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Synthesis and polymerization of optically active itaconamate bearing an (*R*)-α-methylbenzyl group

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Two types of optically active itaconamates, α-ethyl β-*N*-((*R*)-α'-methylbenzyl)itaconamate (MBEI) and α-*N*-((*R*)-α'-methylbenzyl)β-ethyl itaconamate (EMBI) were synthesized from itaconic anhydride, (*R*)-α-methylbenzylamine and ethanol. Radical polymerizations of MBEI and EMBI were performed in bulk and in several solvents at 50 to 130°C. But only bulk polymerization gave appreciably optically active polymers. It was found that MBEI has higher polymerization reactivity than EMBI. Radical copolymerizations of MBEI (M_1) (EMBI (M_1)) were performed with styrene (ST, M_2), methyl methacrylate (MMA, M_2), or *N*-phenylmaleimide (PhMI, M_2) in benzene at 60°C. The monomer reactivity ratios (r_1, r_2) and Alfrey–Price Q–e values were determined as follows: $r_1 = 0.35$, $r_2 = 0.14$ (MBEI/ST), $r_1 = 0.03$, $r_2 = 1.12$ (EMBI/ST), $r_1 = 0.02$, $r_2 = 2.39$ (EMBI/MMA), $r_1 = 4.35$, $r_2 = 0.17$ (MBEI/PhMI), $r_1 = 1.04$, $r_2 = 0.13$ (EMBI/PhMI), $Q = 1.80$, $e = 0.94$ for MBEI, $Q = 0.21$, $e = 1.04$ for EMBI. Chiroptical properties of homopolymers and copolymers were also investigated. Copyright © 1996 Elsevier Science Ltd.

(Keywords: optically active itaconamates; asymmetric induction; asymmetric perturbation)

INTRODUCTION

In recent years, polymerizations and copolymerizations of dialkyl itaconate (DRI)[1-7] and *N*-alkyl itaconimide (RII)[8-12] with various substituents have been widely investigated. It was reported that itaconic acid derivatives can be readily polymerized in spite of bulky substituents[13-15]. There have been a few reports on polymerization and characterization of itaconamates[15-17]. The authors[17] synthesized 19 types of itaconamate and clarified effects of *N*-(4-substituted phenyl) groups on their copolymerization with styrene (ST) and methyl methacrylate (MMA). Sato and co-workers[16] investigated methyl *N*-phenylitaconamate kinetically and by electron spin resonance (e.s.r.) spectroscopy. Otsu and co-workers[15] synthesized two types of isomers of itaconamate and studied radical polymerization reactivities. There have been few reports on the synthesis and chiroptical properties of optically active itaconic acid derivative polymers except for our reports concerning optically active mono-L-menthyl[18] and di-L-menthyl itaconates[19]. Thus, the authors recently reported polymerization reactivities of *N*-[4-*N'*-((*R*)-α-methylbenzyl)-aminocarbonylphenyl]itaconimide[20] and chiroptical properties of the polymers and copolymers. However, there have been no reports on optically active itaconamate.

On the other hand, polymerization reactivities of cyclic 1,2-disubstituted ethylene type monomer, i.e. *N*-substituted maleimides (RMI) bearing an optically active group such as (*R*)-α-methylbenzyl[21-24], L-menthyl[25,26] and cholesteryl[27-29] group, and chiroptical properties of the polymers and copolymers were investigated. These reports[21-29] found that chiroptical properties of the polymers and copolymers were significantly influenced by asymmetric induction into the polymer main chain and asymmetric perturbation by the side chain chromophore. In addition, we clarified that (*R*)-α-methylbenzyl group can most strongly influence chiroptical properties of the polymers and copolymers in all optically active substituents studied so far[21-29]. Thus, we tried to investigate optically active itaconamates bearing (*R*)-α-methylbenzyl group.

In this study, two types of optically active itaconamate, α-ethyl β-*N*-((*R*)-α-methylbenzyl)itaconamate (MBEI) and α-*N*-((*R*)-α-methylbenzyl)β-ethyl itaconamate (EMBI) are synthesized from itaconic anhydride, (*R*)-α-methylbenzylamine and ethanol. MBEI and EMBI are polymerized and copolymerized with styrene (ST), methyl methacrylate (MMA) or *N*-phenylmaleimide (PhMI) in the presence of radical initiators. From the results, monomer reactivity ratios (r_1, r_2) and Alfrey–Price Q–e values are determined. Based on specific rotations $[\alpha]_D$ and circular dichroism (CD) spectra, chiroptical properties of poly(MBEI), poly(EMBI), and the copolymers are investigated, as compared with those of model compounds for the homopolymers.

EXPERIMENTAL

MBEI and EMBI monomers

MBEI and EMBI monomers were synthesized from itaconic anhydride, (*R*)-α-methylbenzylamine and ethanol, as shown in *Scheme 1*.

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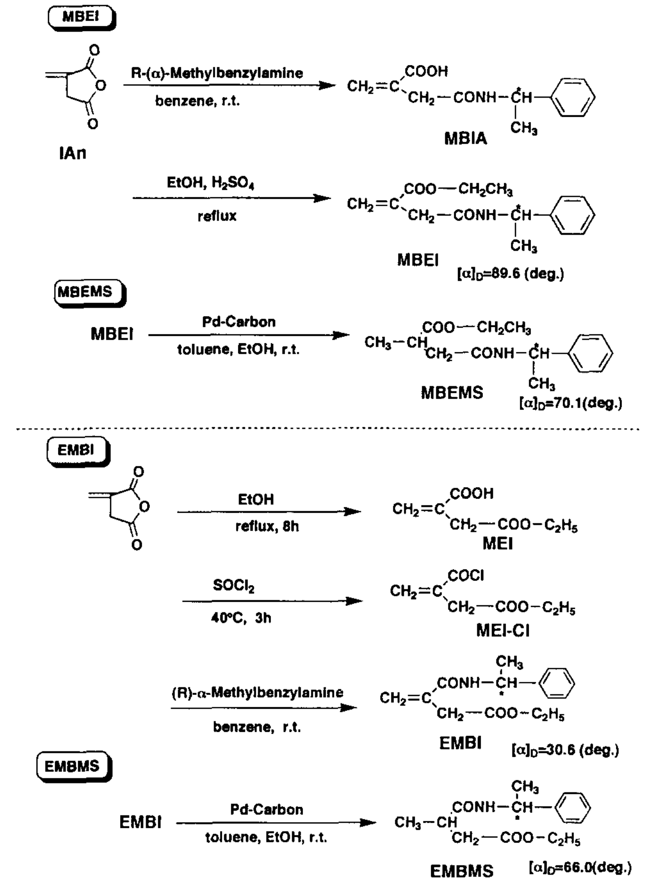

Scheme 1

β-N-((R)-α-Methylbenzyl)itaconamic acid (MBIA). A solution of (*R*)-α-methylbenzylamine (9.7 g, 0.1 mol) in benzene (10 ml) was added dropwise to a solution of itaconic anhydride (11.0 g, 0.10 mol) in benzene (100 ml) at room temperature (r.t.) and then the mixture was stirred at r.t. for 10 h. After the reaction was completed, the resulting product was filtered and recrystallized twice from chloroform to obtain pure MBIA: yield 56.6%; m.p. 143–145°C. I.r. (KBr disk; cm^{-1}): 3270 (NH), 2300 (COOH), 1690 (CONH), 1590 (COO), 1535 (CONH). ^{1}H n.m.r. (δ, ppm from TMS in deuterium dimethyl sulfoxide (DMSO-d_6)); 8.32 (d, $J = 8.25$ Hz, 1H, NH), 7.32–7.14 (m, 5H in phenyl), 6.09 and 5.63 (ss, 2H, CH_2 =C), 4.93–4.10 (m, 1H, CH–N), 3.14 (s, 2H, CH_2–CO), 1.33 (d, $J = 7.26$ Hz, 3H, CH_3).

α-Ethyl β-N-((R)-α-methylbenzyl) itaconamate (MBEI). A solution of MBIA (4.0 g; 17 mmol) in 40 ml of ethanol containing a small amount of sulfuric acid as catalyst was refluxed for 8 h. After the reaction was completed, the reaction mixture was neutralized by an addition of aqueous sodium hydrogen carbonate (1%) solution. The organic product was extracted with diethyl ether from the mixture, and then the organic layer was dried on magnesium sulfate. The ether solution was evaporated and distilled under reduced pressure to obtain crude MBEI. The distillation was repeated twice to give pure MBEI: 3.0 g, yield 32.6%; b.p. 158–160°C (7.4×10^{-2} mmHg), $[\alpha]_D = 89.6°$ ($c = 1.0$ g dl^{-1}, $l =$ 10 cm, THF). I.r. (neat; cm^{-1}): 3300 (NH), 3050 (CH in phenyl), 1730 (CONH), 1650 (CO), 1550 (CONH). ^{1}H n.m.r. (δ, ppm from TMS in $CDCl_3$): 7.35–7.20 (m, 5H, in phenyl), 6.28 (d, $J = 5.94$, 1H, CONH), 6.31 and 5.82 (ss, 2H, CH_2 =C), 5.14–5.03 (m, 1H, N–CH), 4.19 (q, $J = 7.26$ Hz, 2H, O–CH_2), 3.21 (s, 2H, CH_2–CO), 1.45 (d, $J = 6.93$ Hz, 3H, N–C–CH_3), 1.27 (t, $J =$ 6.92 Hz, 3H, O–CCH_3). ^{13}C n.m.r. (σ, ppm from TMS in $CDCl_3$): 168.66 (C=O), 166.92 (C=O), 143.16 and 134.47 (CH_2 =C), 128.90, 128.57, 127.22 and 126.04 (6 carbons in phenyl), 61.26 (O–CH_2), 48.78 (CH), 40.54 (*C*H_2CO), 21.80 (CH–*C*H_3), 14.07 (CH_2–*C*H_3).

Elemental analysis: found: C = 68.96%, H = 7.29%, N = 5.34%; calcd for $C_{15}H_{19}NO_3$: C = 68.94%, H = 7.33%, N = 5.36%.

EMBI monomer

β-Monoethyl itaconate (MEI). MEI was synthesized from itaconic anhydride and ethanol: yield 65.3%; m.p. 58–59°C.

α-Chloro β-ethyl itaconyl (MEI-Cl). A mixture of MEI (7.7 g, 49 mmol) and thionyl chloride (20 ml) was heated at 40°C for 3 h. Unreacted thionyl chloride was evaporated out to obtain MEI-Cl: 8.8 g; yield 99%. I.r. (neat, cm^{-1}): 1730 (C = O), 1140 (COO). ^{1}H n.m.r. (δ, ppm from TMS in $CDCl_3$): 6.71 and 6.17 (ss, 2H, CH_2 = C), 4.17 (q, $J = 7.26$ Hz, 2H, OCH_2), 3.36 (s, 2H, CH_2–CO), 1.26 (t, $J = 7.26$ Hz, 3H, CH_3).

α-N-((R)-α-Methylbenzyl)β-ethyl itaconamate (EMBI). A solution of MEI-Cl (8.3 g, 47 mmol) in benzene (30 ml) was added dropwise to a mixture of (*R*)-α-methylbenzylamine (5.1 g, 32 mmol) and triethylamine (3.9 g, 43 mmol) in benzene (150 ml) below 10°C under nitrogen atmosphere. After the addition was completed, the mixture was stirred at 10°C for 1 h, then at r.t. for 10 h. The reaction mixture was filtered to exclude precipitating triethylammonium chloride salt. The filtrate was washed with water and aqueous solution containing 1 N of hydrochloric acid three times, and then the organic layer was dried on magnesium sulfate. Organic reagents were evaporated out to give solid product. The organic produce was treated by column chromatography on silica gel using chloroform as developing solvent. Chloroform was evaporated, and then the residue was recrystallized three times from n-hexane to obtain pure EMBI: 4.0 g; yield 32.6%; m.p. 72–74°C; $[\alpha]_D = 30.6°$ ($c = 1.0$ g dl^{-1}, $l = 10$ cm, THF). I.r. (KBr disk; cm^{-1}): 3270 (NH), 1735 (CONH), 1650 (C = O), 1605 (CO). ^{1}H n.m.r. (δ, ppm from TMS in $CDCl_3$): 7.35–7.24 (m, 5H, in phenyl), 6.46 (d, $J = 6.20$ Hz, 1H, CONH), 5.79 and 5.46 (ss, 2H, CH_2 = C), 5.19–5.14 (m, 1H, N–CH), 4.09 (q, $J = 6.93$ Hz, 2H, O–CH_2), 3.38–3.36 (dd, $J = 4.62$ Hz, 2H, CH_2–CO), 1.54 (d, $J = 6.60$ Hz, 3H, N–C–CH_3), 1.23 (t, $J = 7.26$ Hz, 3H, O–C–*C*H_3). ^{13}C n.m.r. (δ, ppm from TMS in $CDCl_3$): 171.16 (CONH), 166.76 (C = O), 143.07 and 138.54 (CH_2 = C), 128.66, 127.35, 126.15 and 121.58 (6 carbons in phenyl), 61.13 (O–CH_2), 49.04 (N–CH), 38.44 (*C*H_2–CO), 21.78 (CH–CH_3), 14.07 (CH_2–*C*H_3).

Elemental analysis: found: C = 68.93%, H = 7.30%; calcd for $C_{15}H_{19}NO_3$: C = 68.94%, H = 7.33%, N = 5.36%.

Model compounds for homopolymers

α-Ethyl β-N-((R)-α′-methylbenzyl)-(RS)-methyl succinamate (MBEMS). MBEMS was prepared by hydrogen reduction of MBEI monomer using palladium–carbon (Pd-C, 10 wt%) as a catalyst. A mixture of MBEI monomer (1.0 g, 2.7 mmol), activated Pd-C (0.10 g), toluene (50 ml) and ethanol (50 ml) was contacted with a theoretical amount of hydrogen gas using a hydrogen reduction apparatus. After the reaction was completed, the Pd-C was filtered from the reaction mixture, and then the filtrate was concentrated with evaporator. To the residual mixture was added methylene dichloride, the solution was washed with water three times, then the organic layer was dried on magnesium sulfate. The organic solution was evaporated and treated by column chromatography on activated alumina, using n-hexane/ethyl acetate (50/50 vol/vol) as a developing solvent to obtain crude MBEMS. The crude MBEMS was purified by distillation: yield 67.5%; b.p. 120–123°C; $[\alpha]_D = 70.1°$ ($c = 1.0\,\mathrm{g\,dl^{-1}}$, $l = 10\,\mathrm{cm}$, THF). I.r. (neat; $\mathrm{cm^{-1}}$): 3250 (NH), 2950 (CH), 1725 (CONH), 1640 (CO), 1540 (CONH), and 1170 (COO). ^{1}H n.m.r. (δ, ppm from TMS in $CDCl_3$): 7.33–7.23 (m, 5H, in phenyl), 5.89 (bs, 1H, CONH), 5.16–5.06 (m, 1H, N–CH), 4.19–4.04 (m, 2H, COO–CH_2), 3.03–2.91 (m, 1H, CH_3–*CH*–CO), 2.62–2.53 and 2.29–2.21 (mm, 2H, CH–CH_2–CON), 1.48 (d, $J = 6.93$ Hz, 3H, N–C–CH_3), 1.28–1.17 (m, 6H, CH_3–CH, CH_2–CH_3). ^{13}C n.m.r. (δ, ppm from TMS in $CDCl_3$): 176.01 (CONH), 169.90 (C = *O*), 143.14, 128.64, 127.97 and 126.15 (6 carbons in phenyl), 60.68 (O–CH_2), 48.71 (N–CH), 40.02 (*C*HCO), 36.48 (*C*H_2CO), 21.84 (PhCH–*C*H_3), 17.33 (CH_2–*C*H_3), 14.09 (*C*H_3CHCO).

α-N-((R)-α′-Methylbenzyl)β-ethyl-(RS)-methyl succinamate (EMBMS). EMBMS was prepared by hydrogen reduction of EMBI monomer, according to a method similar to that of MBEMS. Yield 68.5%; b.p. 133–135°C; $[\alpha]_D = 66.0°$ ($c = 1.0\,\mathrm{g\,dl^{-1}}$, $l = 10\,\mathrm{cm}$, THF). I.r. (neat; $\mathrm{cm^{-1}}$): 3250 (NH), 1730 (CO), 1640 (CONH), 1510 (CONH). ^{1}H n.m.r. (δ, ppm from TMS in $CDCl_3$): 7.26–7.11 (m, 5H, in phenyl), 5.89 (bs, 1H, CONH), 5.06–5.00 (m, 1H, N–CH), 4.11–3.95 (m, 2H, COO–CH_2), 2.75–2.58 (m, 2H, CH–CH_2–CO), 2.33–2.25 (m, 1H, *CH*CO), 1.40 (d, $J = 6.93$ Hz, 3H, N–C–CH_3), 1.21–1.09 (m, 6H, CH_3–CH, CH_2–CH_3). ^{13}C n.m.r. (δ, ppm from TMS in $CDCl_3$): 174.07 (CONH), 172.54 (C = O), 143.25, 128.57, 127.29 and 126.07 (6 carbons in phenyl), 60.61 (O–CH_2), 48.66 (N–CH), 38.26 (*C*HCO), 37.06 (*C*H_2CO), 21.84 (Ph-CH-*C*H_3), 17.74 (OCH_2*C*H_3), 14.09 (*C*H_3CHCO).

Other materials

N-Phenylmaleimide (PhMI) was synthesized from maleic anhydride and aniline, according to the usual method of synthesis for RMI compounds[30]. ST and MMA were purified by the ordinary method[31]. THF and benzene were purified by distillation after being refluxed in the presence of sodium. Other solvents were purified by the usual method[32]. 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized twice from methanol and chloroform, and benzoyl peroxide (BPO) was purified by recrystallization twice from chloroform[31]. Commercially available tert-butyl peroxypivalate (PBPV), tert-butyl peroxyneodecanate (PBND) and di-tert-butyl peroxide (DTBP) were used without further purification.

Homopolymerization and copolymerization

Radical homopolymerizations were carried out with various initiators in several solvents or bulk in a sealed tube at 50 to 130°C. After polymerization, MBEI

Table 1 Radical polymerization of MBEI

Run	MBEI ($\mathrm{mol\,l^{-1}}$)	Initiator[a] ($\times 10^2\,\mathrm{mol\,l^{-1}}$)	Polym. solvent[b] (ml)	Polym. temp. (°C)	Polym. time (h)	Convn (%)	$\bar{M}_n$ ($\times 10^{-4}$)	$\bar{M}_w/\bar{M}_n$	$[\alpha]_D^{25e}$ (deg.)
1	1.90[c]	AIBN(2.0)[d]	none	70	22	0			
2	0.95	AIBN(1.0)	THF(2.0)	70	22	0			
3	0.97	AIBN(5.0)	THF(5.0)	70	24	0			
4	1.91[c]	DTBP(5.0)[d]	none	130	24	0			
5	1.91[c]	PBPV(5.0)[d]	none	70	24	4.6			
6	1.91[c]	AIBN(5.0)[d]	none	70	24	trace			
7	0.96	AIBN(5.0)	BEN(2.0)	70	24	0			
8	0.97	AIBN(10.0)	THF(2.0)	70	24	0			
9	0.96	AIBN(10.0)	BEN(2.0)	70	24	0			
10	1.92	PBND(10.0)	BEN(1.0)	50	24	7.4			
11	1.92	AIBN(10.0)	BEN(1.0)	60	24	1.9			
12	1.90[c]	PBND(10.0)[d]	none	50	24	68.2	1.31	2.91	30.9
13	1.92[c]	AIBN(10.0)[d]	none	60	24	54.0	1.52	2.80	31.4
14	1.92[c]	BPO(10.0)[d]	none	80	24	trace			
15	1.90	BPO(10.0)	BEN(1.0)	80	24.5	0			
16	1.94	DTBP(10.0)	CB(1.0)	130	24	0			
17	1.93[c]	DTBP(10.0)[d]	none	130	24	0			

[a] DTBP, di-t-butyl peroxide; PBPV, t-butyl peroxypivalate; PBND, t-butyl peroxyneodecanoate; BPO, benzoyl peroxide
[b] THF, tetrahydrofuran; BEN, benzene; CB, chlorobenzene
[c] $\times 10^{-3}$ mol
[d] Amount of initiator: mol% of MBEI
[e] $c \approx 1.0\,\mathrm{g\,dl^{-1}}$; $l = 5\,\mathrm{cm}$; THF

Table 2 Radical polymerization of EMBI

Run	EMBI ($\mathrm{mol\,l^{-1}}$)	Initiator[a] ($\times 10^2\,\mathrm{mol\,l^{-1}}$)	Polym. solvent[a] (ml)	Polym. temp. (°C)	Polym. time (h)	Convn (%)	$\bar{M}_n$ ($\times 10^{-3}$)	$\bar{M}_w/\bar{M}_n^b$	$[\alpha]_D^c$ (deg.)
1	1.89	AIBN(1.0)	BEN(1.0)	60	24	0			
2	1.91	AIBN(10.0)	BEN(1.0)	60	24	trace	–[d]	–[d]	–[d]
3	1.91	AIBN(10.0)	DMF(1.0)	60	24	0			
4	1.91[e]	BPO(10.0)[f]	none	80	24	57.5	1.1	1.73	54.5
5	1.91	AIBN(10.0)	BEN(1.0)	80	50	0			

[a] DMF, *N,N*-dimethylformamide; BEN, benzene
[b] By g.p.c.
[e] $c \approx 1.0\,\mathrm{g\,dl^{-1}}$; $l = 5\,\mathrm{cm}$; THF
[d] No measurements
[e] $\times 10^{-3}$ mol
[f] mol% of EMBI

polymer solution was poured into a large amount of methanol to precipitate the polymers. The obtained MBEI polymer was purified by reprecipitation from the THF solution to methanol three times. In EMBI polymers, methanol/water (2/1 vol/vol) was used as precipitant instead of methanol. The polymer was filtered and dried *in vacuo* for a day at 40°C. Radical copolymerizations of MBEI (or EMBI) with ST or MMA were carried out in benzene at 60°C, according to a procedure similar to that of homopolymerization. The composition of the copolymer was calculated from elemental analysis (N) and ^{1}H n.m.r. spectra.

Measurement

D-line specific rotations ($c = 1.0\,\mathrm{g\,dl^{-1}}$, $l = 5$ or 10 cm, THF) were measured at 25°C with a Jasco DIP-140 (Japan Spectroscopic Co.). Circular dichroism (c.d.) spectra ($c = 0.025$–$0.05\,\mathrm{g\,dl^{-1}}$, $l = 0.2$ or 1 mm, THF) were obtained at 25°C using a Jasco J-20C (Japan Spectroscopic Co.), equipped with a xenon source and computing data processor. U.v. spectra ($c = 0.01$–$0.04\,\mathrm{g\,dl^{-1}}$, $l = 1$ mm, THF) were obtained with a Shimadzu 200A spectrophotometer. Molecular weights of the polymers were measured by gel permeation chromatography (g.p.c.) using the same technique as described earlier[26]. I.r., n.m.r. measurement and elemental analysis were determined using the same instruments as reported previously[26].

RESULTS AND DISCUSSION

Radical homopolymerizations of MBEI and EMBI

Radical homopolymerizations of MBEI and EMBI were performed under several conditions. The results of radical homopolymerizations of MBEI and EMBI are shown in *Tables 1* and *2*, respectively. As can be seen from the tables, the polymerization reactivities were very low. Only bulk polymerization of MBEI gave the polymers in 55 to 68% yields. All polymerizations proceeded homogeneously throughout. Radical bulk polymerizations of MBEI gave higher yields than solution polymerizations. Polymerization of MBEI in benzene with PBND and AIBN even at 50 and 60°C gave polymers in low yield. But no MBEI homopolymers could be obtained over 80°C. Thus, it was considered that MBEI monomer has a ceiling temperature around 80°C.

No EMBI homopolymers could be obtained in solution polymerization, but bulk polymerization of EMBI gave the homopolymer in 57% yield. Number average molecular weight ($\overline{M_n}$) of MBEI homopolymer was higher than that of EMBI homopolymer. Thus, MBEI monomer has higher polymerizability than EMBI monomer. The reason for this is the different position of the *N*-substituent. MBEI is an α-substituted acrylic ester derivative, and EMBI is an α-substituted acrylamide derivative. Since an amide group of EMBI is attached directly to the reacting double bond, the effect of steric hindrance in EMBI monomer may be larger than that of MBEI. Otsu and co-workers[15] reported the polymerizations of two isomers of methyl itaconamate derivatives. The polymerizability of isomer with an *N*-substituent at the α-position in itaconic acid, i.e. α-substituted acrylamide, was inferior to that of isomer with an *N*-substituent at the β-position, α-substituted acrylic ester, because of different conformations[15]. Since EMBI takes twist or s-*trans* conformation[15] due to the bulky (*R*)-α-methylbenzyl group, the polymerization reactivities of EMBI may be lower than those of MBEI.

Optical properties of homopolymers

C.d. spectra for poly(MBEI), the model compounds, and MBEI monomer are shown in *Figure 1*. In all c.d. spectra some small negative peaks and a large positive peak were observed at about 260 nm and 225 nm, respectively. Both peaks were attributable to the n–π^* electron transition of two carbonyl groups and the π–π^* transition of phenyl groups, as can be seen from the u.v. spectra shown in *Figure 1*. The c.d. pattern and molecular ellipticity [θ] for the poly(MBEI) were similar to those of MBEMS (the model compound for poly(MBEI)), as shown in *Figure 1*.

In u.v. spectra (*Figure 2*), ϵ values for the EMBI system were greater than those for the MBEI system. However, there was little difference of pattern between the systems. The c.d. pattern and molecular ellipticity for poly(EMBI) were also similar to those of MBEMS (the model compound for poly(EMBI)), as can be seen from *Figure 2*.

The authors have tried to synthesize a better model compound for poly(MBEM) than MBEMS. That is, 2,2-dimethylsuccinic anhydride was used as the starting material to substitute the α-proton of MBEMS with a methyl group. However, it was difficult to synthesize pure model compound since the additional product from dimethylsuccinic anhydride and α-methylbenzylamine was a mixture of α- and β-types which could not be

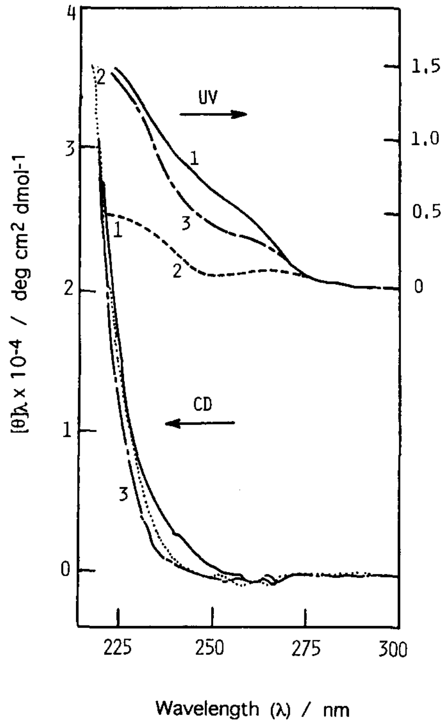

Figure 1 C.d. and u.v. spectra for (1) MBEI monomer, (2) MBEMS (model compound for poly(MBEI)), and (3) poly(MBEI) obtained in bulk (run 13 in *Table 1*)

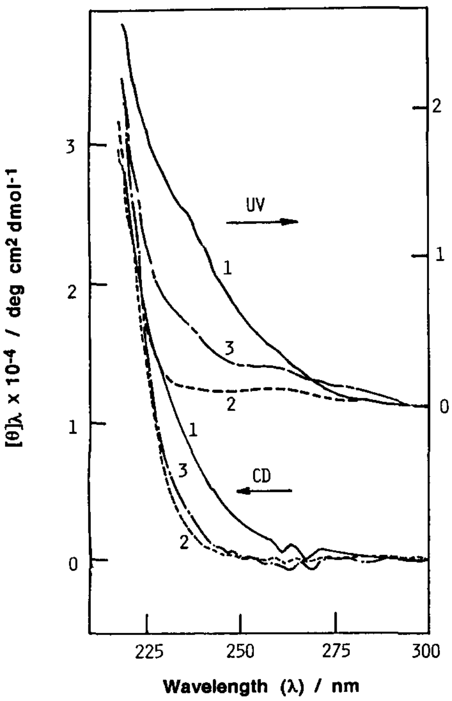

Figure 2 C.d. and u.v. spectra for (1) EMBI monomer, (2) EMBMS (model compound for poly(EMBI)), and (3) poly(EMBI) obtained in bulk (run 4 in *Table 2*)

separated. Thus the desired pure model compound has not yet been synthesized.

In the maleimide derivative polymers bearing an optically active α-methylbenzyl group at the side chain, chiroptical properties of the polymers can be significantly influenced by the π–π^* electron transition based on the benzyl chromophore[21–29]. In this study, however, the influence is considered to be very small since there was little difference of the c.d. patterns between the polymers and model compound in spite of the practical difference of the optical rotation between them.

Radical copolymerizations of MBEI (or EMBI) with ST, MMA or PhMI

The results of radical copolymerizations of MBEI (or EMBI) (M_1) with ST (M_2), MMA (M_2) or PhMI (M_2) in benzene at 60°C are summarized in *Tables 3* and *4*. All copolymerizations proceeded homogeneously throughout. The obtained copolymers were white powders and were optically active. In all systems, both yields and $\overline{M}_n$ of the copolymers become lower with increasing amount of MBEI and EMBI in the feed, as can be seen from *Tables 3* and *4*. When the amount of MBEI or EMBI was the highest in the monomer feed, the copolymerizations were performed at 60°C over 6 days to obtain the copolymer. This indicates that MBEI and EMBI have very low reactivity in solution polymerization, as described in the homopolymerization section.

Copolymer composition curves for MBEI/ST, MBEI/MMA, MBEI/PhMI, EMBI/ST, EMBI/MMA and EMBI/PhMI systems are shown in *Figures 3* and *4*. Monomer reactivity ratios, r_1 and r_2, were determined as $r_1 = 0.35$, $r_2 = 0.14$ for MBEI/ST, $r_1 = 0.03$, $r_2 = 1.12$ for EMBI/ST, $r_1 = 0.02$, $r_2 = 2.39$ for EMBI/MMA, $r_1 = 4.35$, $r_2 = 0.17$ for MBEI/PhMI, $r_1 = 1.04$, $r_2 = 0.13$ for EMBI/PhMI, according to the high-conversion method reported by Tüdos *et al.*[33]. Both MBEI and EMBI monomers had high copolymerization reactivities with PhMI. But in the MMA systems the reactivities were very low. Alfrey–Price[34] Q–e values for MBEI and EMBI were calculated as $Q_1 = 1.80$, $e_1 = 0.94$ for MBEI/ST, and $Q_1 = 0.21$, $e_1 = 1.04$ for the EMBI/ST system. The e values calculated from both systems were almost the same, but the Q values were very different. It seems that the Q value calculated from the MBEI/ST system was abnormally large, as compared with that of *N*-(4-substituted phenyl)itaconamate reported previously[17]. The reason for the larger Q value cannot be explained clearly. In the Alfrey–Price Q–e theory, no steric effect is considered[34]. It is considered that steric hindrance in our MBEI monomer cannot be negligible because the *N*-substituent of MBEI is the very bulky α-methylbenzyl group. In the EMBI/ST and EMBI/MMA systems, r_1 values were generally lower than those of acrylamide derivatives[35]. The reason may be that the polymerization reactivity of EMBI is inferior to that of acrylamide derivatives because of steric hindrance of EMBI containing an ethoxy group at the β-position of itaconic acid.

Optical behaviour of copolymers

The c.d. spectra for copolymers are shown in *Figure 5*. In general, the c.d. patterns for MBEI copolymers were similar to those for corresponding EMBI copolymers. A positive Cotton effect was observed at about 220 nm, based on the n–π^* electron transition of carbonyl groups of MBEI (or EMBI, MMA) monomeric units and the π–π^* transition of phenyl groups of the MBEI (or EMBI, ST, PhMI) monomeric units. The molecular ellipticity $[\theta]$ (calculated from the average molecular weight of the monomeric units) for poly(EMBI-*co*-ST) was practically smaller than that for poly(MBEI-*co*-ST) although the

Table 3 Copolymerization of MBEI (M_1) in benzene (1 ml) at 60°C[a]

Run	M_2	M_1 in monomer (mol%)	Polym. time (h)	Convn (%)	M_1 in[b] copolymer (mol%)	$\overline{M}_n^c$ ($\times 10^{-4}$)	$\overline{M}_w/\overline{M}_n$	$[\alpha]_D^{25d}$ (deg.)
1	ST	4.7	11	18.2	13.4	0.57	1.04	14.9
2	ST	10.2	11	21.0	23.9	3.99	1.92	22.0
3	ST	16.9	11	18.8	36.4	3.77	1.90	25.4
4	ST	29.9	6.5	16.5	46.0	3.46	1.89	28.9
5	ST	47.9	24	19.1	59.6	1.92	1.58	29.2
6	ST	68.9	24	19.0	71.0	1.16	1.92	37.6
7	ST	86.0	178	13.2	83.2	0.98	1.92	39.2
8	ST	92.7	184	6.8	91.5	0.64	1.87	41.3
9	MMA	5.2	3.5	16.1	6.9	5.92	3.15	10.1
10	MMA	10.2	3.5	16.7	11.5	6.01	2.65	17.3
11	MMA	20.1	7	17.5	18.3	6.08	1.94	23.6
12	MMA	30.1	7	10.6	24.3	1.31	5.36	34.8
13	PhMI	10.3	3.5	21.1	20.7	2.27	2.32	26.7
14	PhMI	30.0	8	14.1	54.9	1.53	1.86	43.7
15	PhMI	51.1	8	11.2	78.3	1.63	1.47	49.6
16	PhMI	70.0	15.5	11.8	95.8	1.28	1.38	53.9
17	PhMI	89.8	153	9.0	96.9	0.18	3.65	57.7

[a] [AIBN] = 1.0×10^{-2} mol l^{-1}; $M_1 + M_2 = 0.5$ g
[b] Determined by ^{1}H n.m.r. and elemental analysis
[c] By g.p.c.
[d] $c = 1.0$ g dl^{-1}; $l = 5$ cm; THF

Table 4 Copolymerization of EMBI (M_1) in benzene (1 ml) at 60°C[a]

Run	M_2	M_1 in monomer (mol%)	Polym. time (h)	Convn (%)	M_1 in[b] copolymer (mol%)	$\overline{M}_n^c$ ($\times 10^{-4}$)	$\overline{M}_w/\overline{M}_n$	$[\alpha]_D^{25d}$ (deg.)
1	ST	5.1	9.3	12.4	6.6	3.46	1.79	3.9
2	ST	10.1	9.5	11.6	8.6	2.76	1.93	8.2
3	ST	16.7	13	13.0	13.8	2.02	1.86	11.4
4	ST	23.8	13	9.4	17.3	1.89	1.45	15.8
5	ST	48.9	23	22.6	30.5	0.78	1.33	27.7
6	ST	69.9	46.5	10.2	41.1	0.48	1.41	39.9
7	ST	79.1	60.5	7.4	43.3	0.63	1.08	39.7
8	MMA	5.1	4	25.6	2.8	1.46[e]	1.94	2.1
9	MMA	10.1	5	25.4	6.3	6.88	2.51	2.6
10	MMA	20.2	9	34.1	7.6	4.40	2.43	5.6
11	MMA	30.2	14	29.8	13.2	4.31	1.79	10.5
12	MMA	50.3	54	17.8	22.8	1.04	2.21	21.8
13	MMA	69.5	98	17.4	34.1	0.67	1.58	28.5
14	MMA	76.9	146	16.7	35.4	0.75	1.36	34.4
15	PhMI	10.2	8.5	26.4	27.1	1.74	2.25	24.4
16	PhMI	30.0	16	11.2	59.4	1.20	1.94	42.1
17	PhMI	50.8	16.5	6.5	64.9	0.30	4.74	47.2
18	PhMI	69.6	48	11.7	72.6	0.47	1.77	57.4
19	PhMI	89.3	118	0				

[a] [AIBN] = 1.0×10^{-2} mol l^{-1}; $M_1 + M_2 = 0.5$ g
[b] Determined by ^{1}H n.m.r. and elemental analysis
[c] By g.p.c.
[d] $c = 1.0$ g dl^{-1}; $l = 5$ cm; THF
[e] $\times 10^{-5}$

content of chiral unit in the copolymer was almost the same. This tendency was also observed in the specific rotation of both systems, as shown in *Tables 1* and *2*. *Figures 6* and *7* show the dependence of specific rotations $[\alpha]_D$ on the compositions (wt%) of copolymers in the MBEI and EMBI copolymerization systems, respectively. In both systems the absolute values of specific rotations of the MBEI and EMBI copolymers increased with the content of MBEI and EMBI monomeric unit. A dotted line (1 in *Figures 6* and *7*), connecting 0 with $[\alpha]_D$ of the homopolymer, shows that chiroptical properties of the copolymers are influenced not by co-unit (i.e. M_1–M_2

successive unit) but by optically active units (i.e. M_1–M_1 successive units).

In *Figure 6*, the specific rotations of poly(MBEI-*co*-ST) showed deviation from a dotted line (line 1), which suggests that chiroptical properties of MBEI/ST copolymers were appreciably influenced by a MBEI–ST diad sequence. This tendency was also observed in the MBEI/PhMI system. In the MBEI/PhMI system, deviation from line 1 was much larger than in the MBEI/ST system. This may be due to the different structure of PhMI (cyclic olefin type) from that of ST (vinyl type). That is, PhMI monomer can give polymers containing four types of additional structures, i.e. *trans* (threo-diisotactic and threo-disyndiotactic) and *cis* type (erythro-diisotactic and erythro-disyndiotactic)[36].

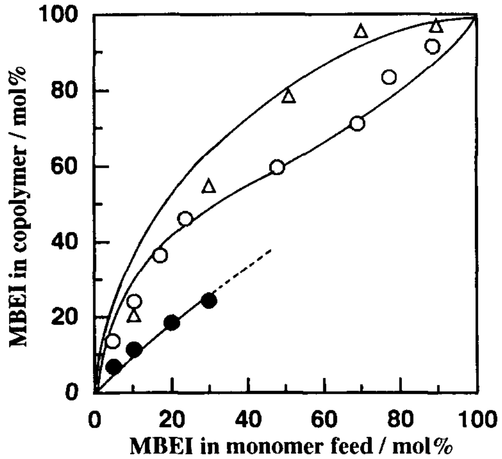

Figure 3 Copolymer composition curves for (○) MBEI/ST, (●) MBEI/MMA and (△) MBEI/PhMI systems

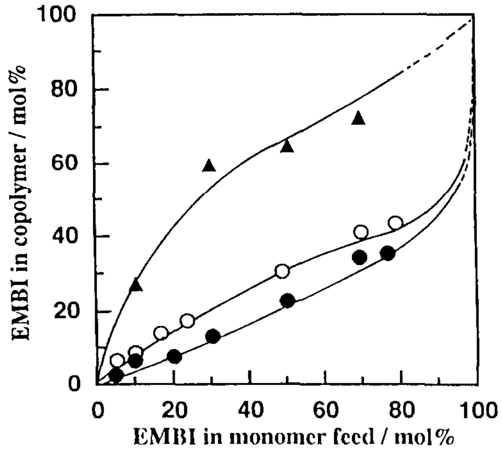

Figure 4 Copolymer composition curves for (○) EMBI/ST, (●) EMBI/MMA and (▲) EMBI/PhMI systems

In the EMBI systems, deviation from line 1 was generally smaller than in the MBEI systems. The specific rotations of poly(EMBI-*co*-ST)s and poly(EMBI-*co*-MMA)s increased almost linearly with the content of the EMBI monomeric unit. This linearity suggests that asymmetric induction in the copolymer was considerably influenced not by a EMBI–ST and EMBI–MMA diad sequence but by EMBI–EMBI successive units. In the copolymerizations of *N*-[4-((α-methylbenzyl)-aminocarbonyl)phenyl]itaconimide with ST or MMA reported previously[20], a similar tendency was observed. In the EMBI/PhMI system, the deviation was larger than in other systems.

It was found that the chiroptical properties of MBEI copolymers were significantly influenced by the M_1–M_2 diad sequence and that the chiroptical properties of EMBI copolymers were strongly affected rather by the M_1–M_1 diad sequence than by the M_1–M_2 diad sequence. The difference in chiroptical properties for MBEI and EMBI copolymers may be ascribed to the different structures of monomer and copolymer main chain. That is, MBEI is an α-substituted acrylic ester derivative, and EMBI is an α-substituted acrylamide derivative, as described above. In the EMBI systems, an optically active α-methylbenzylaminocarbonyl group can influence the chiroptical properties of the copolymer since the group is adjacent to a carbon of the polymer main chain. Thus, even though chromophores may exist in the comonomer, the chiroptical properties of the copolymers are most strongly influenced by the chromophore of EMBI itself. Consequently, in the EMBI systems the deviation from line 1 became

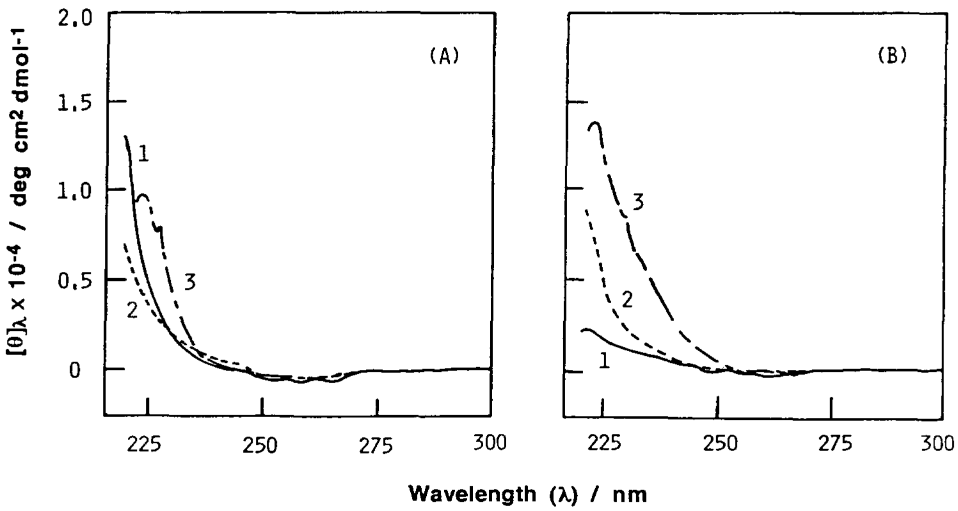

Figure 5 C.d. spectra. (A) (1) Poly(MBEI-*co*-ST) (run 1 in *Table 3*), (2) poly(MBEI-*co*-MMA) (run 12 in *Table 3*) and (3) poly(MBEI-*co*-PhMI) (run 14 in *Table 3*). (B) (1) Poly(EMBI-*co*-ST) (run 3 in *Table 4*), (2) poly(EMBI-*co*-MMA) (run 11 in *Table 4*) and (3) poly(EMBI-*co*-PhMI) (run 16 in *Table 4*)

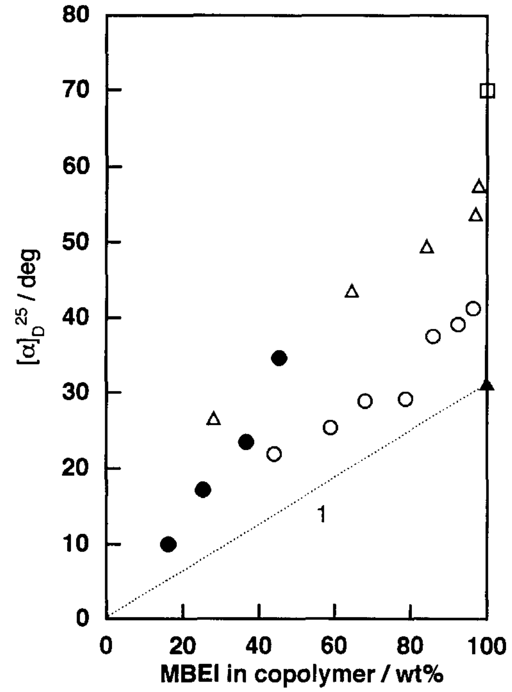

Figure 6 Dependence of specific rotation $[\alpha]_D$ on the composition (wt%) of (○) poly(MBEI-*co*-ST), (●) poly(MBEI-*co*-MMA), (△) poly(MBEI-*co*-PhMI), (▲) poly(MBEI) (run 13 in *Table 1*) and (□) MBEMS (model compound)

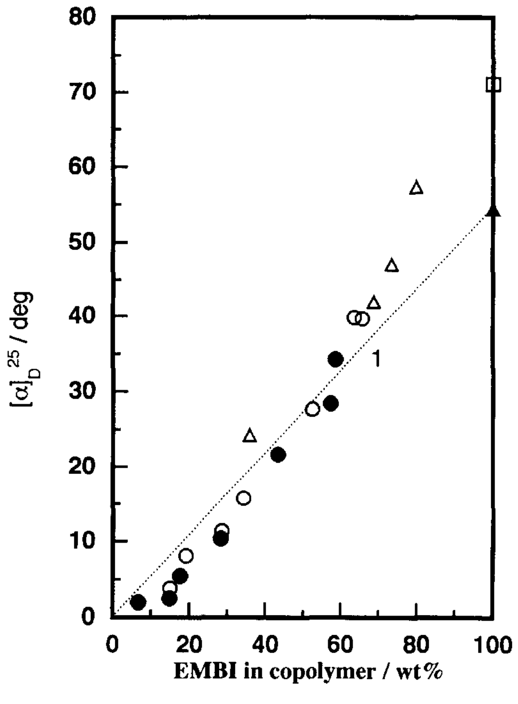

Figure 7 Dependence of specific rotation $[\alpha]_D$ on the composition (wt%) of (○) poly(EMBI-*co*-ST), (●) poly(EMBI-*co*-MMA), (△) poly(EMBI-*co*-PhMI), (▲) poly(EMBI) (run 4 in *Table 2*) and (□) EMBMS (model compound)

relatively small, as compared with that in MBEI systems. The chromophore can hardly influence the chiroptical properties of the copolymers since a methylene group in the MBEI exists between an α-methylbenzylaminocarbonyl group and a carbon of the main chain. Consequently the chromophores (a phenyl group in ST, carbonyl group in MMA, carbonylimido group in PhMI) in the comonomers had more influence on the chiroptical properties of the copolymers.

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