed with AIBN in the same solvents as here to obtain a polymer having an $\overline{M}_n$ of 4.4×10^3 to 8.9×10^3 and only one peak in the g.p.c. curves. Thus, the polymerization reactivities of ChPMI were found to be affected by the phenyl group in the maleimide. It is difficult to explain the reason clearly but it may result from some kind of inclusion characteristic of the cholesteryl moiety.

The specific rotation ($[\alpha]_D$) and the molecular ellipticity ($[\theta]$) of the polymers obtained with AIBN were 2.3–41.1° and 1.3×10^4 to 2.7×10^4 deg cm^2 dmol^{-1}, respectively, and decreased with increase of $\overline{M}_n$ of the polymers. This

Table 1 Radical polymerizations of ChPMI in several solvents at 70°C[a]

Run no.	ChPMI ($\times 10^{-4}$ M)	Solvent[b] (ml)	Polymerization time (h)	Yield (%)	$\overline{M}_n$[c] ($\times 10^{-3}$)	$\overline{M}_w/\overline{M}_n$[c]	$[\alpha]_D^{25}$ (deg)[d]	$[\theta]_\lambda^{25}$ ($\times 10^{-4}$)[e]
A-1	8.6	THF(3)	24	42.1[f]	4.1[g]	4.3[g]	41.1[g]	2.7[g]
A-2	8.6	CB(3)	24	69.1	52.0	7.4	2.3	1.4
A-3	8.6	DCB(3)	24	73.6	46.0	8.6	4.6	1.3
A-4	8.6	TOL(5)	24	70.3	18.0	9.8	16.8	2.0
A-5	8.7	CHO(3)	24	23.7	10.0	9.4	6.5	1.4
A-6	8.6	DOX(5)	24	59.9	18.0	9.0	25.0	2.2

[a] $[\text{AIBN}] = 1.0 \times 10^{-2}$ mol l^{-1}

[b] THF, tetrahydrofuran, TOL, toluene, CHO, chloroform, DOX, dioxane, CB, chlorobenzene, DCB, *o*-dichlorobenzene

[c] By g.p.c.

[d] $c = 1.0$ g dl^{-1}; $l = 5$ cm; in THF

[e] Deg cm^2 dmol^{-1}; $c = \sim 0.2$ g dl^{-1}; $l = 1.0$ mm; in THF; $\lambda = 242 \pm 2$ nm

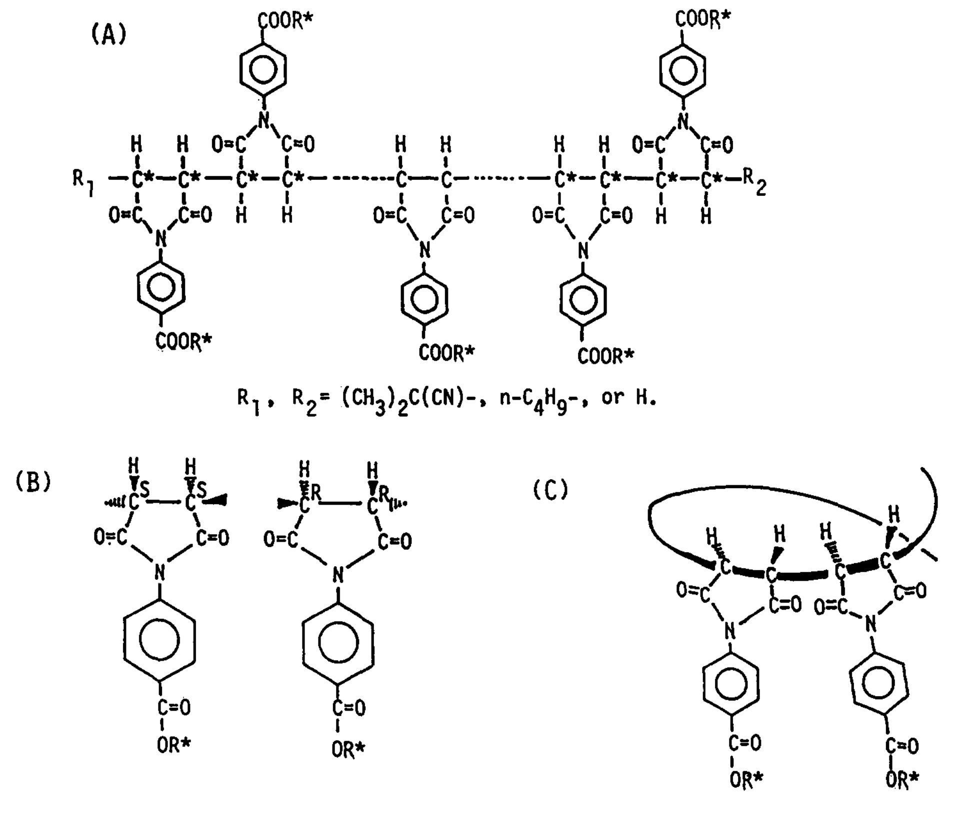
[f] Total yield: 42.1%; the yield of the polymer insoluble in THF: 7.8%

[g] Polymer soluble in THF

Table 2 Anionic polymerizations of ChPMI at 0°C

Run no.	ChPMI ($\times 10^{-4}$ M)	Solvent[a] (ml)	Catalyst[b] (mol% (wt%))	Polymerization time (h)	Yield (%)	$\overline{M}_n$[c] ($\times 10^{-3}$)	$\overline{M}_w/\overline{M}_n$[c]	$[\alpha]_D^{25}$ (deg)[d]	$[\theta]_\lambda^{25}$ ($\times 10^{-4}$)[e]
B-1	8.8	THF(5)	3.5(0.4)	24	40.7	6.3	2.8	5.4	10.6
B-2	8.5	THF(5)	7.0(0.8)	24	53.1	7.4	1.6	6.6	10.8
B-3	17.4	TOL(20)	3.5(0.4)	24	28.6	6.0	2.5	10.1	11.5
B-4	16.6	TOL(20)	7.0(0.8)	24	33.5	4.8	1.4	10.5	12.2
B-5	17.0	TOL(20)	8.2(0.9)	24	27.6	4.3	1.1	7.1	8.8
B-6	16.8	TOL(20)	16.4(1.9)	24	25.7	3.6	1.4	11.6	8.1

[a] THF, tetrahydrofuran, TOL, toluene
[b] Catalyst = n-BuLi; ([cat.]/([ChPMI] + [cat.])) × 100
[c] By g.p.c.
[d] $c = 1.0\ \mathrm{g\ dl^{-1}}$; $l = 5$ cm; in THF
[e] $\mathrm{Deg\ cm^2\ dmol^{-1}}$; $c = \sim 0.2\ \mathrm{g\ dl^{-1}}$; $l = 1.0$ mm; in THF; $\lambda = 242 \pm 4$ nm



R_1, R_2 = $(CH_3)_2C(CN)$-, n-C_4H_9-, or H.

C*=Chiral Carbon, R*=Cholesteryl.

Scheme 2

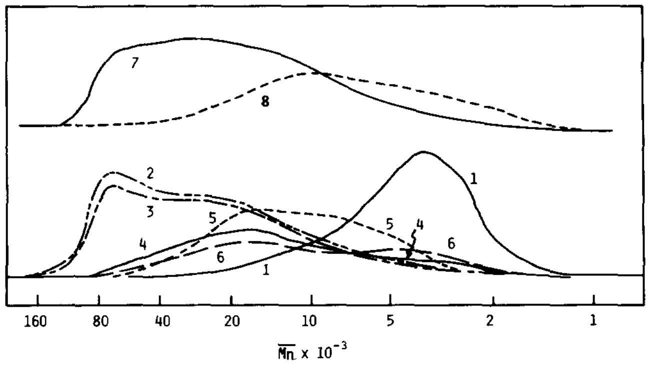


Figure 3 G.p.c. curves for the poly(ChPMI)s obtained with AIBN in several solvents: (1) THF, (2) CB, (3) DCB, (4) TOL, (5) CHO, (6) DOX; and the copolymers: (7) poly(ChPMI-*co*-ST) (run C-4), (8) poly(ChPMI-*co*-MMA) (run D-4)

indicates that the optical activity may be attributed to the asymmetric induction around both the terminal ChPMI units of the polymer, as illustrated in *Scheme 2A*, and to an excess of chiral centres of (*R*,*R*) or (*S*,*S*) in the polymer main chain (*Scheme 2B*). *Scheme 2B* indicates not a helical but a linear polymer.

^{1}H and ^{13}C n.m.r. spectra of all obtained polymers were similar. Typical ^{1}H and ^{13}C n.m.r. spectra are shown in *Figure 4*. The structural differences between the polymers could not be observed from the i.r., ^{1}H and ^{13}C n.m.r. spectra.

All the anionic polymerizations proceeded homogeneously throughout. Values of $\overline{M}_n$ and polydispersity ($\overline{M}_w/\overline{M}_n$) were 3.6×10^3 to 7.4×10^3 and 1.1 to 1.4, respectively, and were much smaller than those for the polymers obtained with AIBN. The value of $[\alpha]_D$ was

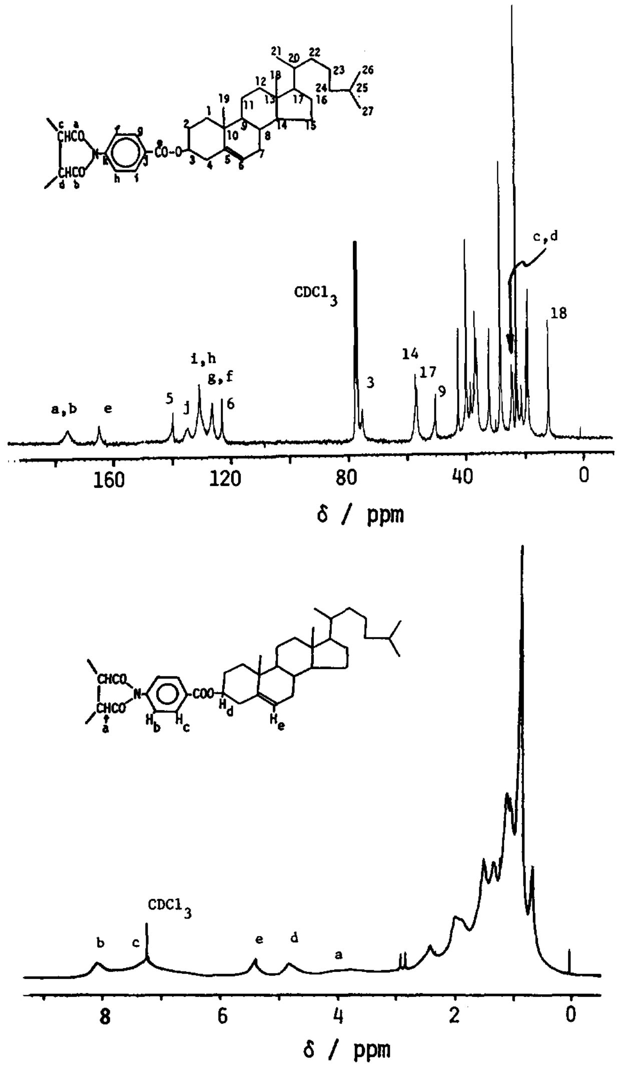


Figure 4 ^{1}H and ^{13}C n.m.r. spectra for the polymers (run A-2)

from 5.4 to 11.6, and its variation was smaller. ^{1}H and ^{13}C n.m.r. spectra of the polymers obtained with n-BuLi were similar to those of the polymers obtained with AIBN. This suggests that there are no structural differences among the polymers obtained using radical and anionic initiators.

The c.d. spectra for poly(ChPMI)s obtained with AIBN and n-BuLi in toluene are shown in *Figure 5*. In both c.d. spectra, one large positive peak, which is ascribed to the $\pi \rightarrow \pi^*$ transition, was observed at about 245 nm. A model compound of poly(ChPMI), i.e. *N*-[4-(cholesteroxycarbonyl)phenyl]succinimide (ChPSI) indicated a similar pattern to that obtained with n-BuLi, as shown in *Figure 5*, trace 3. In the polymerization of ChMI, the c.d. spectrum of the polymer obtained with AIBN indicated quite a different pattern from that obtained with n-BuLi, which suggested that each polymer obtained with AIBN or n-BuLi had a different structure[29]. In the case of ChPMI, however, such a tendency was not observed.

Cubbon[1] has reported that eight achiral *N*-substituted maleimides (RMI) were polymerized by free radical and n-BuLi, and both types of initiator gave rise to polymers which contain a predominantly *threo*-diisotactic polymer, based only on X-ray analysis[1]. 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 stereospecificity 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]. Inspection[1] of a poly(RMI) model indicates that *threo*-diisotactic polymer can form the 3_1 helix in which the repeat distance is 4.7 Å, and that the diameter of the helix with no substituents on the nitrogen is about 10 Å.

The poly(ChPMI)s obtained in this study from radical and anionic initiators were not crystalline but amorphous, as judged from X-ray diffraction diagrams.

Temperature dependence of the specific rotations for the poly(ChPMI) was studied. The relationship between the specific rotations of the copolymers and the temperature (3–60°C) was linear, and the slopes were very small [the temperature coefficients $(\Delta[\alpha]_D/\Delta T) = 0.06$ to 0.08]. When the specific rotation was plotted against the solvent concentration ([THF]/([THF] + [ethanol])), a straight line was obtained. Accordingly, there may scarcely be helical conformation in the poly(ChPMI), as shown in *Scheme 2C*.

Radical copolymerizations of ChPMI with ST and MMA

The results of radical copolymerizations of ChPMI (M_1) with ST (M_2), MMA (M_2) in toluene (6 ml) at 70°C in the presence of AIBN (1.0×10^{-2} mol l^{-1}) are summarized in *Table 3*. Copolymerization proceeded homogeneously throughout. The obtained copolymers were white powders and optically active. The $\overline{M}_n$ of poly(ChPMI-*co*-ST)s were generally greater than those

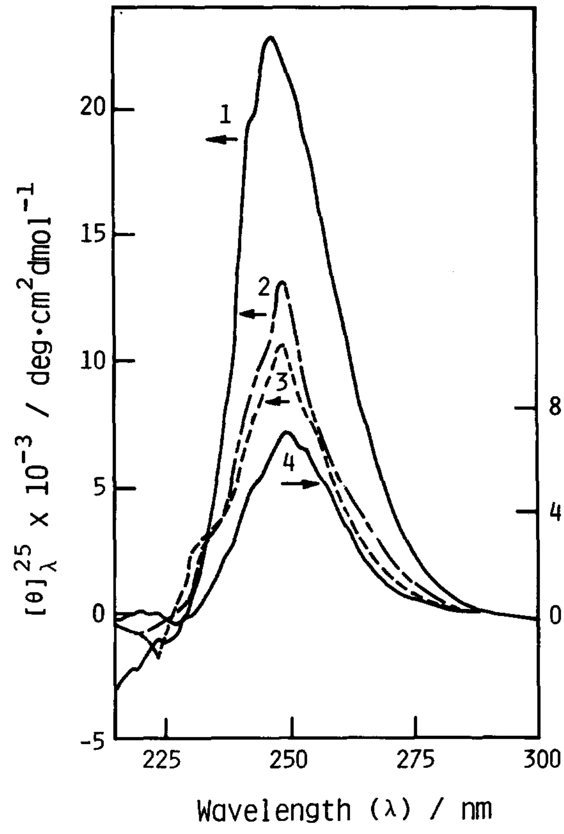


Figure 5 C.d. spectra for (1) poly(ChPMI) obtained with AIBN in toluene (run A-4), (2) poly(ChPMI) obtained with n-BuLi in toluene (run B-4), (3) ChPSI (a model compound for poly(ChPMI)) and (4) hydrolysed polymer (run H-2)

Table 3 Radical copolymerizations of ChPMI (M_1) with ST (M_2) or MMA (M_2) in toluene (6 ml) at 70°C[a]

Run no.	M_1 in monomer (mol%)	M_2	Yield (%)	M_1 in copolymer[b] (mol%)	$\overline{M}_n$[c] ($\times 10^{-3}$)	$\overline{M}_w/\overline{M}_n$[c]	$[\alpha]_D^{25}$ (deg)[d]	$[\theta]_\lambda^{25}$ ($\times 10^{-4}$)[e]
C-1	10.1	ST	20.9	47.8	102.0	1.6	2.6	1.1
C-2	19.8	ST	28.1	48.5	94.0	1.9	3.0	1.2
C-3	40.1	ST	31.8	50.1	79.5	2.1	2.8	1.1
C-4	47.9	ST	32.7	50.3	56.3	5.6	1.5	1.2
C-5	61.4	ST	32.4	52.7	36.1	6.6	1.9	1.3
C-6	78.2	ST	20.9	57.9	26.5	7.8	2.5	1.4
C-7	90.1	ST	19.9	70.2	21.6	10.1	3.4	1.6
D-1	10.2	MMA	25.3	10.3	19.3	12.3	1.7	0.8
D-2	20.3	MMA	27.1	20.1	14.9	10.1	1.9	1.1
D-3	39.7	MMA	32.0	31.4	7.4	8.7	2.5	1.2
D-4	49.0	MMA	30.8	41.5	5.8	5.9	3.6	1.2
D-5	58.3	MMA	34.4	47.1	5.0	3.8	4.8	1.3
D-6	78.0	MMA	30.9	59.2	3.9	2.3	8.1	1.4
D-7	90.2	MMA	25.8	72.5	3.5	2.1	9.8	1.8

[a] [AIBN] $= 1.0 \times 10^{-2}$ mol l^{-1}; $M_1 + M_2 = 1.0$ g; polymerization time = 12 h
[b] Determined by ^1H n.m.r.
[c] Estimated by g.p.c.
[d] $c = 1.0$ g dl^{-1}; $l = 5$ cm; in THF
[e] Deg cm^2 dmol^{-1}; $c = \sim 0.3$ g dl^{-1}; $l = 1$ mm; in THF; $\lambda = 242 \pm 2$ nm

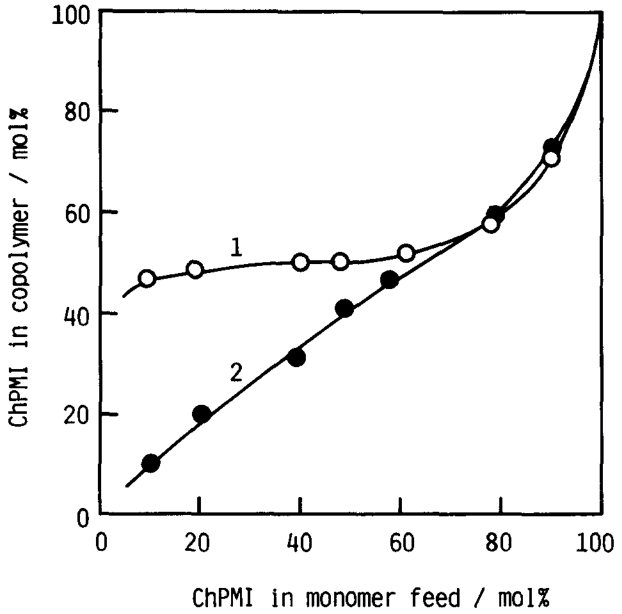


Figure 6 Copolymer composition curves for (○) ChPMI-ST and (●) ChPMI-MMA systems

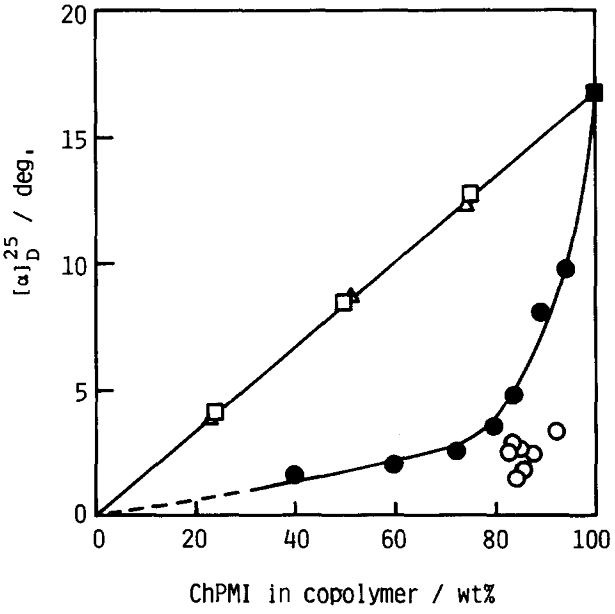


Figure 7 Relationships between specific rotation $[\alpha]_D$ and content (wt%) of the monomeric unit of ChPMI in copolymers: (○) poly(ChPMI-*co*-ST)s, (●) poly(ChPMI-*co*-MMA)s, (■) poly(ChPMI) obtained with AIBN (run A-4), (□) a mixture of poly(ChPMI) and poly(ST), and (△) a mixture of poly(ChPMI) and poly(MMA)

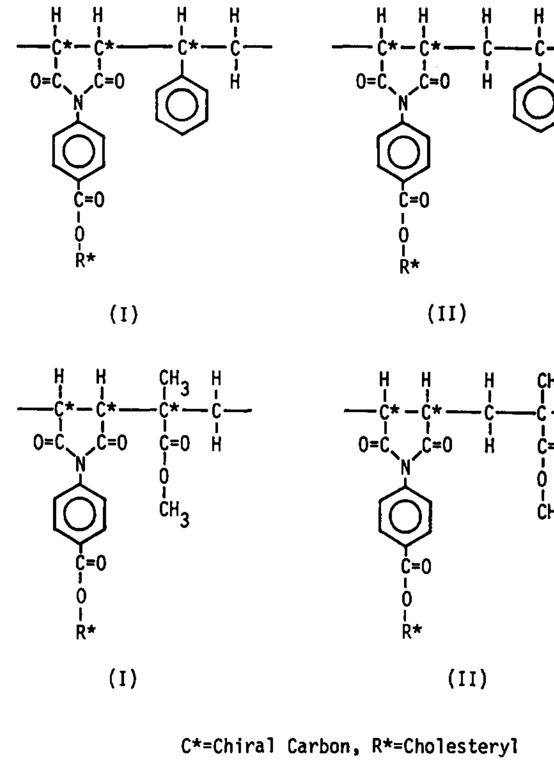
of poly(ChPMI-*co*-MMA)s, as shown in *Table 3* and *Figure 3*.

Copolymer composition curves of the ChPMI-ST and ChPMI-MMA systems are shown in *Figure 6*. Monomer reactivity ratios, r_1 and r_2, determined by the integration method[33] and Alfrey–Price[34] Q, e values were as follows: $r_1 = 0.080$, $r_2 = 0.020$, $Q_1 = 6.57$, $e_1 = 1.74$ in the ChPMI-ST system and $r_1 = 0.11$, $r_2 = 0.80$, $Q_1 = 1.73$, $e_1 = 1.96$ in the ChPMI-MMA system. These copolymerization parameters were similar to those for other RMI copolymers reported previously[35].

Optical behaviour of the copolymers

Figure 7 shows the relationship between the specific rotation and the content (wt%) of the monomeric unit of ChPMI in both copolymer systems. The specific rotations of a mixture of poly(ChPMI) and poly(ST) gave a good linear relation, as shown in *Figure 7*. The absolute values of specific rotations of poly(ChPMI-*co*-ST)s increased with the content (wt%) of ChPMI unit. However, a significant deviation from linearity was observed. This suggests that asymmetry may be introduced into the copolymer main chain, as shown in *Scheme 3*. In poly(ChPMI-*co*-MMA)s, the same tendency could be observed, as shown in *Figure 7*.

In the c.d. spectra for poly(ChPMI-*co*-ST)s, as shown in *Figure 8*, a positive peak around 245 nm was observed,



Scheme 3

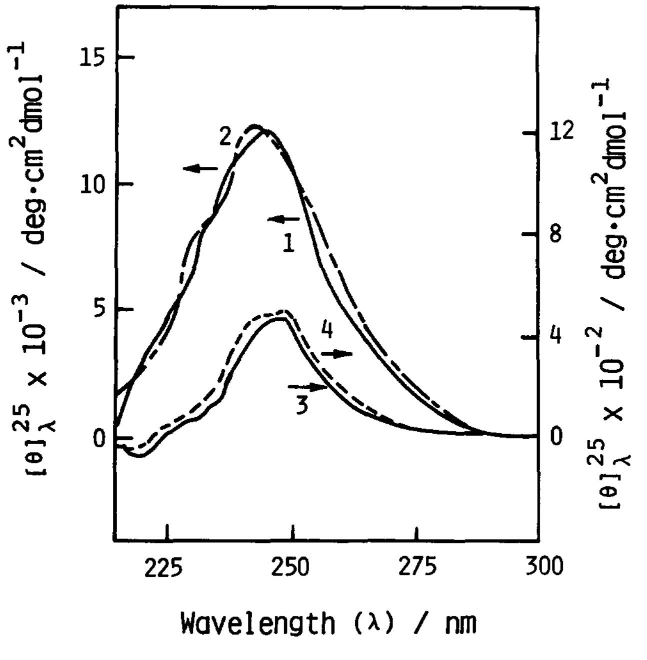


Figure 8 C.d. spectra for (1) poly(ChPMI-*co*-ST) (run C-4), (2) poly(ChPMI-*co*-MMA) (run D-4), (3) hydrolysed poly(ChPMI-*co*-ST) (run H-6) and (4) hydrolysed poly(ChPMI-*co*-MMA) (run H-7)

which was ascribed both to the π→π* transition of phenyl groups in the ST and ChPMI units and to the n→π* transition of carbonyl groups in the ChPMI unit. In the poly(ChPMI-*co*-MMA)s, a positive c.d. peak was observed at about 243 nm, based on the n→π* transition of carbonyl groups of the MMA and ChPMI units and on the π→π* transition of the ChPMI unit.

The relationship between the molecular ellipticities [θ] (owing to the average molecular weight of monomeric units) and the composition (wt%) of the copolymers indicated a considerable deviation, as shown in *Figure 9*. This suggests that the asymmetric induction copolymerization may take place, as shown in *Scheme 3*.

In order to confirm the asymmetric induction, the polymers and copolymers were hydrolysed in a mixture of THF and methanol (vol. ratio 1:1) with potassium hydroxide. As shown in *Table 4*, the specific rotations of the hydrolysed poly(ChPMI)s, poly(ChPMI-*co*-ST)s and poly(ChPMI-*co*-MMA)s had very small values, but were still optically active after the hydrolysis. A very small positive peak was observed in c.d. spectra of all hydrolysed polymers and copolymers, as shown in *Figures 5* and *8*. This confirmed the induction of asymmetry into the polymer and copolymers, as illustrated in *Scheme 4*.

In both the ChPMI-ST and the ChPMI-MMA

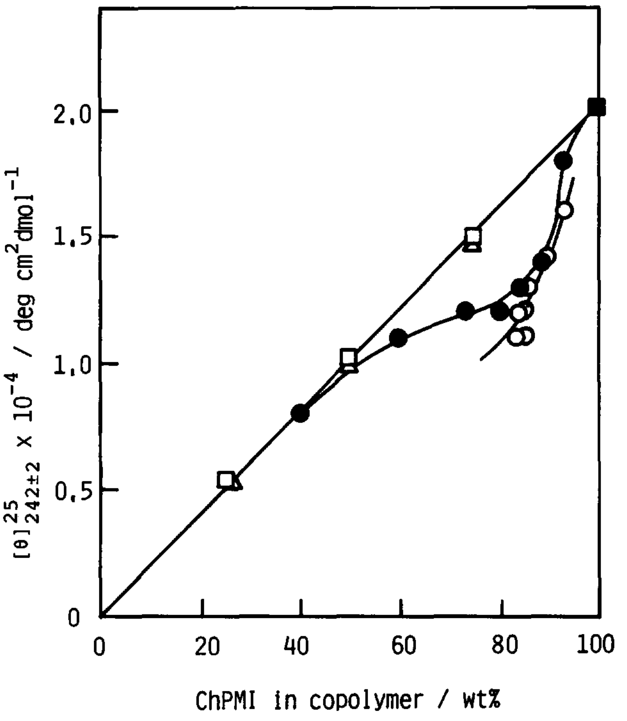
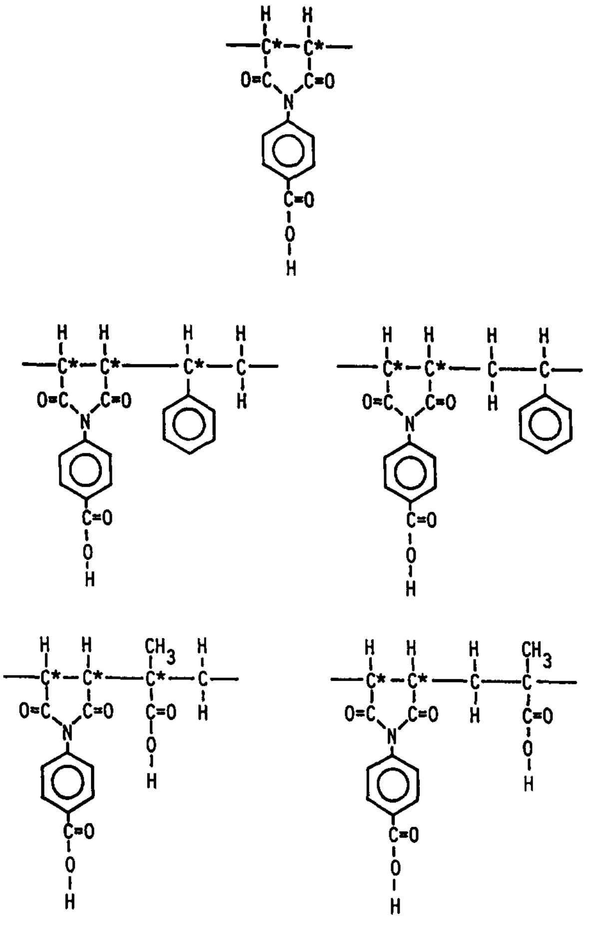


Figure 9 Relationships between molecular ellipticities [θ] and content (wt%) of the monomeric unit of ChPMI in copolymers: (○) poly(ChPMI-*co*-ST)s, (●) poly(ChPMI-*co*-MMA)s, (■) poly(ChPMI) obtained with AIBN (run A-4), (□) a mixture of poly(ChPMI) and poly(ST), and (△) a mixture of poly(ChPMI) and poly(MMA)

Table 4 Optical behaviour of hydrolysed poly(ChPMI), poly(ChPMI-*co*-ST) and poly(ChPMI-*co*-MMA)

	Original polymers[a]			Hydrolysed polymers	
Run	Run	$[\alpha]_D$ (deg)	$[\theta] \times 10^{-4}$	$[\alpha]^{25}_D$ (deg)[b]	$[\theta]^{25}_{\lambda}$[c]
H-1	A-3	4.6	1.3	1.8	680
H-2	A-4	16.8	2.0	2.1	720
H-3	B-2	6.6	1.1	2.2	620
H-4	B-4	10.5	1.2	1.7	580
H-5	C-3	2.8	1.1	1.3	480
H-6	C-5	1.9	1.3	1.0	510
H-7	D-3	2.5	1.2	1.1	500
H-8	D-5	4.8	1.3	1.7	560

[a] See run no. in *Tables 1*, *2* and *3*
[b] $c = 0.4$–0.9 g dl^{-1}; $l = 5$ cm; in THF
[c] Deg cm^2 dmol^{-1}; $c = 0.2$–0.4 g dl^{-1}; in THF; $\lambda = 249 \pm 2$ nm



Scheme 4

systems, the relationship between the specific rotations of the copolymers and the temperature gave linearity, and the slopes were very small [the temperature coefficients ($\Delta[\alpha]_D/\Delta T$) = 0.03 to 0.07]. When the specific rotation was plotted against the solvent concentration ([THF]/([THF] + [ethanol])), a straight line was obtained. Thus, there may scarcely be helical conformation in the copolymers, as well as in the homopolymers.

From polarization microscope measurements, it was found that the ChPMI monomer indicated a cholesteric phase from 168 to 170°C. Both the polymers and the copolymers showed a liquid-crystalline phase from 222 to 228°C. Details on these will be reported in the near future.

CONCLUSIONS

1. A novel type of optically active *N*-[4-(cholesteroxycarbonyl)phenyl]maleimide (ChPMI) was synthesized and polymerized with radical and anionic initiators to obtain chiral polymers.
2. The specific rotations of the ChPMI polymers obtained with AIBN were influenced by the polymerization solvents, and could be correlated to the molecular weight. The optical activity may be attributable to both the chiral cholesteryl moiety and asymmetric induction into the polymer main chain. This was confirmed by the fact that the hydrolysed polymers were optically active.
3. The polymers obtained with AIBN and n-BuLi showed almost the same c.d. pattern.
4. From the results of the radical copolymerizations of ChPMI (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: $r_1 = 0.080$, $r_2 = 0.020$, $Q_1 = 6.57$, $e_1 = 1.74$ in the ChPMI-ST system, $r_1 = 0.11$, $r_2 = 0.80$, $Q_1 = 1.73$, $e_1 = 1.96$ in the ChPMI-MMA system.
5. Asymmetric induction copolymerization took place in the ChPMI-ST and ChPMI-MMA systems. This was confirmed by hydrolysis of the original copolymers.

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