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Synthesis and polymerization of *N*-substituted maleimides based on L-alanine ester

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Four types of *N*-maleoyl-L-alanine esters [RAM; ester substituents: butyl (BAM), cyclohexyl (CHAM), phenyl (PHOAM) and naphthyl (NOAM)] were synthesized, and radically and anionically polymerized to obtain optically active polymers. Radical copolymerizations of RAM (M_1) with styrene (ST; M_2) or methyl methacrylate (MMA; M_2) were performed and monomer reactivity ratios and Alfrey–Price Q–e were determined. Chiroptical properties of the polymers and copolymers were significantly affected by *N*-substituents. This could be attributed to asymmetric induction into the polymer main chain. Chiroptical properties of the copolymers except for CHAM–MMA and BAM–MMA systems were strongly influenced by M_1–M_2 successive units and isolated M_1 units, but not M_1–M_1 successive units. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: asymmetric induction; asymmetric perturbation; *N*-substituted maleimide)

INTRODUCTION

Recently, asymmetric polymerizations were extensively, vigorously and systematically investigated by many groups[1–11]. The authors have been interested in asymmetric polymerizations of 1,2-disubstituted ethylene-type monomers, particularly *N*-substituted maleimide (RMI) since RMI has characteristic polymerization reactivity, i.e. RMI can afford two *trans*-openings of the double bond to produce stereogenic centres (*S,S*) and (*R,R*)[7]. Optical activity of poly(RMI) and the copolymer could be ascribed to a *threo-diisotactic* structure, which can arise from helical structures and/or from the excess of chiral stereogenic centers (*S,S*) or (*R,R*). From this point of view, the authors have systematically studied many optically active RMI[12–25]. In the radical homopolymerizations of *N*-maleoyl-L-phenylalanine alkyl ester (RPAM: *Scheme 1*), ester groups in the *N*-substituents can significantly influence asymmetric induction on the polymer main chain[23,24]. Especially in the polymerization of monomers bearing a bulky substituent, asymmetric induction took place more strongly in the polymer main chain. Radical copolymerizations of RPAM with styrene (ST) or methyl methacrylate (MMA) induced asymmetry into the polymer main chain. In the radical copolymerizations ester substituents influenced the reactivity, but scarcely affected chiroptical properties of the copolymers. The chiroptical properties were affected by comonomer units (ST or MMA units). RPAM has $\pi \rightarrow \pi^*$ chromophore in the monomeric unit itself.

In this paper, the authors synthesized optically active *N*-maleoyl-L-alanine ester [RAM; ester group: butyl (BAM), cyclohexyl (CHAM), phenyl (PHOAM) and naphthyl (NOAM)]. RAM was polymerized with radical or anionic initiators and copolymerized with styrene (ST) or methyl methacrylate (MMA). Monomer reactivity ratios and Alfrey–Price Q–e values were determined. Asymmetric induction into the polymer main chain and asymmetric perturbation by the side chain chromophores were discussed by comparing $[\alpha]_D$ and c.d. spectra of the polymers with those of the corresponding model compounds. The objective of this paper is to clarify polymerization reactivity of RAM and chiroptical properties of the polymers and copolymers obtained from RMI without $\pi \rightarrow \pi^*$ chromophores in the α-amino-acid unit.

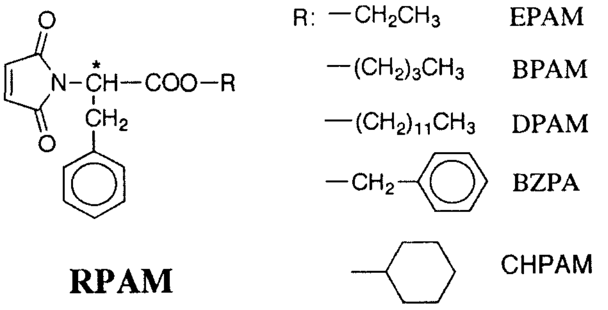
EXPERIMENTAL

Monomers

RAM were synthesized from maleic anhydride, L-alanine and, alcohols, as shown in *Scheme 2*.

N-*Maleoyl*-L-*alanine (AIM: precursor).* AIM was synthesized from maleic anhydride and L-alanine according to a previous paper[16]: yield 54.5% (based on AMI); m.p. 99–100°C; $[\alpha]_D = -24.3°$ ($c = 1.0$ g dl^{-1}, $l = 10$ cm, THF).

N-*Maleoyl*-L-*alanine butyl ester (BAM).* A mixture of AMI (9.0 g, 0.05 mol), butanol (16.2 g, 0.16 mol), and



RPAM

Scheme 1

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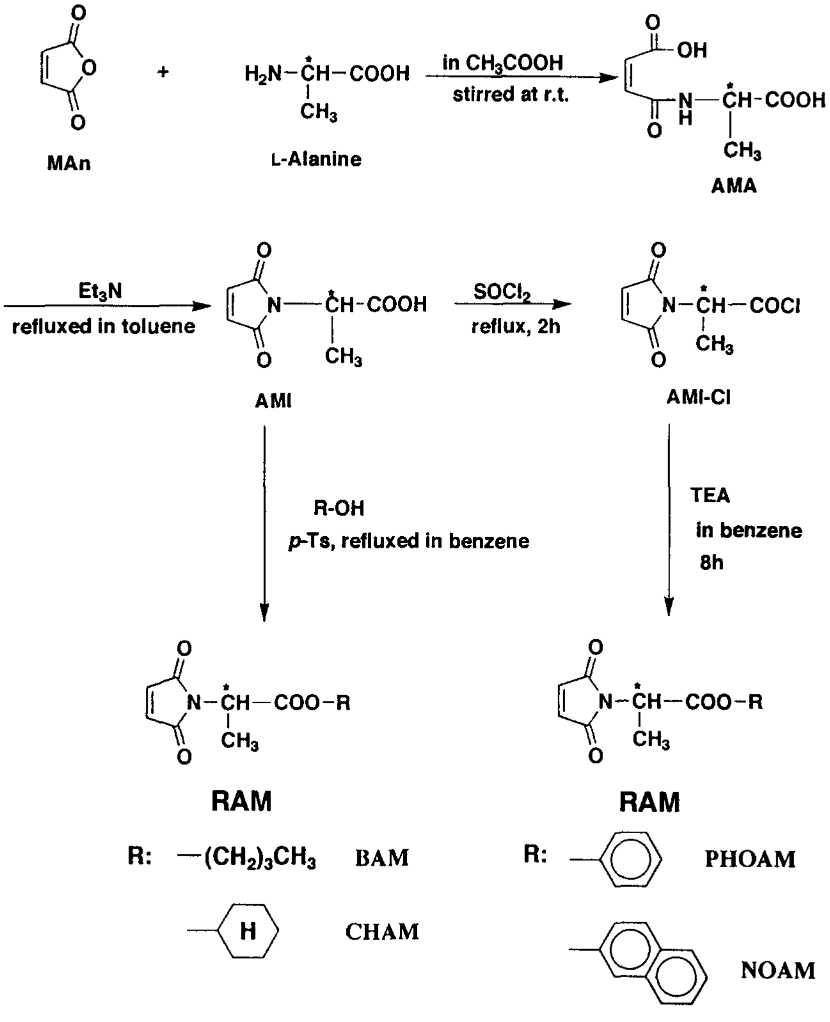


Scheme 2

p-toluene sulfonic acid (*p*-Ts; 0.9 g) in a benzene (50 ml) solution was refluxed for 15 h. After cooling to room temperature, the benzene solution was washed with sodium hydrocarboxide in an aqueous solution and water, dried on anhydrous magnesium sulfate, and evaporated to obtain crude BAM. The concentrate was distilled under reduced pressure to obtain pure BAM. Yield 48.3% (based on AMI); b.p. 91°C/3.6 × 10^{-2} mm Hg; $[\alpha]_D = -20.3°$ ($c = 1.0$ g dl^{-1}, l = 10 cm, THF); ^{1}H n.m.r. (δ in ppm from TMS in $CDCl_3$): 6.75 (s, 2H, CH=CH), 4.76 (gem, J = 14.85 Hz, 1H, CH*), 4.14 (t, J = 6.60 Hz, 2H, COO-CH_2–), 1.64–1.54 (m, 5H, C*-CH_3 and COO-CH_2-CH_2–), 1.40–1.27 (m, 2H, COO-CH_2-CH_2-CH_2–), 0.91(t, J = 7.26 Hz, 3H, CH_3 in butyl group). Elemental analysis. Found (%): C = 58.31; H = 6.70; N = 5.91. Calculated for $C_{11}H_{15}NO_4$ (%): C = 58.65; H = 6.71; N = 6.22.

N-*Maleoyl-*L*-alanine cyclohexyl ester (CHAM).* CHAM was synthesized from AMI and cyclohexanol according to the same method as that of BAM. Yield 52.4% (based on AMI); b.p. 132°C/7.0 × 10^{-2} mm Hg; $[\alpha]_D = -17.0°$ (c = 1.0 g dl^{-1}, l = 10 cm, THF); ^{1}H n.m.r. (δ in ppm from TMS in $CDCl_3$): 6.74 (s, 2H, CH=CH), 4.85–4.72 (m, 2H, CH* and COO–CH), 1.82–1.25 (m, 13H, C*–CH_3 and CH_2 in cyclohexyl group). Elemental analysis. Found (%): C = 61.63; H = 6.65; N = 5.04. Calculated for $C_{13}H_{17}NO_4$ (%): C = 62.13; H = 6.82; N = 5.58.

N-*Maleoyl-*L*-alaninyl chloride (AMI-Cl).* A mixture of AMI (10.0 g, 0.06 mol) and thionyl chloride (40 ml) was refluxed for 2 h. Unreacted thionyl chloride was evaporated out, and then residual product was distilled *in vacuo* to obtain pure AMI-Cl. Yield 75.7% (based on AMI); b.p. 74°C/6.8 × 10^{-2} mm Hg; ^{1}H n.m.r. (δ in ppm from TMS in $CDCl_3$): 6.91 (s, 2H, CH=CH), 5.07 (gem, J = 14.85 Hz, 1H, CH*), 1.82 (d, J = 7.25 Hz, 3H, C*–CH_3).

N-*Maleoyl-*L*-alanine phenyl ester (PHOAM).* A benzene (50 ml) solution of phenol (3.8 g, 0.04 mol) and triethylamine (TEA; 3.1 g, 0.03 mol) was added dropwise to a solution of AMI-Cl (6.2 g, 0.03 mol) in benzene (50 ml) at room temperature, and the mixture was refluxed for 8 h. After cooling to room temperature, the benzene solution was washed with hydrochloric acid aqueous solution and water, and dried on anhydrous magnesium sulfate. The solution was evaporated to obtain crude PHOAM. The residue was recrystallized twice from benzene to obtain pure PHOAM. Yield 23.3% (based on AMI-Cl); m.p. 74–76°C; $[\alpha]_D = -72.1°$ (c = 1.0 g dl^{-1}, l = 10 cm, THF); ^{1}H n.m.r. (δ in ppm from TMS in $CDCl_3$): 7.33–6.98 (m, 5H, phenyl group), 6.70 (s, 2H, CH=CH), 4.95 (gem, J = 15.4 Hz, 1H, CH*), 1.66 (d, J = 7.26 Hz, 3H, C*–CH_3). Elemental analysis. Found (%): C = 63.31; H = 4.60; N = 5.64. Calculated for $C_{13}H_{11}NO_4$ (%): C = 63.67; H = 4.25; N = 5.71.

N-*Maleoyl*-L-*alanine naphthyl ester (NOAM).* NOAM was prepared from TEA, AMI-Cl and 2-naphthol according to the same method as that of PHOAM. The residue was recrystallized twice from ethanol to obtain pure NOAM. Yield 27% (based on AMI-Cl); m.p. 115–117°C; $[\alpha]_D = -102.1°$ ($c = 1.0\ \mathrm{g\,dl^{-1}}$, $l = 10$ cm, THF); ^{1}H n.m.r. (δ in ppm from TMS in $CDCl_3$): 7.32–6.98 (m, 7H, naphthyl group), 6.69 (s, 2H, CH=CH), 4.95 (gem, J = 14.84 Hz, 1H, CH*), 1.66 (d, J = 7.26 Hz, 3H, C*–CH_3). Elemental analysis. Found (%): C = 69.29; H = 4.73; N = 4.73. Calculated for $C_{17}H_{13}NO_4$ (%): C = 69.10; H = 4.45; N = 4.74.

Model compounds of homopolymer

N-*Succinoyl*-L-*alanine butyl ester (BAS).* BAS was synthesized from succinic anhydride, L-alanine, and butanol according to a method similar to that of BAM. Yield: 68.4%; b.p. 122°C/0.12 mmHg; $[\alpha]_D = -41.5°$ ($c = 1.0\ \mathrm{g\,dl^{-1}}$, l = 10 cm, THF); ^{1}H n.m.r. (δ in ppm from TMS in $CDCl_3$): 4.80 (gem, J = 14.51 Hz, 1H, CH*), 4.15 (t, J = 6.60 Hz, 2H, COO–CH_2–), 2.75 (s, 4H, CH_2–CH_2 in imide ring), 1.64–1.56 (m, 5H, C*–CH_3 and COO–CH_2–CH_2–), 1.39–1.31 (m, 2H, COO–CH_2–CH_2–CH_2–), 0.93 (t, J = 7.26 Hz, 3H, CH_3 in butyl group). Elemental analysis. Found (%): C = 57.18; H = 7.36; N = 5.87. Calculated for $C_{11}H_{17}NO_4$ (%): C = 58.05; H = 7.61; N = 6.22.

N-*Succinoyl*-L-*alanine cyclohexyl ester (CHAS).* CHAS was synthesized from succinic anhydride, L-alanine, and cyclohexanol according to a method similar to that of CHAM. Yield: 54.0%; b.p. 150°C/0.16 mm Hg; $[\alpha]_D = -36.4°$ ($c = 1.0\ \mathrm{g\,dl^{-1}}$, l = 10 cm, THF); ^{1}H n.m.r. (δ in ppm from TMS in $CDCl_3$): 4.85–4.75 (m, 2H, CH* and COO–CH), 2.74 (s, 4H, CH_2–CH_2), 1.84–1.31 (m, 13H, C*–CH_3 and CH_2 in cyclohexyl group). Elemental analysis. Found (%): C = 60.55; H = 7.38; N = 5.37. Calculated for $C_{13}H_{19}NO_4$ (%): C = 61.64; H = 7.56; N = 5.53.

N-*Succinoyl*-L-*alanine phenyl ester (PHOAS).* PHOAS was synthesized from succinic anhydride, L-alanine, and phenol according to a method similar to that of PHOAM. Yield: 20.2%; m.p. 200–201°C; $[\alpha]_D = -94.4°$ ($c = 1.0\ \mathrm{g\,dl^{-1}}$, $l = 10$ cm, THF); ^{1}H n.m.r. (δ in ppm from TMS in $CDCl_3$): 7.56–7.21 (m, 5H, phenyl group), 5.19 (gem, J = 14.50 Hz, 1H, CH*), 2.95 (s, 4H, CH_2–CH_2), 1.81 (d, J = 7.26 Hz, 3H, C*–CH_3). Elemental analysis. Found (%): C = 65.71; H = 5.35; N = 5.86. Calculated for $C_{13}H_{13}NO_4$ (%): C = 63.67; H = 5.34; N = 5.71.

N-*Succinoyl*-L-*alanine naphthyl ester (NOAS).* NOAS was synthesized from succinic anhydride, L-alanine, and 2-naphthol according to a method similar to that of NOAM. Yield: 79.4%; m.p. 173–175°C; $[\alpha]_D = -117.6°$ ($c = 1.0\ \mathrm{g\,dl^{-1}}$, $l = 10$ cm, THF); ^{1}H n.m.r. (δ in ppm from TMS in $CDCl_3$): 7.79–7.12 (m, 7H, naphthyl group), 5.03 (gem, J = 14.50 Hz, 1H, CH*), 2.75 (s, 4H, CH_2–CH_2), 1.63 (d, J = 7.26 Hz, 3H, C*–CH_3). Elemental analysis. Found (%): C = 73.47; H = 5.31; N = 4.44. Calculated for $C_{17}H_{15}NO_4$ (%): C = 69.15; H = 5.12; N = 4.74.

Other materials

ST and MMA were purified by the ordinary methods[26]. Solvents were purified by the usual methods[27] just before use. 2,2′-Azobis(isobutyronitrile) (AIBN) was recrystallized from methanol. Commercially available *n*-butyllithium (*n*-BuLi), Kanto Chemical Co., Inc., in an *n*-hexane solution (1.55 $\mathrm{mol\,l^{-1}}$) was used without further purification.

Homopolymerization and copolymerization

Radical homopolymerizations and copolymerizations were performed with AIBN as a radical initiator in a sealed tube at 60°C. After polymerization, the polymer solution was poured into excess methanol to precipitate the polymer. The polymer was filtered, purified by reprecipitation twice from THF solution to excess methanol, and dried *in vacuo* for two days. The composition of the copolymer was determined by ^{1}H n.m.r. spectra and nitrogen analysis.

Anionic polymerizations were performed with *n*-BuLi as initiator in a Shlenk's reaction tube at 0°C. After polymerizations, the polymer solution was poured into excess methanol containing a few drops of dilute hydrochloric acid to precipitate the polymer. The polymer was treated by the same method as that of radical polymerizations.

Table 1 Radical and anionic polymerizations of RAM

Run No.	RAM	Monomer feed ($\mathrm{mol\,l^{-1}}$)	Initiator ($\times 10^{-2}\ \mathrm{mol\,l^{-1}}$)	Polymerization solvent[a] (ml)	Polymerization temperature (°C)	Polymerization time (h)	Yield[b] (%)	$\bar{M}_n^c$ $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$[c]	$[\alpha]_D^{25}$[d] (deg.)
1	BAM	1.16	AIBN(1.0)	BEN(2)	60	21	27.2	1.8	1.6	− 25.3
2	BAM	1.12	AIBN(2.0)	BEN(2)	60	21	21.2	0.5	2.1	− 25.5
3	CHAM	0.99	AIBN(1.0)	BEN(2)	60	29	69.2	1.3	2.7	− 15.1
4	CHAM	1.01	AIBN(2.0)	BEN(2)	60	29	73.9	0.8	3.0	− 16.0
5	NOAM	0.56	AIBN(2.0)	BEN(3)	60	24	54.1	0.5	1.7	− 76.2
6	PHOAM	1.00	AIBN(1.0)	BEN(2)	60	24	55.7	1.6	2.5	− 63.7
7	NOAM	0.56	AIBN(1.0)	BEN(3)	60	24	34.8	0.5	1.7	− 75.7
8	BAM	1.33	BuLi(2.2)	THF(2)	0	20	39.8	1.9	2.5	+ 48.3
9	BAM	1.13	BuLi(5.5)	THF(2)	0	20	13.3	2.7	2.6	+ 23.8
10	CHAM	1.01	BuLi(2.0)	THF(2)	0	20	31.4	0.7	1.5	− 28.6
11	CHAM	1.14	BuLi(4.9)	THF(2)	0	20	49.6	0.7	1.3	− 7.3
12	PHOAM	0.69	BuLi(3.5)	THF(3)	0	24	17.8	0.8	1.4	− 24.3
13	NOAM	0.57	BuLi(2.9)	THF(3)	0	24	32.9	0.7	1.5	− 43.0

[a] BEN: benzene; THF: tetrahydrofuran
[b] Insoluble in CH_3OH
[c] Determined by g.p.c.
[d] $c = 1.0\ \mathrm{g\,dl^{-1}}$, THF, l = 10 cm; error: ± 0.2°

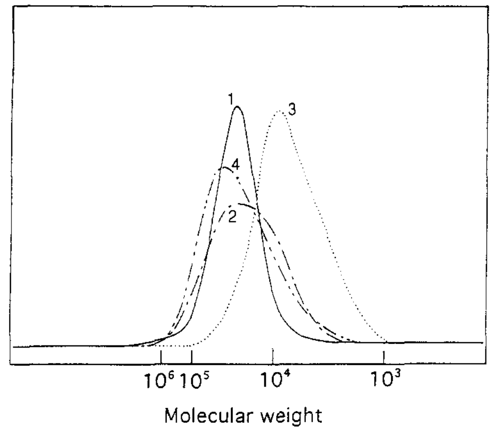


Figure 1 G.p.c. curves for poly(RAM) obtained with AIBN in benzene: (1) poly(BAM) (Run 1 in *Table 1*); (2) poly(CHAM) (Run 4 in *Table 1*); (3) poly(NOAM) (Run 5 in *Table 1*); and (4) poly(PHOAM) (Run 6 in *Table 1*)

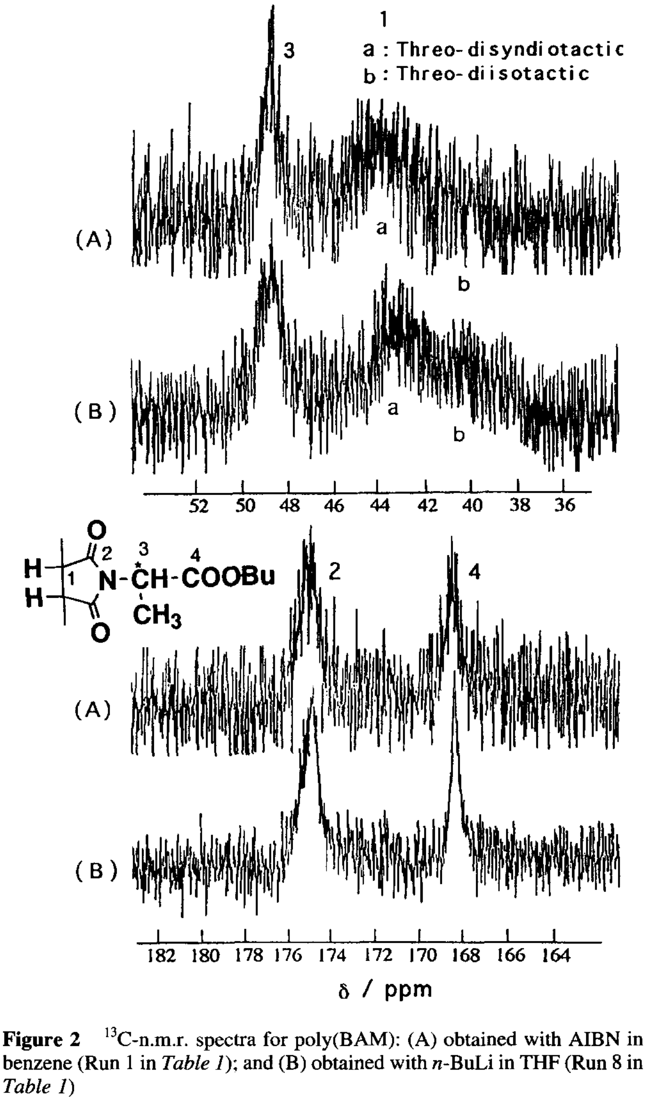


Figure 2 ^{13}C-n.m.r. spectra for poly(BAM): (A) obtained with AIBN in benzene (Run 1 in *Table 1*); and (B) obtained with *n*-BuLi in THF (Run 8 in *Table 1*)

Measurements

D-line-specific optical rotations were measured at 25°C in THF on a JASCO DIP-140 (Japan Spectroscopic Co.). 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 (quartz cell length: 0.1 and 1.0 mm; *ca.* 0.5–1.0 g dl^{-1} in THF).

Uultraviolet (u.v.) spectra were obtained with a Shimadzu UV 2200 spectrophotometer (quartz cell length: 1.0 mm and approximately 1.2×10^{-2}–4.0×10^{-2} g dl^{-1} in THF). Molecular weights of polymers were measured by gel permeation chromatography (g.p.c.) on Shimadzu LC 3A-equipped with a data processor and u.v. detector (Shimadzu SPD-10A), using THF as eluent and Shimadzu polystyrene gels HGS-10-15-20-40. N.m.r. spectra were recorded at 25°C with a JEOL EX-270 (JEOL Ltd.) instrument. Elemental analysis was carried out with a CHN recorder (Yanagimoto Co.).

RESULTS AND DISCUSSION

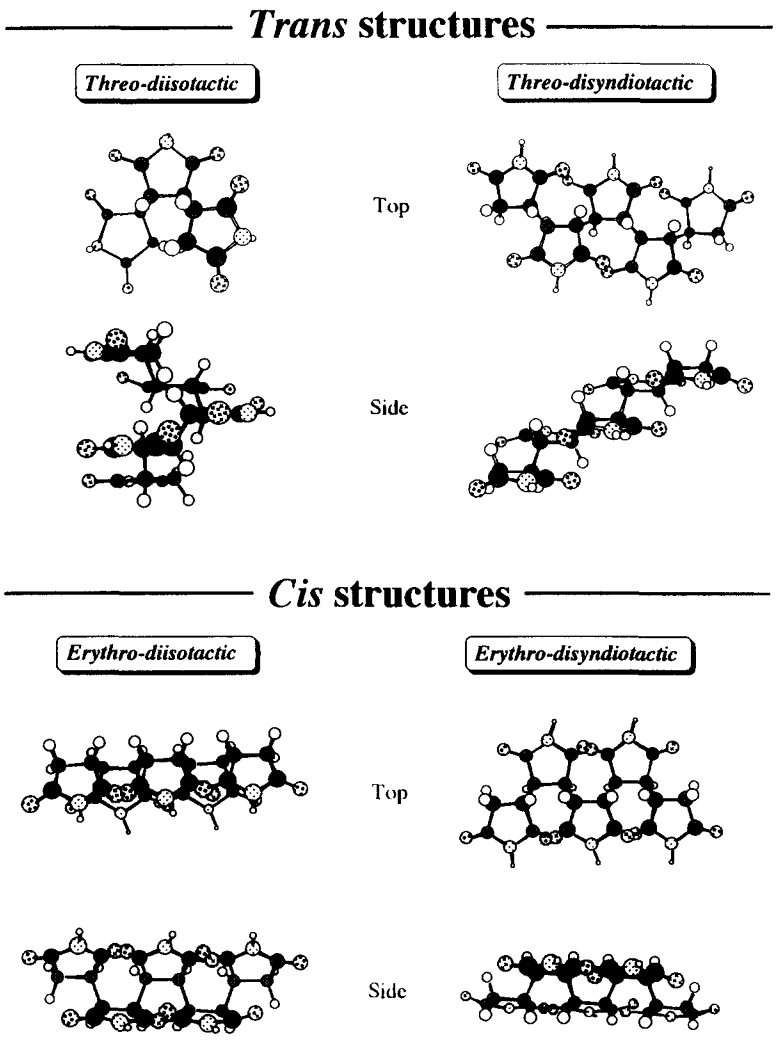
Homopolymerization of RAM

The results of the homopolymerizations of RAM are summarized in *Table 1*. All polymerizations proceeded homogeneously throughout, and the resulting polymers were soluble in ordinary polar solvents such as chloroform and THF.

In the radical polymerizations of RAM (runs 1–7 in *Table 1*), the number average molecular weight ($\bar{M}_n$) of poly(RAM) was 5×10^3 to 1.8×10^4 and relatively low. This tendency was similar to those for poly(RPAM) reported previously[23,24]. *Figure 1* shows g.p.c. curves of the polymers. The $\bar{M}_n$ of the poly(BAM), poly(CHAM) and poly(PHOAM) were similar, and one of the poly(NOAM) (curve 3 in *Figure 1*) was lower than those for other polymers. This may be attributed to the bulky ester substituent of a naphthyl group. The conversion of poly(RAM) was 21 to 73% and that of poly(BAM) was much lower than those for other poly(RAM). Such a tendency was similar to that in the polymerizabilities of RPAM[23,24], but the reason for this has not been clarified. Generally, the $\bar{M}_n$ values of the polymers obtained with lower concentration of AIBN initiator (1×10^{-2} mol l^{-1}) were higher than those with the AIBN concentration of 2×10^{-2} mol l^{-1}.

In anionic polymerizations of RAM (runs 8–13 in *Table 1*), yields were lower than those for the radical polymerizations. This tendency was also similar to that in the polymerizabilities of RPAM[23,24].

^{1}H and ^{13}C n.m.r. spectra of the polymers obtained from radical and anionic initiators were almost similar except for peaks assigned to the polymer main chain, as shown in *Figure 2*, which suggests that both polymers have almost similar structures, i.e. ordinary vinyl additions took place in both systems. All possible structures of poly(RMI) are shown in *Scheme 3*. Since RMI has a pentagonal plane structure with polymerizable double bond, RMI polymerizes not by *cis*-addition but by *trans*-addition due to steric hindrance. This is supported by ^{13}C n.m.r. spectral analysis[28–30] of the model compounds, as described below. At present *N*-substituted 3,4-dimethylsuccinimide can be regarded as the best model compound of poly(RMI). *N*-Phenyl-3,4-dimethylsuccinimide has two structures, i.e. *cis* and *trans* forms. Methine carbons of the *trans* form appeared at much lower magnetic field (42.4 ppm) than the *cis* form at 38.4 ppm[28]. Lately the authors investigated *cis–trans* isomerization of *N*-cyclohexyl-3,4-dimethylsuccinimide[29] (CHDMSI) and *N*-α-methylbenzyl-3,4-dimethylsuccinimide[30] (MBDMSI) in order to clarify δ values of model compounds in the ^{13}C n.m.r. measurement. From the results, signals assigned to methine carbons of *cis*-CHDMSI appeared at 37.7 ppm ($CDCl_3$) and those of



Scheme 3

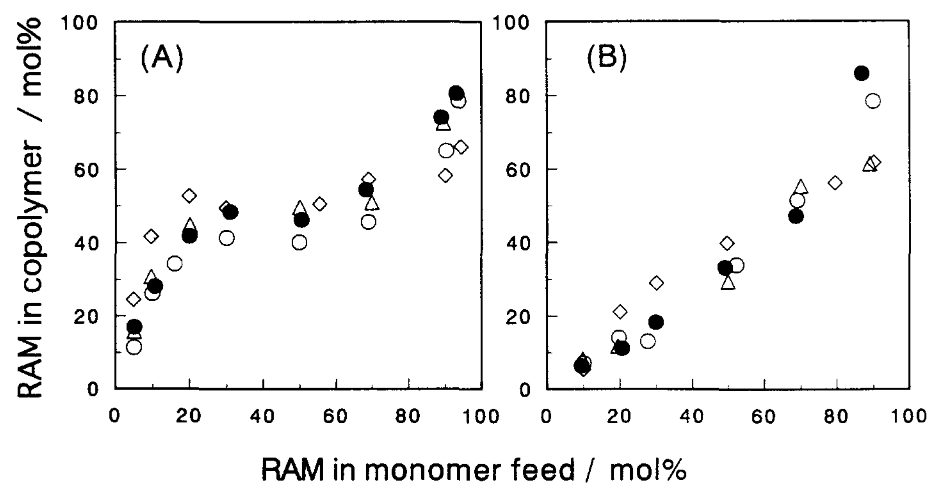


Figure 3 Copolymer composition curves for (A) RAM–ST and (B) RAM–MMA systems: RAM = (○) BAM; (●) CHAM; (△)PHOAM; and (◇) NOAM

trans-CHDMSI at 42.7 ppm ($CDCl_3$). As to MBDMSI, the methine carbon of the *cis*-form appeared at 37.4 ppm and the *trans*-form at 41.9 ppm.

In addition, Cubbon reported that eight types of RMI were polymerized by radical initiators and *n*-BuLi to produce the polymers with predominantly *threo-diisotactic* structures[31]. In this study, with respect to slightly different peaks due to the main chain, as shown in *Figure 2*, *threo-diisotactic* and *threo-disyndiotactic* structures should be considered. There were no peaks above 38 ppm, which suggests that the polymerization of RAM proceeded through not *trans*-addition rather *cis*-addition. In the ^{13}C n.m.r. spectrum of the polymer prepared with radical initiator a broad peak having a maximum at 44.5 ppm was observed

Table 2 Radical copolymerization of RAM (M_1) with ST (M_2) in benzene (2 ml) at 60°C[a]

Run	M_1	M_1 in monomer (mol%)	Polymerization time (h)	Yield[b] (%)	M_1 in copolymer[c] (mol%)	$\bar{M}_n$[d] $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$[d]	$[\alpha]_D^{25}$[e] (deg.)
A-1	BAM	5.0	11.5	27.6	11.4	3.3	3.1	− 6.5
A-2		10.0	5.7	33.3	26.2	5.6	3.4	− 9.4
A-3		16.1	2.5	35.8	34.4	15.7	3.2	− 10.3
A-4		30.0	2.0	55.9	41.4	20.8	3.4	− 12.0
A-5		49.8	2.0	68.3	40.1	27.9	3.5	− 13.3
A-6		68.9	2.5	47	45.7	17.5	3.5	− 15.6
A-7		90.3	6.7	31.2	65.0	1.7	5.3	− 24.8
A-8		93.8	11.5	37.1	78.2	1.5	2.6	− 25.6
B-1	CHAM	5.2	9.0	21.3	17.0	3.6	2.1	− 5.4
B-2		10.6	6.0	30.3	28.2	3.7	3.5	− 8.3
B-3		20.2	2.0	16.5	41.9	10.5	2.7	− 7.0[f]
B-4		31.1	2.0	27.4	39.6	13.2	2.8	− 8.8
B-5		50.6	1.5	28.5	46.3	18.5	2.8	− 9.1
B-6		70.1	2.0	39.6	54.8	13.2	3.3	− 11.1
B-7		85.0	9.0	46.8	74.2	1.6	5.9	− 15.0
B-8		88.4	11.3	70.1	72.6	0.8	4.2	− 15.5
C-1	PHOAM	5.0	24.0	39.2	15.7	2.3	3.1	− 14.6
C-2		9.7	8.9	41.4	30.8	4.8	3.6	− 31.7
C-3		20.0	1.4	34.0	44.7	22.8	1.5	− 42.5
C-4		50.0	1.4	54.6	49.6	23.8	1.4	− 46.0
C-5		69.9	1.9	48.0	50.9	15.4	1.8	− 50.1
C-6		89.6	24.0	30.0	72.4	3.1	3.0	− 56.2
D-1	NOAM	4.8	10.5	35.5	24.5	3.3	3.2	− 27.7
D-2		9.4	7.5	52.7	41.7	5.0	2.9	− 44.6
D-3		19.7	2.0	48.2	52.8	21.8	1.6	− 57.8
D-4		29.8	1.7	56.9	49.6	23.5	1.6	− 63.3
D-5		55.4	3.0	47.5	50.6	23.8	1.7	− 67.8
D-6		69.0	8.3	9.7	57.3	17.5	1.9	− 69.6[f]
D-7		90.0	8.3	30.4	58.3	1.1	3.9	− 79.4
D-8		94.3	12.7	24.6	66.1	0.9	1.9	− 74.5

[a] [AIBN] = 1.0×10^{-2} mol l^{-1}; $M_1 + M_2 = 0.5$ g
[b] Insoluble in CH_3OH
[c] Determined by ^1H n.m.r. and *N*-analysis; error: ±2.7 mol%.
[d] Determined by g.p.c.
[e] $c = 1.0$ g dl^{-1}, $l = 10$ cm, THF; error: ±0.2°
[f] $c = 1.0$ g dl^{-1}, $l = 5$ cm, THF; error: ±0.4°

over the range from 40 ppm to 46 ppm, which was assigned to *trans*-addition[29,30]. The reason for the broad peak could be attributed to the fact that the polymer consists of a mixture of *threo-diisotactic* and *threo-disyndiotactic* structures.

Radical copolymerizations of RAM with ST or MMA

The results of the radical copolymerizations of RAM (M_1) with ST (M_2) and MMA (M_2) are summarized in *Tables 2* and *3*, respectively. All copolymerizations proceeded homogeneously throughout. The copolymers were white powders and optically active. Generally, $\bar{M}_n$ values of the copolymers were much higher than those of homopolymers. $\bar{M}_n$ values of poly(RAM-*co*-ST)s were 8.0 × 10^3 to 2.79 × 10^5 and poly(RAM-*co*-ST) consisting of composition of near to 50 mol% RAM exhibited relatively higher $\bar{M}_n$. The $\bar{M}_n$ values of poly(RAM-*co*-ST)s were greater than those of poly(RAM-*co*-MMA)s. In contrast to the homopolymerization of NOAM, there was little obvious influence of ester substituents with respect to the $\bar{M}_n$, i.e.

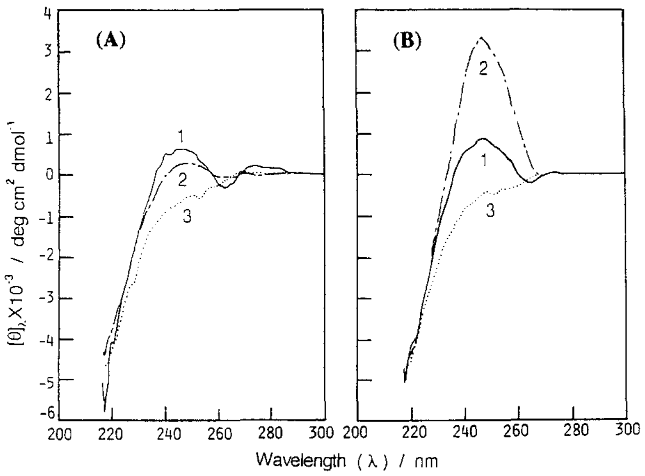


Figure 4 C.d. spectra for RAM: (A) (1) poly(CHAM) obtained with AIBN (Run 4 in *Table 1*), (2) poly(CHAM) obtained with *n*-BuLi (Run 11 in *Table 1*), and (3) model compounds of poly(CHAM); and (B) (1) poly(BAM) obtained with AIBN (Run 1 in *Table 1*), (2) poly(BAM) obtained with *n*-BuLi (Run 8 in *Table 1*) and (3) model compounds of poly(BAM)

Table 3 Radical copolymerizations of RAM (M_1) with MMA (M_2) in benzene (2 ml) at 60°C[a]

Run	M_1	M_1 in monomer (mol%)	Polymerization time (h)	Yield[b] (%)	M_1 in copolymer[c] (mol%)	$\bar{M}_n$[d] $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$[d]	$[\alpha]_D^{25}$[e] (deg.)
E-1	BAM	10.2	5.3	31.4	7.1	5.5	2.3	− 5.7
E-2		19.8	5.3	26.2	14.0	3.1	3.9	− 10.8
E-3		27.8	6.8	33.6	13.0	4.2	2.7	− 14.3
E-4		52.4	7.0	26.0	33.9	0.7	1.2	− 23.3
E-5		69.1	7.0	38.8	51.5	1.9	2.5	− 28.4
E-6		90.0	9.3	13.8	78.4	1.3	1.7	− 29.7[f]
F-1	CHAM	9.6	6.0	29.0	6.4	2.6	5.3	− 3.4
F-2		20.7	6.0	26.0	11.2	6.1	2.6	− 8.1
F-3		30.1	7.0	24.0	18.2	1.5	7.3	− 12.7
F-4		49.3	7.0	25.4	33.1	3.0	4.4	− 19.1
F-5		68.8	7.7	34.0	47.2	3.1	3.1	− 23.4
F-6		87.1	11.7	46.4	85.9	1.6	2.6	− 19.1
G-1	PHOAM	9.9	5.0	20.9	8.1	4.8	2.8	− 9.2
G-2		19.5	5.0	34.7	11.6	5.6	2.6	− 22.5
G-3		50.0	5.5	26.0	29.2	7.0	2.2	− 38.3
G-4		70.0	5.5	55.2	55.2	3.4	4.3	− 55.4
G-5		89.0	6.0	19.1	61.3	2.8	2.9	− 55.2
H-1	NOAM	10.0	6	42.8	5.5	4.2	2.1	− 17.5
H-2		20.0	6.3	31.1	8.6	6.1	1.6	− 30.8
H-3		30.1	6.3	43.7	17.7	2.9	2.8	− 43.4
H-4		49.6	7	54.0	39.8	3.2	2.4	− 63.2
H-5		79.4	8.3	36.8	56.2	1.2	2.8	− 76.7
H-6		90.1	9	24.9	61.8	0.7	2.3	− 80.2

[a] $[AIBN] = 1.0 \times 10^{-2}$ mol l^{-1}; $M_1 + M_2 = 0.5$ g
[b] Insoluble in CH_3OH
[c] Determined by ^1H n.m.r. and *N*-analysis; error: ± 2.7 mol%
[d] Determined by g.p.c.
[e] $c = 1.0$ g dl^{-1}, $l = 10$ cm, THF; error: ± 0.2°
[f] $c = 1.0$ g dl^{-1}, $l = 5$ cm, THF; error: ± 0.4°

Table 4 Monomer reactivity ratios and Alfrey–Price *Q–e* values

M_1	M_2	r_1	r_2	Q_1	e_1
BAM	ST	0.001	0.21	0.46	2.13
CHAM	ST	0.06	0.11	1.45	1.43
PHOAM	ST	0.05	0.04	3.56	1.69
NOAM	ST	0.007	0.004	19.7	2.44
BAM	MMA	0.20	1.76	0.63	1.42
CHAM	MMA	0.46	1.95	0.43	0.73
PHOAM	MMA	0.07	1.54	0.88	1.91
NOAM	MMA	0.03	1.99	0.74	2.09

poly(NOAM-*co*-ST) and poly(NOAM-*co*-MMA) exhibited $\bar{M}_n$ similar to those for the other poly(RAM-*co*-ST) and poly(RAM-*co*-MMA).

Copolymer composition curves for the copolymerizations of RAM(M_1) with ST(M_2) or MMA(M_2) are shown in *Figure 3A* and *B*. *Table 4* shows monomer reactivity ratios (r_1, r_2) calculated from the high-conversion method reported by Tüdös *et al.*[32] * and Alfrey and Price[33] *Q–e*. The *Q* and *e* calculated from ST systems indicated very high values, which may be due to the formation of a charge transfer (CT) complex[34,35]. This tendency was observed in the copolymerization of ST and maleic anhydride[36]. On the whole, copolymerization parameters for RAM were similar to those for other RMI reported previously[12–25]. This suggests that ester substituents in RAM hardly influence copolymerization reactivity.

Chiroptical properties of homopolymers

RAM could exhibit similar Cotton effects since they contain the same chiral L-alanine residue. Both c.d. spectra of poly(CHAM) and poly(BAM) exhibited Cotton effects based on the $n-\pi^*$ transitions at 220 and 250 nm, as shown in *Figure 4*. The c.d. spectrum of the polymer obtained with *n*-BuLi was different from those for poly(CHAM) obtained by the radical polymerization (1 in *Figure 4A*). This tendency was also observed with BAM (*Figure 4B*). In addition, c.d. spectra of the polymers differed from that of the corresponding model compound, which suggests that asymmetric induction took place into the polymer backbone. Poly(PHOAM) and poly(NOAM) also showed Cotton effects based on the $n-\pi^*$ and $\pi-\pi^*$ transitions at 220 and 250 nm, as shown in *Figure 5*. Thus, it is considered that differences of c.d. spectra were due to different main chain structures. Poly(RAM) and poly(CHAM) without $\pi-\pi^*$ chromophore exhibited relatively lower molecular ellipticity than poly(PHOAM) and poly(NOAM) with the $\pi-\pi^*$ chromophore. In both systems, poly(RAM) with or without the $\pi-\pi^*$ chromophore exhibited different c.d. spectra at about 250 nm. In the anionic polymerizations of both systems, c.d. spectra were different. Thus, it was found that

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* Reactivity ratios were determined by Method 6 described in this article

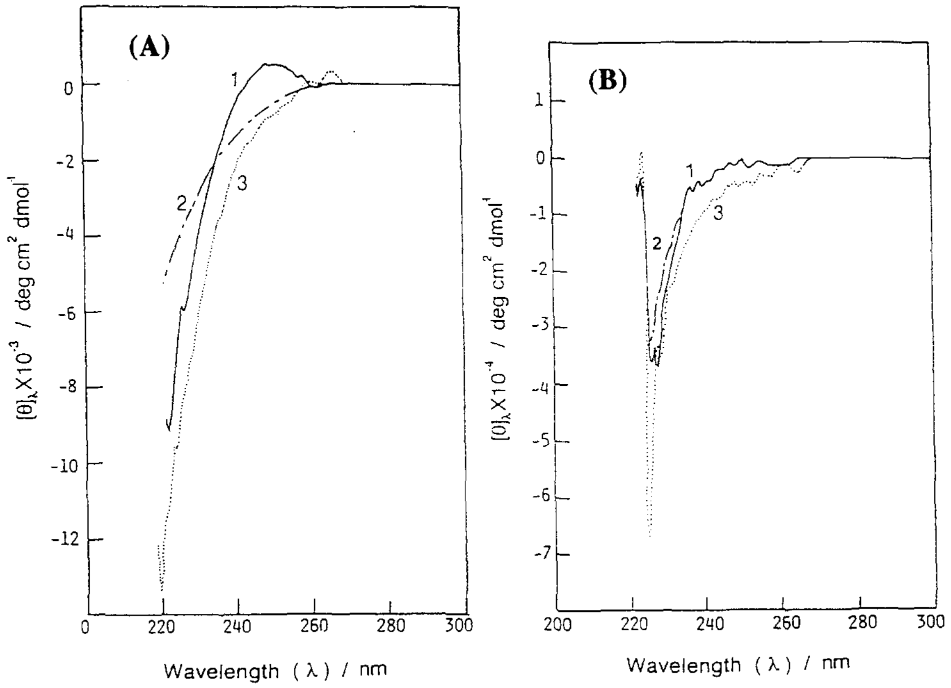

Figure 5 C.d. spectra for RAM: (A) (1) poly(PHOAM) obtained with AIBN (Run 6 in *Table 1*), (2) poly(PHOAM) obtained with *n*-BuLi (Run 12 in *Table 1*) and (3) model compounds for poly(PHOAM); and (B) (1) poly(NOAM) obtained with AIBN (Run 5 in *Table 1*), (2) poly(NOAM) obtained with *n*-BuLi (Run 13 in *Table 1*) and (3) model compounds for poly(NOAM)

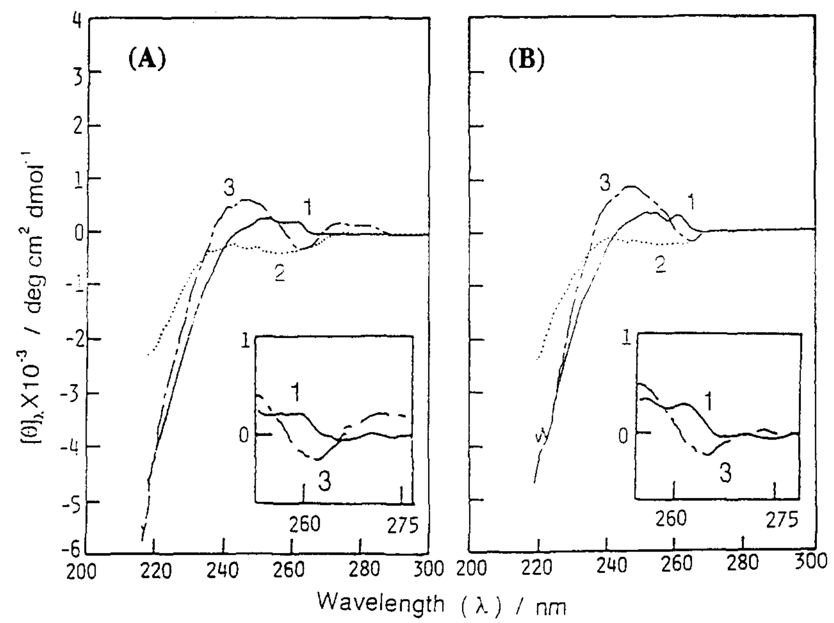

Figure 6 C.d. spectra for RAM copolymers: (A) (1) poly(CHAM-*co*-ST) (Run B-8 in *Table 2*), (2) poly(CHAM-*co*-MMA) (Run F-6 in *Table 3*) and (3) poly(CHAM) (Run 4 in *Table 1*) obtained with AIBN; and (B) (1) poly(BAM-*co*-ST) (Run A-5 in *Table 2*), (2) poly(BAM-*co*-MMA) (Run E-5 in *Table 3*) and (3) poly(BAM) (Run 1 in *Table 1*) obtained with AIBN

Table 5 Specific rotations ($[\alpha]_D^{25}$) for monomers, model compounds and homopolymers

	Monomer (deg.)	Model compound (deg.) *A*	Homopolymer[a] (deg.) *B*	$(\|B\| - \|A\|)/\|A\|$
BAM	− 20.3	− 41.5	− 25.3	0.585
CHAM	− 17.0	− 36.4	− 15.1	0.390
PHOAM	− 72.1	− 94.4	− 63.7	0.356
NOAM	− 120.1	− 117.6	− 75.7	0.325

[a] Obtained with AIBN

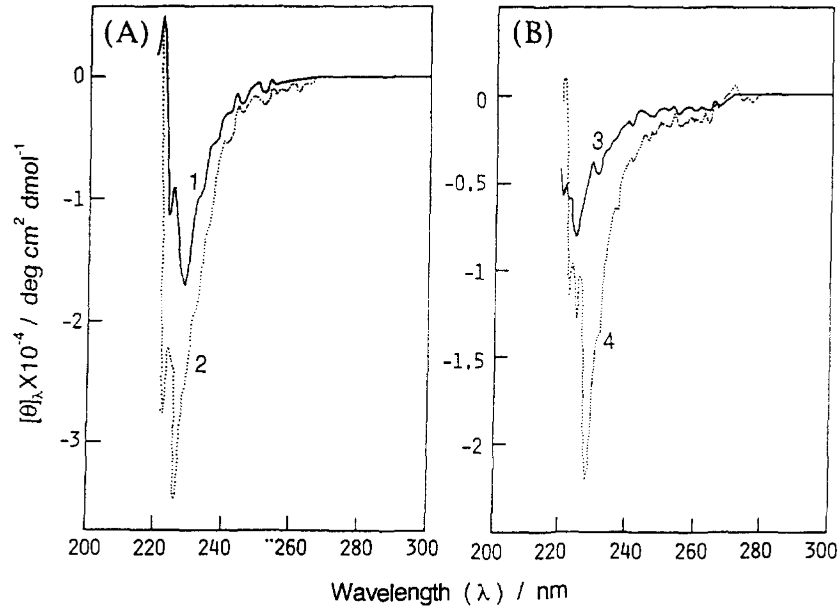

Figure 7 C.d. spectra for RAM copolymers: (A) (1) poly(PHOAM-*co*-ST) (Run C-2 in *Table 2*) and (2) poly(PHOAM-*co*-ST) (Run C-6 in *Table 3*); and (B) (3) poly(PHOAM-*co*-MMA) (Run G-3 in *Table 3*) and (2) poly(PHOAM-*co*-MMA) (Run G-5 in *Table 3*)

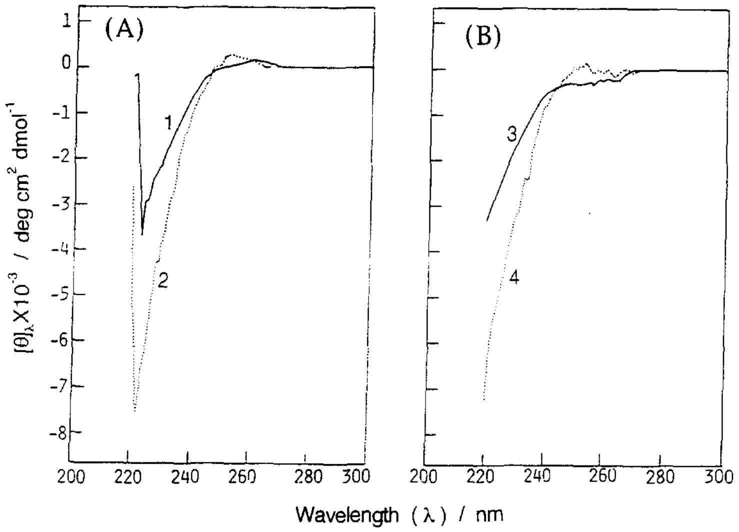

Figure 8 C.d. spectra for RAM copolymers: (A) (1) poly(NOAM-*co*-ST) (Run D-2 in *Table 2*) and (2) poly(NOAM-*co*-ST) (Run D-4 in *Table 3*); and (B) (3) poly(NOAM-*co*-MMA) (Run H-2 in *Table 3*) and (2) poly(NOAM-*co*-MMA) (Run H-4 in *Table 3*)

chiroptical properties of the poly(RAM) were remarkably affected by the presence of the $\pi-\pi^*$ chromophore.

Table 5 summarizes specific rotations $[\alpha]_D^{25}$ of the monomers, the model compounds of the polymers, and the polymers obtained by radical polymerizations in benzene. The ratio $[(B - A)/A]$ represents to what extent chirality of the polymers differed from that of the model compound. A difference between the polymer and the model compound suggests the occurrence of asymmetric induction in the backbone. The order of the ratio was CHAM > NOAM > BAM > PHOAM. CHAM, which bears a bulky cyclohexyl group, had a greater value than BAM, which has a linear butyl ester group, where neither has the $\pi-\pi^*$ chromophore. On the other hand, NOAM, with a bulkier naphthyl group, had a slightly greater value than PHOAM. It seems that the value is concerned with bulkiness of ester groups. The order suggests that bulkiness of *N*-substituents may be advantageous for asymmetric induction in ordinary radical polymerizations as well as RPAM[23,24]. In addition, in the case of RAM, asymmetric induction may depend on the presence or absence of the $\pi-\pi^*$ chromophore.

In the poly(CHAM) and poly(BAM) without the $\pi-\pi^*$ chromophore, chiroptical properties were significantly affected by the occurrence of asymmetric induction more than asymmetric perturbation based on the $n-\pi^*$ chromophore. In the poly(PHOAM) and poly(NOAM) having the $\pi-\pi^*$ chromophore, chiroptical properties were affected by asymmetric perturbation due to the chromophore more than the occurrence of asymmetric induction.

Chiroptical properties of copolymers

Figure 6 shows c.d. spectra of the CHAM and BAM system copolymers. In both the ST and MMA systems, c.d. patterns did not differ even though composition of the copolymers varied. In the CHAM and BAM systems, a negative Cotton effect at about 220 nm and a positive

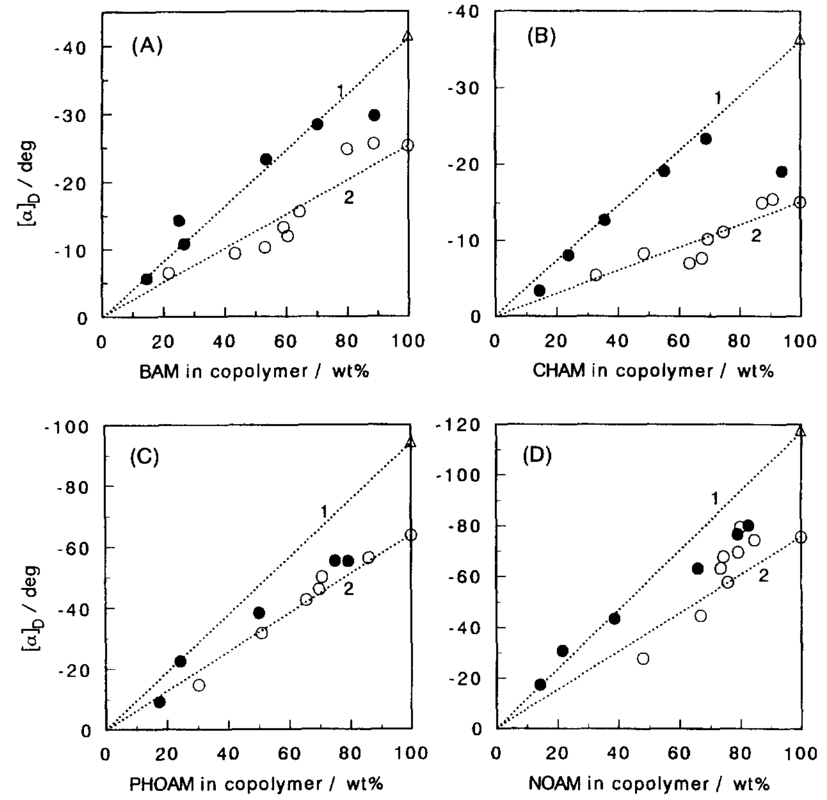

Figure 9 Relationships between specific rotations ($[\alpha]_D$) and RAM contents (wt%) in copolymer: RAM = (A) BAM, (B) CHAM, (C) PHOAM, and (D) NOAM; (○) poly(RAM-*co*-ST) and (●) poly(RAM-*co*-MMA)

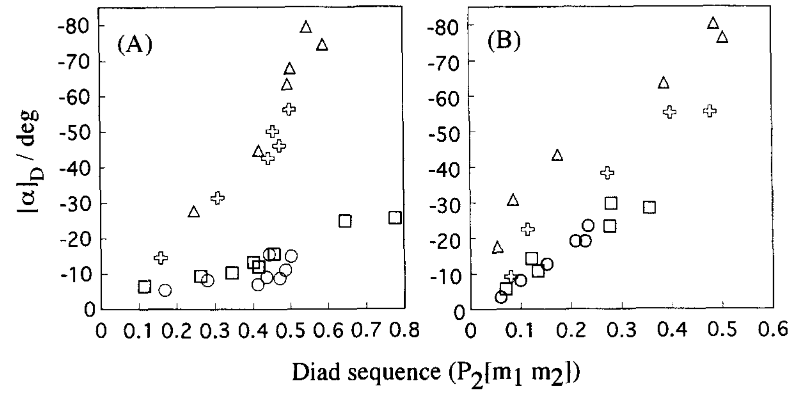

Figure 10 Relationship between $[\alpha]_D$ and a RAM–ST, a RAM–MMA diad sequence $P_2[m_1m_2]$ of (A) RAM–ST and (B) RAM–MMA copolymers: (□) BAM, (○) CHAM, (✥) PHOAM, and (△) NOAM

Cotton effect at about 250 nm were observed as well as in the homopolymers. However, the c.d. patterns at the range from 260 to 270 nm for the poly(RAM-*co*-ST) were different from those of the homopolymers (curves 3), as drawn in the expanded figures. This is attributed to the $\pi-\pi^*$ chromophore of the ST unit. In the MMA copolymers (curves 2) there were no c.d. peaks over the range from 250 to 270 nm.

The PHOAM–ST copolymer exhibited a large negative and a very small positive c.d. peak at about 220 nm and the range from 250 to 260 nm, respectively, as shown in *Figure 7*. This pattern was similar to that of the polymers obtained by radical polymerizations. On the other hand, all the PHOAM–MMA copolymers also exhibited a negative Cotton effect at 220 nm. However, the c.d. peak at about 250–260 nm changed from negative to positive with an increase of the M_1 content in the copolymer.

In both NOAM–ST and NOAM–MMA systems, the c.d. patterns were not different as the composition of the copolymers varied, as shown in *Figure 8*. The molecular ellipticity $[\theta]$ was greater than those for CHAM, BAM and PHOAM copolymers. In both systems, a negative Cotton effect was observed, which was in agreement with that of the homopolymer.

Figure 9 shows the relationship between $[\alpha]_D$ and RAM content (wt%) in the copolymer. A dotted line (1) depicts a relationship in which no asymmetric induction takes place in the copolymers because the line (1) was connected to the $[\alpha]_D$ of the model compound (Δ) with zero. A dotted line (2) indicates a relationship in which chiroptical properties of the copolymers were affected by the *co*-unit such as ST or MMA because the line (2) was connected to the $[\alpha]_D$ of the homopolymer (○ at 100 wt%) with zero. The $[\alpha]_D$ of the copolymers showed

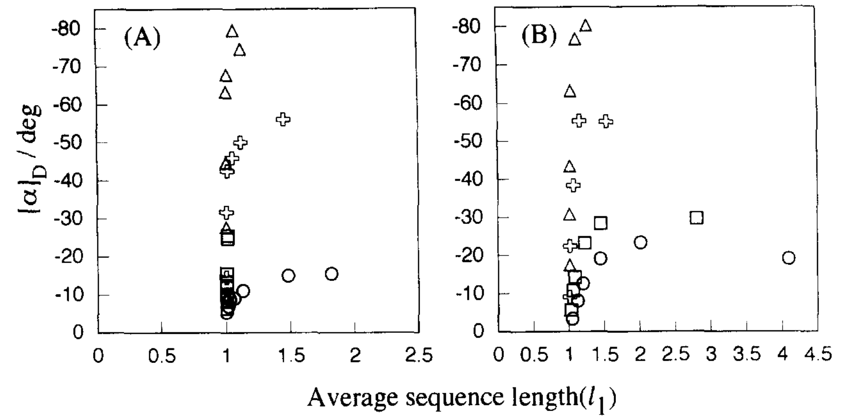

Figure 11 Relationship between $[\alpha]_D$ and average sequence length (l_1) of RAM in (A) RAM–ST and (B) RAM–MMA copolymers: (□) BAM, (○) CHAM, (✥) PHOAM, and (△) NOAM

deviation from these straight lines. In the radical copolymerizations of RMI, the authors reported[22] that effects of asymmetric induction on chiroptical properties were very small. Thus, it is considered that such deviation was mostly attributed to asymmetric perturbation caused by the *co*-units.

As can be seen from *Figure 9*, in all cases, generally speaking, incorporation of large amounts of optically active monomer RAM results in higher optical activity of the copolymer. For the RAM–MMA systems, the deviation of the specific rotation from the theoretical lines (2) seems larger at higher ratio of optically active monomer RAM (wt%), but this tendency is not clearly seen for the RAM–ST systems.

Figure 10 shows the dependence of a diad sequence[37,38] $P_2[m_1m_2]$ on specific rotations of the copolymers. The $P_2[m_1m_2]$ value indicates the probability of a RAM–ST or a RAM–MMA diad sequence. $P_2[m_1m_2]$ was derived as follows:

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

$$P_2[m_1m_2] = P_1[m_1]P(m_1m_2)$$

$$P(m_1m_2) = 1/(1 + r_1X)$$

where $P_1[m_1]$ and $P_1[m_2]$ are the molar fraction of the copolymer, $P(m_1m_2)$ is given by the monomer ratio in the feed ($X = [M_1]/[M_2]$), and r_1 is the monomer reactivity ratio of RAM. The term $1 + r_1X$ indicates an average sequence length (l_1) of M_1. As can be seen from *Figure 10*, for ST (*Figure 10A*) and MMA (*Figure 10B*) systems, specific rotations of the copolymers increased linearly with an increasing number of diad sequences $P_2[m_1m_2]$. This suggests that chiroptical properties of the copolymers were strongly influenced by M_1–M_2 successive units.

Specific rotations of the copolymers were generally independent of the average sequence length (l_1) of RAM except for BAM–MMA and CHAM–MMA copolymers, as shown in *Figure 11*. This suggests that chiroptical properties of the copolymers were practically influenced not by M_1–M_1 successive units but by isolated M_1 units. For the BAM–MMA and CHAM copolymer systems, the specific rotation slightly increased with the average sequence length (l_1), which suggests that the chiroptical properties of the copolymers were slightly influenced by M_1–M_1 successive units. The relatively large deviation for the BAM–MMA and CHMI–MMA systems shown in *Figure 9* could be ascribed to the M_1–M_1 successive units.

CONCLUSIONS

(1) Four types of *N*-substituted maleimide polymers bearing an optically active L-alanine ester (RAM) were synthesized. Polymerizabilities of RAM increased with decreasing steric hindrance of ester groups.
(2) From the results of radical copolymerizations of RAM (M_1) with ST (M_2) or MMA (M_2), the monomer reactivity ratios (r_1, r_2) and the Alfrey–Price *Q–e* values were determined.
(3) Chiroptical properties of the polymers and copolymers were significantly affected by *N*-substituents. This could be attributed to asymmetric induction into the polymer main chain.
(4) Chiroptical properties of the copolymers, except those for CHAM–MMA and BAM–MMA systems, were strongly influenced by M_1–M_2 successive units and isolated M_1 units, but not by M_1–M_1 successive units.

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REFERENCES

1. Okamoto, Y. and Nakano, T., *Chem. Rev.*, 1994, **94**, 349.
2. Nakano, T., Shikisai, Y. and Okamoto, Y., *Polym. J.*, 1996, **28**, 51.
3. Choi, S., Yashima, E. and Okamoto, Y., *Macromolecules*, 1996, **29**, 1880.
4. Wulff, G. CHEMTECH, 1991, p. 364.
5. Wulff, G., *Angew. Chem., Int. Engl.*, 1989, **28**, 21.
6. Wulff, G. and Gladow, S., *Macromol. Chem. Phys.*, 1995, **196**, 3341.
7. Farina, M., *Top. Stererochem.*, 1989, **17**, 1.
8. Kakuchi, T., Haba, O., Fukui, N., Uesaka, T., Obata, M., Morimoto, Y. and Yokota, K., *Polymer*, 1997, **37**, 5703.
9. Kakuchi, T., Haba, O., Uesaka, T., Obata, M., Morimoto, Y. and Yokota, K., *Macromolecules*, 1996, **29**, 3812.
10. Angiolini, L., Caretti, D., Calini, C. and Salatelli, E., *Polymer*, 1995, **36**, 1071.
11. De, B. B., Sivaram, S. and Dhal, P. K., *Polymer*, 1992, **33**, 1756.
12. Oishi, T. and Fujimoto, M., *J. Polym. Sci. Polym. Chem. Ed.*, 1984, **22**, 2789.
13. Oishi, T., Kamori, A. and Fujimoto, M., *J. Macromol. Sci. Pure Appl. Chem.*, 1992, **A29**, 231.
14. Oishi, T. and Fujimoto, M., *J. Polym. Sci., Part A: Polym. Chem.*, 1992, **30**, 1821.
15. Oishi, T., Otsubo, Y. and Fujimoto, M., *Polym. J.*, 1992, **24**, 527.
16. Oishi, T., Matsusaki, K. and Fujimoto, M., *Polym. J.*, 1992, **24**, 1281.

17. Oishi, T., Kagawa, K. and Fujimoto, M., *Macromolecules*, 1993, **26**, 24.
18. Oishi, T., Kagawa, K. and Fujimoto, M., *Polym. J.*, 1993, **25**, 977.
19. Oishi, T., Kagawa, K. and Fujimoto, M., *Polymer*, 1993, **34**, 2644.
20. Oishi, T., Morikawa, H., Matsusaki, K. and Fujimoto, M., *Polym. J.*, 1994, **26**, 1332.
21. Kagawa, K., Oishi, T., Matsusaki, K. and Fujimoto, M., *Polymer*, 1995, **36**, 941.
22. Oishi, T., Kagawa, K. and Fujimoto, M., *J. Polym. Sci., Part A: Polym. Chem.*, 1995, **33**, 1341.
23. Kagawa, K. and Oishi, T., *Polym. J.*, 1995, **27**, 579.
24. Kagawa, K. and Oishi, T., *Polym. J.*, 1996, **28**, 1.
25. Oishi, T., Kagawa, K. and Nagata, H., *Polymer*, 1997, **38**, 1461.
26. Otsu, T. and Kinoshita, M., *Koubunshigousei no Jikkenhou.* Kagakudojin, Kyoto, 1972, pp. 69–91.
27. Riddick, J. A., Bunger, W. B. and Sakano, T. K., *Organic Solvent.* John Wiley and Sons, New York, 1986.
28. Olson, K. G. and Butler, B., *Macromolecules*, 1984, **17**, 2480.
29. Onimura, K., Tsutsumi, H. and Oishi, T., *Polym. Bull.*, 1997, 1997, **39**, 437.
30. Oishi, T., Fujii, K., Onimura, K. and Tsutsumi, H., *Kobunshi Ronbunshu*, 1997, **54**, 914.
31. Cubbon, R. C. B., *Polymer*, 1965, **6**, 419.
32. Tüdös, F., Kelen, T., Folde-Berezsnich, T. and Turcsanyi, B., *J. Macromol. Sci. Chem.*, 1976, **A10**, 1513.
33. Alfrey, T. Jr. and Price, C. C., *J. Polym. Sci.*, 1947, **2**, 101.
34. Oishi, T., Iwahara, M. and Fujimoto, M., *Polym. J.*, 1991, **23**, 1409.
35. Oishi, T., Sase, K., Saeki, K., Yano, S. and Ohdan, K., *Polymer*, 1995, **36**, 3935.
36. Brandrup, J. and Immergut, E. H., in *Polymer Hand Book* 3rd edn, ed. J. Brandrup and E. H. Immergut. John Wiley and Sons, New York, 1989, p. II-221.
37. Harwood, H. J. and Ritchey, W. M., *J. Polym. Sci., Polym. Lett. Ed.*, 1964, **2**, 601.
38. Kurokawa, M., Yamaguchi, H. and Minoura, Y., *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**, 2241.