Polymerizability and Chiroptical Properties of the *N*-Substituted Maleimide Bearing L-Phenylalanine Alkyl Ester

Kensoh KAGAWA and Tsutomu OISHI*

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering,
Yamaguchi University, 2557 Tokiwadai, Ube, Yamaguchi 755, Japan

(Received May 11, 1995)

ABSTRACT: Four types of *N*-maleoyl-L-phenylalanine alkyl ester (RPAM) polymers were synthesized from maleic anhydride, L-phenylalanine and the corresponding alcohols, *i.e.*, ethyl, butyl, dodecyl, or benzyl alcohol. Radical and anionic polymerizations were performed. Bulkiness of the ester group decreased polymerizability. However, bulkiness was favorable to asymmetric induction into the homopolymer main chain. In addition, polymers obtained by radical polymerizations had regular main chain structures smaller than those obtained by anionic polymerizations. The difference of the regularity caused different chiroptical properties of the polymers. Radical copolymerizations with styrene (ST) or methyl methacrylate (MMA) were performed and monomer reactivity ratios and Alfrey-Price $Q-e$ were determined. Chiroptical properties of the copolymers were significantly influenced by the ST or MMA *co*-unit. Bulkiness of the ester group hardly influenced chiroptical properties of the copolymers.

KEY WORDS Asymmetric Induction / Asymmetric Perturbation / *N*-Substituted Maleimide / Styrene / Methyl Methacrylate / L-Phenylalanine Ester / Optically Active Polymer /

We reported polymerizations of *N*-substituted maleimide (RMI) bearing optically active groups.¹⁻¹⁰ In the reports, the polymers obtained showed asymmetric induction in the main chain and asymmetric perturbation in the side chain chromophore. Since RMI has a pentagonal plane structure with a polymerizable double bond and a pair of imide chromophores exhibiting the $n \rightarrow \pi^*$ transition, there is large possibility of asymmetric induction and asymmetric perturbation. In the recent systematic studies of optically active RMI,^{5,9} chiroptical properties of poly(RMI) were significantly influenced by the location of the chiral carbon in the side chain. That is, the shorter the distance between the imide ring and chiral carbon, the greater the influence for chirality of the polymer.

On the other hand, we reported asymmetric polymerization of achiral *N*-alkyl maleimides with *n*-butyllithium/(–)-sparteine and optical activity of the resulting polymers.¹¹ In the report, *N*-cyclohexyl maleimide polymer showed larger specific rotation ($[\alpha]_D$) and Cotton effect than other RMI polymers. This suggests that bulkiness of *N*-substituent may be advantageous for asymmetric polymerization and asymmetric induction polymerization.

Recently, we reported polymerizations and copolymerizations of RMI bearing L-amino acid, *i.e.*, L-phenylalanine, L-alanine,⁸ or its cyclohexyl ester(CHPAM).¹⁰ Chiroptical properties of poly(CHPAM) exhibited significant differences between poly(CHPAM) and the corresponding model compound in chiroptical property. This is mostly attributable to the influence of the location of a chiral carbon in *N*-substituent. However, the influence of the bulkiness of ester group is not found yet. The objective of our investigation is to explore whether bulkiness of the ester group in *N*-substituent affects polymerizabilities and chiroptical properties of the polymers and the copolymers. The final purpose of a

series of studies is to estimate quantitatively asymmetric induction (formation of new asymmetric centers in the polymer main and asymmetric perturbation by the side chain chromophore) with and without cleavage of optically active groups.

In this article, we synthesized optically active *N*-(maleoyl-L-phenylalanine ester)[RPAM; ester group: ethyl (EPAM), butyl (BPAM), dodecyl (DPAM), and benzyl (BZPA)]. These RMI have a L-phenylalanine residue as well as CHPAM,¹⁰ but bulkiness of *N*-substituent is different from CHPAM. Accordingly, these RMI could give more detailed information on the relation between chiroptical properties of the polymers and bulkiness of *N*-substituent, in particular, the effects of bulkiness on asymmetric induction. RPAM are polymerized with radical or anionic initiators and copolymerized with styrene (ST) or methyl methacrylate (MMA). The monomer reactivity ratios and Alfrey-Price $Q-e$ values are determined. We discuss the asymmetric induction in the polymer main chain and asymmetric perturbation of side chain chromophores by comparing $[\alpha]_D$ and CD spectra of the polymers with those of the corresponding model compounds.

EXPERIMENTAL

Monomers

RPAM were synthesized from maleic anhydride, L-phenylalanine and alcohols, as shown in Scheme I. General synthetic procedure was the same as that of CHPAM.¹⁰ The detailed procedure of EPAM synthesis is given as follows.

N-Maleoyl-L-phenylalanine (PAMI): PAMI was synthesized from maleic anhydride and L-phenylalanine according to the previous paper⁸: mp 162–163 °C; $[\alpha]_D = -128.6^\circ$ ($c = 1.0$ g dl⁻¹, tetrahydrofuran (THF))

N-Maleoyl-L-phenylalanine ethyl ester (EPAM): A mixture of PAMI (12.3 g, 0.05 mol), ethanol (100 ml), and *p*-toluene sulfonic acid (*p*Ts) (2.0 g) in benzene

* To whom all correspondence should be addressed.

Scheme 1. Synthesis of RPAM and RPAS.

(100 ml) solution was refluxed for 12 h. After cooling to room temperature, the benzene solution was washed with sodium hydrogen carbonate aqueous solution and water, and dried on anhydrous magnesium sulfate. The solution was evaporated to obtain crude EPAM, which was recrystallized twice from benzene-*n*-hexane (2:1) to give pure EPAM. Yield 60% (based on PAMI); mp 79–80 °C; $[\alpha]_D = -95.2^\circ$ ($c = 1 \text{ g dl}^{-1}$, $l = 10 \text{ cm}$, THF); ^1H NMR (δ in ppm from tetramethylsilane (TMS) in CDCl_3): 7.27–7.11 (m, 5H in phenyl group), 6.59 (s, 2H, CH=CH), 4.97–4.91 (gem, $J = 11.54 \text{ Hz}$, 2H, C*H), 4.29–4.18 (m, 2H, COO-CH₂), 3.55–3.37 (m, 2H, CH₂ connecting phenyl group), 1.27 (t, $J = 7.26$, 3H, CH₃); ^{13}C NMR (δ in ppm from TMS in CDCl_3): 169.79 (C=O in imide ring), 168.66 (C=O in ester group), 136.62 (*ipso* carbon in phenyl group), 133.96 (C=C in imide ring), 128.76 (*ortho* carbons in phenyl group), 128.54 (*meta* carbons in phenyl group), 126.86 (*para* carbon in phenyl group), 62.01 (C*H), 53.30 (COO-CH₂), 34.49 (methylene carbon connecting phenyl group), 14.05 (CH₃).

N-Maleoyl-L-phenylalanine butyl ester (BPAM): BPAM was synthesized from maleic anhydride, L-phenylalanine, and butanol. BPAM was purified by distillation twice under reduced pressure. Yield 62% (based on PAMI); bp 176–178 °C/ $1.5 \times 10^{-1} \text{ mmHg}$; $[\alpha]_D = -90.2^\circ$ ($c = 1 \text{ g dl}^{-1}$, $l = 10 \text{ cm}$, THF); ^1H NMR (δ in ppm from TMS in CDCl_3): 7.26–7.11 (m, 5H in phenyl group), 6.59 (s, 2H, CH=CH), 4.94 (gem, $J = 11.57 \text{ Hz}$, 1H, C*H), 4.18 (t, $J = 6.43 \text{ Hz}$, 2H, COO-CH₂), 3.55–3.37 (m, 2H, CH₂ connecting phenyl group), 3.52–3.37 (m, 2H, COO-CH₂-CH₂-), 1.67–1.56 (m, 2H, -CH₂-CH₃), 0.92 (t, $J = 7.26$, 3H, CH₃); ^{13}C NMR (δ in ppm from TMS in CDCl_3): 169.79 (C=O in imide ring), 168.71 (C=O in ester group), 136.62 (*ipso* carbon in phenyl group), 133.94 (C=C in imide ring), 128.73 (*ortho* carbons in phenyl group), 128.51 (*meta* carbons in phenyl group), 126.85 (*para* carbon in phenyl group), 65.81 (C*H), 53.50 (COO-CH₂), 34.45 (methylene carbon connecting phenyl group), 30.41 (COO-CH₂-CH₂), 18.96 (-CH₂-CH₃), 13.57 (CH₃).

N-Maleoyl-L-phenylalanine dodecyl ester (DPAM): DPAM was synthesized from maleic anhydride, L-phenylalanine, and dodecanol. DPAM was purified by recrystallization twice in hexane. Yield 55% (based on PAMI); mp 36–37 °C; $[\alpha]_D = -78.7^\circ$ ($c = 1 \text{ g dl}^{-1}$, $l = 10 \text{ cm}$, THF); ^1H NMR (δ in ppm from TMS in CDCl_3): 7.27–7.11 (m, 5H in phenyl group), 6.59 (s, 2H, CH=CH), 4.95 (gem, $J = 11.54 \text{ Hz}$, C*H), 4.17 (t, $J = 6.6 \text{ Hz}$, 2H, COO-CH₂), 3.55–3.41 (m, 2H, CH₂ connecting phenyl group), 1.62 (t, $J = 6.60 \text{ Hz}$, 2H, COO-CH₂-CH₂-), 1.40–1.18 (br, 18H, -(CH₂)_n-), 0.88 (t, $J = 6.60 \text{ Hz}$, 3H, CH₃); ^{13}C NMR (δ in ppm from TMS in CDCl_3): 169.81 (C=O in imide ring), 168.75 (C=O in ester group), 136.66 (*ipso* carbon in phenyl group), 133.96 (C=C in imide ring), 128.77 (*ortho* carbons in phenyl group), 128.55 (*meta* carbons in phenyl group), 126.88 (*para* carbon in phenyl group), 66.17 (C*H), 53.34 (COO-CH₂), 34.50 (methylene carbon connecting phenyl group), 31.90 (COO-CH₂-CH₂), 29.62, 29.53, 29.47, 29.33, 29.13, 28.41, 25.75 (methylene carbons in dodecyl group), 22.66 (-CH₂-CH₃), 14.09 (CH₃).

N-Maleoyl-L-phenylalanine benzyl ester (BZPA): BZPA was synthesized from maleic anhydride, L-phenylalanine and benzyl alcohol. BZPA was purified by distillation twice under reduced pressure. Yield 62% (based on PAMI); bp 195–197 °C/ $1.5 \times 10^{-1} \text{ mmHg}$; $[\alpha]_D = -97.2^\circ$ ($c = 1 \text{ g dl}^{-1}$, $l = 10 \text{ cm}$, THF); ^1H NMR (δ in ppm from TMS in CDCl_3): 7.4–7.09 (m, 10H in phenyl group), 6.56 (s, 2H, CH=CH), 5.20 (s, 2H, COO-CH₂), 5.00 (gem, $J = 11.54 \text{ Hz}$, 1H, C*H), 3.51–3.40 (m, 2H, CH₂ connecting phenyl group); ^{13}C NMR (δ in ppm from TMS in CDCl_3): 169.72 (C=O in imide ring), 168.55 (C=O in ester group), 136.42 (*ipso* carbon in L-phenylalanine residue), 135.02 (*ipso* carbon in benzyl ester), 133.93 (C=C in imide ring), 128.90, 128.73, 128.54, 128.41, 128.104, 126.88 (phenyl groups), 67.62 (C*H), 53.28 (COO-CH₂), 34.45 (methylene carbon connecting phenyl group).

Model Compounds of Poly(RPAM)

Model compounds of poly(RPAM) were prepared from succinic anhydride, L-phenylalanine and alcohols according to a method similar to those of monomers.

N-Succinoyl-L-phenylalanine (PASI, Precursor): PASI was synthesized from maleic anhydride and L-phenylalanine according to the synthesis procedure of PAMI: mp 167–168 °C; $[\alpha]_D = -138.3^\circ$ ($c = 1.0 \text{ g dl}^{-1}$, THF).

Model Compound of Poly(EPAM): *N*-succinoyl-L-phenylalanine ethyl ester (EPAS): Yield 50% (based on PASI); mp 165–166 °C; $[\alpha]_D = -136.3^\circ$ ($c = 1 \text{ g dl}^{-1}$, $l = 10 \text{ cm}$, THF); ^1H NMR (δ in ppm from TMS in CDCl_3): 7.28–7.11 (m, 5H in phenyl group), 5.00 (gem, $J = 10.23 \text{ Hz}$, 1H, C*H), 3.52–3.37 (m, 2H, CH₂ connecting phenyl group), 3.18 (t, $J = 7.26 \text{ Hz}$, 2H, COO-CH₂), 2.64–2.41 (m, 4H in succinimide ring), 1.30 (t, $J = 7.26 \text{ Hz}$, 3H, CH₃); ^{13}C NMR (δ in ppm from

TMS in CDCl_3): 176.08 (C=O in imide ring), 168.21 (C=O in ester group), 136.48 (*ipso* carbon in phenyl group), 128.76 (*ortho* carbons in phenyl group), 128.43 (*meta* carbons in phenyl group), 126.85 (*para* carbon in phenyl group), 65.73 (C*H), 53.51 (COO-CH₂), 33.59 (methylene carbon connecting phenyl group), 27.73 (methylene carbons in imide ring), 13.55 (CH₃).

Model Compound of Poly(BPAM): *N*-succinoyl-L-phenylalanine butyl ester (BPAS): Yield 60% (based on PASI); bp 163–165°C/ 1.1×10^{-2} mmHg; $[\alpha]_D = -103.2^\circ$ ($c = 1 \text{ g dl}^{-1}$, $l = 10 \text{ cm}$, THF); ^1H NMR (δ in ppm from TMS in CDCl_3): 7.28–7.11 (m, 5H in phenyl group), 5.00 (gem, $J = 10.89 \text{ Hz}$, 1H, C*H), 4.18 (t, $J = 6.60 \text{ Hz}$, 2H, COO-CH₂), 3.53–3.37 (m, 2H, CH₂ connecting phenyl group), 2.65–2.41 (m, 4H in succinimide ring), 1.68–1.57 (m, 2H, COO-CH₂-CH₂), 1.43–4.29 (m, 2H, CH₂-CH₃), 0.93 (t, $J = 7.26 \text{ Hz}$, 3H, CH₃); ^{13}C NMR (δ in ppm from TMS in CDCl_3): 176.08 (C=O in imide ring), 168.21 (C=O in ester group), 136.48 (*ipso* carbon in phenyl group), 128.76 (*ortho* carbons in phenyl group), 128.43 (*meta* carbons in phenyl group), 126.85 (*para* carbon in phenyl group), 65.73 (C*H), 53.51 (COO-CH₂), 33.59 (methylene carbon connecting phenyl group), 30.37 (COO-CH₂-CH₂-), 27.73 (methylene carbons in imide ring), 18.96 (-CH₂-CH₃), 13.55 (CH₃).

Model Compound of Poly(DPAM): *N*-succinoyl-L-phenylalanine dodecyl ester (DPAS): Yield 55% (based on PASI); bp 226–228°C/ 4.0×10^{-2} mmHg; $[\alpha]_D = -76.4^\circ$ ($c = 1 \text{ g dl}^{-1}$, $l = 10 \text{ cm}$, THF); ^1H NMR (δ in ppm from TMS in CDCl_3): 7.28–7.11 (m, 5H in phenyl group), 5.00 (gem, $J = 10.89 \text{ Hz}$, 1H, C*H), 4.17 (t, $J = 6.60 \text{ Hz}$, 2H, COO-CH₂), 3.53–3.41 (m, 2H, CH₂ connecting phenyl group), 2.65–2.42 (m, 4H in succinimide ring), 1.66–1.59 (m, 2H, COO-CH₂-CH₂), 1.40–1.18 (br, 18H, -(CH₂)₉-), 0.88 (t, $J = 6.6 \text{ Hz}$, 3H, CH₃); ^{13}C NMR (δ in ppm from TMS in CDCl_3): 176.19 (C=O in imide ring), 168.28 (C=O in ester group), 136.51 (*ipso* carbon in phenyl group), 128.82 (*ortho* carbons in phenyl group), 128.50 (*meta* carbons in phenyl group), 126.92 (*para* carbon in phenyl group), 66.13 (C*H), 53.59 (COO-CH₂), 33.61 (methylene carbon connecting phenyl group), 31.86 (COO-CH₂-CH₂-), 29.60, 29.53, 29.47, 29.29, 29.13, 28.39, 27.80, 25.77 (methylene carbons in dodecyl group), 27.80 (methylene carbons in imide ring), 22.64 (-CH₂-CH₃), 14.07 (CH₃).

Model Compound of Poly(BZPA): *N*-succinoyl-L-phenylalanine benzyl ester (BZPAS): Yield 55% (based on PASI); bp 208–210°C/ 1.1×10^{-1} mmHg; $[\alpha]_D = -103.2^\circ$ ($c = 1 \text{ g dl}^{-1}$, $l = 10 \text{ cm}$, THF); ^1H -NMR (δ in ppm from TMS in CDCl_3): 7.46–7.10 (m, 10H in phenyl group), 5.21 (s, 2H, COO-CH₂), 5.06 (gem, $J = 10.56 \text{ Hz}$, 1H, C*H), 3.55–3.40 (m, 2H, CH₂ connecting phenyl group), 2.59–2.43 (m, 4H in succinimide ring); ^{13}C NMR (δ in ppm from TMS in CDCl_3): 176.17 (C=O in imide ring), 168.16 (C=O in ester group), 136.33 (*ipso* carbon in L-phenylalanine residue), 135.09 (*ipso* carbon in benzyl ester), 128.57, 128.50, 128.43, 128.36, 128.16, 126.95 (phenyl groups), 67.64 (C*H), 53.59 (COO-CH₂), 33.51 (methylene carbon connecting phenyl group), 27.78 (methylene carbons in imide ring).

Other Materials

ST and MMA were purified by the ordinary methods.¹² Benzene, toluene and 1,4-dioxane were purified by the usual methods just before use.¹² α, α' -Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Commercially available *n*-butyllithium (BuLi) *n*-hexane solution was used without further purification.

Homopolymerization and Copolymerization

All polymerizations were done in nitrogen atmosphere. Radical homopolymerization and copolymerization were performed with AIBN as an initiator in a sealed tube at 60°C. After polymerization, the polymer solution was poured into a large amount of methanol. To remove the monomer completely, reprecipitation was repeated twice from THF solution in a large amount of methanol. The compositions of the copolymers were determined by ^1H NMR spectra and nitrogen analysis data. Anionic polymerization was performed with BuLi as an initiator in Schlenk's reaction tube at 0°C. After polymerization, the polymer solution was poured into a large amount of methanol containing a few drops of dilute hydrochloric acid. The polymer was treated by the same method as the polymer obtained by radical polymerization.

Measurements

D-Line specific rotations were measured in THF at 25°C with a Jasco DIP-140 (Japan Spectroscopic Co.). Circular dichroism (CD) spectra were obtained in THF as solvent at 25°C by a JASCO J-20C (Japan Spectroscopic Co.) equipped with a xenon source and a computing data processor ($c = 0.05$ – 0.1 g dl^{-1} , $l = 0.2 \text{ mm}$, THF). UV spectra were obtained with a Shimadzu 200 A spectrophotometer ($c = 0.01$ – 0.04 g dl^{-1} , $l = 1 \text{ mm}$, THF). Molecular weights of polymers were measured by gel permeation chromatography (GPC) using the same techniques as described earlier.¹³ NMR spectra were recorded in the presence of tetramethylsilane (TMS) as an internal standard in CDCl_3 solution at 25°C using JNM-EX-270 (JEOL Ltd.). IR and elemental analysis were achieved, using the same instruments as reported previously.¹⁴

RESULTS AND DISCUSSION

Homopolymerization of RPAM

The polymerization conditions and results are summarized in Table I. All polymerizations proceeded homogeneously throughout, and the resulting polymers were soluble in chloroform and THF. The polymers were white powders except for poly(DPAM) and showed negative optical rotations in THF at sodium D-line. Poly(DPAM) was a highly viscous oil.

In radical polymerizations of RPAM (upper paragraph in Table I), polymerization solvents influenced yields of the polymers and their number-average molecular weights ($\bar{M}_n$). Generally, the use of benzene for polymerization solvent gave better yields and higher polymer molecular weights than 1,4-dioxane. This tendency was observed in other RMI reported previously.^{1–10} This may result from small chain transfer of propagating polymer to benzene. $\bar{M}_n$ of poly(BPAM) and

Table I. Radical and anionic polymerizations of RPAM

Run	Monomer feed mol l ⁻¹	Initiator × 10 ² mol l ⁻¹	Polymn. solvent ^a ml	Polymn. temp. °C	Polymn. time h	Convsn. %	$\bar{M}_n^b$ × 10 ⁻³	$\bar{M}_w/\bar{M}_n^b$	$[\alpha]_D^{25c}$ deg
EPAM	0.95	AIBN(1.0)	BEN(2)	60	24	74.3	7.1	3.7	-115.0
EPAM	0.93	AIBN(1.0)	DOX(2)	60	24	88.1	6.8	1.8	-120.0
BPAM	0.83	AIBN(1.0)	BEN(2)	60	24	74.9	19.6	3.0	-91.7
BPAM	0.83	AIBN(1.0)	DOX(2)	60	24	47.6	2.9	1.5	-96.8
DPAM	0.61	AIBN(1.0)	BEN(2)	60	23	72.0	15.4	2.7	-65.2
DPAM	0.61	AIBN(1.0)	DOX(2)	60	25	66.6	4.4	1.5	-66.6
BZPA	0.76	AIBN(1.0)	BEN(2)	60	23	77.8	6.6	3.6	-77.4
BZPA	0.75	AIBN(1.0)	DOX(2)	60	25	66.6	2.5	1.7	-78.1
EPAM	0.95	BuLi(1.9)	THF(2.0)	0	18	17.3	8.0	4.8	-222.0
BPAM	0.67	BuLi(1.5)	THF(2.5)	0	20	32.1	5.6	1.6	-156.1
BPAM	0.67	BuLi(0.77)	TOL(2.5)	0	24	48.9	8.9	1.8	-104.1
BPAM	0.67	BuLi(1.5)	DMF(2.5)	0	24	79.4	9.1	2.4	-126.1
DPAM	0.61	BuLi(1.2)	DMF(2)	0	25	83.0	7.2	1.6	-77.3
DPAM	0.61	BuLi(2.4)	DMF(2)	0	25	78.9	6.5	1.7	-81.5
BZPA	0.59	BuLi(1.1)	TOL(2.5)	0	20	14.1	4.8	1.3	-91.0

^a BEN, benzene; THF, tetrahydrofuran; DMF, *N,N*-dimethylformamide; DOX, dioxane; TOL, toluene. ^b Determined by GPC. ^c $c = 1.0 \text{ g dl}^{-1}$; $l = 10 \text{ cm}$, THF.

Figure 1. ¹³C NMR spectra for poly(BPAM): (A) obtained with BuLi in DMF and (B) obtained with AIBN in benzene.

poly(DPAM) polymerized in benzene were 19.6×10^3 and 15.4×10^3 , respectively, higher than those of others. GPC curves indicate that poly(BPAM) and poly(DPAM) had narrower molecular weight distributions than others. This suggests that a long alkyl chain of the ester group in the *N*-substituent was favorable for the polymerizabilities of RMI. The tendency was identical with the radical polymerizations of RMI having *N*-alkyl chain reported by Matsumoto *et al.*¹⁵ That is, a long alkyl chain could not inhibit the propagation reaction but decrease the termination reaction because of high viscosity in the polymerization mixture. Consequently, it is considered that the polymerization reactivities were higher.¹⁵

In anionic polymerizations of RPAM (lower paragraph in Table I), generally, yields of the polymers in DMF were higher than in other solvents because DMF was a good solvent for the polymers. Concerning $\bar{M}_n$, solvent effects during the polymerization were less than

in the radical polymerizations. Generally, there were little differences among the polymers in several solvents. Anionic polymerization of BZPA in toluene gave smaller yield compared to others. Furthermore, anionic polymerizations of BZPA in other solvents (*e.g.*, DMF or THF) gave only traces of polymer. This is due to steric hindrance of *N*-substituent.

The polymerizabilities of RPAM in this study were higher than that of CHPAM reported previously.¹⁰ This may be attributed to less bulkiness of the *N*-substituent of RPAM than that of CHPAM.

Figure 1 shows ^{13}C NMR spectra for poly(BPAM). The poly(BPAM) obtained with BuLi showed splitting peaks assigned to methine carbons in imide ring [Figure 1(A)]. According to ^{13}C NMR studies on poly(*N*-phenylmaleimide)¹⁶ and poly(2-propenyl isocyanate-*alt*-maleic anhydride),¹⁷ peaks at 42 and at 45 ppm were assigned to the *cis* and *trans* form, respectively (Scheme 2). The former has larger peak area compared to the latter, as shown in the expanded spectrum [Figure 1(A)]. However, poly(BPAM) obtained with AIBN showed broad peaks at around 43 ppm, as shown in Figure 1(B). This suggests that the polymers obtained with BuLi are predominantly the *trans* form. It can be seen from these NMR spectra that the polymers obtained with BuLi have more regular main chain structures compared to

Scheme 2.

Figure 2. CD spectra for poly(RPAM): (1) poly(BPAM) obtained with AIBN, (2) model compound of poly(BPAM), (3) poly(BZPA) obtained with AIBN, (4) model compound of poly(BZPA).

Table II. Specific rotations ($[\alpha]_D^{25}$) for monomer, model compound and homopolymer

Specific rotations/deg.					
Monomer	Model compound (A)	Homopolymer (B)	(B)–(A) ^a	$\frac{(B)-(A)^a}{(A)}$	%
EPAM	–95.2	–136.3	–115.0	21.3	15.6
BPAMI	–90.2	–103.2	–91.7	11.5	11.1
DPAM	–78.7	–76.4	–65.2	11.2	14.6
BZPA	–97.2	–103.2	–77.4	25.8	25.0
CHPAM ^b	–86.0	–106.8	–66.6	40.2	37.6

^a Absolute value. ^b Data taken from ref 8.

Figure 3. CD spectra for poly(BPAM) polymerized anionically in (1) DMF, (2) toluene, (3) THF, and (4) poly(BPAM) obtained with AIBN.

those obtained with AIBN. The differences of main chain regularity may influence chiroptical properties of the polymer.

Chiroptical Properties of Homopolymers

Fundamentally, RPAM may have similar chirality because they have the same chiral unit (*i.e.*, L-phenylalanine residue). Accordingly, it is considered that each poly(RPAM) exhibits similar Cotton effect. In fact, both CD spectra of poly(BPAM) and poly(BZPA) exhibited Cotton effects based on $n \rightarrow \pi^*$ and the $\pi \rightarrow \pi^*$ transitions at 223 and 250 nm, as shown in Figure 2. Other poly(RPAM), *i.e.*, poly(EPAM) and poly(DPAM) also

Figure 4. UV spectra for (1) poly(BPAM) obtained with AIBN, (2) poly(BPAM) obtained with BuLi in DMF, (3) BPASI [model compound for poly(BPAM)] and (4) BPAM monomer.

Figure 5. ¹H NMR spectra for poly(BPAM) polymerized anionically in (A) DMF and (B) THF; (C) poly(BPAM) obtained with AIBN in benzene.

showed Cotton effects identical with those shown in Figure 2. In comparison with specific rotations ($[\alpha]_D^{25}$) of poly(RPAM), however, difference was observed. Table II summarizes $[\alpha]_D^{25}$ of monomers, model compounds of the polymers, and polymers obtained by radical polymerizations in benzene. Ratios $[(B-A)/A]$ represent to what extent chirality of the polymers differed from that of the model compound. The difference between the polymer and model compound indicates asymmetric induction in the backbone. The order of the ratios was $\text{CHPAM}^{10} > \text{BZPA} > \text{EPAM} \geq \text{DPAM} \geq \text{BPAM}$. This order almost agrees with the bulkiness of ester groups. It seems that the order reflects a small difference in asymmetric induction. In addition, the order suggests that *bulkiness* of *N*-substituent may be advantageous for asymmetric induction in ordinary radical polymerizations. However, the ratio for EPAM was slightly greater than those for DPAM and BPAM, which suggests that asymmetric induction could be influenced not by length of methylene unit in the ester group but steric hindrance, especially *bulkiness*. From a reaction point of view, a long alkyl chain may not be concerned with bulkiness. Otsu and co-workers reported¹⁵ that a long alkyl chain could not interfere with the propagation reaction of RMI, as described for the *homopolymerization of RPAM*.

Figure 3 shows CD spectra for poly(BPAM) obtained

with BuLi and AIBN. UV spectra for poly(BPAM) obtained with BuLi and AIBN, the model compound for poly(BPAM), *i.e.*, (BPASI), and BPAM monomer are shown in Figure 4. In the anionic polymerization of BPAM, polymerization solvents influenced the chiroptical properties of the polymers. The polymers obtained with BuLi in DMF and toluene showed the same CD patterns (1 and 2 in Figure 3), but the polymer obtained in THF showed different Cotton effect at around 260 nm (3 in Figure 3). These polymers exhibited the same ¹³C NMR spectra as shown in Figure 1(A), suggesting the ratios of *trans/cis* form in the polymer main chain to equal for the three polymers. But slight differences in ¹H NMR spectra for poly(BPAM) obtained in *N,N*-dimethylformamide (DMF) and in THF were observed, as shown in Figure 5. Peaks around 2.5 to 5.2 ppm were slightly different for two polymers, though they overlapped with methine and other protons. This indicates that the conformation and/or configuration of the main chain structure was different for the two polymers. Thus, it is considered that the differences of CD spectra are due to different main chain structures, which due to the fact that *trans*-addition contains *threo*-diisotactic and *threo*-disyndiotactic, and *cis*-addition contains *erythro*-diisotactic and *erythro*-disyndiotactic structures.

These CD spectra were different from those for

Table III. Radical copolymerization of RPAM(M_1) with ST (M_2) in benzene (2 ml) at 60°C^a

Run	M_1	M_1 in monomer	Polymn. time	Convsn.	M_1 in copolymer	$\bar{M}_n^b$ $\times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$[\alpha]_D^{25c}$
		mol%	h	%	mol%			deg
A-1	EPAM	5.1	9.3	31.5	21.5	1.6	4.0	-62.5
-2		10.1	4.4	21.2	28.4	6.4	2.3	-87.2
-3		20.1	2.8	26.0	39.7	9.5	4.8	-105.7
-4		29.1	2	36.8	46.9	12.9	2.7	-114.2
-5		49.2	2	31.2	49.1	7.8	3.8	-121.7
-6		69.2	2	30.9	53.8	9.2	3.6	-124.6
-7		89.2	3.3	26.4	76.9	4.2	3.6	-118.5
-8		93.7	3.5	27.2	92.4	3.3	3.4	-117.4
B-1	BPAM	5.0	9	25.7	25.7	2.2	3.5	-54.4
-2		10.0	6	32.0	31.5	4.5	2.8	-78.1
-3		19.9	2	22.9	37.6	8.0	2.9	-94.3
-4		29.9	2	27.3	45.3	8.5	5.1	-102.4
-5		50.0	1.5	23.8	48.2	14.1	3.8	-107.5
-6		70.1	1.5	21.6	49.4	18.7	2.8	-110.8
-7		89.6	6	24.3	71.5	2.0	5.6	-99.7
-8		94.9	9	29.3	85.1	1.1	2.6	-95.9
C-1	DPAM	6.0	8	27.5	15.8	4.2	2.6	-54.7
-2		11.6	8	39.2	29.4	4.2	3.2	-63.7
-3		23.1	2	39.4	43.3	8.3	2.7	-74.9
-4		33.9	2	39.5	43.7	8.9	2.6	-77.5
-5		54.3	2	32.6	49.4	6.6	3.6	-82.5
-6		73.7	2	30.6	50.1	5.7	3.1	-82.5
-7		90.0	5	17.5	57.1	3.5	3.6	-69.0
-8		93.9	5	19.6	73.8	1.5	5.7	-66.3
D-1	BZPA	5.0	6.5	22.4	13.6	3.3	2.4	-61.0
-2		10.0	6.5	33.4	26.6	3.9	2.8	-76.6
-3		20.0	2.5	8.6	48.5	2.5	4.6	-86.0
-5		50.4	2.5	13.5	54.7	2.1	6.6	-98.0
-6		70.1	2.5	14.8	56.6	4.8	3.9	-99.0
-7		89.8	5.5	33.2	73.3	2.5	4.0	-84.2
-8		95.0	5.5	20.5	78.8	2.0	4.2	-81.6

^a $M_1 + M_2 = 1.0$ g. ^bBy GPC. ^c $c = 1.0$ g dl⁻¹; $l = 10$ cm, THF.

poly(BPAM) obtained by radical polymerization (1 in Figure 3).

Radical Copolymerizations of RPAM with ST or MMA

Radical copolymerizations of RPAM(M_1) with ST(M_2) and MMA(M_2) were carried out in benzene at 60°C. The results of the copolymerization are summarized in Tables III and IV. All copolymerizations proceeded homogeneously throughout. The copolymers were white powders and optically active. Generally, $\bar{M}_n$'s of poly(RPAM-co-ST)s were greater than those of poly(RPAM-co-MMA)s and RPAM homopolymers. Further, $\bar{M}_n$'s

of poly(BPAM-co-ST), poly(BPAM-co-MMA), poly(DPAM-co-ST), and poly(DPAM-co-MMA) were greater than those of other RPAM copolymers. Similar tendency was observed in RPAM homopolymer system.

Copolymer composition plots in the copolymerizations of RPAM(M_1) with ST(M_2) or MMA(M_2) are shown in Figure 6. Table V gives monomer reactivity ratios (r_1, r_2) calculated by the High-conversion method reported by Tüdös *et al.*¹⁸ and Alfrey-Price Q-e.¹⁹ It can be seen from Figure 6 and Table V that copolymerization systems of RPAM with ST or MMA exhibited similar reactivities. Q_1 in the RPAM-ST system were

Table IV. Radical copolymerization of RPAM(M_1) with MMA (M_2) in benzene (2 ml) at 60°C^a

Run	M_1	M_1 in monomer	Polymn. time	Convsn.	M_1 in copolymer	$\bar{M}_n^b \times 10^{-4}$	$\bar{M}_w/\bar{M}_n$	$[\alpha]_D^{25c}$
		mol%			mol%			deg
E-1	EPAM	5.0	4.5	27.0	5.2	2.7	2.7	-10.4
-2		10.2	4.5	26.5	7.6	3.3	2.9	-20.8
-3		20.1	4.5	24.3	11.9	2.7	3.0	-40.5
-4		30.0	4.5	23.3	20.9	4.2	2.4	-57.1
-5		50.0	4.5	25.4	37.6	3.5	3.4	-90.8
-6		70.3	4.5	34.3	64.9	2.6	4.0	-109.6
-7		80.3	4.5	34.9	74.1	2.4	3.9	-114.1
-8		90.0	4.5	31.8	86.4	2.0	3.7	-114.8
F-1	BPAM	5.08	6	32.2	5.3	4.6	2.7	-6.8
-2		10.0	6	35.7	3.4	5.4	2.3	-14.5
-3		20.0	7	37.3	7.3	4.7	2.2	-29.8
-4		29.7	7	34.2	11.5	3.7	2.4	-43.6
-5		49.8	7	32.2	23.2	3.8	2.3	-71.2
-6		69.8	8	33.8	34.9	3.1	2.3	-92.1
-7		89.9	7	20.0	62.1	1.0	2.7	-95.7
-8		94.8	8	16.9	85.6	1.0	2.2	-95.1
G-1	DPAM	4.8	6	39.4	1.6	9.5	1.4	-6.6
-2		9.7	6	37.3	9.3	7.5	1.6	-13.6
-3		19.4	7	36.4	12.8	4.8	2.5	-27.3
-4		29.2	7	35.4	17.3	4.1	2.6	-39.3
-5		49.0	7	33.0	30.3	3.4	3.4	-59.3
-6		69.0	4	26.4	45.1	3.4	2.5	-68.1
-7		89.7	4	31.5	63.7	7.7	2.7	-66.6
-8		94.8	4	28.6	78.1	1.6	4.0	-69.9
H-1	BZPA	5.1	6	19.8	2.9	4.6	2.6	-8.7
-2		10.0	6	36.6	7.1	3.9	2.7	-17.2
-3		20.1	7	35.6	12.9	3.7	2.6	-34.0
-4		30.1	7	38.1	17.3	3.2	2.7	-48.2
-5		50.3	8	36.4	30.3	2.7	3.0	-72.7
-6		69.9	8	47.5	49.8	2.5	3.8	-84.0
-7		89.9	8	35.4	75.2	2.2	3.7	-79.9
-8		94.1	8	30.3	82.5	1.8	3.8	-79.7

^a $M_1 + M_2 = 1.0$ g. ^b By GPC. ^c $c = 1.0$ g dl⁻¹; $l = 10$ cm, THF.

Figure 6. Copolymer composition curves for (1) RPAM-ST system and (2) RPAM-MMA system: (○) EPAM, (●) BPAM, (□) DPAM, and (■) BZPA.

Table V. Monomer reactivity ratios and Alfrey-Price $Q-e$

M_1	M_2	r_1	r_2	Q_1	e_1
EPAM	ST	0.05	0.06	2.29	1.60
BPAM	ST	0.02	0.08	1.76	1.71
DPAM	ST	0.01	0.12	1.10	1.72
BZPA	ST	0.06	0.07	2.21	1.56
EPAM	MMA	0.16	1.33	0.75	1.99
BPAM	MMA	0.04	2.78	0.49	1.92
DPAM	MMA	0.05	2.01	0.68	1.94
BZPA	MMA	0.06	1.80	0.75	1.91

larger than those in the RPAM-MMA system. This may be due to the formation of charge transfer (CT) complex.^{20,21} The copolymerization parameters for RPAM were similar to those for other RMI reported previously¹⁻⁸ as well as CHPAM.¹⁰ This suggests that the ester substituent in RPAM hardly affects copolymerization reactivity.

Chiroptical Properties of Copolymers

Figures 7 and 8 show the CD spectra for BPAM (or BZPA) copolymers with ST or MMA. Copolymers containing more than 50–60 mol% of BPAM (or BZPA)

Figure 7. CD spectra for (A) poly(BPAM-co-ST) and (B) poly(BPAM-co-MMA): (1) 71.5 mol% of BPAM, (2) 48.2 mol% of BPAM, (3) 62.1 mol% of BPAM, (4) 34.9 mol% of BPAM, and (5) 23.2 mol% of BPAM in the copolymer.

Figure 8. CD spectra for (A) poly(BZPA-co-ST) and (B) poly(BZPA-co-MMA): (1) 73.3 mol% of BZPA, (2) 56.5 mol% of BZPA, (3) 75.2 mol% of BZPA, and (4) 12.9 mol% of BZPA in the copolymer.

Figure 9. Relationships between specific rotations ($[\alpha]_D$) and RPAM content (wt%) in a copolymer: (○) poly(RPAM-*co*-ST); (●) poly(RPAM-*co*-MMA).

showed CD patterns similar to those of the corresponding homopolymers (solid line spectra in Figures 7 and 8). That is, a positive Cotton effect at 225 nm and some negative Cotton effects at about 260 nm were observed. On the other hand, copolymers containing less than 50 mol% BPAM (or BZPA) showed quite different CD patterns from those of the corresponding homopolymers (dotted or slashed line spectra in Figures 7 and 8). In our previous investigation on optically active RMI,¹⁻⁹ even if the content of RMI in the copolymer varied, the copolymers showed similar CD spectra except for molecular ellipticity. In the present work, the resulting copolymers in all RPAM systems showed significant change in CD spectra when they contained less than 50 mol% of RPAM. This was also observed in both poly(CHPAM-*co*-ST) and poly(CHPAM-*co*-MMA).¹⁰ This suggests that: (1) *co*-units (ST or MMA) can affect chiroptical properties of the copolymers, (2) bulkiness of the ester group can hardly influence chiroptical properties of the copolymers, which are different from chiroptical properties of the homopolymers.

Figure 9 shows the relation between $[\alpha]_D$ and RPAM content (wt%) in the copolymer, where the slashed line indicates that neither asymmetric induction nor asymmetric perturbation occurs in the copolymers, because the line is connected $[\alpha]_D$ of the model compound (◇) with zero. The dotted line indicates that chiroptical properties of the copolymers are influenced by *co*-unit such as ST or MMA, because the line is connected $[\alpha]_D$ of the homopolymer (○ at 100 wt%) with zero. $[\alpha]_D$ of the copolymers showed deviation from these straight lines. In the free radical copolymerizations of RMI, the effects of asymmetric induction on chiroptical properties are very small.⁹ Thus, the deviations were mostly attributable to asymmetric perturbation caused by *co*-units. The deviation in Figure 9 was also observed in

CHPAM copolymers.¹⁰ That is, chiroptical properties of poly(RPAM-*co*-ST) and poly(RPAM-*co*-MMA) were similar to those of CHPAM copolymers.¹⁰ This suggests that not bulkiness of ester group but the *co*-units (ST or MMA) is a determining factor of chiroptical properties of the copolymer.

CONCLUSIONS

(1) Four types of *N*-substituted maleimide polymers bearing an optically active L-phenylalanine ester (RPAM) were synthesized. Polymerizabilities of RPAM increased with decreasing steric hindrance of the ester group.

(2) From the results of radical copolymerizations of RPAM (M_1) with ST(M_2) or MMA(M_2), the monomer reactivity ratios (r_1, r_2) and Alfrey-Price Q were determined.

(3) Chiroptical properties of poly(RPAM) were influenced by ester group bulkiness. Bulkiness was advantageous for asymmetric induction polymerization.

(4) Chiroptical properties of poly(RPAM-*co*-ST) and poly(RPAM-*co*-MMA) showed significant change whether RPAM was present at more than or less than 50–70 mol%. Chiroptical properties of the copolymer were remarkably influenced by ST or MMA *co*-units. However, bulkiness of the ester group hardly influenced the chiroptical properties of the copolymers.

Acknowledgments. We are thankful to Mr. M. Momoi for carrying out the elemental analysis.

REFERENCES

1. T. Oishi and M. Fujimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 2789 (1984).
2. T. Oishi, A. Kamori, and M. Fujimoto, *J. Macromol. Sci., Pure Appl. Chem.*, **A29**, 231 (1992).
3. T. Oishi and M. Fujimoto, *J. Polym. Sci., Part A, Polym. Chem.*, **30**, 1821 (1992).
4. T. Oishi, Y. Otsubo, and M. Fujimoto, *Polym. J.*, **24**, 527 (1992).
5. T. Oishi, K. Kagawa, and M. Fujimoto, *Macromolecules*, **26**, 24 (1993).
6. T. Oishi, K. Kagawa, and M. Fujimoto, *Polym. J.*, **25**, 977 (1993).
7. T. Oishi, K. Kagawa, and M. Fujimoto, *Polymer*, **34**, 2644 (1993).
8. T. Oishi, K. Matsusaki, and M. Fujimoto, *Polym. J.*, **24**, 1281 (1992).
9. T. Oishi, K. Kagawa, and M. Fujimoto, *J. Polym. Sci., Part A, Polym. Chem.*, **33**, 1341 (1995).
10. K. Kagawa and T. Oishi, *Polym. J.*, in press.
11. T. Oishi, H. Yamasaki, and M. Fujimoto, *Polym. J.*, **23**, 795 (1991).
12. T. Otsu and M. Kinoshita, "Koubunshigousei no Jikkenhou," Kagakudojin, Kyoto, 1972, pp 69–91.
13. T. Oishi, Y. Morioka, and M. Fujimoto, *Polym. J.*, **21**, 287 (1989).
14. T. Oishi and M. Fujimoto, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 2727 (1982).
15. A. Matsumoto, A. Oki, and T. Otsu, *Polym. J.*, **23**, 201 (1991).
16. K. G. Olson and G. B. Butler, *Macromolecules*, **17**, 2486 (1984).
17. W. Mormann and K. Schmalz, *Macromolecules*, **27**, 7115 (1994).
18. F. Tüdös, T. Kelen, T. Folde-Berezsnich, and B. Turcsanyi, *J. Macromol. Sci.-Chem.*, **A10**, 1513 (1976).
19. T. Alfrey, Jr. and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).
20. T. Oishi, M. Iwahara, and M. Fujimoto, *Polym. J.*, **23**, 1409 (1991).
21. T. Oishi, K. Sase, K. Saeki, S. Yano, and K. Ohdan, *Polymer*, **36**, 3935 (1995).