Synthesis and Polymerization of N-(Cholesteroxycarbonylmethyl)maleimide

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ABSTRACT: A new type of optically active N-(cholesteroxycarbonylmethyl)maleimide (ChMI) was synthesized from maleic anhydride, glycine and cholesterol. Radical homopolymerizations of ChMI were performed at 70°C for 24 h to give optically active polymers having $[\alpha]_D = -25.7$ to $-34.2°$. Radical copolymerizations of ChMI (M_1) were performed with styrene (ST, M_2), methyl methacrylate (MMA, M_2) in benzene at 70°C. From the results, the monomer reactivity ratios (r_1, r_2) and Alfrey–Price Q, e values were determined as follows: $r_1 = 0.090$, $r_2 = 0.082$, $Q_1 = 2.07$, $e_1 = 1.42$ for the ChMI–ST system; $r_1 = 0.13$, $r_2 = 1.22$, $Q_1 = 1.04$, $e_1 = 1.76$ for the ChMI–MMA system. Anionic homopolymerizations of ChMI were also carried out. Chiroptical properties of the polymers and copolymers were investigated.
   KEY WORDS   Polymerization / N-(Cholesteroxycarbonylmethyl)maleimide / Optically Active Polymer / Monomer Reactivity Ratio / Q, e Values / Asymmetric Induction Copolymerization /

It is well known that many cholesteryl derivatives are thermotropic liquid crystallines, and indicate a cholesteric phase.[1] Cholesterol is the most commonly encountered pendant chiral moiety; both homopolymers[2-4] and copolymers[5-8] with a pendant cholesteryl group have been reported. These are related to liquid crystalline polymers. On the other hand, cholesterol is also interesting as an inclusion compound.[9] To the best of our knowledge, there have been no detailed reports on the polymerization reactivities of monomers containing cholesteryl moiety. No N-substituted maleimide (RMI) containing a cholesteryl group has been investigated. Since the cholesteryl moiety is chiral and very bulky, it is interesting to clarify the polymerization reactivities of RMI vearing cholesteryl moiety, and the chiroptical properties of the polymers and copolymers obtained, concerning asymmetric induction copolymerization of cis-cyclic

olefin.

There have been many reports[10-18] including patents[19] on the polymerization and copolymerization of RMI. However, only a few investigations on the polymerization of optically active RMI have been made.[20,21] The polymerization reactivities and chiroptical properties of chiral N-(α-methylbenzyl)maleimide (MBZMI)[22] and N-(L-menthoxycarbonylmethyl)maleimide[23] were investigated. Polymerizations of cis-cyclic alkene derivatives can yield two trans-openings of the double bond, chiral centers of (S,S) and (R,R). If one is produced more than the other, the obtained polymer can be optically active.[24] Asymmetric polymerizations of non-chiral RMI were performed with n-BuLi/(−)-sparteine (Sp) to obtain chiral poly(RMI)s containing a relatively high specific rotation ($[\alpha]_D = -40°$, RMI = N-cyclohexylmaleimide).[25,26] Asymmetry could be attributable to

a *threo*-diisotactic structure of the RMI polymer main chain, *i.e.*, arising from a helical structure and/or from the excess of chiral stereogenicity, (*S,S*) or (*R,R*).[25]

In this paper, a novel, optically active *N*-(cholesteroxycarbonylmethyl)maleimide (ChMI) was synthesized from maleic anhydride, glycine, and cholesterol. ChMI is polymerized and copolymerized with styrene (ST) and methyl methacrylate (MMA) in the presence of a radical initiator. Monomer reactivity ratios and *Q–e* values are determined. From the specific rotations and molecular ellipticities measurements of the copolymers, asymmetric induction into the copolymer main chain is discussed. ChMI is also polymerized with an anionic initiator; *n*-BuLi, to obtain a chiral polymer. Structural differences of the ChMI polymers obtained with radical or anionic initiator are described. Thermotropic properties of ChMI monomer, the polymers, and copolymers are also described.

EXPERIMENTAL

ChMI Monomer

The ChMI monomer was synthesized from maleic anhydride, glycine, and cholesterol, as shown in Scheme 1.

N-Glycinyl maleamic acid (GMA)[23]: GMA was synthesized from maleic anhydride (MAn) and glycine in acetic acid at room temperature; yield 95%; mp 197°C [lit.[27] 187—188.5°C].

N-Glycinyl maleimide (GMI)[23]: GMI was prepared by dehydration of GMA in the presence of triethylamine in toluene; yield 42%; mp 118°C [lit.[27] 113.5°C].

N-[(Chloroformyl)methyl]maleimide (CGMI)[23]: GMI was treated with thionyl chloride to obtain CGMI: bp 85—87°C/1.6×10^{-2} mmHg; yield 76%.

N-(Cholesteroxycarbonylmethyl)maleimide: A solution of CGMI (27.9 g, 0.16 mol) in 100 ml of chloroform was added dropwise to 200 ml of chloroform solution dissolved cholesterol (62.3 g, 0.16 mol) and triethylamine (14.2 g, 0.14 mol), keeping the temperature below 5°C. After the addition, the solution was stirred for 24 h at room temperature. The reaction was performed under nitrogen atmosphere throughout. The reaction mixture was poured into 100 ml of ice water containing 2 ml of hydrochloric acid. The solution was extracted with chloroform to obtain a crude ChMI. The ChMI was purified by reprecipitation four times from the chloroform solution
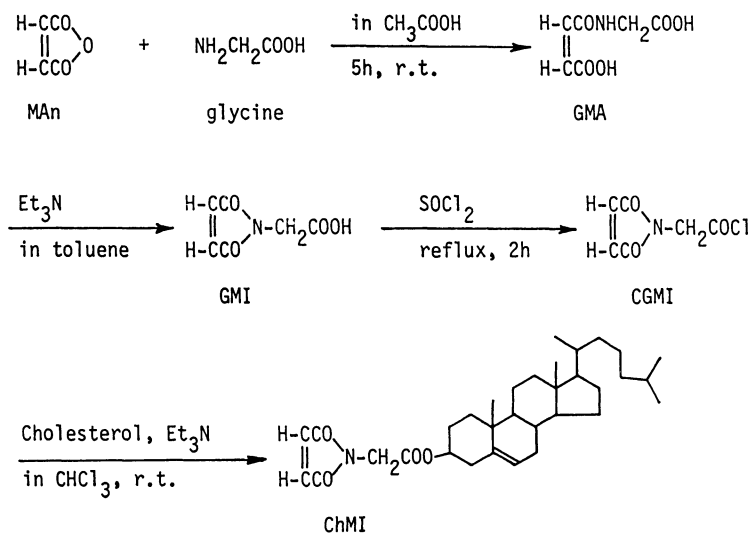
Scheme 1.

to methanol, and then recrystallized from ethanol to obtain pure ChMI (76 g, 91% based on CGMI; total yield: 20.1%): mp 190—193°C; $[\alpha]_D = -27.8°$ ($c = 1.0 \, \text{g dl}^{-1}$; $l = 10 \, \text{cm}$; THF).

IR (KBr disk, cm^{-1}): 2850 (CH, CH$_2$, CH$_3$), 1740 and 1719 (CO–N–CO), 1640 (C=C), 1450, 1420 and 1380 (CH, CH$_2$, CH$_3$), 1205 and 1140 (OC=O), 830 and 695 (*cis* CH=CH). ^{1}H NMR (δ, ppm from TMS in CDCl$_3$): 6.79 (s, 2H, CH=CH), 5.38—5.36 (m, 1H, C=CH in cholesteryl), 4.68—4.62 (m, 1H, O–CH in cholesteryl), 4.25 (s, 2H, N–CH$_2$CO), 2.34—0.67 (m, 43H, other protons of cholesteryl group). ^{13}C NMR (δ, ppm from TMS in CDCl$_3$): 170.13 (CO–N–CO), 166.88 (COO), 139.73 (–C= in cholesteryl), 134.88 (C=C in maleimide ring), 123.38 (=CH– in cholesteryl), 76.34 (O–CH in cholesteryl), 42.84 (N–CH$_2$) and 57.21, 56.74, 50.59, 40.26, 40.01, 39.44, 38.43, 37.88, 37.06, 36.71, 36.22, 32.39, 28.64, 28.44, 28.16, 24.74, 24.34, 23.18, 22.96, 21.56, 19.71, 19.21, 12.33 (24C, other carbons of cholesteryl group).

Elemental analysis (%): Found, C = 75.62, H = 9.15, N = 2.30; Calcd. for C$_{33}$H$_{49}$O$_4$N, C = 75.68, H = 9.43, N = 2.67.

Model Compound of Poly(ChMI): *N*-(Cholesteroxycarbonylmethyl)succinimide (ChSI)

ChSI was prepared from succinic anhydride, glycine, and cholesterol, according a method similar to that of ChMI. Yields and melting points of precursors are as follows: *N*-(L-glycinyl)succinamic acid (GSA): yield 98%; mp. 150—153°C; *N*-(L-glycinyl)succinimide (GSI): yield 63%, mp 111—116°C, *N*-(L-chloroformylmethyl)succinimide (CGSI) recrystallized from benzene (50)/cyclohexane(50): yield 93%, mp 81— 84°C.

ChSI: total yield 4.3%; mp 178—181°C; $[\alpha]_D = -26.8°$ ($c = 1.0 \, \text{g dl}^{-1}$, $l = 10 \, \text{cm}$, THF). IR (KBr disk, cm^{-1}): 2850 (CH$_2$ and CH$_3$), 1745 and 1710 (CO–N–CO), 1420 and 1375 (CH$_3$), 1200 and 1145 (OC=O). ^{1}H NMR (δ, ppm from TMS in CDCl$_3$): 5.38—5.11 (m, 1H, C=CH in cholesteryl), 4.76—4.31 (m, 1H, O–CH in cholesteryl), 4.15 (s, 2H, N–CH$_2$–CO), 2.74 (s, 4H, CH$_2$CH$_2$ in succinimide ring), 2.46—0.67 (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.

Homopolymerization and Copolymerization

Radical homopolymerization and copolymerization were carried out with 2,2′-azobisisobutyronitrile (AIBN, mp 102°C) as an initiator in tetrahydrofuran (THF), chlorobenzene (CB), *o*-dichlorobenzene (DCB), toluene (TOL), chloroform (CF), 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. The composition of the copolymer obtained was calculated by ^{1}H NMR spectra.

Anionic homopolymerization was achieved in toluene or THF at 0°C using *n*-butyllithium (*n*-BuLi) as a catalyst under a nitrogen atmosphere. The polymerization was terminated with a few drops of methanol using a syringe. The solution was poured into a large amount of acetone. The obtained polymer was purified by reprecipitation three times from chloroform solution to acetone, 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

room temperature. Optical rotatory dispersion (ORD) and circular dichroism (CD) spectra were obtained at room temperature by a Jasco J-20C (Japan Specroscopic Co.), equipped with a xenon source and a computing data processor. Molecular weights of the polymers were measured by gel permeation chromatographic (GPC) analysis, using the same technique described earlier,[28] and by a vapor pressure osmometer (VPO) on Corona 114 using the vapor of chloroform. IR and NMR spectra were obtained and elemental analysis was carried out, using the same instruments as reported previously.[29]

RESULTS AND DISCUSSION

Radical and Anionic Homopolymerizations of ChMI

Radical and anionic polymerizations of ChMI were performed under several conditions. The results are summarized in Tables I

Table I. Radical polymerizations of ChMI in various solvents at 70°C[a]

Run No.	[ChMI] $\times 10^{-4}$ mol	Solvent[b] ml	Polym. time h	Yield %	N-Analysis %	$\bar{M}_n$[c] $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$	$\bar{M}_n$[d] $\times 10^{-3}$	$[\alpha]_D$[e] deg	$[\theta]_\lambda$[f]
A-1	9.6	THF (3)	24.0	58.3	2.42	4.4	1.2	3.9	−25.9	−680
A-2	9.5	CB (5)	17.3	67.8	2.39	8.5	1.9	8.2	−27.7	−1400
A-3	9.5	DCB (5)	17.3	76.5	2.36	7.2	1.6	6.5	−27.4	−1200
A-4	9.6	TOL (5)	24.0	71.6	2.56	6.4	1.4	5.8	−26.1	−930
A-5	9.6	CF (5)	24.0	62.9	2.38	8.9	1.8	8.2	−30.7	−1800
A-6	9.5	DOX (5)	24.0	73.6	2.45	4.9	1.4	4.6	−29.4	−1700

[a] $[AIBN] = 1.0 \times 10^{-2}$ mol l^{-1}.
[b] THF, tetrahydrofuran; TOL, toluene; CF, chloroform; DOX, dioxane; CB, chlorobenzene; DCB, dichlorobenzene.
[c] By GPC.
[d] By VPO.
[e] $c = 1.0$ g dl^{-1}; $l = 10$ cm; THF.
[f] deg cm^2 dmol^{-1}; $c = 1.0$ g dl^{-1}; $l = 0.1$ cm; $\lambda = 220 \pm 4$ nm.

Table II. Anionic polymerizations of ChMI at 0°C

Run No.	[ChMI] $\times 10^{-4}$ mol	Solvent[a] ml	Cat.[b] mol% [wt%]	Polym. time h	Yield %	N-Analysis %	$\bar{M}_n$[c] $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$[c]	$\bar{M}_n$[d] $\times 10^{-3}$	$[\alpha]_D$[e] deg	$[\theta]_\lambda$[f]
B-1	9.5	THF (10)	3.5 [0.4]	18	64.7	2.55	7.2	2.8	6.8	−37.1	−1200
B-2	9.5	THF (10)	7.0 [0.7]	24	30.3	—	—	—	—	—	—
B-3	9.6	TOL (20)	3.5 [0.4]	24	1.5	—	—	—	—	—	—
B-4	9.6	TOL (20)	7.0 [0.7]	24	15.4	—	—	—	—	—	—
B-5	9.6	TOL (20)	8.2 [1.0]	24	52.3	2.63	4.4	3.2	4.1	−40.1	−970
B-6	9.6	TOL (20)	16.4 [3.5]	24	65.2	2.58	6.0	2.5	5.7	−32.7	−820
B-7	9.6	TOL (20)	28.6 [7.0]	24	31.1	2.59	6.7	3.0	—	−36.4	−710

[a] THF, tetrahydrofuran; TOL, toluene.
[b] Cat., n-BuLi.
[c] By GPC.
[d] By VPO.
[e] $c = 1.0$ g dl^{-1}; $l = 10$ cm; THF.
[f] deg cm^2 dmol^{-1}; $c = 0.1$ g dl^{-1}; $l = 0.1$ cm; THF; $\lambda = 220 \pm 4$ nm.

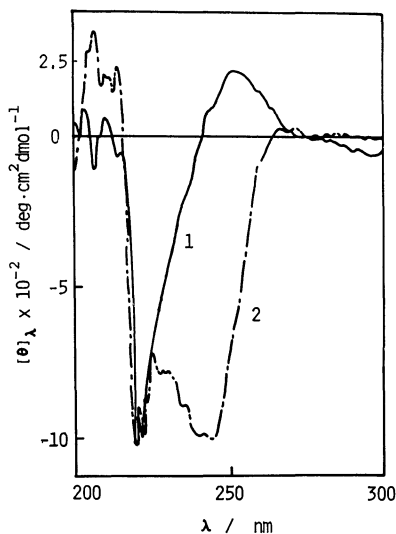**Figure 1.** CD spectra ($c = ca.$ $1.0\,g\,dl^{-1}$; THF, $l = 1.0$ mm) for (1) poly(ChMI) obtained with AIBN in toluene (run A-4), and (2) poly(ChMI) obtained with n-BuLi in toluene (run B-5).

Figure 2. CD spectra ($c = ca.$ $1.0\,g\,dl^{-1}$, THF, $l = 1.0\,mm$) for (1) poly(ChMI) obtained with AIBN in THF (run A-1), (2) poly(ChMI) obtained with n-BuLi in THF (run B-1), and (3) ChSI [a model compound for poly(ChMI)].

and II. The polymerizations proceeded homogeneously throughout. The obtained polymers were white powders and had negative optical activities. The number-average molecular weights ($\bar{M}_n$) of poly(ChMI)s obtained with the radical initiator were 4.4×10^3 to 8.9×10^3. However, the $\bar{M}_n$ of the poly(ChMI)s could not be correlated with dielectric constants (ε_r) of the polymerization solvents. The specific rotation ($[\alpha]_D$) and the molecular ellipticity ($[\theta]$) of the polymers were -25.9 to $-30.7°$, and -6.8×10^2 to $-1.8 \times 10^3\,deg\,cm^2\,dmol^{-1}$, respectively.

The CD spectra for poly(ChMI)s obtained with AIBN and n-BuLi in toluene are shown in Figure 1. The CD patterns for the poly(ChMI)s obtained with AIBN in other solvents were similar to that of the poly(ChMI) obtained in toluene, except for the poly(ChMI) obtained in THF. In the poly(ChMI) obtained with AIBN, large negative and small positive CD peaks were observed at about 220 nm and 255 nm, respectively. The former could be attributed to the $n \rightarrow \pi^*$ transition of two carbonyl groups in the imide ring, the latter
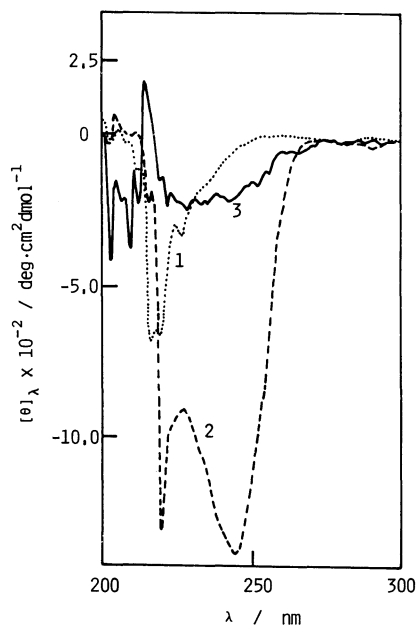
was based on the $\pi \rightarrow \pi^*$ transition of cholesteryl group. The poly(ChMI) obtained in THF revealed only negative CD, as shown in Figure 2 (1). This difference in CD may be attributable to conformation of the main chain, as will be described later.

As shown in Figures 1 and 2, the CD patterns for poly(ChMI)s obtained with n-BuLi were quite different from those for polymers obtained with AIBN. That is, the polymers obtained with anionic initiator exhibited large negative CD peaks at about 245 nm. Both CD patterns for the poly(ChMI)s obtained with AIBN and n-BuLi were quite different from that for a model compound of poly(ChMI), i.e., N-(cholesteroxycarbonylmethyl)succinimide (ChSI), as shown in Figure 2 (3). This suggests that the asymmetry of both polymers obtained with AIBN and n-BuLi could be ascribed not only to the N-substituent, a chiral cholesteryl group, but also to the following chiral factors, (A) helical conformation, (B)

(A)

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

(C)

R* = cholesteryl
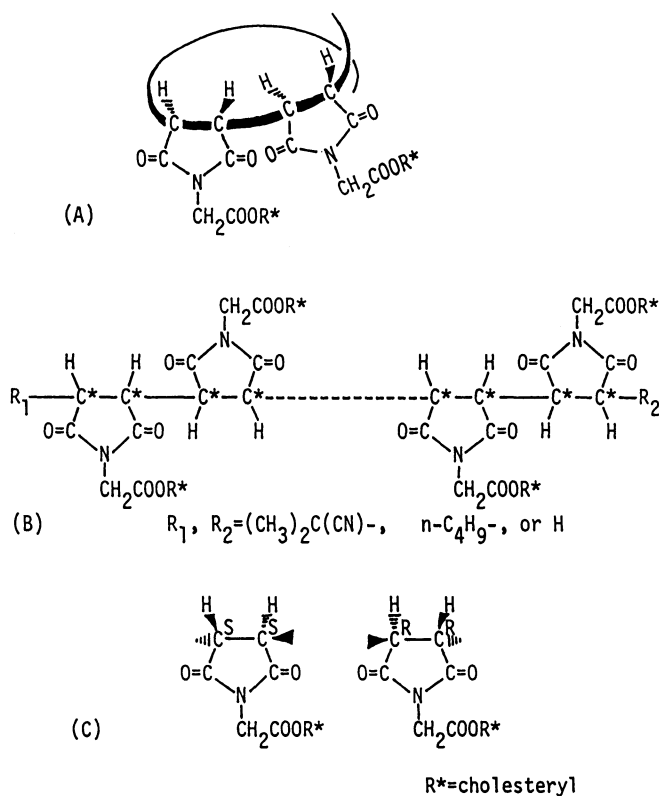
Scheme 2.

asymmetric induction around both terminal ChMI of the polymers, and (C) excess of chiral centers of (R,R) or (S,S) in the polymer main chain.

In the case of poly(ChMI)s, CD peaks of the polymers obtained with n-BuLi at about 245 nm were quite negative. The polymers obtained with AIBN also indicated weak positive CD peaks, except for the polymerization in THF. It is interesting to note that positive or negative Cotton Effects were observed around 250 nm in the CD curves for maleimide polymers containing cholesteryl moiety, as well as RMI polymers obtained with n-BuLi/(−)-Sp.[25]

Cubbon has reported[10] that eight N-substituted maleimide monomers (RMI) were polymerized by free radical and n-BuLi, and both types of initiator gave rise to polymers containing a predominantly *threo*-diisotactic

polymer. The RMI polymers may not be completely stereoregular and predominantly *threo*-diisotactic with occasional *threo*-disyndiotactic placements which disrupt crystallinity to some extent[10]. In addition, the stereospecificity of RMI polymers was due to the geometry of the monomer unit, which requires *trans* opening of the double bonds and leads to the formation of a helix.[10]

Our poly(ChMI)s obtained from radical and anionic initiators were not crystalline but amorphous, judging from both X-ray diffraction diagrams.

Solvents effects of poly(ChMI)s on CD spectra for the poly(ChMI) obtained with n-BuLi are shown in Figure 3. The CD patterns in THF, cyclohexane, and chloroform are slightly different. However, the magnitude of the molecular ellipticities $[\theta]$ at 241 nm scarcely varied even with rise or fall of temperature (3
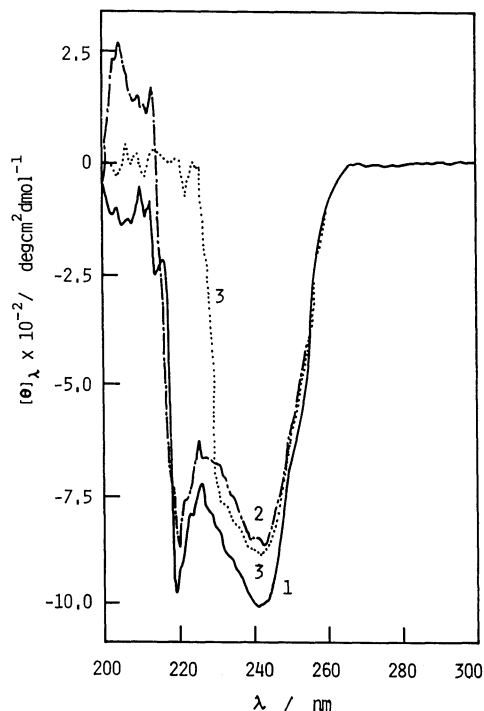
Figure 3. CD spectra for poly(ChMI)s [(run B-5); $l = 1.0$ mm, $c = 1.0$ g dl^{-1}] at 25°C in solvents: (1) cyclohexane; (2) THF; (3) chloroform.

R*=cholesteryl group

Scheme 3.

to 60°C). This tendency was also observed in the poly(ChMI) obtained with AIBN (run A-4). In addition, the relationship between the specific rotations of polymers (run A-1 and run B-5) and temperature gave linearity, and the slopes were very small [temperature coefficients $(\Delta[\alpha]_D/\Delta T) = 0.05$ to 0.14]. When specific rotation was plotted against solvent concentration ([THF]/([THF] + [ethanol])), a straight line was observed. These suggest that the main chains of poly(ChMI)s scarcely contain a helical structure. In fact, the degree of polymerization (DP = 9 to 17) of poly(ChMI) is too small to take a helix. Consequently, poly(ChMI) obtained with *n*-BuLi may take almost a linear structure as illustrated in Scheme 3.

If the chirality for the polymer obtained with *n*-BuLi and AIBN is attributed to both cholesteryl moiety and excess chiral centers of
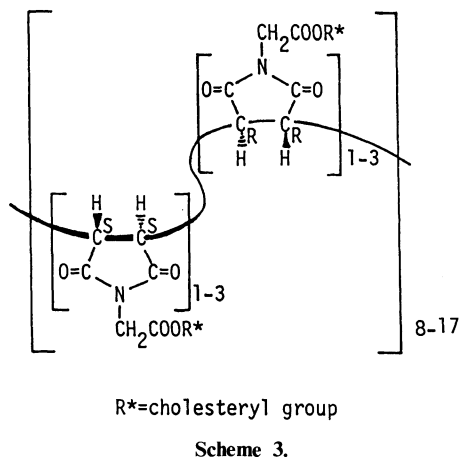
(S,S) or (R,R) [Type C in Scheme 2], no more than four successive units of (S,S) or (R,R) may exist. Because, more than a four-unit sequence of (S,S) or (R,R), *i.e.*, a continuous *threo*-diisotactic structure, would produce a helix. This can be confirmed by inspection of a poly(ChMI) model.

Asymmetric induction around both the terminal ChMI unit of the polymers [Type B in Scheme 2] may not be ignored, because the degree of polymerizations for the polymers are very small.

The ^{1}H NMR and ^{13}C NMR spectra for polymers obtained with AIBN or *n*-BuLi were slightly different. The IR for both polymers showed the same spectra. All polymers obtained showed only one GPC peak. On the basis of IR, NMR, and GPC, however, it is not possible to discuss the detailed structural differences, though the CD patterns for the poly(ChMI)s obtained with AIBN in THF was slightly different from that in other solvents, as shown in Figures 2 and 3.

Radical Copolymerizations of ChMI with ST and MMA

The results of radical copolymerizations of ChMI (M_1) with ST (M_2), MMA (M_2) in THF (6 ml) at 70°C in the presence of AIBN (1.0×10^{-2} mol l^{-1}) are summarized in Table III. Copolymerization proceeded homogene-

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Table III. Radical Copolymerizations of ChMI (M_1) with ST (M_2) or MMA (M_2) in THF (6 ml) at 70°C[a]

Run No.	M_1 in monomer mol%	Yield %	M_1 in copolymer[b] mol%	$\bar{M}_n{}^c$ $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n{}^c$	$[\alpha]_D{}^d$ deg	$[\theta]_\lambda{}^e$
C-1	20.1	26.5	45.9	23.9	1.7	-22.4	-270
C-2	40.1	30.9	46.5	19.2	1.8	-23.9	-290
C-3	50.1	33.3	48.6	14.8	1.6	-24.1	-300
C-4	60.7	33.5	53.6	10.1	1.5	-24.2	-410
C-5	80.2	20.6	60.1	7.2	1.5	-26.1	-630
D-1	20.4	15.8	15.5	9.3	1.9	-14.1	—
D-2	39.8	29.5	28.8	4.6	1.3	-20.0	—
D-3	50.1	27.8	35.6	4.1	1.5	-22.1	—
D-4	61.2	28.8	45.6	4.7	1.7	-24.8	—
D-5	79.6	19.9	56.1	5.5	1.8	-27.3	—

[a] $[AIBN] = 1.0 \times 10^{-2}$ mol l^{-1}; $M_1 + M_2 = 1.0$ g; ChMI–ST, C-1—C-5; ChMI–MMA, run D-1—D-5; polymerization time, 10 h.
[b] Calculated from ^{1}H NMR spectra.
[c] Estimated by GPC.
[d] $c = 1.0$ g dl^{-1}; $l = 10$ cm; THF.
[e] deg cm^2 dmol^{-1}; $c = 1.0$ g dl^{-1}; $l = 0.1$ cm; THF; $\lambda = 220 \pm 4$ nm.
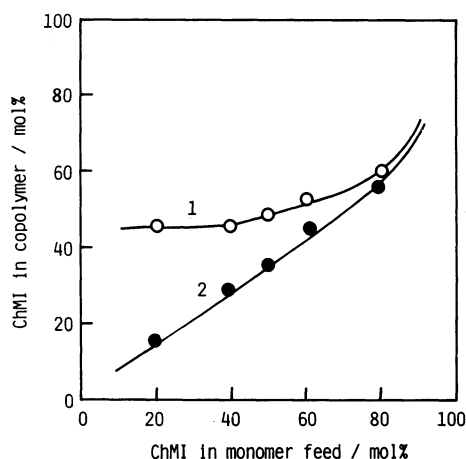

Figure 4. Copolymer composition curves for (1) the ChMI–ST and ChMI–MMA system.

ously throughout. The obtained copolymers were white powders and optically active. Copolymer–composition curves of the ChMI–ST and ChMI–MMA systems are shown in Figure 4. Monomer reactivity ratios, r_1 and r_2 determined by both the Integration Method by Mayo and Lewis[30] and High Conversion

Method reported by Kelen–Tüdos and co-workers,[31] and Alfrey Price[32] Q, e values were as follows: $r_1 = 0.090$, $r_2 = 0.082$, $Q_1 = 2.07$, $e_1 = 1.42$ in the ChMI–ST system and $r_1 = 0.13$, $r_2 = 1.22$, $Q_1 = 1.04$, $e_1 = 1.76$ in the ChMI–MMA system. These copolymerization parameters were similar to those for other RMI copolymers reported previously.[33]

Optical Behavior of the Copolymers

Figure 5 shows the relation between the specific rotation and content (wt%) of the monomeric unit of ChMI in both copolymer systems. The absolute values of specific rotations of a mixture of poly(ChMI) and poly(ST) gave a good linear relationship, as shown in Figure 5 ($\square$). The absolute values of specific rotations of poly(ChMI-co-ST)s increased with content (wt%) of ChMI unit. However, a little deviation from the linearity was observed, which suggests that asymmetric induction occurred in the main chain of the copolymers. In poly(ChMI-co-MMA)s, the same tendency was observed.
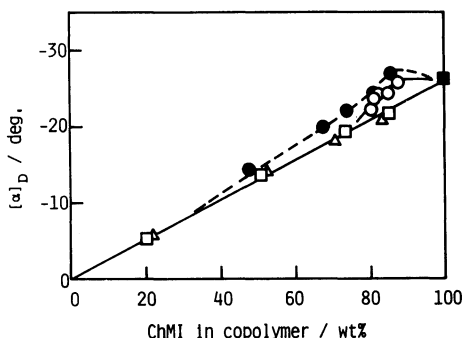
Figure 5. Relationships between specific rotation $[\alpha]_D$ and content of the monomeric unit of ChMI in copolymers: (○) poly(ChMI-*co*-ST)s; (●) poly(ChMI-*co*-MMA)s; (■) poly(ChMI) obtained with AIBN [run A-1]; (□) a mixture of poly(ChMI) and poly(ST); (△) a mixture of poly(ChMI) and poly(MMA).
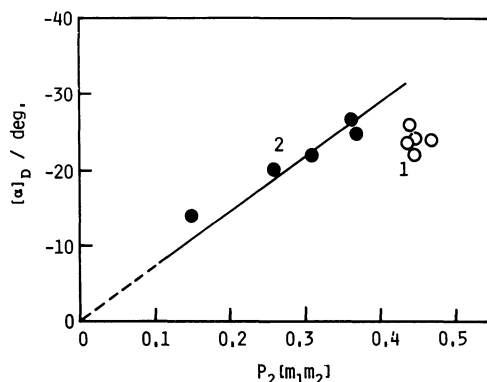

Figure 7. Relationships between specific rotation $[\alpha]_D$ of the copolymer and $P_2[m_1m_2]$: (1) poly(ChMI-*co*-ST)s and (2) poly(ChMI-*co*-MMA)s.
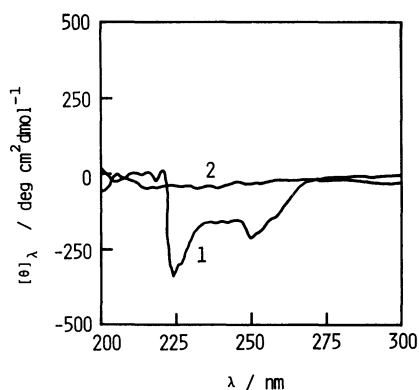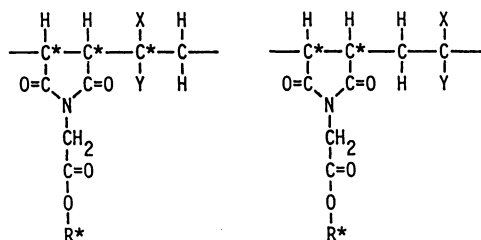

Figure 6. CD spectra for (1) poly(ChMI-*co*-ST) [run C-3] and (2) poly(ChMI-*co*-MMA) [run D-3].

ST (X=H, Y=phenyl); MMA (X=CH$_3$, Y=COOCH$_3$);

R*= cholesteryl group; C*=chiral carbon

Scheme 4.

In the CD spectra for poly(ChMI-*co*-ST)s, as shown in Figure 6, negative and positive peaks around 250 and 225 nm were ascribed to the $\pi \rightarrow \pi^*$ transition of phenyl groups of ST unit and to the $n \rightarrow \pi^*$ transition of carbonyl groups of ChMI unit, respectively. In the CD spectra for poly(ChMI-*co*-MMA)s, a broad and small, negative peak was observed, based on the $n \rightarrow \pi^*$ transition of carbonyl groups of MMA and ChMI units, as shown in Figure 6.

In both the ChMI–ST and ChMI–MMA systems, the relationship between the specific rotations of the copolymers and temperature gave linearity, and the slopes were very small [temperature coefficients $(\varDelta[\alpha]_D/\varDelta T) =$ 0.06 to 0.11]. When the specific rotation was plotted against solvent concentration ([THF]/ ([THF]+[ethanol])), a straight line was observed. Accordingly, it seems that there is no helical conformation in the copolymers.

Figure 7 shows the dependence of a diad sequence,[34,35] $P_2[m_1m_2]$, on specific rotations of the copolymers. The $P_2[m_1m_2]$ values indicate the probability of a ChMI–ST or a ChMI–MMA diad sequence. In the ChMI–ST system, linear relation was not clear because of the alternating copolymer. But in the ChMI–MMA system, a linear relation was clearly observed. This suggests that the new asymmetric center appeared in the copolymer main chain by the addition of a ST or a MMA

monomer to a growing chain end of ChMI, as shown in Scheme 4 (C^* is a chiral carbon).

From polarization microscope measurements, it was found that the ChMI monomer indicated a cholesteric phase from 188° to 192°C. But neither the polymers nor copolymers showed a liquid crystalline phase. Details on these will be reported in the near future, as well as for N-(cholesteroxycarbonylpentyl)- and N-(cholesteroxycarbonylundecyl)-maleimides.

CONCLUSIONS

(1)   A novel type of optically active N-(cholesteroxycarbonylmethyl)maleimide (ChMI) was synthesized and polymerized with radical and anionic initiator to obtain chiral polymers.

(2)   The conformation of the ChMI polymer obtained with an anionic initiator was different from that of the polymer obtained with a radical initiator, judged from the CD spectra.

(3)   From the results of radical copolymerizations of ChMI(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: $r_1 = 0.090$, $r_2 = 0.082$, $Q_1 = 2.07$, $e_1 = 1.42$ in the ChMI–ST system, $r_1 = 0.13$, $r_2 = 1.22$, $Q_1 = 1.04$, $e_1 = 1.76$ in the ChMI–MMA system.

(4)   Asymmetric induction copolymerization took place in the ChMI–ST and ChMI–MMA systems.

REFERENCES

1. N. Kusabayashi and S. Takenaka, *Yukigouseikyoukaishi*, **42**, 2 (1984); T. Gunjima, *ibid.*, **42**, 13 (1984); S. Iwayanagi, "Ekisyou," Kyouritsu Syuppan, Tokyo, 1986.
2. Y. S. Freidzon, Y. G. Tropsha, V. P. Shibaev, and N. A. Plate, *Makromol. Chem., Rapid Commun.*, **6**, 625 (1985).
3. T. Yamaguchi, T. Hayashi, and N. Nakamura, *Mol. Cryst. Liq. Cryst.*, **5**, 23 (1987).
4. G. M. Janini, R. J. Laub, and T. J. Shaw, *Makromol. Chem., Rapid Commun.*, **6**, 57 (1985).
5. M. L. Tsai and S. H. Chen, *Macromolecules*, **23**, 1908 (1990).
6. Y. S. Freidzon, N. I. Boiko, V. P. Shibaev, and N. A. Plate, *Eur. Polym. J.*, **22**, 13 (1986).
7. H. Finkelmann, H. Ringsdorf, W. Siol, and H. Wendorff, *Makromol. Chem.*, **179**, 829 (1978).
8. J. Pinsl, C. Brauchle, and F. H. Kreuzer, *J. Mol. Electron*, **3**, 9 (1987).
9. K. Tanaka, O. Kakinoki, and F. Toda, Nippon Kagakukai 61 Syukinennkai Kouen Yokousyu, II (1991), p 2005.
10. R. C. P. Cubbon, *Polymer*, **6**, 419 (1966).
11. T. Oishi and T. Kimura, *Kobunshi Ronbunshu*, **32**, 380 (1975); *ibid.*, **33**, 141 (1976); *ibid.*, **33**, 685 (1976).
12. M. Yamada, I. Takase, and T. Mishima, *Kobunshi*, **26**, 393, (1969); M. Yamada, I. Takase, T. Tsukano, and Y. Ueda, *Kobunshi*, **26**, 401 (1969).
13. A. Matsumoto, T. Kubota, and T. Otsu, *Macromolecules*, **23**, 4508 (1990).
14. T. Otsu, A. Matsumoto, T. Kubota, and S. Mori, *Polym. Bull.*, **23**, 43 (1990).
15. A. Matsumoto, T. Kubota, and T. Otsu, *Polym. Bull.*, **24**, 459 (1990).
16. T. Otsu, A. Matsumoto, and A. Tatsumi, *Polym. Bull.*, **24**, 467 (1990).
17. A. Matsumoto, Y. Oki, and T. Otsu, *Makromol. Chem. Rapid Commun.*, **11**, 507 (1990).
18. A. Matsumoto, Y. Oki, and T. Otsu, *Polym. J.*, **23**, 201 (1991).
19. For example: H. Kawakami, A. Kobayashi, and T. Saitoh, Jpn Kokai Tokkyo Koho, Japanese Patent 02-29405 (1990); S. Tsunoda, T. Yamada, Y. Haruta, and T. Oishi, Jpn. Kokai Tokkyo Koho, Japanese Patent 62-109811 (1987); Y. Koinuma, K. Doinai, and K. Kato, Jpn. Kokai Tokkyo Koho, Japanese Patent 02-158653 (1990).
20. H. Yamaguchi and Y. Minoura, *J. Polym. Sci., A–1*, **8**, 929, (1970).
21. H. Yamaguchi and Y. Minoura, *J. Polym. Sci., A–1*, **8**, 1467 (1970).
22. T. Oishi and M. Fujimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2789 (1984).
23. T. Oishi, A. Kamori, and M. Fujimoto, *J. Macromol. Sci.*, in press.
24. M. Farina, "The Stereochemistry of Linear Macromolecules," Topics in Stereochemistry, Vol. 17, E. L. Eliel and S. H. Wilen, Ed., John Wiley & Sons, Inc., New York, 1987.
25. T. Oishi, H. Yamasaki, and M. Fujimoto, *Polym. J.*, **23**, 795 (1991).
26. Y. Okamoto, T. Nakano, H. Kobayashi, and K. Hatada, *Polym. Bull. (Berlin)*, **25**, 5 (1991).
27. D. H. Rich and P. D. Gesellchen, *J. Med. Chem.*, **18**,

1004 (1975).

28. T. Oishi, Y. Morioka, and M. Fujimoto, *Polym. J.*, **21**, 287 (1989).

29. T. Oishi and M. Fujimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 2727 (1982).

30. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.*, **66**, 1594 (1944).

31. F. Tudos, T. Kelen, T. Foldes-Berezsnich, and B. Turcsanyi, *J. Macromol. Sci-Chem.*, **A10**, 1513 (1976).

32. T. Alfrey Jr. and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).

33. L. J. Young, "Tabulation of *Q–e* Values," in "Polymer Handbook," J. Brandrup and E. H. Immergut, Ed., Wiley, New York, 1975, p II—387.

34. H. J. Harwood and W. M. Ritchey, *J. Polym. Sci., Polym. Lett. Ed.*, **2**, 601 (1964).

35. M. Kurokawa, H. Yamaguchi, and Y. Minoura, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 2241 (1979).