

# Synthesis and polymerization of maleimide containing an L-menthyl group

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Two types of optically active *N*-(L-menthoxy-carbonyl-*n*-pentyl)maleimide (MPMI) and *N*-(L-menthoxy-carbonyl-*n*-undecyl)maleimide (MUMI) were synthesized. Radical homopolymerizations of MPMI and MUMI were performed at 60°C for 24 h to give optically active polymers. Radical copolymerizations of MPMI ( $M_1$ ) and MUMI ( $M_1$ ) were performed with styrene ( $M_2$ ), methyl methacrylate ( $M_2$ ) in toluene at 60°C. Monomer reactivity ratios and the Alfrey–Price  $Q$ ,  $e$  values were also determined. Anionic homopolymerizations of MPMI and MUMI were also carried out. Chiroptical properties of the polymers and copolymers were investigated. Hydrolysed MPMI and MUMI polymers and copolymers still had optical activity judged from specific rotation and circular dichroism spectra. This suggests that chiral carbons in the polymer main chains were formed and that asymmetric induction took place. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: *N*-(L-menthoxy-carbonyl-*n*-alkyl)maleimide; optically active polymer; monomer reactivity ratio)

## INTRODUCTION

There have been many reports on polymerizations and copolymerizations of *N*-substituted maleimide (RMI)<sup>1–6</sup> but not so many studies on the polymerization of optically active RMI<sup>7,8</sup>. Since RMI is a 1,2-disubstituted cyclic ethylene type monomer, it has characteristic polymerization reactivities. That is, RMI can yield two *trans*-openings of the double bond to produce stereogenicity (*S*, *S*) and (*R*, *R*)<sup>9</sup>. Chiroptical properties of RMI polymer and copolymer could be attributed to a three-diisotactic structure, which can arise from helical structure and/or from the excess of chiral stereogenic centres (*S*, *S*), or (*R*, *R*). From this point of view, the authors have recently investigated many optically active RMI<sup>10–20</sup> bearing an (*R*)- $\alpha$ -methylbenzyl, menthyl and cholesteryl groups. Our previous papers<sup>13,16–18</sup> suggested that specific rotations  $[\alpha]_D^{25}$  and circular dichroism (c.d.) spectra for the copolymers could be attributed not only to chiral maleimide repeat units but also to comonomer units. In addition, it was found that asymmetric induction (formation of chiral carbon and/or asymmetric perturbation by the side chain chromophore) into the homopolymer and copolymer main chains took place, judged from chiroptical properties of a model compound of the polymer and of the copolymers.

In this article, two types of novel, optically active *N*-[(L-menthoxy)carbonyl-*n*-alkyl]maleimide (MAMI), i.e. *N*-[(L-menthoxy)carbonyl-*n*-pentyl]maleimide (MPMI;  $n = 5$  in Scheme 1) and *N*-[(L-menthoxy)carbonyl-*n*-undecyl]maleimide (MUMI;  $n = 11$  in Scheme 1), are prepared from maleic anhydride, corresponding  $\alpha$ ,

$\omega$ -amino acid, and L-menthol. MAMI is polymerized and copolymerized with styrene (ST) and methyl methacrylate (MMA) in the presence of radical initiators. The monomer reactivity ratios and the Alfrey–Price  $Q$ ,  $e$  values are determined. From the specific rotation and molecular ellipticity of the copolymers, chiroptical properties for the copolymers contributed to both chiral RMI residue and the comonomer unit are discussed, compared with that of *N*-[(L-menthoxy-carbonyl)methyl]maleimide (MGMI) ( $n = 1$  in Scheme 1), reported lately<sup>20</sup>. The obtained polymers and copolymers are hydrolysed to confirm asymmetric induction in the main chain. MAMI is also polymerized with an anionic initiator, *n*-BuLi, to obtain chiral polymers.

## EXPERIMENTAL

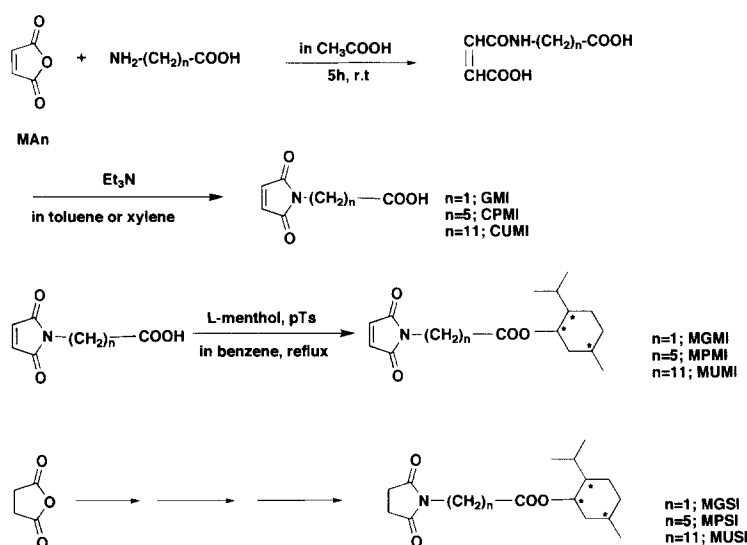
### MAMI monomers

*N*-(5-Carboxy-*n*-pentyl)maleimide (CPMI) and *N*-(11-carboxy-*n*-undecyl)maleimide (CUMI) were synthesized, according to a method reported previously<sup>21</sup>, with some modifications<sup>22</sup>. MAMI monomer was synthesized from CPMI (or CUMI) and L-menthol, as shown in Scheme 1.

*N*-(5-Carboxy-*n*-pentyl)maleamic acid (CPMA)<sup>22</sup>: yield 87%; mp 159–160°C (lit.<sup>21</sup> 159.5–161°C). <sup>1</sup>H nuclear magnetic resonance (n.m.r.): chemical shift,  $\delta$ , ppm from tetramethylsilane (TMS) in deuterium dimethyl sulfoxide (DMSO- $d_6$ ): 9.27 (s, 2H, 2COOH), 6.65 (2d,  $J = 12.1$  Hz, 2H, CH=CH), 6.12 (s, 1H, NH), 2.48 (m, 2H, N-CH<sub>2</sub>), 2.20 (t,  $J = 4.8$  Hz, 2H, COCH<sub>2</sub>), 1.35 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

*N*-(5-Carboxy-*n*-pentyl)maleimide (CPMI)<sup>22</sup>: yield 31%, mp 82–83°C (lit.<sup>21</sup> 79–80°C). <sup>1</sup>H n.m.r. ( $\delta$ , ppm from TMS in CDCl<sub>3</sub>): no peaks assigned to COOH can

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Scheme 1

be observed in  $\text{CDCl}_3$ , but it was observed at 7.80 ppm (s, 1H, COOH) in  $\text{DMSO}-d_6$ : 6.70 (s, CH=CH); 3.52 (t,  $J = 7.3$  Hz, 2H, N-CH<sub>2</sub>), 2.35 (t,  $J = 7.3$  Hz, 2H, COCH<sub>2</sub>), 1.72–1.56 (m, 4H, N-CH<sub>2</sub>-CH<sub>2</sub> and OOCCH<sub>2</sub>-CH<sub>2</sub>), and 1.40–1.31 (m, 2H, CH<sub>2</sub>).

*N*-[(5-Chlorocarbonyl)-*n*-pentyl]maleimide (CCPMI)<sup>22</sup>: yield 73.9%; bp 142–143°C/ $3.6 \times 10^{-2}$  mmHg. <sup>1</sup>H n.m.r. ( $\delta$ , ppm from TMS in  $\text{CDCl}_3$ ): 6.70 (s, 2H, CH=CH), 3.50 (t,  $J = 6.0$  Hz, 2H, N-CH<sub>2</sub>), 2.88 (t,  $J = 6.0$  Hz, 2H, CH<sub>2</sub>COCl), and 1.48 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>).

MPMI: A benzene (BEN 100 ml) solution of CCPMI (21.1 g, 0.1 mol) was added dropwise to a solution of *L*-menthol (18.8 g, 0.12 mol) in BEN (100 ml) at room temperature, and the mixture was refluxed for 4 h. The solution was cooled to room temperature and was then washed with dilute hydrochloric acid solution and with water. The BEN was evaporated to obtain crude MPMI, which was redistilled under reduced pressure to obtain pure MPMI: 20.0 g, 57.2%, bp 184–185°C/ $2.3 \times 10^{-2}$  mmHg,  $[\alpha]_D^{25} = 44.0^\circ$  ( $c = 1$  g dl<sup>-1</sup>,  $l = 10$  cm, tetrahydrofuran, THF). Infra-red (i.r., KBr disk, cm<sup>-1</sup>): 2800 (CH<sub>2</sub>), 1700 (C=O), 1448 (CH<sub>2</sub>), 830 (*cis* CH=CH), 690 (CH=CH). <sup>1</sup>H n.m.r. ( $\delta$ , ppm from TMS in  $\text{CDCl}_3$ ): 6.69 (s, 2H, CH=CH), 4.71–4.61 (m, 1H, COOCH), 3.51 (t,  $J = 7.26$  Hz, 2H, NCH<sub>2</sub>), 2.27 (t,  $J = 7.43$  Hz, 2H, COCH<sub>2</sub>), 2.06–0.69 (m, 24H, (CH<sub>2</sub>)<sub>3</sub> and other protons in menthyl). <sup>13</sup>C n.m.r. ( $\delta$ , ppm from TMS in  $\text{CDCl}_3$ ): 172.96 (COO), 170.73 (CO-N-CO), 133.98 (CH=CH in maleimide ring), 73.93 (COO-CH), 46.92, 40.86, 37.59, 34.40, 34.20, 31.31, 28.16, 26.18, 24.51, 23.34, 21.96, 20.69, 16.23 (14 carbons of other methylene in alkyl group and menthyl group).

Elemental analysis (%): found, C = 68.51, H = 8.63, N = 3.88; calcd for C<sub>20</sub>H<sub>31</sub>O<sub>4</sub>N, C = 68.74, H = 8.94, N = 4.01.

*N*-(11-Carboxy-*n*-undecyl)maleamic acid (CUMA)<sup>22</sup>: yield: 77.3%, mp 149–151°C (lit.<sup>21</sup> 152–153°C). <sup>1</sup>H n.m.r. ( $\delta$ , ppm from TMS in  $\text{DMSO}-d_6$ ): 9.12 (m, 1H, NH), 8.65–7.81 (m, 2H, 2COOH), 6.32 (d,  $J = 12.1$  Hz, 2H, CH=CH), 3.15 (t,  $J = 7.3$  Hz, 2H, N-CH<sub>2</sub>), 2.18 (t,  $J = 7.4$  Hz, 2H, CH<sub>2</sub>COO), 1.63–1.52 (m, 4H, N-CH<sub>2</sub>-CH<sub>2</sub> and OOCCH<sub>2</sub>-CH<sub>2</sub>), and 1.23 (m, 14H, (CH<sub>2</sub>)<sub>7</sub>).

*N*-(11-Carboxy-*n*-undecyl)maleimide (CUMI)<sup>22</sup>: yield

20.0%, mp 89–91°C (lit.<sup>21</sup> mp 81–84°C). <sup>1</sup>H n.m.r. ( $\delta$ , ppm from TMS in  $\text{CDCl}_3$ ): 6.69 (s, 2H, CH=CH), 3.50 (t,  $J = 7.3$  Hz, 2H, N-CH<sub>2</sub>), 2.34 (t,  $J = 7.4$  Hz, 2H, CH<sub>2</sub>COO), 1.65–1.55 (m, 4H, N-CH<sub>2</sub>-CH<sub>2</sub> and OOCCH<sub>2</sub>-CH<sub>2</sub>), and 1.26 (m, 14H, (CH<sub>2</sub>)<sub>7</sub>).

MUMI: MUMI was synthesized from CUMI and *L*-menthol in the presence of *p*-toluenesulfonic acid (*p*Ts). A mixture of CUMI (14.8 g, 0.05 mol), *L*-menthol (15.6 g, 0.1 mol), and *p*Ts (1.0 g,  $5.0 \times 10^{-3}$  mol) in benzene (250 ml) was refluxed for 48 h. During the reaction, the formed water was excluded from the reaction mixture system with a Dean–Stark trap. The reaction mixture was cooled to room temperature, and was washed with dilute sodium carbonate solution, following with water fully. Then it was dried with magnesium sulfate, and evaporated to exclude BEN. The residue was distilled under reduced pressure to obtain crude MUMI, which was purified by repeating distillation: yield 14.5 g (67.0%), bp 220–222°C/ $4.6 \times 10^{-2}$  mmHg.  $[\alpha]_D^{25} = -36.6^\circ$  ( $c = 1.0$  g dl<sup>-1</sup>,  $l = 10$  cm, THF). I.r. (neat, cm<sup>-1</sup>): 2800 (CH<sub>2</sub>), 1700 (C=O), 1448 (CH<sub>2</sub>), 830 (*cis* CH=CH), 690 (CH=CH). <sup>1</sup>H n.m.r. ( $\delta$ , ppm from TMS in  $\text{CDCl}_3$ ): 6.69 (s, 2H, CH=CH), 4.72–4.62 (m, 1H, COOCH), 3.50 (t,  $J = 7.26$  Hz, 2H, NCH<sub>2</sub>), 2.26 (t,  $J = 7.43$  Hz, 2H, COCH<sub>2</sub>), 2.29–0.74 (m, 36H, (CH<sub>2</sub>)<sub>9</sub> and other protons in menthyl). <sup>13</sup>C n.m.r. ( $\delta$ , ppm from TMS in  $\text{CDCl}_3$ ): 173.40 (COO), 170.84 (CO-N-CO), 133.98 (CH=CH in maleimide ring), 73.80 (COO-CH), 46.97, 40.91, 37.86, 34.70, 34.25, 31.31, 29.38, 29.17, 29.06, 28.48, 26.69, 26.20, 25.09, 23.38, 21.98, 20.72, 16.25 (20 carbons of other methylene in alkyl and in menthyl groups).

Elemental analysis (%): found, C = 71.79, H = 9.98, N = 3.36; calcd for C<sub>26</sub>H<sub>43</sub>O<sub>4</sub>N, C = 72.02, H = 10.00, N = 3.23. Model compound of poly(MPMI): *N*-(*L*-menthoxy-carbonyl)-*n*-pentylsuccinimide (MPSI): MPSI was prepared from succinic anhydride, 6-aminocarproic acid and *L*-menthol, according to a method similar to that for MPMI. Yields and melting points of precursors are as follows: *N*-(5-carboxy-*n*-pentyl)succinamic acid: yield 70.7%; mp 100–101°C; *N*-(5-carboxy-*n*-pentyl)succinimide: yield 32%, mp 79–81°C; *N*-(5-chlorocarbonyl)-*n*-pentylsuccinimide: yield 85%, mp 162–163°C/ $3.4 \times 10^{-2}$  mmHg.

MPSI: total yield 31.0%; bp 194–195°C/7.2 × 10<sup>-2</sup> mmHg;  $[\alpha]_D^{25} = -44.7^\circ$  ( $c = 1.0 \text{ g dl}^{-1}$ ,  $l = 10 \text{ cm}$ , THF). I.r. (neat, cm<sup>-1</sup>): 2900 (CH<sub>2</sub> and CH<sub>3</sub>), 1726 and 1697 (CO–N–CO), 1462, 1401 and 1372 (CH<sub>3</sub> and CH<sub>2</sub>), 1180 and 1145 (OC=O). <sup>1</sup>H n.m.r. ( $\delta$ , ppm from TMS in CDCl<sub>3</sub>): 4.70–4.61 (m, 1H, COOCH), 3.48 (t,  $J = 6.3 \text{ Hz}$ , 2H, NCH<sub>2</sub>), 2.78 (s, 4H, CH<sub>2</sub>CH<sub>2</sub> in succinimide ring), 2.28 (t,  $J = 6.1 \text{ Hz}$ , 2H, COCH<sub>2</sub>), 2.00–1.00 (m, 6H, (CH<sub>2</sub>)<sub>3</sub>), 0.88 (d,  $J = 8.0 \text{ Hz}$ , 3H, CCH<sub>3</sub>) and 0.68 (s, 3H, CCH<sub>3</sub>). <sup>13</sup>C n.m.r. ( $\delta$ , ppm from TMS in CDCl<sub>3</sub>): 177.12 (CO–N–CO), 172.96 (COO), 73.96 (COO–CH), 46.97 (N–CH<sub>2</sub>), 28.09 (CH<sub>2</sub>–CH<sub>2</sub> in succinimide ring), 40.90, 38.56, 34.40, 34.21, 31.32, 27.30, 26.48, 26.08, 25.07, 23.29, 21.96, 20.68, 16.26 (four carbons of methylene groups and nine carbons in a menthyl group).

Elemental analysis (%): found, C = 69.20, H = 9.18,

N = 3.29; calcd for C<sub>20</sub>H<sub>33</sub>O<sub>4</sub>N, C = 68.34, H = 9.46, N = 3.58.

Model compound of poly(MUMI): *N*-[*L*-(menthoxy-carbonyl)-*n*-undecyl)succinimide (MUSI): MUSI was prepared from succinic anhydride, 12-amino-*n*-dodecanoic acid, and *L*-menthol, according to a similar method to that for MUMI: yields and melting points of precursors are as follows: *N*-(11-carboxy-*n*-undecyl)succinamic acid: yield 98%; mp 150–153°C; *N*-(11-carboxyundecyl)succinimide: yield 63%, mp 111–116°C.

MUSI: total yield 30.0%, bp 220–222°C/2.0 × 10<sup>-2</sup> mmHg;  $[\alpha]_D^{25} = -36.5^\circ$  ( $c = 1.0 \text{ g dl}^{-1}$ ,  $l = 10 \text{ cm}$ , THF). I.r. (neat, cm<sup>-1</sup>): 2900 (CH<sub>2</sub> and CH<sub>3</sub>), 1725 and 1695 (CO–N–CO), 1460, 1400 and 1370 (CH<sub>3</sub> and CH<sub>2</sub>), 1180 and 1145 (OC=O). <sup>1</sup>H n.m.r. ( $\delta$ , ppm from TMS in CDCl<sub>3</sub>): 4.71–4.61 (m, 1H, COOCH), 3.50 (t,

**Table 1** Radical and anionic polymerizations of MPMI

Run	MPMI (×10 <sup>3</sup> mol)	Initiator (×10 <sup>2</sup> mol l <sup>-1</sup> )	Polymerization solvent <sup>a</sup> (ml)	Polymerization temp. (°C)	Polymerization time (h)	Conversion (%)	$\bar{M}_n^b$ (×10 <sup>-3</sup> )	$\bar{M}_w/\bar{M}_n^b$	$[\alpha]_D^{25c}$ (deg.)
1-1	1.45	AIBN (1.0)	TOL (2)	60	24	52.8	4.3	1.5	-45.1
1-2	1.44	AIBN (2.0)	TOL (2)	60	24	53.3	4.6	1.4	-43.9
1-3	1.44	AIBN (1.0)	THF (2)	60	24	21.3	3.3	1.3	-47.5
1-4	1.44	AIBN (2.0)	THF (2)	60	24	30.7	3.3	1.3	-44.9
1-5	1.44	AIBN (1.0)	XY (2)	60	24	16.3	8.6	2.0	-43.5
1-6	1.46	AIBN (1.0)	DOX (2)	60	24	46.7	4.2	1.4	-45.0
1-7	1.43	AIBN (1.0)	CF (2)	60	24	3.1	2.6	25.3	-54.9
1-8	1.44	PV <sup>d</sup>		60	24	64.0	114	1.9	-43.8
1-9	1.46	DBPO <sup>e</sup> (2.0)	TOL (2)	110	24	59.9	3.3	2.4	-43.5
1-10	1.44	BuLi (3.0)	TOL (3)	0	24	54.7	6.2 (3.4)	2.2 (1.1)	-47.6
1-11	1.47	BuLi (3.0)	THF (2)	0	15	23.5	6.6	2.1	-44.8

<sup>a</sup> TOL, toluene; THF, tetrahydrofuran; DOX, dioxane; XY, *o*-xylene; CF, chloroform

<sup>b</sup> By g.p.c.

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

<sup>d</sup> *t*-Butyl peroxyvalerate 7 mol% of MPMI

<sup>e</sup> Di-*t*-butyl peroxide

**Table 2** Radical and anionic polymerizations of MUMI

Run	MUMI (×10 <sup>3</sup> mol)	Initiator (×10 <sup>2</sup> mol l <sup>-1</sup> )	Polymerization Solvent <sup>a</sup> (ml)	Polymerization temp. (°C)	Polymerization time (h)	Conversion (%)	$\bar{M}_n^b$ (×10 <sup>-3</sup> )	$\bar{M}_w/\bar{M}_n^b$	$[\alpha]_D^{25c}$ (deg.)
2-1	1.15	AIBN (1.0)	TOL (1)	60	24	16.1	14.9	2.02	-36.3
2-2	1.15	AIBN (2.0)	TOL (1)	60	24	83.5	6.8	1.84	-36.2
2-3	1.16	AIBN (1.0)	THF (1)	60	24	80.2	5.0	1.53	-36.3
2-4	1.15	AIBN (2.0)	THF (1)	60	24	76.6	5.0	1.54	-36.3
2-5	1.16	AIBN (1.0)	BEN (2)	60	24	87.6	34.4	3.02	-36.3
2-6	1.15	AIBN (2.0)	BEN (2)	60	24	85.8	27.3	3.31	-33.5
2-7	1.15	AIBN (1.0)	DOX (1)	60	24	78.1	6.3	3.77	-36.3
2-8	1.15	AIBN (2.0)	DOX (1)	60	24	78.8	8.8	2.57	-36.5
2-9	1.16	AIBN <sup>d</sup>		60	24	84.8	31.7	1.58	-35.0
2-10	1.15	PV <sup>e</sup>		60	24	89.1	30.5	2.06	-35.5
2-11	2.31	BuLi (2.5)	TOL (2)	0	24	4.0	11.8 (5.4)	2.16 (1.09)	-35.1
2-12	2.32	BuLi (5.7)	TOL (2)	0	24	30.9	9.7	1.91	-35.0
2-13	2.34	BuLi (2.5)	THF (2)	0	24	12.0	11.0	17.6	-34.0
2-14	2.31	BuLi (5.7)	THF (2)	0	20	90.2	11.0	17.5	-37.5

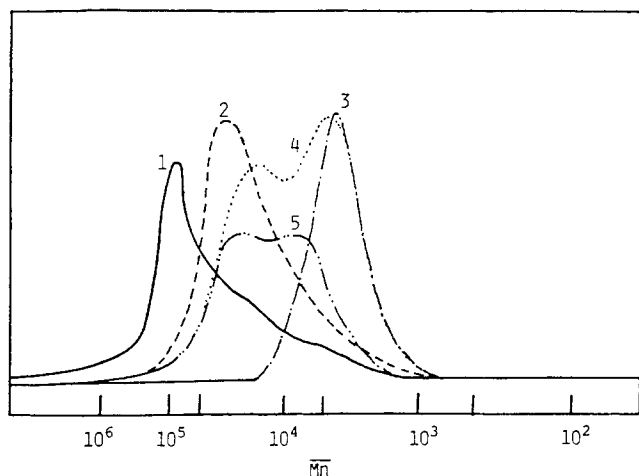
<sup>a</sup> TOL, toluene; THF, tetrahydrofuran; BEN, benzene; DOX, dioxane

<sup>b</sup> By g.p.c.

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

<sup>d</sup> AIBN 2.1 mol% of MUMI

<sup>e</sup> *t*-Butyl peroxyvalerate 6 mol% of MUMI



**Figure 1** G.p.c. curves for poly(MAMI): (1) poly(MUMI) obtained with AIBN in BEN (run 2-5); (2) poly(MUMI) obtained with AIBN in TOL (run 2-1); (3) poly(MPMI) obtained with AIBN in TOL (run 1-1); (4) poly(MPMI) obtained with *n*-BuLi in TOL (run 1-10); and (5) poly(MUMI) obtained with *n*-BuLi in TOL (run 2-11)

$J = 6.3$  Hz, 2H, NCH<sub>2</sub>), 2.68 (s, 4H, CH<sub>2</sub>CH<sub>2</sub> in succinimide ring), 2.28 (t,  $J = 6.1$  Hz, 2H, COCH<sub>2</sub>), 2.06–0.69 (m, 35H, (CH<sub>2</sub>)<sub>9</sub> and other protons in menthyl). <sup>13</sup>C n.m.r. ( $\delta$ , ppm from TMS in CDCl<sub>3</sub>): 177.21 (CO–N–CO), 173.40 (COO), 73.78 (COO–CH), 28.09 (CH<sub>2</sub>–CH<sub>2</sub> in succinimide ring), 46.96, 40.88, 38.82, 34.68, 34.22, 31.52, 31.31, 29.34, 29.15, 29.06, 27.46, 26.78, 26.17, 25.07, 23.34, 21.96, 20.70, 16.23 (19 carbons of methylene in alkyl groups and menthyl group).

Elemental analysis (%): found, C = 71.80, H = 10.54, N = 3.43; calcd for C<sub>26</sub>H<sub>45</sub>O<sub>4</sub>N, C = 71.68, H = 10.41, N = 3.22.

#### Other materials

ST, MMA, BEN, THF, toluene (TOL), and

other solvents were purified by the usual methods<sup>23</sup>. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization twice from methanol, but commercially available *t*-butyl peroxyvalate (PV) and *n*-butyllithium (*n*-BuLi) hexane solution were used without further purification.

#### Homopolymerization and copolymerization

Radical homopolymerization and copolymerization were carried out with radical initiators in THF, BEN, TOL, *o*-xylene (XY), chloroform (CF) or dioxane (DOX) in a sealed tube at 60°C. After polymerization, the polymer solution was poured into a large amount of methanol to precipitate the polymer. The obtained polymer was purified by reprecipitation from the THF solution to methanol twice. The polymer was filtered and dried *in vacuo* for 3 days at 40°C. The composition of the copolymer obtained was calculated by <sup>1</sup>H n.m.r. spectra and elemental analysis (N).

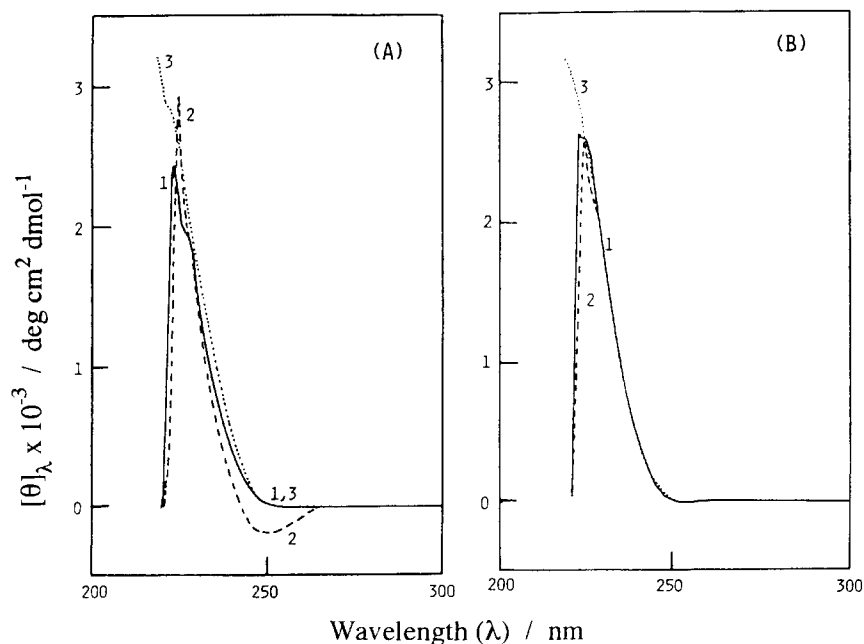
Anionic homopolymerization was achieved in TOL or THF at 0°C by using *n*-BuLi as a catalyst under a nitrogen atmosphere. The polymerization was terminated with a few drops of methanol by using a syringe. The solution was poured into a large amount of methanol. The obtained polymer was purified by reprecipitation twice from the THF solution to methanol, then filtered and dried *in vacuo* at 40°C.

#### Hydrolysis of the polymers and copolymers

The polymers and copolymers were hydrolysed with potassium hydroxide, according to the same method as reported previously<sup>24,25</sup>.

#### Measurements

D-line specific rotations were measured with a Jasco DIP-140 (Japan Spectroscopic Co.) at 25°C (quartz cell length: 5 and 10 cm; *ca* 1.0 g dl<sup>-1</sup> in THF). C.d. spectra were obtained at 25°C using a Jasco J-20C (Japan Spectroscopic Co.), equipped with a xenon source and a



**Figure 2** C.d. spectra for poly(MAMI): (A-1) poly(MPMI) obtained with AIBN in TOL (run 1-1), (A-2) poly(MPMI) obtained with *n*-BuLi in TOL (run 1-10), (A-3) MPSI (model compound for poly(MPMI)), (B-1) poly(MUMI) obtained with AIBN in TOL (run 2-1), (B-2) poly(MUMI) obtained with *n*-BuLi in TOL (run 2-12), and (B-3) MUSI (model compound for poly(MUMI))

computing data processor (quartz cell length: 0.1 and 1.0 mm; *ca* 0.5–1.0 g dl<sup>-1</sup> in THF). Ultraviolet (u.v.) spectra were obtained with a Shimadzu UV 2200 spectrophotometer (quartz cell length: 1 mm and *ca* 1.2 × 10<sup>-2</sup>–4.0 × 10<sup>-2</sup> g dl<sup>-1</sup> in THF). Molecular weights of polymers were measured by gel permeation chromatographic (g.p.c.) analysis, using the same technique as described in an earlier paper<sup>18</sup>. I.r. and n.m.r. spectra were obtained and elemental analysis was carried out, using the same instruments as reported previously<sup>18</sup>.

## RESULTS AND DISCUSSION

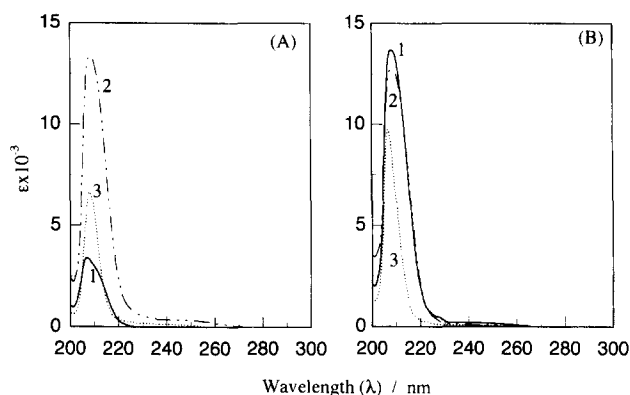
### Radical and anionic homopolymerization of MPMI and MUMI

Radical and anionic polymerizations of MPMI and MUMI were performed under several conditions. The results are summarized in *Tables 1* and *2*. The polymerizations proceeded homogeneously throughout. The obtained polymers were colourless powders and had negative optical activities. In the polymerization of MPMI in chloroform the yield and the number-average molecular weights ( $\bar{M}_n$ ) were very low ( $2.6 \times 10^5$ ). In addition, polydispersity [weight-average molecular weight ( $\bar{M}_w$ )/ $\bar{M}_n$ ] was very large (25.3), as shown in *Table 1*. This may result from chain transfer of propagating radical to solvent (chloroform). The bulk polymerization of MPMI with PV, which was a liquid initiator, gave much higher yield and  $\bar{M}_n$  ( $1.14 \times 10^5$ ) than in other systems. As can be seen from *Table 2*, generally, both the yields and  $\bar{M}_n$  of the poly(MUMI) were higher than those for the MPMI polymers. That is, polymerizabilities of MUMI were superior to those of MPMI because steric hindrance of menthyl groups locating far from the maleimide ring decreased.

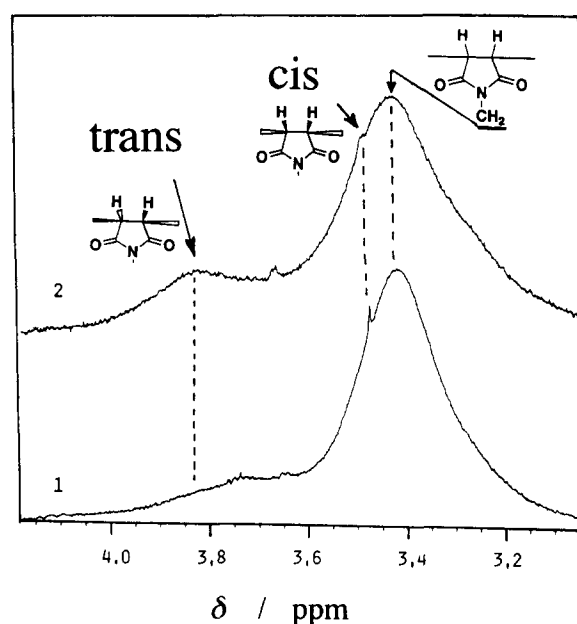
In the g.p.c. curve of the polymer obtained with AIBN in benzene (run 2–5), one peak was observed at about  $1 \times 10^5$ , but was very broad. Thus  $\bar{M}_n$  was relatively low and  $3 \times 10^4$ , as shown in *Figure 1 (1)*. Poly(MUMI) showed higher  $\bar{M}_n$  than poly(MPMI) and both had only one peak [*Figures 1 (2) and 1 (3)*]. For poly(MPMI) (run 1–11) and poly(MUMI) (run 2–13, 14) obtained with *n*-BuLi in THF, only one peak such as the curves drawn in *Figures 1 (2) and 1 (3)* was observed. For poly(MPMI) (run 1–10) and poly(MUMI) (run 2–11) obtained with *n*-BuLi in toluene, however, two peaks appeared [*Figures 1 (4) and 1 (5)*]. This difference could not be explained clearly since there were little differences of <sup>1</sup>H n.m.r. spectra between poly(MUMI)s obtained with *n*-BuLi in THF and in toluene. However, the reason may be attributed to solubility of forming polymers in the polymerization solvent. The  $\bar{M}_n$ s of poly(MUMI)s obtained with the radical initiator were  $5.0 \times 10^3$ – $3.4 \times 10^4$ , and higher than those ( $4.4 \times 10^3$ – $8.9 \times 10^3$ ) of poly(MGMI)<sup>20</sup> ( $n = 1$  in *Scheme 1*). Thus, the homopolymerizabilities of maleimide containing an *L*-menthyl group were found to be higher when the *L*-menthyl group existed far from a maleimide ring. The reason for this may be that the steric hindrance of the bulky *L*-menthyl group decreased during the propagation reaction.

The c.d. spectra for poly(MAMI) obtained with AIBN and *n*-BuLi in TOL are shown in *Figure 2*. The c.d. pattern for poly(MPMI) obtained with *n*-BuLi in toluene

showed a negative Cotton effect at about 250 nm, ascribed to the  $n \rightarrow \pi^*$  transition of two carbonyl groups as shown in *Figure 3A*, and was different from those for other polymers. This suggests that confirmation of the poly(MPMI) obtained with *n*-BuLi differed from other polymers obtained with radical initiators. It seemed that both poly(MPMI)s obtained with *n*-BuLi and AIBN consisted of much more *cis*-forms (erythro-diisotactic and -disyndiotactic) than *trans*-forms (threo-diisotactic and disyndiotactic). The peaks assigned to *cis*- and *trans*-forms appeared at about 3.5 ppm and 3.8 ppm<sup>26</sup>, respectively, as shown in *Figure 4*, even though peaks due to the *cis*-form included those at 3.45 ppm assigned to methylene groups connecting a nitrogen (N–CH<sub>2</sub>). Compared to both the spectra, poly(MPMI) obtained with *n*-BuLi contained more *trans*-form than that with AIBN. This may result from the fact that the anionic polymerization at low temperature was more stereoregularly controlled than the radical one.



**Figure 3** U.v. spectra for poly(MAMI): (A-1) poly(MPMI) obtained with AIBN in TOL (run 1–1), (A-2) poly(MPMI) obtained with *n*-BuLi in TOL (run 1–10), (A-3) MPSI (model compound for poly(MPMI)), (B-1) poly(MUMI) obtained with AIBN in TOL (run 2–1), (B-2) poly(MUMI) obtained with *n*-BuLi in TOL (run 2–12), and (B-3) MUSI (model compound for poly(MUMI))



**Figure 4** <sup>1</sup>H n.m.r. spectra for poly(MPMI) obtained with (1) AIBN [run 1–1] and (2) *n*-BuLi [run 1–10]

The c.d. patterns for poly(MUMI) obtained with AIBN in other solvents were similar to those of the poly(MUMI) obtained in toluene. There were little differences between the c.d. patterns for poly(MUMI) obtained with *n*-BuLi and the radical initiator, as shown in Figure 2B. Both the c.d. patterns were similar to that of the model compound (MUSI) in spite of each polymer having different molecular ellipticity  $[\theta]$ . In all c.d. spectra, a large positive peak was observed at about 225 nm, which was based on the  $n \rightarrow \pi^*$  transition of two carbonyl groups in the imide ring, as can be seen from u.v. spectra shown in Figure 3B. For poly(MGMI) obtained with *n*-BuLi as reported previously<sup>20</sup>, one negative c.d. peak at about 255 nm obviously appeared. In the c.d. patterns for poly(MUMI) obtained with *n*-BuLi, however, no c.d. peaks at about 255 nm could be observed. This was quite different from that of poly(MGMI)<sup>20</sup> ( $n = 1$  in Scheme 1).

In the MGMI system, the asymmetric induction could be supported by the fact that there was an obvious difference of the optical rotation between poly(MGMI)<sup>20</sup> ( $[\alpha]_D = -56.1^\circ$ ) and the model of poly(MGMI)

( $[\alpha]_D = -47.6^\circ$ ). In poly(MPMI), there was very little difference of the optical rotation between the homopolymer and model compound (MPSI). There was no difference between poly(MUMI) and the model compound (MUSI). That is, when the methylene unit became longer, the difference gradually decreased. This suggests that asymmetric induction (formation of chiral carbon and/or asymmetric perturbation by the side chain chromophore) was strongly influenced by the distance from the reacting site of maleimide ring to the optically active group, i.e. length of the methylene units.

#### Radical copolymerizations of MPMI, MUMI with ST or MMA

The results of the radical copolymerizations of MPMI ( $M_1$ ), MUMI ( $M_1$ ) with ST ( $M_2$ ), MMA ( $M_2$ ) in benzene (2 ml) at 60°C in the presence of AIBN ( $1.0 \times 10^{-2} \text{ mol l}^{-1}$ ) are summarized in Tables 3 and 4. All the copolymerizations proceeded homogeneously throughout. The resulting copolymers were colourless powders and optically active.

Copolymer composition curves of the MPMI-ST,

**Table 3** Radical copolymerization of MPMI ( $M_1$ ) in TOL (2 ml) at 60°C<sup>a</sup>

Run	$M_2$	$M_1$ in monomer (mol%)	Polymerization time (h)	Conversion (%)	$M_1$ in copolymer (mol%)	$M_n^b$ ( $\times 10^{-3}$ )	$\bar{M}_w/\bar{M}_n^b$	$[\alpha]_D^{25}{}^c$ (deg.)
3-1	ST	10.7	7	23.6	25.8	4.5	4.3	-22.0
3-2	ST	30.3	8	36.1	40.1	1.6	2.6	-31.6
3-3	ST	50.2	9	43.4	41.5	2.0	1.7	-35.7
3-4	ST	68.9	9	49.6	58.2	0.89	19.4	-38.2
3-5	ST	90.1	7	23.6	69.7	0.80	4.8	-44.1
3-6	MMA	10.3	8	28.8	10.9	2.4	1.7	-8.7
3-7	MMA	30.7	9	30.7	21.6	6.8	4.2	-21.4
3-8	MMA	50.9	9	31.0	44.4	11.0	2.7	-31.3
3-9	MMA	70.4	11	34.5	68.0	0.45	3.6	-39.1
3-10	MMA	89.3	12	36.3	92.0	0.61	2.7	-43.7

<sup>a</sup>  $[\text{AIBN}] = 1.0 \times 10^{-2} \text{ mol l}^{-1}$ ;  $M_1 + M_2 = 0.5 \text{ g}$

<sup>b</sup> By g.p.c.

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

**Table 4** Radical copolymerization of MUMI ( $M_1$ ) in BEN (2 ml) at 60°C<sup>a</sup>

Run	$M_2$	$M_1$ in monomer (mol%)	Polymerization time (h)	Conversion (%)	$M_1$ in copolymer (mol%)	$M_n^b$ ( $\times 10^{-3}$ )	$\bar{M}_w/\bar{M}_n^b$	$[\alpha]_D^{25}{}^c$ (deg.)
4-1	ST	5.0	7	30.3	22.7	23.8	4.1	-21.3
4-2	ST	10.0	7	40.0	31.9	16.1	9.7	-23.3
4-3	ST	20.1	2	29.6	44.6	34.6	3.1	-28.0
4-4	ST	30.0	4	31.7	50.7	34.8	6.1	-26.9
4-5	ST	50.1	3	35.7	55.5	31.5	4.0	-29.1
4-6	ST	70.0	7	31.7	63.4	29.4	6.6	-29.3
4-7	ST	90.0	8	41.5	87.6	16.8	4.7	-32.6
4-8	MMA	5.0	6	22.3	2.4	38.0	6.9	-3.8
4-9	MMA	10.7	5	23.4	7.5	39.1	2.0	-7.9
4-10	MMA	20.1	13	25.6	14.4	45.1	2.3	-12.6
4-11	MMA	30.1	12	23.8	19.1	35.2	2.7	-17.9
4-12	MMA	50.0	15	5.7	31.5	44.3	2.5	-22.4
4-13	MMA	69.5	7	38.8	64.7	19.6	4.2	-29.8
4-14	MMA	90.0	8	29.9	82.5	16.0	3.5	-32.9

<sup>a</sup>  $[\text{AIBN}] = 1.0 \times 10^{-2} \text{ mol l}^{-1}$ ;  $M_1 + M_2 = 0.5 \text{ g}$

<sup>b</sup> By g.p.c.

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

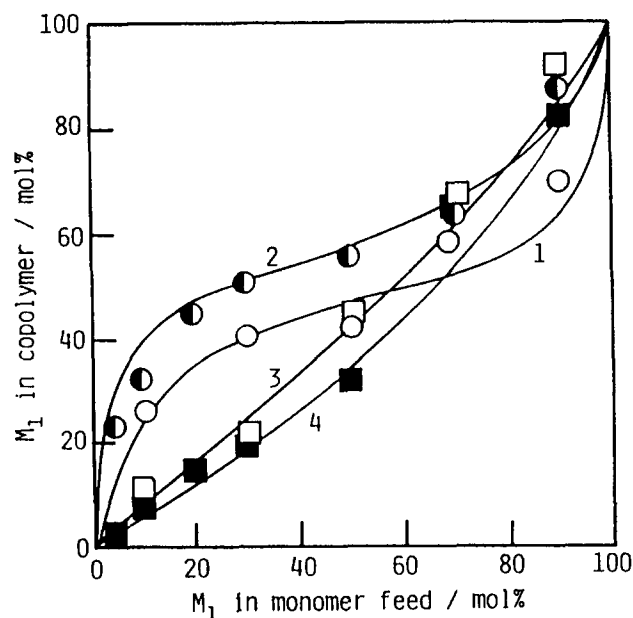


Figure 5 Copolymer composition curves for (1) MPMI-ST, (2) MUMI-ST, (3) MPMI-MMA, and (4) MUMI-MMA system

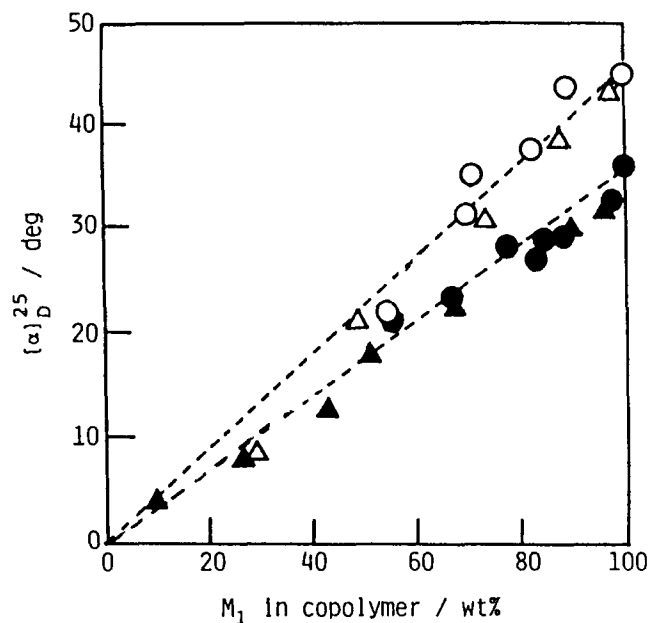


Figure 6 Relationships between  $[\alpha]_D^{25}$  and monomer content (wt%); (O) poly(MPMI-co-ST), ( $\Delta$ ) poly(MUMI-co-ST), ( $\bullet$ ) poly(MPMI-co-MMA), and ( $\blacktriangle$ ) poly(MUMI-co-MMA)

MPMI-MMA, MUMI-ST, and MUMI-MMA systems are shown in Figure 5. Monomer reactivity ratios,  $r_1$  and  $r_2$  determined according to the high conversion method reported by Tüdös and coworkers<sup>27</sup>, and Alfrey-Price<sup>28</sup>  $Q$ ,  $e$  values are as follows:  $r_1 = 0.08$ ,  $r_2 = 0.24$ ,  $Q_1 = 0.86$ ,  $e_1 = 1.12$  in the MPMI-ST system;  $r_1 = 0.62$ ,  $r_2 = 1.12$ ,  $Q_1 = 0.84$ ,  $e_1 = 1.00$  in the MPMI-MMA system;  $r_1 = 0.43$ ,  $r_2 = 0.06$ ,  $Q_1 = 3.59$ ,  $e_1 = 1.11$  in the MUMI-ST system;  $r_1 = 0.51$ ,  $r_2 = 1.85$ ,  $Q_1 = 0.44$ ,  $e_1 = 0.60$  in the MUMI-MMA system. These copolymerization parameters were similar to those for other RMI copolymers reported previously<sup>29</sup>.

#### Optical behaviour of the copolymers

Figure 6 shows the relationship between the specific

rotation and the content (wt%) of the monomeric unit of MAMI ( $M_1$ ) in both copolymer systems. The absolute values of specific rotations of a simple mixture of poly(MAMI) and poly(ST) (or poly(MMA)) gave a good linear relationship, as shown in Figure 6 (dashed line). In the poly(MPMI-co-ST)s and poly(MPMI-co-MMA)s, there was very little deviation from linearity. These tendencies were also observed in the poly(MUMI-co-ST) and poly(MUMI-co-MMA). This strongly suggests that chiroptical properties of the MAMI copolymers can very slightly be affected by the comonomer unit; ST or MMA. That is, it was expected that slight asymmetric induction (formation of chiral carbons and/or perturbation by the side chain chromophore) occurred in the main chain of the copolymers. This was evidenced by the fact that hydrolysed polymers and copolymers practically had a little specific rotation, as described later. Thus, occurrence of only a very little asymmetric induction was attributable to the distance from the maleimide ring to the optically active group. This tendency was also recognized in  $N$ -[ $N'$ -( $\alpha$ -methylbenzyl)amino-carbonyl- $n$ -alkyl]maleimide<sup>22</sup> (MBAM)-ST and MBAM-MMA systems, and  $N$ -[(cholesteroxycarbonyl)- $n$ -alkyl]maleimide<sup>24</sup> (ChAM)-ST and ChAM-MMA systems.

The c.d. and u.v. spectra for poly(MPMI-co-ST) and poly(MPMI-co-MMA) are shown in Figures 7 and 8, respectively. Molecular ellipticities  $[\theta]$  were calculated from the number average molecular weight of the monomeric units. Poly(MUMI-co-ST) and poly(MUMI-co-MMA) gave the c.d. patterns similar to those for MPMI copolymers systems. In the c.d. spectra a positive peak around 225 nm was ascribed to the  $\pi \rightarrow \pi^*$  transition assigned to phenyl groups of ST unit and to the  $n \rightarrow \pi^*$  transition based on carbonyl groups of MPMI and/or MMA units. A positive c.d. peak was very small when MPMI monomer feed was low. The c.d. peaks for other copolymers were present between curves 1 and 2 in Figure 7.

To confirm asymmetric induction, i.e. formation of chiral carbons on the main chain, the polymers and copolymers were hydrolysed with potassium hydroxide in a mixture of THF and methanol<sup>24</sup>.

Hydrolysed poly(MAMI), poly(MAMI-co-ST), and

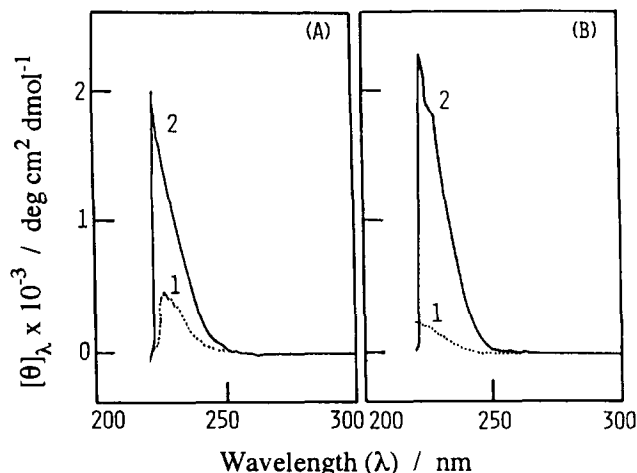
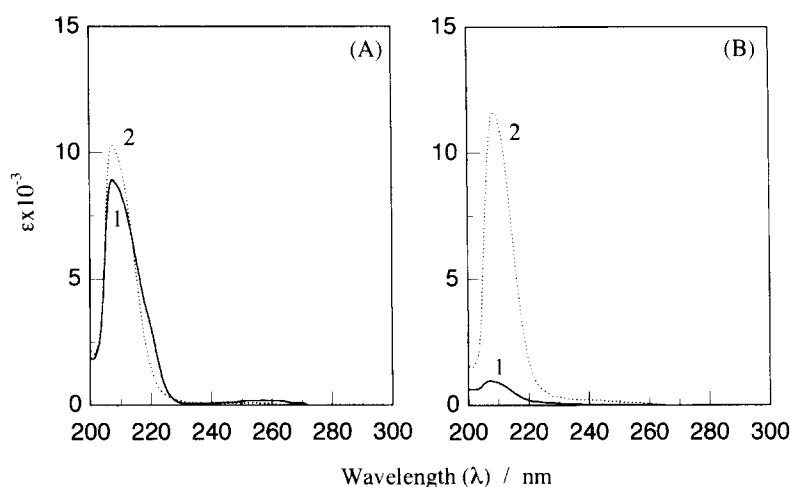


Figure 7 C.d. spectra for (A) poly(MPMI-co-ST) and (B) poly(MPMI-co-MMA): (1) 10 mol% of MPMI in monomer feed (run 3-1 and 3-6) and (2) 90 mol% of MPMI in monomer feed (run 3-5 and 3-10)



**Figure 8** U.v. spectra for (A) poly(MPMI-co-ST) and (B) poly(MPMI-co-MMA): (1) 10 mol% of MPMI in monomer feed (run 3-1 and 3-6) and (2) 90 mol% of MPMI in monomer feed (run 3-5 and 3-10)

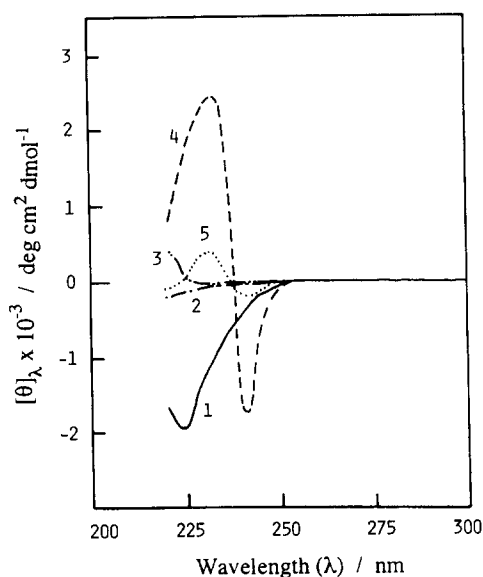
**Table 5** Optical behaviour of poly(MAMI), poly(MAMI-co-ST), and poly(MAMI-co-MMA)

Run	M <sub>1</sub>	M <sub>2</sub>	Original polymer		Hydrolysed polymer
			MAMI in copolymer (mol%)	$[\alpha]_D^{25}$ <sup>a</sup> (deg)	$[\alpha]_D^{25}$ <sup>b</sup> (deg)
5-1	MPMI	–	100	–45.1	+1.0
5-2	MPMI	ST	40.1	–31.6	+0.4
5-3	MPMI	MMA	21.6	–21.4	+0.1
5-4	MUMI	–	100	–36.3	+0.1
5-5	MUMI	ST	50.7	–26.9	–0.3 <sup>c</sup>

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

<sup>b</sup>  $c = 1.0 \text{ g dl}^{-1}$ ,  $l = 10 \text{ cm}$ , H<sub>2</sub>O

<sup>c</sup>  $c = 1.0 \text{ g dl}^{-1}$ ,  $l = 10 \text{ cm}$ , CH<sub>3</sub>OH



**Figure 9** C.d. spectra for hydrolysed polymers copolymers: (1) poly(MPMI) [run 5-1], (2) poly(MPMI-co-ST) [run 5-2], (3) poly(MPMI-co-MMA) [run 5-3], (4) poly(MUMI) [run 5-4], and poly(MUMI-co-ST) [run 5-5]

poly(MAMI-co-MMA) still had optical activity after hydrolysis, as shown in Table 5. In the c.d. spectra of hydrolysed polymers and copolymers, as displayed in Figure 9, negative and positive peaks were observed in the range of about 225–250 nm. Both specific rotations

and c.d. patterns were quite different from those for the corresponding original polymers and copolymers, which suggests that the hydrolysed polymers contained different conformations from the original ones. It was confirmed that asymmetric carbons were formed in the polymer and copolymer main chains, as illustrated in Scheme 2. However, it seemed that the asymmetric induction was very little.

## CONCLUSIONS

(1) Two types of optically active *N*-[(*L*-menthoxy-carbonyl)-*n*-alkyl]maleimide (MAMI: MPMI and MUMI) were synthesized and polymerized with radical and anionic initiators to obtain chiral polymers.

(2) From the results of the radical copolymerizations of MAMI (M<sub>1</sub>) with ST (M<sub>2</sub>) or MMA (M<sub>2</sub>), monomer reactivity ratios ( $r_1$ ,  $r_2$ ) and the Alfrey-Price  $Q$ ,  $e$  values were determined as follows:

$r_1 = 0.08$ ,  $r_2 = 0.24$ ,  $Q_1 = 0.86$ ,  $e_1 = 1.12$  in the MPMI-ST;

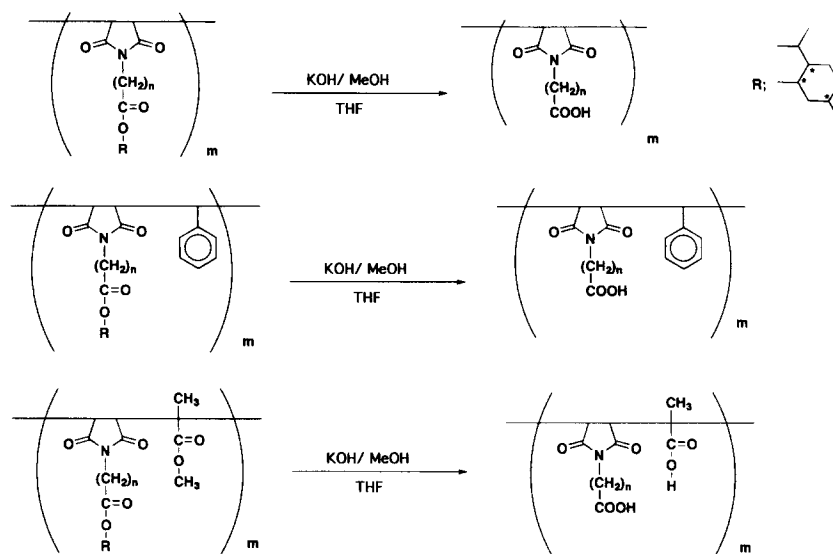
$r_1 = 0.62$ ,  $r_2 = 1.12$ ,  $Q_1 = 0.84$ ,  $e_1 = 1.00$  in the MPMI-MMA;

$r_1 = 0.43$ ,  $r_2 = 0.06$ ,  $Q_1 = 3.59$ ,  $e_1 = 1.11$  in the MUMI-ST; and

$r_1 = 0.51$ ,  $r_2 = 1.85$ ,  $Q_1 = 0.44$ ,  $e_1 = 0.65$  in the MUMI-MMA system.

(3) The specific rotations and molecular ellipticities for the copolymers were significantly influenced by the distance from the maleimide ring to the optically active group, i.e. length of the methylene units.





Scheme 2

(4) In the radical polymerizations of MPMI and MUMI, it was confirmed that a very little asymmetric induction in the polymer and copolymer main chains occurred from chirality of the hydrolysed polymers and copolymers.

#### ACKNOWLEDGEMENT

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