Synthesis and Polymerization of Optically Active N-[4-N'-(α-Methylbenzyl)aminocarbonylphenyl]itaconimide

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ABSTRACT: A new type of optically active N-[4-N'-(α-methylbenzyl)aminocarbonylphenyl]-itaconimide (MBPI) was synthesized from itaconic anhydride, p-aminobenzoic acid, and (R)-α-methylbenzylamine. The radical homopolymerization of MBPI was performed in tetrahydrofuran (THF) at 60—130°C for 22 h to give optically active polymers having $[\alpha]_D^{25} = -46.6$ to $-51.8°$. Anionic polymerizations of MBPI with n-butyllithium in THF and N,N-dimethylformamide were performed. But the yields were quite small. Radical copolymerizations of MBPI (M_1) were performed with styrene (ST, M_2), methyl methacrylate (MMA, M_2), or indene (ID, M_2) in THF at 70°C. Monomer reactivity ratios (r_1, r_2) and Alfrey–Price Q–e values were calculated. Chiroptical properties of the polymers and copolymers were also investigated.
KEY WORDS Optically Active Itaconimide / Radical Polymerization / Monomer Reactivity Ratio / Q–e values / Chiroptical Properties / Asymmetric Perturbation /

There have been some reports on the polymerization and copolymerization of N-substituted itaconimides (RII).[1-4] However, no studies on polymerization of optically active RII have been made. Thus, polymerization reactivity and chiroptical property of RII including a chiral group were of interest to us. We reported that radical copolymerizations of optical active N-[4-N'-(α-methylbenzyl)aminocarbonylphenyl]maleimide [(R)-MBPM[5] and (S)-MBPM[6]] were performed with styrene (ST) or methyl methacrylate (MMA). In these systems, relationships between specific rotation of the copolymers and content (wt%) of chiral MBPM monomeric unit indicated great deviation from linearity. This deviation could be attributed to (1) asymmetric induction into the copolymer main chain and/or (2) asymmetric perturbation of chromophore of the chiral side chain.

In this paper, a novel, optically active N-[4-N'-(α-methyl-benzyl)aminocarbonylphenyl]itaconimide (MBPI), is prepared from itaconic anhydride, p-aminobenzoic acid, and (R)-$(+)$-α-methylbenzylamine. MBPI is polymerized and copolymerized with styrene, methyl methacrylate, and indene (ID) in the presence of radical initiators. From the results, monomer reactivity ratios and Q–e values were determined. Based on specific rotations and molecular ellipticities of the copolymers, asymmetric induction into the copolymer main chain and asymmetric perturbation of chromophore of the chiral side chain are discussed and compared with that of (R)-MBPM[5] containing the same N-substituent as MBPI. MBPI was also polymerized with an anionic initiator.

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EXPERIMENTAL

MBPI Monomer

The MBPI monomer was synthesized from itaconic anhydride, *p*-aminobenzoic acid, and (*R*)-(+)-α-methylbenzylamine, as shown in Scheme 1.

N-(4-Carboxyphenyl)itaconamic acid (p-CPIA). Itaconic anhydride (42.6 g, 0.38 mol) and *p*-aminobenzoic acid (52.1 g, 0.38 mol) were dissolved in *N,N*-dimethylformamide (DMF; 240 ml). The mixture was stirred at room temperature for 16 h under nitrogen atmosphere. The resulting solution was poured into a large amount of water to precipitate crude *p*-CPIA. It was filtered, dried, and recrystallized three times from water to obtain pure *p*-CPIA (86.8%); mp 233—235°C. ^{1}H NMR (δ, ppm from tetramethylsilane (TMS) in deuterium dimethyl sulfoxide (DMSO-d_6): 12.63 (s, 1H, COOH), 10.34 (s, 1H, CONH), 7.92, 7.89, 7.72, 7.69 (4H, protons of phenyl), 6.19 and 5.78 (2H, CH$_2$=), 3.40 (2H, CH$_2$-CO-); ^{13}C NMR (δ, ppm from TMS in DMSO-d_6): 169.11 (carbon in COOH connecting phenyl), 167.60 (COOH), 166.97 (CONH), 135.60 and 127.89 (CH$_2$=C), 143.31, 130.46, 124.98, and 118.24 (other carbons in phenyl), and 38.56 (CH$_2$ in itaconimide).

N-(4-Carboxyphenyl)itaconimide (p-CPII). A mixture of *p*-CPIA (50.0 g; 0.2 mol), acetic anhydride (150 ml), and sodium acetate (1.6 g) was stirred at 60°C for 10 h. The reaction mixture was poured into a large amount of water to give crude *p*-CPII. The crude *p*-CPII was filtered, washed with water, dried, and recrystallized three times from methanol–water (2:5) mixture solution; yield 68.5%, mp 196—197°C; IR (cm^{-1}): 3100 (OH); 2950 (CH); 2300 (COOH); 1730 and 1700 (C=O); 1660 and 1600(C=C); 1375 (CH); 890(C=CH$_2$). ^{1}H NMR (δ, ppm from TMS in DMSO-d_6: 13.09 (s, 1H, COOH); 8.06, 7.48 (2d, J=8.25 Hz, 4H in phenyl); 6.24 and 5.77 (2H, CH$_2$=C), 3.55 (s, 2H, CH$_2$-CO). ^{13}C NMR (δ, ppm from TMS in DMSO-d_6): 173.37
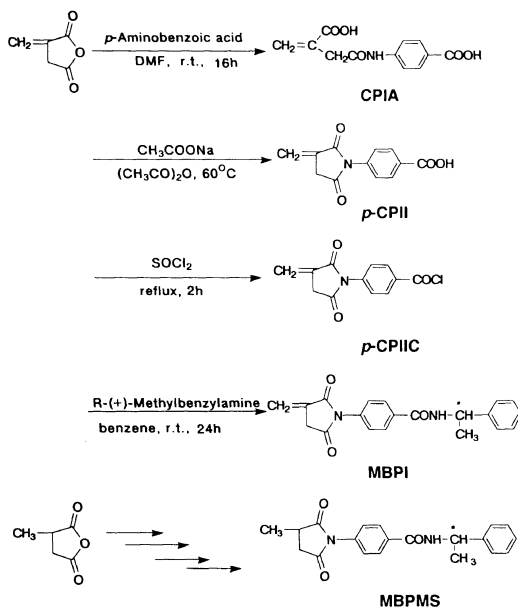
Scheme 1.

(COOH), 168.66 and 167.01 (–CO–N–CO), 136.59 and 127.46 (CH$_2$=C), 136.59, 130.69, 130.29, and 120.60 (other carbons in phenyl), and 34.28 (CH$_2$ in itaconimide).

N-[4-(Chlorocarbonyl)phenyl]itaconimide (p-CPIIC). A mixture of *p*-CPII (8.3 g; 0.036 mol) and thionyl chloride (40 ml) was refluxed for 2 h. Unreacted thionyl chloride was evaporated out, and the residual product was recrystallized from benzene to obtain pure *p*-CPIIC; 7.4 g, yield 83.3%; mp 163—164°C. IR (cm^{-1}): 1765 (COCl); 1710 (CO–N–CO); 1593 (C=C), 1365 (CH). ^{1}H NMR (δ, ppm from TMS in DMSO-d_6): 8.06 (d, J=8.25 Hz, 2H, in phenyl group), 7.48 (d, J=8.25 Hz, 2H in phenyl), 6.24 and 5.78 (2H, CH$_2$=), and 3.56 (s, 2H, CH$_2$-CO). ^{13}C NMR (δ, ppm from TMS in DMSO-d_6): 173.12 (COCl), 168.39 and 166.69 (CO–N–CO), 134.38 and 128.38 (CH$_2$=C), 136.32, 130.44, 130.37, 128.38, and 120.36 (other carbons in phenyl), and 34.04 (CH$_2$ in itaconimide).

N-[4-N'-((R)-α-Methylbenzyl)aminocarbonylphenyl]itaconimide (MBPI). A benzene (30 ml) solution of (*R*)-α-methylbenzylamine

(4.3 g, 0.035 mol) and triethylamine (3.3 g; 0.036 mol) was added dropwise to a solution of p-CPIIC (9.0 g, 0.036 mol) in benzene (400 ml) below 10°C under nitrogen atmosphere. After the addition, the mixture was stirred at room temperature for 24 h. The precipitated product was filtered, dried, and recrystallized from ethanol three times to obtain pure (R)-MBCP; 7.1 g, 61.6%, mp 207—208°C, $[\alpha]_D^{25} = -32.6°$ $(c = ca.\ 0.74\,g$ dl^{-1}, $l = 10$ cm, THF). IR (cm^{-1}): 3280 (NH); 1705 (C=O), 1655 (CONH); 1655 (C=C); 1160 and 1515 (CONH); 1370 (CH$_3$). ^{1}H NMR (δ, ppm from TMS in DMSO-d_6): 8.88 (d, $J = 8.24$ Hz, 1H, CONH); 8.05—7.19 (m, 9H in phenyl groups); 6.23 and 5.77 (2H, CH$_2$=), 5.23—5.12 (m, 1H, N–CH), 3.54 (m, 2H, CH$_2$–CO), and 1.48 (d, $J = 6.93$ Hz, 3H, N–C–CH$_3$). ^{13}C NMR (δ, ppm from TMS in DMSO-d_6): 173.16 (CONH), 168.45 and 164.96 (–CO–N–CO), 134.40 and 128.25 (CH$_2$=C), 144.80, 134.77, 134.32, 127.91, 126.74, 126.61, 126.02, and 120.16 (other carbons in phenyl), 48.56 (CH), 33.96 (CH$_2$ in itaconimide), 22.29 (CH$_3$). *Elemental analysis.* Found: C = 71.62%, H = 5.54%, N = 8.37%; Calcd for C$_{20}$H$_{18}$N$_2$O$_3$: C = 71.84%, H = 5.43%, N = 8.38%.

Model Compound of Poly(MBPI): N-[4-(N'-(R)-α-methylbenzyl)-aminocarbonylphenyl]-(RS)-α-methylsuccinimide (MBPMS). MBPMS was prepared from (RS)-α-methylsuccinic anhydride, p-aminobenzoic acid, and (R)-α-methylbenzylamine, according to a method similar to that of MBPI. Yields and mp of some precursors for MBPMS are as follows: N-(4-carboxyphenyl)-(RS)-α-methylsuccinamic acid (CPMSA): yield 85%; mp 214—216°C; N-(4-carboxyphenyl)-(RS)-α-methyl succinimide (CPMSI) recrystallized from methanol–water (5 : 2): yield 48.2%, mp 212— 213°C. N-[4-(Chlorocarbonyl)phenyl]-(RS)-α-methylsuccinimide recrystallized from benzene: yield 74.7%; mp 132—133°C.

MBPMS: yield 45.7%; mp 202—204°C; $[\alpha]_D^{25} = -23.8°$ $(c = 0.78\,g$ dl^{-1}, $l = 10$ cm,

THF). IR (cm^{-1}): 3300 (NH); 1710 (C=O), 1630 (CH=CH in phenyl); 1390 (CH); 695 (phenyl). ^{1}H NMR (δ, ppm from TMS in DMSO-d_6): 8.88 (d, $J = 8.24$ Hz, 1H, NH); 7.96 (d, $J = 8.57$ Hz, 2H in phenyl group); 7.41—7.20 (m, 7H in phenyl groups); 5.23—5.12 (m, 1H, CO–N–CH), 3.06—3.02 (s, 2H, CH$_2$CO–), 1.48 (d, $J = 7.26$ Hz, 3H, N–C–CH$_3$), 1.30 (d, $J = 6.92$ Hz, 3H, CH$_3$ in succinimide). ^{13}C NMR (δ, ppm from TMS in DMSO-d_6): 180.00 (CONH), 175.98, and 165.27 (CO–N–CO), 145.10, 135.35, 134.45, 128.56, 128.20, 127.05, 126.92, 126.33 (carbons in phenyl), 48.84 (N–CH), 36.57 (CH in succinimide), 34.86 (CH$_2$ in succinimide), 22.57 (CH$_3$), 16.00 (CH$_3$ in succinimide). *Elemental analysis* Found; C = 71.50%, H = 6.21%, N = 8.29% %; Calcd for C$_{20}$H$_{20}$N$_2$O$_3$: C = 71.41%, H = 5.99%, N = 8.33%.

Other Materials

ST and MMA were purified by ordinary methods.[7] Commercially available indene (ID) was purified by redistillation. THF and toluene were purified by distillation after refluxing in the presence of sodium. Methanol and other solvents were purified by the usual methods.[8] 2,2'-Azobisisobutyronitrile (AIBN) was purified from recrystallized twice from methanol and chloroform. Commercially available n-butyllithium (n-BuLi) hexane solution was used without further purification.

Homopolymerization and Copolymerization

Radical homopolymerizations were carried out with AIBN or DTBP as an initiator in several solvents in a sealed tube at 60 to 130°C. After polymerization, the polymer solution was poured into a large amount of methanol. To remove unreacted optically active monomer, reprecipitation was repeated three times from THF solution into a large amount of methanol. The homopolymers insoluble in organic solvents were thoroughly washed with methanol.

Copolymerizations of MBPI with ST, MMA

or ID were performed in THF at 70°C. The copolymerization procedure was similar to that of the polymerization. Composition of the copolymer was determined by nitrogen analysis (N) and ^{1}H NMR.

Anionic homopolymerizations were achieved in DMF at 0°C using n-BuLi as a catalyst under nitrogen atmosphere. Polymerization was terminated with a few drops of methanol using a syringe. The solution was poured into a large amount of methanol to precipitate the polymer. No appreciable polymers were obtained.

Measurements

D-Line specific rotations were measured in THF at 25°C with a Jasco DIP-140 (Japan Spectroscopic Co.), using a quartz cell (5 and 10 cm) and ca. 1.0 g dl^{-1} of sample concentration. Circular dichroism (CD) spectra were obtained in THF at 25°C by a JASCO J-20C (Japan Spectroscopic Co.), equipped with a xenon source and a computing data processor, using a quartz cell (1 mm) and ca. 2.5 × 10^{-2}—

5.0 × 10^{-2} g dl^{-1} of sample concentration. UV spectra were obtained in THF at 25 °C with Shimadzu UV-200A spectrophotometer (Shimadzu Co.), using a quartz cell (1 cm) and ca. 2.5 × 10^{-3}—5.0 × 10^{-3} g dl^{-1} of sample concentration. Molecular weights of the polymers were measured by gel permeation chromatographic (GPC) analysis using the same technique as described earlier.[9] IR and NMR measurements, and elemental analysis were done using the same instruments as reported previously.[10]

RESULTS AND DISCUSSION

Radical and Anionic Homopolymerization of MBPI

Radical and anionic polymerizations of MBPI were performed under several conditions. The results are summarized in Table I. The polymerizations proceeded homogeneously throughout except in chlorobenzene (CB). In chlorobenzene, portions of the polymers were insoluble in the solvent and

Table I. Radical and anionic polymerizations of MBPI

Run	MBPI mol l^{-1}	Initiator × 10^2 mol l^{-1}	Polym. solvent[a] ml	Polym. time °C	Polym. time h	Convn. %	$\bar{M}_n$[b] × 10^{-3}	$\bar{M}_w/\bar{M}_n$[b]	$[\alpha]_D^{25}$[c] deg.
1	0.50	AIBN (1.0)	DMF (3.0)	60	22	Trace	—[e]	—[e]	—[e]
2	0.50	AIBN (2.0)	DMF (3.0)	60	22	Trace	—[e]	—[e]	—[e]
3	0.15	AIBN (1.0)	THF (6.0)	60	22	44.5	8.9	17.9	−51.2
4	0.15	AIBN (1.0)	THF (6.0)	70	15	33.2	9.7	17.2	−52.1
5	0.15	AIBN (0.5)	THF (6.0)	60	22	52.0	13.2	24.8	−50.1
6	0.15	AIBN (1.0)	DOX (6.0)	60	22	59.9	42.1	14.5	−51.8
7	0.15	AIBN (1.0)	DOX (6.0)	70	18.5	47.2	11.7	19.7	−49.6
8	0.20	DTBP (1.0)[d]	CB (4.5)	130	18	72.6	43.2	13.3	−46.6
9	0.75	AIBN (1.0)	DMSO (2.0)	60	22	0			
10	0.75	AIBN (3.8)	DMSO (2.0)	60	22	6.2	4.2	23.2	—[e]
11	0.30	n-BuLi (3.0)	DMF (4.0)	0	19.5	0			
12	0.30	n-BuLi (1.0)	DMF (4.0)	0	19.5	0			

[a] DMF, N,N-dimethylformamide; THF, tetrahydrofuran; DOX, dioxane: CB, chlorobenzene; DMSO, dimethyl sulfoxide.
[b] By GPC.
[c] C = ca. 1.0 g dl^{-1}, THF, l = 5 cm.
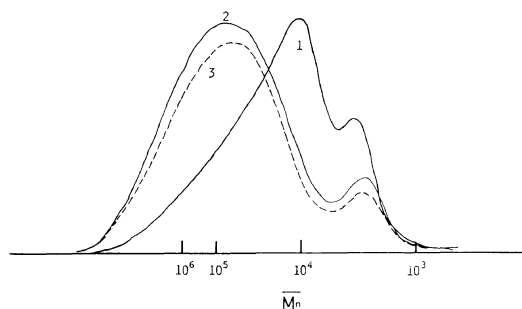[d] Di-t-butylperoxide.
[e] No measurement.

Figure 1. GPC curves for polymers obtained (1) in THF [run 1—3], (2) in dioxane [run 1—5], and (3) in chlorobenzene [run 1—8].
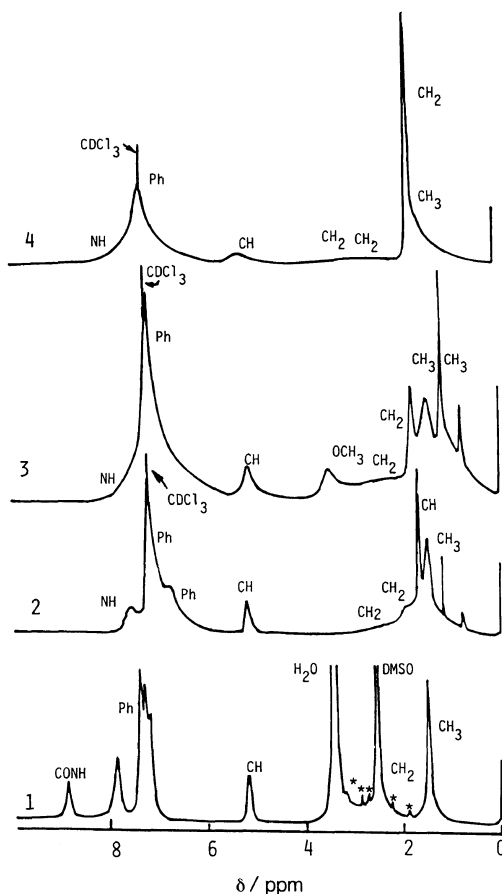

Figure 2. ^{1}H NMR spectra for (1) poly(MBPI) obtained with AIBN in THF [run 1—3], (2) poly(MBPI-co-ST)[run 2—4], (3) poly(MBPI-co-MMA)[run 3—4], and (4) poly(MBPI-co-ID)[run 4—2].

precipitated even at 130°C. The MBPI monomer did not generally dissolve in non-polar organic solvents, and was insoluble in chlorobenzene at 70°C. Thus the heterogeneous system was ascribed to poor solubility of the monomer and polymer.

Figure 1 shows GPC charts for polymers obtained with AIBN in (1) THF, (2) dioxane, and (3) chlorobenzene. On all GPC curves, two peaks were observed. One was 5×10^4 and the other about 5×10^3. Consequently, poly-dispersity ($\bar{M}_w/\bar{M}_n$) for polymers became very large and were 13.3 to 24.8. $\bar{M}_n$ of the polymer obtained in THF was smaller than those in dioxane (DOX), chlorobenzene (CB). The reason for the two peaks in GPC is considered the polymer having relatively small $\bar{M}_n$ based on chain transfer to the monomer. This was confirmed by some small peaks (* in chart) assigned to methine, methylene and/or methyl protons from 3.2 to 1.3 ppm in the ^{1}H NMR spectrum, as shown in Figure 2 (1). That is, the MBPI monomer containing two allylic hydrogens can cause chain transfer reaction.[3] There were no olefinic protons in the spectra for poly(MBPI). Thus, ordinary vinylidene polymerizations took place.

The obtained polymers were white powders and had negative optical activity. The specific rotations $[\alpha]_D$ of polymers were about -46.6 to $-52.1°$ ($C = 1.0\,g\,dl^{-1}$, $l = 10\,cm$, THF), and the absolute values were greater than those

for the monomer ($[\alpha]_D = -31.6°$) and model compound for poly(MBPI), i.e., N-[4-(N'-(R)-α-methylbenzyl)aminocarbonylphenyl]-(RS)-α-methylsuccinimide (MBPMS) ($[\alpha]_D = -23.8°$).

CD and UV spectra for poly(MBPI), model compound, and MBPI monomer are shown in Figures 3 and 4. In all CD spectra only a large negative peak was observed at about 250 nm. The peak was attributable to the n→π* transition of two carbonyl groups in the imide ring and π→π* transition of two phenyl groups. A typical CD peak for the polymer was negatively greater than that of MBPMS (the

Figure 3. CD spectra for (1) poly(MBPI) [run 1—3], (2) MBPI monomer, and (3) MBPMS (a model compound of poly(MBPI).
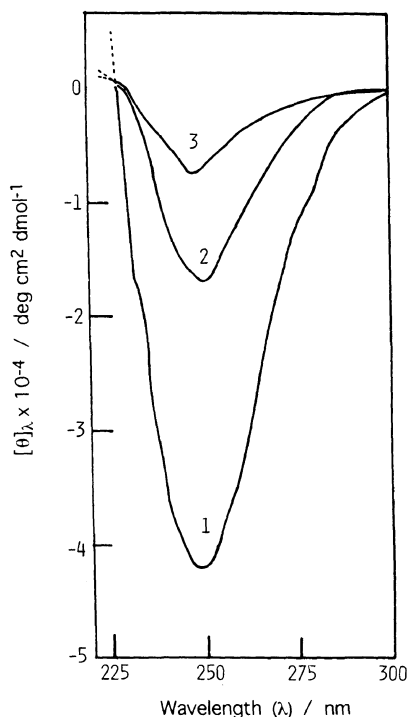
Figure 4. UV spectra for (1) poly(MBPI) [run 1—3], (2) MBPI monomer, and (3) MBPMS (a model compound of poly(MBPI).

model compound for poly(MBPI)), as shown in Figure 3. It is considered that the chiroptical feature of the polymer was affected by asymmetric perturbation[11-13] of the chiral side chain chromophore of α-methylbenzyl group besides the chiral group itself. The specific rotation and CD spectra of optically active polymers containing chromophoric groups show that the chromophores are asymmetrically perturbed by the chirality of the substituents and main chain conformation, as reported previously.[11-13] In the polymerization of optically active maleimide derivatives, similar phenomena have been noted.[5,6] In the case of optically active maleimide polymers, both asymmetric induction into the polymer main chain and asymmetric perturbation of chiral side chain chromophore have to be considered.
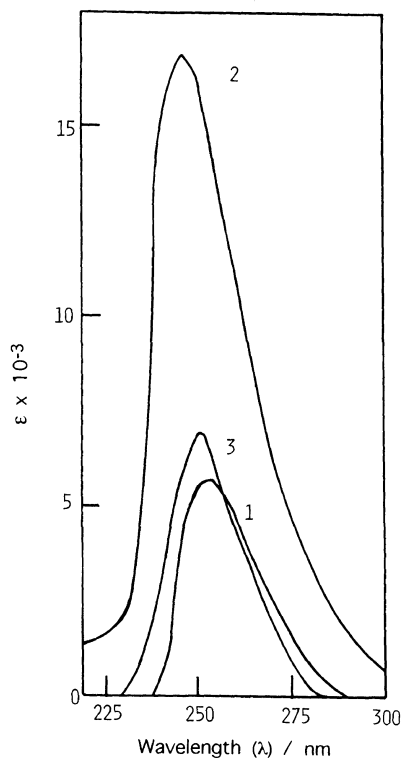
Radical Copolymerizations of MBPI with ST, MMA, or ID

The results of radical copolymerizations of MBPI (M_1) with ST (M_2), MMA (M_2), or ID (M_2) in THF (20 ml) at 70°C in the presence of AIBN (1.0×10^{-2} mol l^{-1}) are summarized in Table II. All copolymerizations proceeded homogeneously throughout. The obtained copolymers were white powders and optically active. Typical NMR spectra for the copolymers are shown in Figure 2. As can be seen from Figure 2, no olefinic protons could be observed, and ordinary vinyl copolymerizations occurred.

Copolymer-composition curves in polymerizations of MBPI with ST, MMA, or ID are shown in Figure 5. Monomer reactivity ratios, r_1 and r_2 were determined as $r_1 = 0.18$, $r_2 = 0.11$ in the MBPI–ST system and $r_1 = 0.81$,

Table II. Copolymerization of MBPI (M_1) with ST (M_2), MMA (M_2),
or ID (M_2) in THF (20 ml) at 70°C[a]

Run	M_2	M_1 in monomer mol%	Polym. time h	Conv. %	N-Anal. %	M_1 in copolymer mol%	$\bar{M}_n{}^b$ ×10^{-3}	$\bar{M}_w/\bar{M}_n{}^b$	$[\alpha]_D^{25\,c}$ deg.
2-1	ST	10.0	1.5	10.3	5.07	32.3	8.1	1.14	−29.6
2-2	ST	20.3	1.5	12.3	5.68	39.5	8.3	2.46	−33.7
2-3	ST	29.7	1.5	23.2	6.03	44.4	8.6	1.49	−37.3
2-4	ST	50.8	1.5	30.4	6.39	50.0	8.0	1.48	−41.8
2-5	ST	70.8	0.3	21.0	7.13	64.0	10.4	2.49	−47.4
2-6	ST	76.7	0.5	30.5	7.14	64.2	6.8	2.74	−47.8
2-7	ST	89.6	0.5	15.9	7.25	66.7	9.0	3.22	−45.3
3-1	MMA	10.1	1.3	25.2	3.90	20.7	11.1	1.93	−18.4
3-2	MMA	20.1	1.3	33.7	5.38	35.0	9.5	1.43	−29.4
3-3	MMA	30.1	1.3	41.7	6.03	43.5	8.0	1.31	−34.8
3-4	MMA	50.7	1.3	46.6	7.16	63.7	8.9	5.23	−44.2
3-5	MMA	70.1	0.5	43.4	7.26	66.0	6.9	4.11	−46.5
3-6	MMA	78.9	0.5	33.4	8.00	86.2	7.6	2.89	−39.4
3-7	MMA	89.6	0.5	39.7	8.00	86.3	9.2	4.43	−51.8
4-1	ID	10.1	3.8	14.9	6.51	54.7	5.1	1.21	−40.3
4-2	ID	29.4	0.6	9.4	6.60	56.4	5.3	1.12	−41.1
4-3	ID	49.8	0.6	11.3	7.25	69.0	4.3	1.74	−44.2
4-4	ID	67.2	1.0	11.9	7.74	80.9	4.7	2.54	−48.9
4-5	ID	86.1	1.0	17.1	7.67	79.0	4.7	2.66	−47.3

[a] $[\text{AIBN}] = 1.0 \times 10^{-2}\,\text{mol}\,l^{-1}$; $M_1 + M_2 = 1.0\,\text{g}$.
[b] By GPC.
[c] $c = 1.0\,\text{g}\,dl^{-1}$, THF, $l = 5\,\text{cm}$, THF.
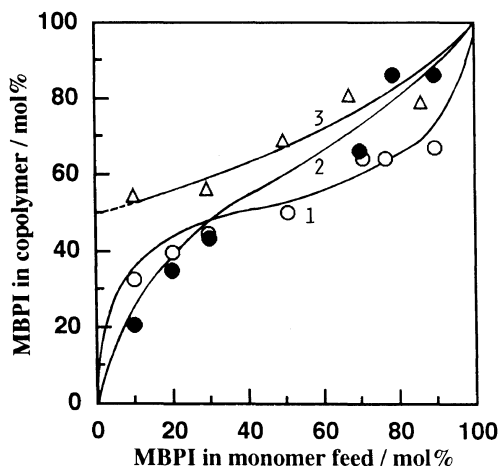
Figure 5. Copolymer composition curves for (1) MBPI–ST, (2) MBPI–MMA, and (3) MBPI–ID systems.

$r_2 = 0.20$ in the MBPI–MMA system and $r_1 = 0.91$, $r_2 = 0.0$ in the MBPI–ID system, according to the High-conversion method

reported by Kelen et al.[14] Alfrey–Price[15] Q–e values for MBPI were calculated as $Q_1 = 1.89$, $e_1 = 1.18$ in the MBPI–ST, and $Q_1 = 6.41$, $e_1 = 1.75$ in the MBPI–MMA system. These values were different in copolymerization systems. In the Alfrey–Price Q and e theory, no steric effect is considered. It seems that MBPI has relatively high steric hindrance because of a large α-methylbenzylaminocarbonylphenyl group as N-substituent. Q and e calculated from the polymerization of MBPI with ST were similar to those reported previously.[16]

Optical Behavior of Copolymers

Figure 6 shows the dependence of specific rotations $[\alpha]_D^{25}$ on the compositions (wt%) of copolymers in each copolymerization system. The absolute values of specific rotations of poly(MBPI-co-ST)s, poly(MBPI-co-MMA)s,
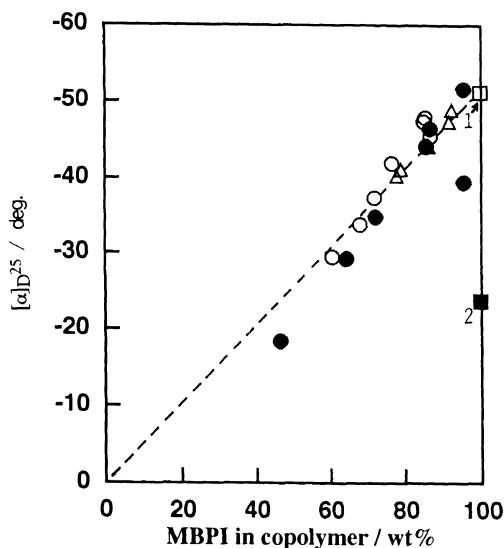
Figure 6. Dependence of specific rotations $[\alpha]_D^{25}$ and composition (wt%) of (○) poly(MBPI-*co*-ST)s, (●) poly(MBPI-*co*-MMA)s, (△) poly(MBPI-*co*-ID)s, (1) poly-(MBPI) and (2) MBPMS.

Wavelength (λ) / nm

Figure 7. CD spectra for (1) poly(MBPI-*co*-ST) [run 2—4], (2) poly(MBPI-*co*-MMA)[run 3—4], and (3) poly(MBPI-*co*-ID) [run 4—2].

and poly(MBPI-*co*-ID)s linearly increased with the content of the MBPI unit. Chiroptical properties for poly(MBPI) were affected by asymmetric perturbation of the side chain chromophore. This linearity suggests that asymmetric perturbation of the copolymer is influenced not by MBPI–ST, MBPI–MMA, or MBPI–ID diad sequences but by MBPI-MBPI successive units.

In both poly((*R*)-MBPM-*co*-ST)s and poly-((*R*)-MBPM-*co*-MMA)s reported previously,[5] great deviation from linearity was observed. Similar tendencies were observed in poly((*S*)-MBPM-*co*-ST)s and poly((*S*)-MBPM-*co*-MMA)s.[6] This suggests that asymmetric induction into the copolymer main chain and/or asymmetric perturbation of chiral side chain chromophore are influenced not by MBPM–MBPM successive units but by MBPM–ST and MBPM–MMA diad sequences.

Differences in chiroptical properties of MBPI and MBPM copolymers may be due to different structures of the copolymer main
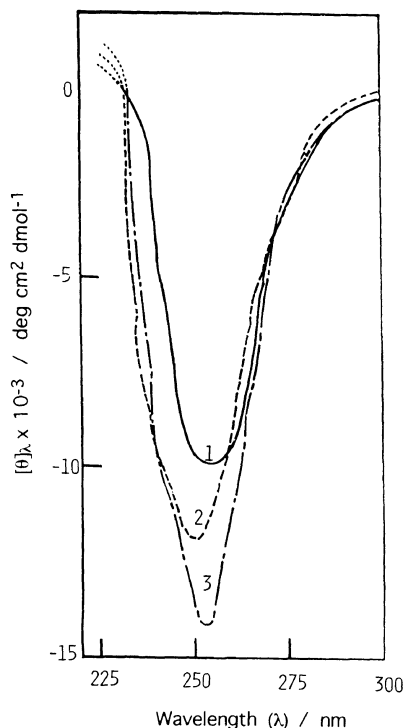
chains. When *threo*-diisotactic addition takes place in the polymerization of a cycloalkene, *i.e.*, maleimide derivatives, polymerization yields two types of *trans* additions, stereogenic centers of (*S,S*) and (*R,R*). If one is produced more than the other, the obtained polymer may be optically active.[11] Optically active itaconimide derivatives, *i.e.*, MBPI polymers cannot take *threo*-diisotactic (*trans*-addition) and/or *threo*-disyndiotactic (*cis*-addition) structures owing to the absence of cyclic olefin[11] of MBPI. However, the chiroptical properties of the MBPI polymer and copolymers were affected by asymmetric perturbation of the chiral side chain chromophore.

CD and UV spectra for poly(MBPI-*co*-ST)s and poly(MBPI-*co*-MMA)s, and poly(MBPI-*co*-ID)s are shown in Figures 7 and 8. Molecular ellipticities [θ] were calculated from average molecular weights of monomeric

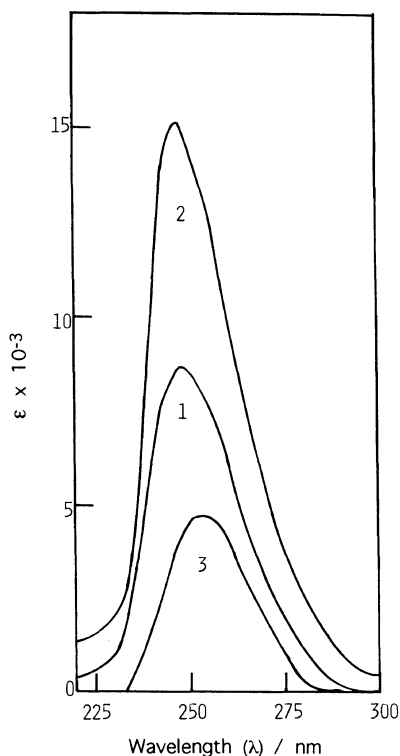**Figure 8.** UV spectra for (1) poly(MBPI-*co*-ST) [run 2—4], (2) poly(MBPI-*co*-MMA)[run 3—4], and (3) poly(MBPI-*co*-ID) [run 4—2].

obtain chiral polymers. In using an anionic initiator, no appreciable amount of polymer was obtained.

(2) From the results of radical copolymerizations of MBPI(M_1) with ST(M_2), MMA(M_2), or ID(M_2), monomer reactivity ratios (r_1, r_2) and Q–e were determined as follows: $r_1 = 0.18, r_2 = 0.11, Q_1 = 1.89, e_1 = 1.18$ in the MBPI–ST system, $r_1 = 0.81$, $r_2 = 0.20$, $Q_1 = 6.41$, $e_1 = 1.75$ in the MBPI–MMA system, and $r_1 = 0.91$, $r_2 = 0.0$ in the MBPI–ID system.

(3) In the polymerization of MBPI, asymmetric perturbation of the chiral side chain chromophore occurs.

(4) In the radical copolymerization of MBPI with ST, MMA, and ID, asymmetric perturbation of the chiral side chain chromophore is not caused by MBPI–ST, MBPI–MMA, or MBPI–ID diad sequences but by conformation of successive MBPI monomeric units.

units. A negative Cotton effect around 250 nm was observed, which was ascribed to the $\pi \rightarrow \pi^*$ transition of two phenyl groups and to $n \rightarrow \pi^*$ transition of carbonyl groups of MBPI and comonomer units. Compared with CD and UV spectra[5] for poly(MBPM-*co*-ST) and poly-(MBPM-*co*-MMA), CD patterns for MBPI copolymers were slightly different. The CD spectra for MBPM copolymers indicated slight splitting peaks. This may be due to different chiroptical properties of MBPI and MBPM copolymers.

CONCLUSIONS

(1) A novel type of optically active *N*-[4-*N'*-(α-methylbenzyl)aminocarbonylphenyl]itaconimide (MBPI) was synthesized and polymerized with radical initiators to

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