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

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A new type of optically active *N*-[4-(cholesteroxy-carbonyl)phenyl]itaconimide (ChPII) was synthesized from itaconic anhydride, aminobenzoic acid and cholesterol. Radical homopolymerizations of ChPII were performed in several solvents at 60°C to give optically active polymers having $[\alpha]_D = 1.7$ to $[\alpha]_D = -6.2°$. Anionic homopolymerizations of ChPII were also carried out. Radical copolymerizations of ChPII(M_1) were performed with styrene (ST, M_2), and methyl methacrylate (MMA, M_2) in toluene at 60°C. From the results, the monomer reactivity ratios (r_1, r_2) and the Alfrey–Price Q, e values were determined as follows: $r_1 = 0.26$, $r_2 = 0.10$, $Q_1 = 2.17$, $e_1 = 1.11$ for the ChPII-ST system; $r_1 = 0.187$, $r_2 = 0.37$, $Q_1 = 2.55$, $e_1 = 1.01$ for the ChPII-MMA system. ChPII polymer and copolymers were still optically active after hydrolysis, which suggests that asymmetric induction into the polymer main chain took place. Chiroptical properties of the polymers and copolymers were investigated. Copyright © 1996 Elsevier Science Ltd.

(Keywords: *N*-[4-(cholesteroxycarbonyl)phenyl]maleimide; optically active polymer; monomer reactivity ratio)

INTRODUCTION

Polymerization reactivities of *N*-substituted maleimide (RMI) containing a cholesteryl group were investigated, and chiroptical properties of polymers and copolymers obtained[1–3]. It was found that asymmetric induction into the polymer main chain and asymmetric perturbation by the side chain chromophore took place in the polymerizations and copolymerizations. RMI is a 1,2-disubstituted cyclic ethylene type monomer, and thus has characteristic polymerization reactivity. That is, RMI can yield two *trans*-openings of the double bond to produce stereogenicity (*S*,*S*) and (*R*,*R*)[4]. Chiroptical properties of RMI polymer and copolymer could be attributed to a threo-diisotactic structure; arising from a helical structure and/or from the excess of chiral stereogenic centres (*S*,*S*), or (*R*,*R*). From this point of view, many optically active RMIs have been investigated recently[5–11].

There is a small number of reports on the polymerizabilities and chiroptical properties of itaconic acid derivatives containing a chiral group[12–14]. Monomenthyl itaconate[12], dimenthyl itaconate[13], and *N*-[4-(α-methylbenzylaminocarbonyl)phenyl]itaconimide (MBPI)[14] have been synthesized and polymerized. However, there are no reports on polymerizabilities of itaconimide (RII) containing a cholesteryl group and chiroptical properties for resulting polymers and copolymers. RII is a 1,1-disubstituted ethylene type monomer. Accordingly, it can be expected that RII has different polymerizability and chiroptical properties from those of RMI polymers.

Synthesis and characterization of the polymers and copolymers from itaconic acid derivatives; itaconic ester[15], itaconamic ester[16], and itaconimide[17] have been investigated by many workers. There have been many reports on polymers and copolymers containing cholesteryl groups[18–24]. However, these all relate to liquid crystalline polymers.

In this article, a novel, optically active *N*-[4-(cholesteroxycarbonyl)-phenyl]itaconimide (ChPII) was synthesized from itaconic anhydride, *p*-aminobenzoic acid and cholesterol. Radical and anionic polymerizations of ChPII were performed to obtain chiral polymers. Chiroptical properties of both polymers were discussed. ChPII was copolymerized with styrene (ST) and methyl methacrylate (MMA) in the presence of radical initiator. From the results, monomer reactivity ratios and Q,e values were determined. Asymmetric induction into the copolymer main chain and asymmetric perturbation of the side chain chromophore were discussed based on specific rotations and molecular ellipticities measurements of polymers and copolymers.

EXPERIMENTAL

ChPII monomer

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

N-*(4-Carboxyphenyl)itaconamic acid* (p-*CPIA*)[25]. *p*-CPIA was synthesized from itaconic anhydride (IAn)

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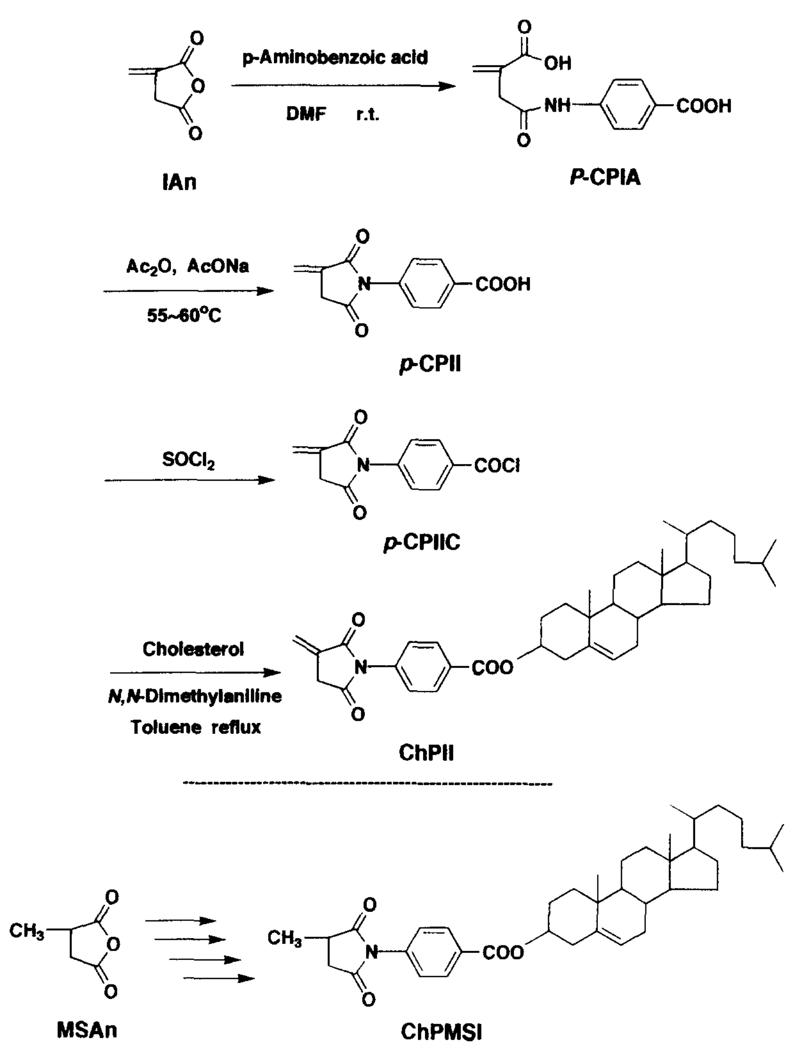


Scheme 1

and *p*-aminobenzoic acid (ABA) in *N*,*N*-dimethylformamide (DMF) at room temperature; yield 86.8%; mp 233–235°C.

N-*(4-Carboxyphenyl)itaconimide (*p-*CPII)*[25]. *p*-CPII was prepared by dehydration of *p*-CPIA in the presence of sodium acetate in acetic anhydride at 55–60°C; yield 85%; mp 244°C.

N-*[4-(Chlorocarbonyl)phenyl]itaconimide (*p-*CPIIC)*[25]. *p*-CPII was treated with thionyl chloride to obtain crude *p*-CPIIC, which was recrystallized from benzene: yield 68.5%; mp 196–197°C.

N-*[4-(Cholesteroxycarbonyl)phenyl]itaconimide (ChPII)*. A mixture of *p*-CPIIC (10.0 g, 40 mmol), *N*,*N*-dimethylaniline (5.8 g, 48 mmol), cholesterol (18.6 g, 48 mmol), and a small amount of hydroquinone in 700 ml of toluene was refluxed for 19 h. All of the reaction was performed under nitrogen atmosphere. After the reaction was completed, the reaction mixture was cooled to room temperature and filtered. The filtrate was washed with aqueous dilute hydrochloric acid, water, aqueous dilute sodium bicarbonate, and then dried with anhydrous magnesium sulfate. Then the solution was evaporated completely, the residue was washed once with a small amount of acetone. The product was dissolved in a small amount of THF, and the solution was poured into a large amount of ethanol to obtain a white precipitate. The crude ChPII was purified by reprecipitation from the THF solution to a large amount of ethanol. The reprecipitation was repeated three times to obtain pure ChPII: yield 24.2%, colourless powder, mp 160°C (decomposed); $[\alpha]_D = 4.9°$ ($c = 1.0\,g\,dl^{-1}$; $l = 10\,cm$; THF). I.r. (KBr disc, cm^{-1}); 2900 (CH, CH_2, CH_3, 1710 (C=O), 1650 (C=C), 1265 (OC=O); ^1H-n.m.r. (ppm from TMS in $CDCl_3$): 8.14 (d, $J = 8.58$ Hz, 2H in phenyl), 7.77 (d, $J = 8.25$ Hz, 1H in phenyl), 6.50 (s, 1*H*, C=CH_2), 5.78 (s, 1H, C=CH), 5.43 (d, $J = 4.29$ Hz, 1H, C=CH- in cholesteryl), 4.85 (m, 1H, O-CH- in cholesteryl), 3.53 (s, 2H, C=C-CH_2-), 2.47–0.69 (m, 43H, other protons of cholesteryl group); ^{13}C-n.m.r. (δ, ppm from TMS in $CDCl_3$); 172.33 and 168.01 (-CO- N-CO), 165.05 (OC=O), 139.53 and 122.88 (C=C in cholesteryl), 135.60, 130.75, 130.37 and 126.02 (in phenyl), 132.65 and 122.26 (C=C in itaconimide), 74.90–11.84 (26C, other carbons of cholesteryl group and itaconimide).

Elemental analysis: found (%): C = 77.64, H = 8.89, N = 2.31.

Calculated for $C_{39}H_{53}O_4N$ (%): C = 78.09, H = 8.86, N = 2.33.

Table 1 Radical and anionic polymerizations of ChPII

Run	ChPII ($mol\,l^{-1}$)	Initiator ($\times 10^{-2}\,mol\,l^{-1}$)	Polymer solvent[a] (ml)	Polymer temp. (°C)	Polymer time (h)	Convn. (%)	$\bar{M}_n$[b] $\times 10^{-3}$	$\bar{M}_w/\bar{M}_n$[b]	$[\alpha]_D^{25}$[c] (deg)
A-1	0.17	AIBN(2.0)	BEN(5)	60	24	66.5	37.5	3.4	−6.2
A-2[d]	0.21	AIBN(2.0)	DOX(4)	60	26	66.3	2.4	3.0	−4.7
A-3	0.21	AIBN(2.0)	THF(4)	60	26	73.8	5.2	4.7	−2.3
A-4	0.17	AIBN(2.0)	TOL(5)	60	26	76.1	6.6 (2.6)		−5.2
B-1	0.17	nBuLi(0.34)	THF(5)	0	24	trace			
B-2	0.17	nBuLi(0.83)	THF(5)	0	24	52.1	6.3	4.0	1.7
B-3	0.042	nBuLi(0.21)	TOL(20)	0	24	trace			
B-4	0.042	nBuLi(0.42)	TOL(20)	0	24	37.4	4.0	2.3	3.9

[a] BEN, benzene; THF, tetrahydrofuran; TOL, toluene; DOX, dioxane
[b] By g.p.c.
[c] $c = 1.0\,g\,dl^{-1}$, THF, $l = 10\,cm$
[d] Heterogeneous system

A model compound of poly(ChPII): N-*[4-(cholesteroxycarbonyl)phenyl]succinimide(ChPMSI)*

ChPMSI was prepared from (R,S)-α-methylsuccinic anhydride, *p*-aminobenzoic acid, and cholesterol, according to a similar method to that of ChPII. Yields and melting points of precursors are as follows: *N*-(4-carboxyphenyl)-(R,S)-α-methylsuccinamic acid (CPMSA)[25]: yield 85%; mp 214–216°C, *N*-(4-carboxyphenyl)-(R,S)-α-methylsuccinimide (CPMSI)[22]: yield 48.2%; mp 212–213°C, *N*-(4-chlorocarbonylphenyl)-(R,S)-α-methylsuccinimide (CPMSIC)[25] recrystallized from benzene: yield 74.7%, mp 132–133°C.

ChPMSI: total yield 22.7%; mp 219°C; white powder, $[\alpha]_D = 2.2°$ ($c = 1.0\,g\,dl^{-1}$; $l = 10\,cm$; THF). i.r. (KBr disc, cm^{-1}), 2900 (CH, CH_2, CH_3), 1700 (C=O), 1265 (OC=O); ^{1}H-n.m.r. (δ, ppm from TMS in $CDCl_3$); 8.15 (d, $J = 8.57\,Hz$, 2H in phenyl), 7.41 (d, $J = 8.58\,Hz$, 2H in phenyl), 5.42 (d, $J = 4.29\,Hz$, 1H, C=CH- in cholesteryl), 4.90–4.82 (m, 1H, O-CH- in cholesteryl), 3.17–3.01 (m, 2H, CH_2-CO), 2.56–2.45 (m, 2H, N-C-CH_3), 2.04–0.69 (m, 43H, other protons of cholesteryl group): ^{13}C n.m.r; (δ, ppm from TMS in $CDCl_3$); 179.03 and 174.90 (-CO-N-CO-), 165.05 (OC=O), 139.53 and 122.86 (C=C in cholesteryl), 135.76, 130.66, 130.35 and 126.04 (phenyl), 74.90–11.84 (28C, other carbons of the cholesteryl group and itaconimide).

Elemental analysis: found (%): C = 76.75, H = 9.26, N = 2.11.

Calculated for $C_{39}H_{55}O_4N$ (%): C = 77.83, H = 9.21, N = 2.33.

Other materials

ST, MMA, THF, toluene (TOL) and other solvents were purified by the usual methods[26,27]. 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. The concentration of *n*-BuLi was determined by titration.

Homopolymerization and copolymerization

Radical homopolymerizations were performed with AIBN as an initiator in THF, benzene (BEN), TOL, or dioxane (DOX) in a sealed tube at 60°C. After polymerization, the polymer solution was poured into a large amount of acetone to precipitate the polymer. The polymer obtained 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 ChPII with ST or MMA were performed in THF at 60°C, according to a similar procedure for the homopolymerizations. Composition of the copolymer obtained was calculated by ^{1}H n.m.r. spectra and elemental analysis.

Anionic homopolymerizations were achieved in toluene or THF at 0°C with *n*-BuLi as a catalyst using a Schlenk's tube under 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 THF 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) (0.05–0.10 g) in THF (20 ml) and methanol (20 ml) with potassium hydroxide was refluxed for 48 h. After the reaction, the solvents in the mixture were completely evaporated out, and 40 ml of water was added to the residue. The mixture was filtered, and 6 N hydrochloric acid was added to the filtrate to give a pH value of 7. The solution was evaporated out, methanol was added to the residue, and the mixture was stirred at room temperature for about 1 h, and then filtered. After the filtrate was evaporated out, a small amount of methanol was added to the residue, and the mixture was filtered. This method was repeated twice, and then the filtrate was concentrated to give hydrolysed polymers. The resultant product was reprecipitated twice from the THF solution into a large amount of ether, and then filtered and dried. The hydrolysed polymers were identified by their n.m.r. spectra.

Measurements

D-line specific rotations were measured with a Jasco DIP-140 (Japan Spectroscopic Co.) at 25°C, using a

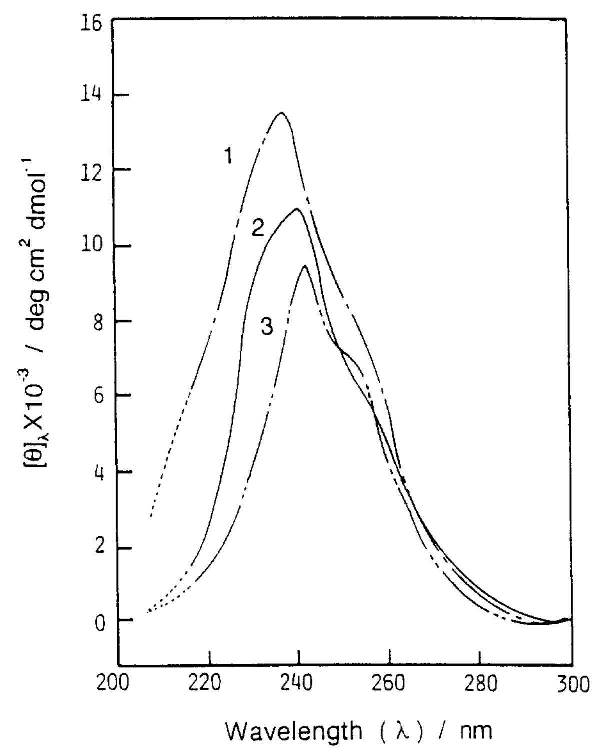


Figure 1 C.d. spectra for (1) poly(ChPII) obtained with AIBN in toluene (run A-4), (2) poly(ChPII) obtained with *n*-BuLi in THF (run B-2) and (3) ChPMSI (model compound for poly(ChPII))

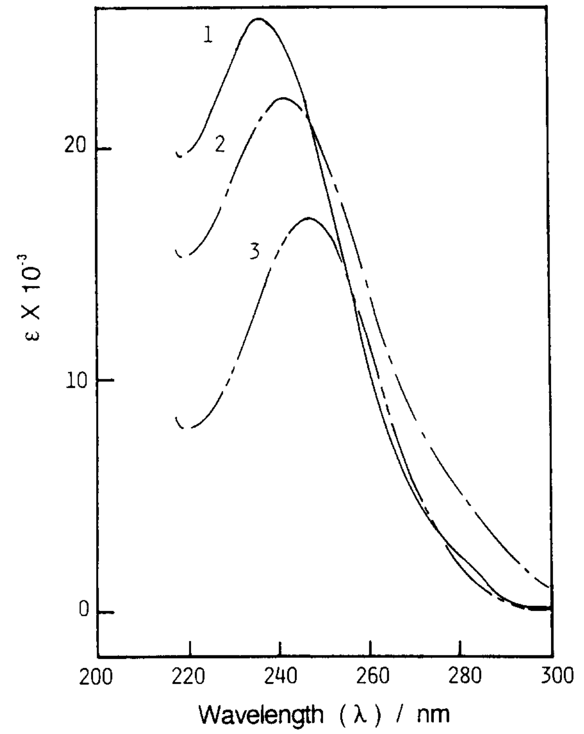


Figure 2 U.v. spectra for (1) poly(ChPII) obtained with AIBN in toluene (run A-4), (2) poly(ChPII) obtained with *n*-BuLi in THF (run B-2) and (3) ChPMSI (model compound for poly(ChPII))

quartz cell (5 and 10 cm) and ca. 1.0 g dl^{-1} of sample concentration. 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, using a quartz cell (0.1 and 1.0 mm) and ca. 0.5–1.0 g dl^{-1} of sample concentration. U.v. spectra were obtained with a Shimadzu UV 200A spectrophotometer, using a quartz cell (1 mm) and ca. $1.2 \times 10^{-2} - 4.0 \times 10^{-2}$ g dl^{-1} of sample concentration. Molecular weights of polymers were measured by gel permeation chromatographic (g.p.c.) analysis, using the same technique as described in an earlier paper[10]. I.r. and n.m.r. spectra were obtained and elemental analysis was carried out, using the same instruments as reported previously[10].

RESULTS AND DISCUSSION

Radical and anionic homopolymerization of ChPII

Radical and anionic polymerizations of ChPII were performed under several conditions. The results are summarized in *Table 1*.

The radical polymerizations proceeded homogeneously throughout, except for the polymerization in DOX. In the polymerization in DOX, part of the polymer produced was insoluble in DOX, and precipitated. The obtained polymers were white powders and had negative optical activities. The number-average molecular weights ($\overline{M_n}$) of poly(ChPII) obtained with the radical initiator were $3.8 \times 10^4 - 2.4 \times 10^3$, and were extremely affected by the solvent. In the radical polymerizations polydispersity ($\overline{M_w}/\overline{M_n}$) for polymers was 3.0–4.7 and relatively large. Especially, using toluene as a solvent, g.p.c. curves exhibited two peaks around 6.6×10^3 and 2.6×10^3. The reason for large polydispersity is due to chain transfer reactions by two allyl protons in ChPII. As compared with $\overline{M_n}$ for poly(ChPMI)[2], $\overline{M_n}$ for ChPII was lower.

All the anionic polymerizations proceeded homogeneously throughout. When the concentration of *n*-BuLi was low, the yield for polymer was trace. In the high concentration the polymers were obtained. The $\overline{M_n}$ and polydispersity ($\overline{M_n}/\overline{M_n}$) were $6.3 \times 10^3 - 4.0 \times 10^3$ and 4.0–2.3, respectively, and were similar to those for the polymers obtained with AIBN. The $[\alpha]_D$ was +1.7 to +3.9° and had a different sign from those ($[\alpha]_D = -2.3$ to $-6.2°$) for polymers obtained with AIBN. $[\alpha]_D$ of a model compound for poly(ChPII), i.e., *N*-[4-(cholesteroxycarbonyl)-phenyl]succinimide [ChPMSI] was +2.2°. Thus the polymer obtained with *n*-BuLi has a structure of conformation and configuration similar to that for the model compound.

The c.d. and u.v. spectra for poly(ChPII) obtained with AIBN and *n*-BuLi, and the model compound for poly(ChPII) [ChPMSI] are shown in *Figures 1* and *2*. In all c.d. spectra, one large positive peak, which is ascribed to the $n-\pi^*$ transition of carbonyl group and the $\pi-\pi^*$ transition of phenyl group, was observed around 240 nm. Three c.d. patterns were slightly different. In addition, molecular ellipticities for both poly(ChPII) were greater than for the polymer model compound (ChPMSI). It can be considered that the model compound (ChPMSI) has no asymmetric induction and asymmetric perturbation of side chain chromophore. Since two c.d. patterns for poly(ChPII) were different from that for ChPMSI, asymmetric induction and asymmetric perturbation of side chain chromophore took place in poly(ChPII), as described later.

There were no olefinic protons in ^{1}H-n.m.r. spectra for both ChPII polymers obtained with AIBN and *n*-BuLi, which suggests that ordinary vinyl polymerization took

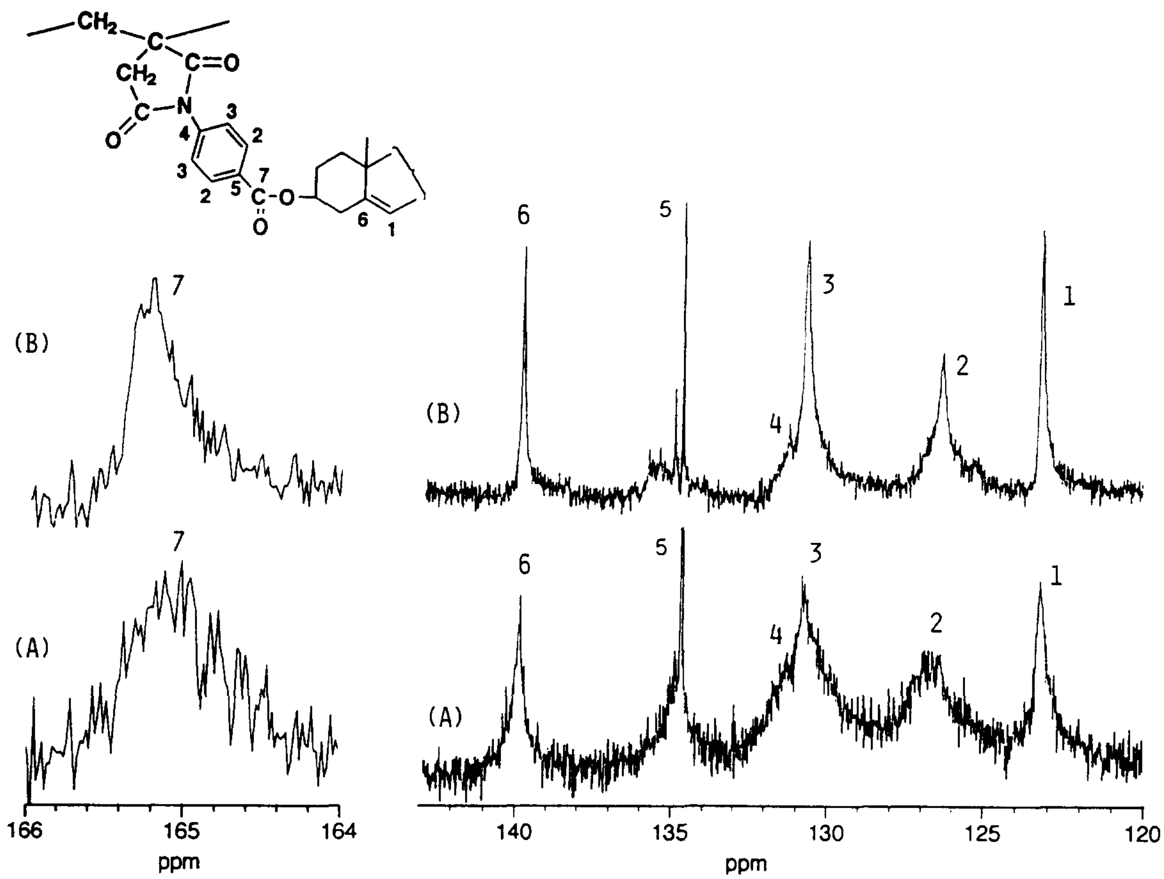


Figure 3 ^{13}C n.m.r. spectra for (A) poly(ChPII) obtained with AIBN and (B) poly(ChPII) obtained with *n*-BuLi

place. However, there was a little difference in ^{13}C n.m.r. spectra of both polymers around 165 ppm and 140 to 120 ppm.

Figure 3 shows expanded ^{13}C n.m.r. spectra for poly(ChPII)s obtained with AIBN and *n*-BuLi. As can be seen from *Figure 3*, signals for the polymer obtained with AIBN were generally broader than those with AIBN. This suggests that both poly(ChPII) have different structures, i.e. different conformations and/or configurations of cholesteryl and phenyl groups. Since signals for the polymer obtained with *n*-BuLi were sharper, the structure of the polymer was more stereoregularly controlled. But detailed structures for both poly(ChPII) have not yet been obtained.

Radical copolymerizations of ChPII with ST and MMA

The results of radical copolymerizations of ChPII (M_1) with ST (M_2) and MMA (M_2) in THF (5 ml) at

Table 2 Radical copolymerization of ChPII(M_1) with ST and MMA in THF (5 ml) at 60°C[a]

Run	M_2	M_1 in monomer (mol%)	Polymer time (h)	Convn. (%)	M_1 in copolymer (mol%)	$\bar{M}_n$[b] $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$[b]	$[\alpha]_D^{25}$[c] (deg)
C-1	ST	9.9	1	15.1	35.0	2.5	1.7	2.4
C-2	ST	19.7	1	30.4	41.3	3.0	2.9	1.1
C-3	ST	38.3	1	41.2	46.9	3.5	3.4	−2.7
C-4	ST	46.9	1	43.2	53.5	3.9	3.6	−1.5
C-5	ST	65.4	1	39.8	56.0	3.4	3.6	−2.1
C-6	ST	78.6	1	34.2	71.1	2.5	3.2	−3.0
D-1	MMA	10.1	1	17.2	21.1	1.5	3.4	3.3
D-2	MMA	20.0	1	23.2	34.0	1.6	2.1	2.9
D-3	MMA	40.9	1	33.8	57.8	1.9	6.0	0.3
D-4	MMA	49.3	0.6	46.5	64.0	2.0	3.5	−0.4
D-5	MMA	66.6	0.6	20.3	80.3	2.6	3.4	−2.5
D-6	MMA	76.1	0.6	33.6	84.7	1.3	4.4	−3.1

[a] $[AIBN] = 2.0 \times 10^{-2}$ M
[b] By g.p.c.
[c] $c = 1.0\,g\,dl^{-1}$, THF, $l = 5$ cm

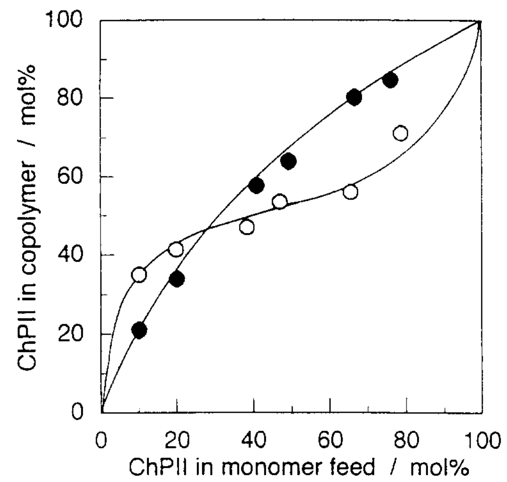


Figure 4 Copolymer–composition curves for (○) poly(ChPII-*co*-ST) and (●) poly(ChPII-*co*-MMA)

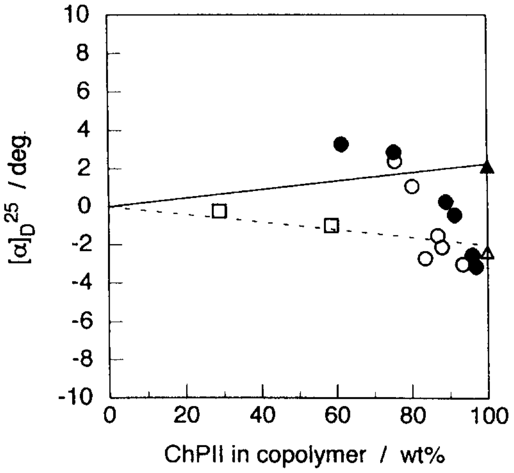


Figure 5 Relationships between specific rotation $[\alpha]_D^{25}$ and content (wt%) of the monomeric unit of ChPII in copolymers: ○, poly(ChPII-*co*-ST)s; ●, poly(ChPII-*co*-MMA)s; △, poly(ChPII), obtained with AIBN (run A-3); □, a mixture of poly(ChPII) and poly(ST); ▲, ChPMSI (model compound of poly(ChPII))

60°C in the presence of AIBN (2.0×10^{-2} mol l^{-1}) are summarized in *Table 2*. Copolymerization proceeded homogeneously throughout. The copolymers obtained were white powders and optically active. The $\overline{M}_n$ of poly(ChPII-*co*-ST)s and poly(ChPII-*co*-MMA)s were 2.5×10^4–3.9×10^4 and 1.3×10^4–2.6×10^4, respectively. These were similar to those for ChPMI copolymers[2], but much higher than those for MBPI copolymers having an amide group in the MBPI monomer unit[10].

Copolymer–composition curves of the ChPII-ST and ChPII-MMA systems are shown in *Figure 4*. Monomer reactivity ratios, r_1, r_2, determined by the high conversion[28] and Alfrey–Price[29] Q,e values were as follows: $r_1 = 0.26$, $r_2 = 0.10$, $Q_1 = 2.17$, $e_1 = 1.11$ for the ChPII-ST system; $r_1 = 1.87$, $r_2 = 0.37$, $Q_1 = 2.55$, $e_1 = 1.01$ for the ChPII-MMA system. In the ST system, the tendency of alternating copolymerization was observed and reactivity of ChPII was higher than that of MMA. These copolymerization parameters were similar to those for other RII copolymers reported previously[30].

Optical behaviour of the copolymers

Figure 5 shows the relationship between specific rotation $[\alpha]_D$ and content (wt%) of the monomeric unit of ChPII in both copolymer systems. Generally, the specific rotations $[\alpha]_D$ of a mixture of poly(ChPII) and poly(ST) exist on a straight line connecting 0 and specific rotation $[\alpha]_D$ for poly(ChPII) (on a dotted line in ChPII). This linear relationship suggests that chirality of the copolymer is strongly affected by monomer successive units. Accordingly, a deviation from this linearity indicates that chirality for copolymer is strongly influenced by comonomer units. As a rule, the homopolymer model compound has neither asymmetric induction nor asymmetric perturbation of the side chain chromophore. Accordingly, a straight line connecting 0 and $[\alpha]_D$ for the model compound suggests that there is neither asymmetric induction nor asymmetric perturbation.

In this ChPII, $[\alpha]_D$ for poly(ChPII) was different from that for ChPMSI. This indicates that asymmetric induction and asymmetric perturbation took place into the main chain of poly(ChPII). The absolute values for $[\alpha]_D$ of poly(ChPII-*co*-ST)s decreased with the content (wt%) of ChPII unit. However, a great deviation from linearity was observed. This suggests that asymmetric induction and asymmetric perturbation of side chain chromophore occurred in the main chain of the copolymers and that chirality of the copolymer was significantly influenced by the comonomer unit (ST). In poly(ChPII-*co*-MMA)s, the same tendency could be observed, as shown in *Figure 5*.

The c.d. and u.v. spectra for poly(ChPII-*co*-ST)s and poly(ChPII-*co*-MMA) are shown in *Figures 6* and *7*. In the c.d. spectra, a positive peak at about 245 nm was

Table 3 Optical behaviour of poly(ChPII) and poly(ChPII-*co*-ST,MMA)

	Original copolymers			Hydrolysed copolymer
Run	M_2	ChPII (mol%)	$[\alpha]_D^{25\,a}$ (deg.)	$[\alpha]_D^{25}$ (deg.)
E-1		100	−7.0	+2.0[b]
E-2	ST	20.5	+0.8	−2.8[c]
E-3	MMA	20.2	+1.5	+2.0[b]

[a] $C = 1.0$ g dl^{-1}, THF, $l = 5$ cm
[b] $C = 0.3$ g dl^{-1}, MeOH, $l = 5$ cm
[c] $C = 0.5$ g dl^{-1}, AcOH, $l = 5$ cm

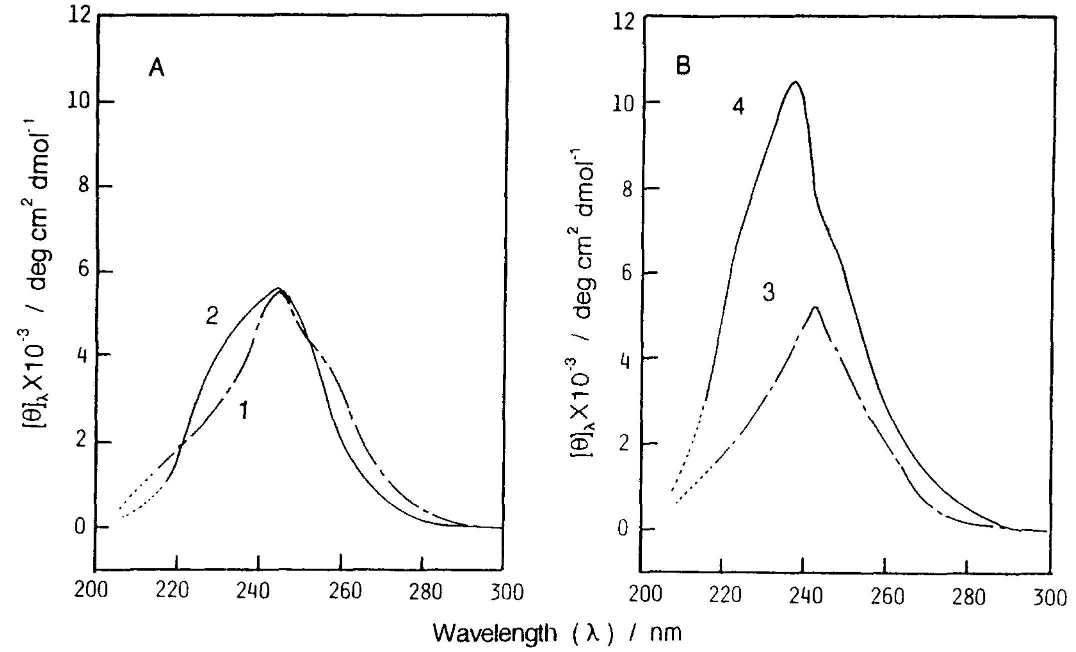


Figure 6 C.d. spectra for (A) poly(ChPII-*co*-ST) and (B) poly(ChPII-*co*-MMA): (1) 41.3 mol% of ChPII in copolymer (run C-2), (2) 56.0 mol% of ChPII in copolymer (run C-5), (3) 34.0 mol% of ChPII in copolymer (run D-2), and (4) 80.3 mol% of ChPII in copolymer (run D-2)

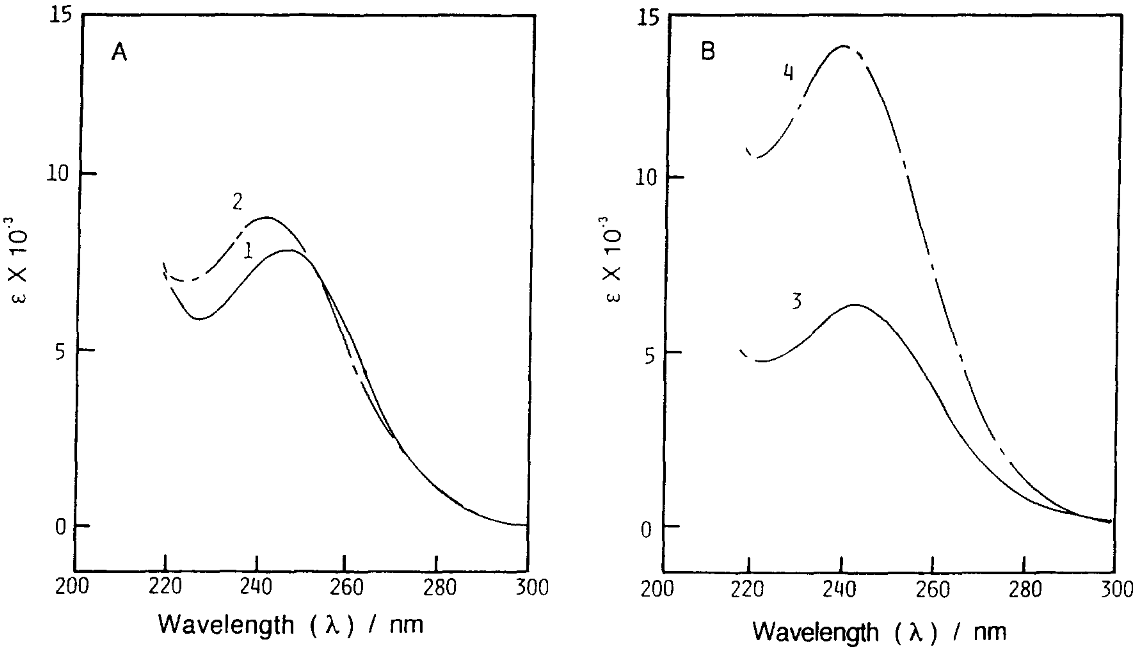


Figure 7 U.v. spectra for (A) poly(ChPII-*co*-ST) and (B) poly(ChPII-*co*-MMA): (1) 41.3 mol% of ChPII in copolymer (run C-2), (2) 56.0 mol% of ChPII in copolymer (run C-5), (3) 34.0 mol% of ChPII in copolymer (run D-2), and (4) 80.3 mol% of ChPII in copolymer (run D-2)

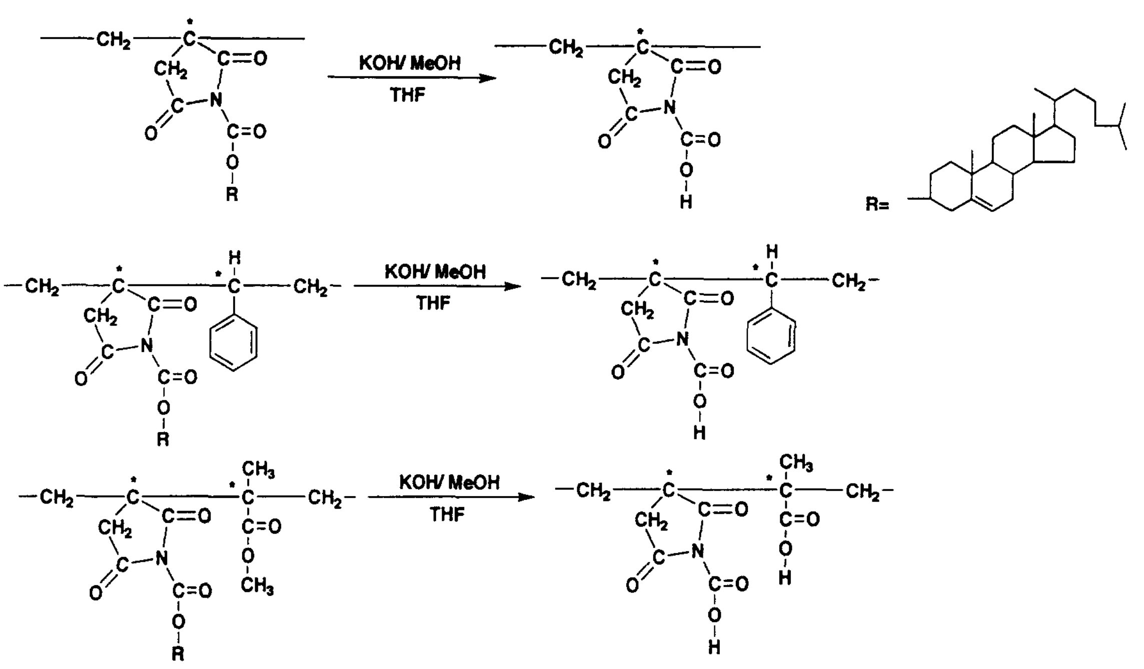
observed, which was ascribed both to the $n-\pi^*$ transition of carbonyl groups of ChPII and to the $\pi-\pi^*$ transition of phenyl groups in the ST and ChPII unit. In the poly(ChPII-*co*-MMA)s, a positive c.d. peak was observed at about 240 nm, based on the $n-\pi^*$ transition of carbonyl groups of MMA and ChPII units and on the $\pi-\pi^*$ transition of the ChPII unit.

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.

Table 3 shows optical behaviour of hydrolysed poly(ChPII), poly(ChPII-*co*-ST), and poly(ChPII-*co*-MMA), which were still optically active after the hydrolysis. The c.d. spectra of hydrolysed polymer and copolymers, as shown in *Figure 8*, indicated some positive and negative peaks. Both specific rotation and c.d. patterns were quite different from those for the corresponding original polymer and copolymers. This suggests that conformation of the polymers was different after hydrolysis. Consequently, it was confirmed that the asymmetric induction into the polymer and copolymers main chain took place, as illustrated in *Scheme 2*.

CONCLUSIONS

1. A novel type of optically active *N*-[4-(cholesteroxycarbonyl)phenyl]itaconimide (ChPII) was synthesized



Scheme 2

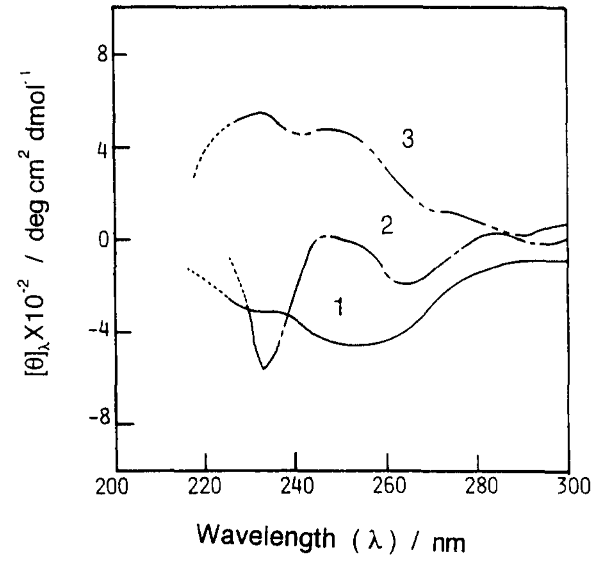


Figure 8 C.d. spectra for (1) hydrolysed poly(ChPII) (run E-1), (2) hydrolysed poly(ChPII-*co*-ST) (run E-2) and hydrolysed poly-(ChPII-*co*-MMA) (run E-3)

and polymerized with radical and anionic initiators to obtain optically active polymers.

2. From the results of the radical copolymerizations of ChPII(M_1) with ST(M_2) or MMA(M_2), the monomer reactivity ratios (r_2, r_2) and the Alfrey–Price Q, e values were determined as follows.

   $r_1 = 0.26$, $r_2 = 0.10$, $Q_1 = 2.17$, $e_1 = 1.11$ in the ChPII-ST system.

   $r_1 = 1.87$, $r_2 = 0.37$, $Q_1 = 2.55$, $e_1 = 1.01$ in the ChPII-MMA system.

3. In the ChPII homopolymer, asymmetric induction into the polymer main chain and asymmetric perturbation by the side chain chromophore took place. This was confirmed by hydrolysis of the original homopolymer and copolymers.

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