Asymmetric Anionic Polymerizations of (*R*)-*N*-Maleoyl-D-Phenylglycine Alkyl Esters and Optical Resolution Using Their Polymers

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ABSTRACT: In the pursuing of optically active polymers synthesized from *N*-substituted maleimides (RMIs) for the application on optical resolution of racemates by being used as chiral stationary phase (CSP) of high performance liquid chromatography (HPLC), poly((*R*)-*N*-maleoyl-D-phenylglycine alkyl ester)s (poly((*R*)-RPGMI)s) were obtained by asymmetric anionic polymerizations of two kinds of (*R*)-RPGMIs with organometal or organometal/chiral ligand complex as initiators. Chiroptical properties and structures of the polymers obtained were investigated by GPC, CD, XRD and NMR measurements. Among these two kinds of polymers, poly((*R*)-*N*-maleoyl-D-phenylglycine methyl ester) (poly((*R*)-MPGMI)) showed excellent optical resolution ability to many racemates because of its high optical activity attributed to the stereoregular *threo*-diisotactic structure in the main chain of the polymer.

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KEY WORDS *N*-Substituted Maleimide / Optically Active Polymer / Asymmetric Anionic Polymerization / Optical Resolution /

Asymmetric induction method was used as early as in 1962 to prepare optically active poly(propylene oxide) by Inoue *et al.*^{1–3} Natta *et al.* obtained optically active polybenzofuran by asymmetric synthesis using AlCl₃ as catalyst complexed with (+)- or (–)-PhCH₂CH(NH₂)CO₂H. This polymer consisted of a series of cyclic monomeric units.⁴ In recent more than twenty years, optically active polymers have been given intensive attention because of their expected applications in asymmetric catalysis, stereoselective recognition, and biological mimics.^{5–15} Polysaccharide derivatives are excellent CSPs because these polymers possess highly ordered structures such as helical conformations which are beneficial to chiral recognition.^{16–20} It is also reported that cellulose derivatives and polymethacrylate derivatives bearing bulky substituents developed by Okamoto *et al.* could optically resolve many racemates when they were used as CSPs of HPLC.^{5,21–26}

N-Substituted maleimides (RMIs) have also been found a kind of important monomers through asymmetric anionic polymerization to provide optically active polymers because of their symmetric characteristic to C₂-axis and 1,2-disubstituted ethylene circle,^{6,27–38} but their application on optical resolution of racemates by being used as CSP of HPLC has not been investigated in detail. Because RMIs can form two chiral centers in the main chains of their polymers through asymmetric polymerization process and the backbones of polymers are very rigid ascribed

to their cyclic plane structures, the chirality of poly(RMI)s comes not only from their configurational but also the conformational aspect. That is if the same configurational pairs successively connect, the main chains of polymers probably form a helical conformation, which will make a large contribution to the optical activity of poly(RMI)s. Therefore, the asymmetric anionic polymerizations of chiral RMIs bearing a chiral amino acid residue in their *N*-substituents are expected to provide high optically active polymers. Some experiments have confirmed this point,^{33,39} but the polymers with good chiral discriminability as CSP of HPLC are being sought for.

In this work, (*R*)-*N*-maleoyl-D-phenylglycine methyl ester ((*R*)-MPGMI) and (*R*)-*N*-maleoyl-D-phenylglycine benzyl ester ((*R*)-BnPGMI) were synthesized from D-phenylglycine and maleic anhydride, and the polymerizations of these monomers (Scheme 1), their chiroptical properties, and polymer structures are discussed based on the measurements of CD, GPC, XRD, and ¹³C NMR. Furthermore, the HPLC analyses for separations of racemates using the CSPs prepared from these polymers are carried out. Optical resolution abilities of these polymers and the difference between esters are also discussed.

EXPERIMENTAL

Reagents

The solvents used in the reactions and polymeriza-

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Scheme 1. Asymmetric anionic polymerization of RPGMI.

tions were purified by the usual methods.⁴⁰ Commercially available *n*-butyllithium (*n*-BuLi) (in *n*-hexane solution, 1.55 mol/L), diethylzinc (Et₂Zn) (in *n*-hexane solution, 1.083 mol/L) and dimethylzinc (Me₂Zn) (in *n*-hexane solution, 0.613 mol/L) (Kanto Chemical Co., Inc.) were used without further purification. Commercially available (–)-sparteine (Sp) (Ishizu Seiyaku, Ltd.) was used after purified by distillation under reduced pressure ($[\alpha]_{435} = -10.3^\circ$ ($c = 1.0$ g/dL, $l = 10$ cm, THF)). (*S,S*)-(1-Ethylpropylidene)-bis(4-benzyl-2-oxazoline) (Bnbox) was prepared as reported previously⁴¹ ($[\alpha]_{435} = -150.7^\circ$ ($c = 1.0$ g/dL, $l = 10$ cm, THF)). Radical initiator, 2,2'-azobisisobutyronitrile (AIBN) (Ishizu Seiyaku, Ltd.) was used after recrystallized from methanol. Racemates were supplied from Tosoh Corporation and used without further purification.

Synthesis of Monomer: (*R*)-MPGMI

Thionyl chloride (SOCl₂) (39 mL) was added dropwise to methanol (150 mL) at -10°C in a three-neck flask which was cooled by ice and NaCl. D-2-Phenylglycine (Tokyo Kasei Industries, Ltd.) (22.7 g, 150 mmol) was added slowly in three portions to this solution at room temperature, and the mixture was stirred for 15 h. After reaction, methanol and SOCl₂ were removed by aspirator under reduced pressure. (*R*)-Phenylglycine methyl ester hydrochloride was obtained by washing the slurry with Et₂O, followed by filtering and drying.

(*R*)-Phenylglycine methyl ester hydrochloride (26.0 g, 129 mmol) was suspended into ethyl acetate (65 mL) at room temperature, the solution of triethylamine (Et₃N) (20.4 mL, 145 mmol) in ethyl acetate (50 mL) was dropwise added into the mixture. After stirred over 10 min, it was collected by suction filtration. Maleic anhydride (Tokyo Kasei Industries, Ltd.)

(12.6 g, 143 mmol) was dissolved into ethyl acetate (50 mL), and then added into the above filtrate at room temperature, followed with stirring for 24 h at room temperature. The solution was washed with H₂O and saturated NaCl solution in sequence, and then dried over Na₂SO₄. (*R*)-*N*-Maleamic acid-D-phenylglycine methyl ester ((*R*)-MPGMA) was obtained by concentrating the above solution with a rotary evaporator. (*R*)-MPGMA (9.0 g, 38.1 mmol) was dissolved in benzene (300 mL) and put into a three-neck flask. After the solution was heated to 50°C , ZnBr₂ (8.6 g, 38.1 mmol) was added. The solution of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (12.1 mL, 57.2 mmol) in benzene (100 mL) was added dropwise into it at 80°C , and refluxed for 12 h with stirring at this temperature. After cooled to room temperature, the insoluble part in benzene was filtered off, and the filtrate was concentrated. Obtained product was dissolved into ethyl acetate (300 mL), then washed and separated by a funnel in a sequence of 0.1 *N* HCl, H₂O, saturated NaHCO₃, and saturated NaCl solution. After dried over Na₂SO₄, filtered, and concentrated by a rotary evaporator, crude (*R*)-MPGMI was obtained, then purified further by column chromatography (solvent: CH₂Cl₂), recrystallized from ethyl acetate/*n*-hexane (5:1) (yield, 4.4 g (47.1%); colorless prism; mp, 87.0 – 88.0°C ; $[\alpha]_{435} = -38.8^\circ$ ($c = 1.0$ g/dL, $l = 10$ cm, in THF) = -167.7° ($c = 1.0$ g/dL, $l = 10$ cm, CHCl₃)). ¹H NMR (δ in ppm from TMS in CDCl₃): 7.48–7.32 (m, 5H, phenyl), 6.73 (s, 2H, –CH=CH–), 5.83 (s, 1H, –C*H), 3.79 (s, 3H); ¹³C NMR (δ in ppm from TMS in CDCl₃): 168.8 (O–C=O), 167.8 (N–C=O), 133.7, 133.6 (–CH=CH–), 128.9, 128.1, 128.0 (phenyl), 55.1 (CH₃), 52.5 (C*H). *Anal.* (%), Calcd for C₁₃H₁₁NO₄: C, 63.67; H, 4.52; N, 5.71; Found: C, 64.70; H, 4.51; N, 6.05.

Synthesis of Model Compound: (*R*)-*N*-Succinoyl-D-phenylglycine Methyl Ester ((*R*)-MPGSI)

(*R*)-MPGMI (0.15 g, 0.61 mmol) was dissolved in ethyl acetate (20 mL) in a Schlenk reaction tube, 10% palladium-activated carbon (Wako Pure Chemical Industries, Ltd., 0.015 g, 10 wt %) was added. The solution was evacuated by aspirator and replaced by hydrogen gas 5 times. After stirred under hydrogen atmosphere for 24 h, the reaction tube was evacuated by aspirator, replaced by nitrogen gas, and then filtered to remove palladium-activated carbon. Filtrate was concentrated under reduced pressure to afford (*R*)-MPGSI (yield, 0.14 g (93%); mp, 101°C ; white solid; $[\alpha]_{435} = +121.7^\circ$ ($c = 1.0$ g/dL, $l = 10$ cm, THF) = -3.4° ($c = 1.0$ g/dL, $l = 10$ cm, CHCl₃)). ¹H NMR (δ in ppm from TMS in CDCl₃): 7.51–7.28 (m, 5H, phenyl), 5.84 (s, 1H, –CH), 3.79 (s, 3H), 2.75 (s, 4H, –CH₂–CH₂–); ¹³C NMR (δ in ppm from

TMS in CDCl_3): 175.3 (N–C=O), 167.3 (O–C=O), 133.3 (C*H–CH), 129.3, 128.1, 127.8 (phenyl), 55.6 (C*H), 52.3 (CH_3), 27.5 ($-\text{CH}_2-\text{CH}_2-$). *Anal.* (%), Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_4$: C, 63.15; H, 5.30; N, 5.66; Found: C, 63.18; H, 5.20; N, 5.50.

Synthesis of Monomer: (R)-BnPGMI

(R)-BnPGMI was synthesized by the similar procedures as synthesizing (R)-MPGMI. (yield, 4.15 g (59%); white solid; mp, 74–75 °C; $[\alpha]_{435} = +24.6^\circ$ ($c = 1.0 \text{ g/dL}$, $l = 10 \text{ cm}$, THF), $= -74.9^\circ$ ($c = 1.0 \text{ g/dL}$, $l = 10 \text{ cm}$, CHCl_3). ^1H NMR (δ in ppm from TMS in CDCl_3): 7.46–7.26 (m, 10H, phenyl), 6.70 (s, 2H, $-\text{CH}=\text{CH}-$), 5.86 (s, 1H, $-\text{CH}$), 5.23 (q, 2H, CH_2); ^{13}C NMR (δ in ppm from TMS in CDCl_3): 168.8 (O–C=O), 167.2 (N–C=O), 134.5 (*ipso* carbon in benzyl ester), 133.6, 133.5 ($-\text{CH}=\text{CH}-$), 129.0, 128.1, 127.9, 127.8, 127.7 (phenyl), 67.2 ($-\text{CH}_2-\text{Ph}$), 55.2 (C*H). *Anal.* (%), Calcd for $\text{C}_{19}\text{H}_{15}\text{NO}_4$: C, 71.02; H, 4.71; N, 4.36; Found: C, 71.49; H, 4.63; N, 4.73.

Synthesis of Model Compound: (R)-N-Succinoyl-D-phenylglycine Benzyl Ester ((R)-BnPGSI)

The model compound (R)-BnPGSI of poly((R)-BnPGMI) was prepared from succinic anhydride and (R)-phenylglycine benzyl ester according to a method similar to synthesis of (R)-BnPGMI. (yield, 1.29 g (64.9%); white solid; mp, 82–83 °C, $[\alpha]_{435} = +137.0^\circ$ ($c = 1.0 \text{ g/dL}$, $l = 10 \text{ cm}$, THF), $= +40.2^\circ$ ($c = 1.0 \text{ g/dL}$, $l = 10 \text{ cm}$, CHCl_3). ^1H NMR (δ in ppm from TMS in CDCl_3): 7.51–7.25 (m, 10H, phenyl), 5.87 (s, 1H, $-\text{CH}$), 5.23 (q, 2H, CH_2), 2.71 (s, 4H, $-\text{CH}_2-\text{CH}_2-$); ^{13}C NMR (δ in ppm from TMS in CDCl_3): 175.3 (N–C=O), 166.8 (O–C=O), 134.5 (*ipso* carbon in benzyl ester), 133.2 (*ipso* carbon in phenylglycine residue), 129.4, 128.2, 127.9, 127.9, 127.8, 127.7 (phenyl), 67.2 ($-\text{CH}_2-\text{Ph}$), 55.9 (C*H), 27.5 ($-\text{CH}_2-\text{CH}_2-$).

Polymerization

Anionic polymerizations were carried out in following procedures. Monomer and chiral ligand were put in a Schlenk reaction tube and a pear-shaped flask, respectively, then evacuated by vacuum pump, and replaced by dry nitrogen gas 5 times. Polymerization solvent (THF or toluene) was added to each vessel by a syringe under nitrogen atmosphere to dissolve them. Organometal ($n\text{-BuLi}$, Me_2Zn , Et_2Zn) in n -hexane solution was introduced into the chiral ligand solution with a syringe to prepare initiator complex. While monomer solution was kept at polymerization temperature, the complex solution was added by a cannula in a stream of nitrogen gas to initiate polymerization. After assigned time, polymerization was

terminated with a small amount of methanol containing 2 drops of 6 *N* hydrochloric acid. The solution was poured into a large amount of methanol to precipitate polymer, which was then collected by suction filtration, washed by methanol, and dried. Purification of the polymer was carried out by reprecipitating twice from THF/methanol system, obtained polymer was dried in vacuum at room temperature for 2 d before measurements.

Radical polymerization was conducted with AIBN as initiator in polymerization solvent (THF or toluene) in a sealed tube at 60 °C for 24 h. After polymerization, the solution was poured into a large amount of methanol to precipitate the polymer. The obtained product was purified by reprecipitating twice from THF solution to excess methanol, filtered and dried *in vacuo* at room temperature for 2 d.

Preparation of Chiral Stationary Phase

Optically active poly(RMI) (0.035 g) was dissolved in dichloromethane (20 mL), microporous silica gel (Si-100, 0.700 g) was added to the solution of poly(RMI). The mixture was evaporated to dryness under reduced pressure, and then 2-propanol (10 mL) was added and dispersed by ultrasonic apparatus to prepare the CSP. The obtained CSP was packed into a stainless-steel column (150 × 2.0 mm I.D.) by a high-pressure slurry method (maximum pressure, 399 kg/cm²) with 2-propanol as an eluent. Theoretical plate number (N) was calculated using toluene or 1,3,5-tri-*tert*-butylbenzene, according to the following equation, $N = 5.54 \times (t_r/w_{1/2})^2$, where t_r is a retention time and $w_{1/2}$ is a half band width.

Measurements

Specific rotations were measured on concentration of 0.5–1.0 g/dL in THF at 25 °C using a quartz cell ($l = 5$ or 10 cm) with a JASCO DIP-140 polarimeter (JASCO Co. Ltd.). CD spectra were measured on the concentration of 0.2 g/dL in THF or CHCl_3 at 25 °C using a quartz cell of 1 or 0.2 mm with a JASCO J-805 spectropolarimeter (JASCO Co. Ltd.). Number-average molecular weights (M_n s) of polymers were measured with gel permeation chromatography (GPC) using THF (50 °C) or CHCl_3 (40 °C) as an eluent and polystyrene as a standard by the Shimadzu LC-10AS instrument equipped with a UV-vis detector SPD-10A, a polarimetric detector (JASCO OR-990), and a data processor. ^1H (270 MHz) and ^{13}C (68 MHz) NMR spectra were obtained with a JEOL-EX270 apparatus (JEOL, Ltd.). X-Ray spectra (XRD) were obtained by a XD-D1 (Shimadzu, Japan) apparatus at room temperature. HPLC analysis was carried out with an apparatus consisting of a LC-10AT liquid chromatography (Shimadzu), CTO-10AS column oven

Table I. Anionic polymerizations of (*R*)-MPGMI^a or (*R*)-BnPGMI^a with *n*-BuLi or *n*-BuLi/ligand as initiators

Run	RMI	Initiator ^b	Polym. Solv.	Polym. Temp.	Polym. Time	Yield ^c	[α] ₄₃₅ ^d (THF)	[α] ₄₃₅ ^e (CHCl ₃)	M_n^f (THF)	M_w/M_n^f (THF)
			(mL)	(°C)	(h)	(%)	(deg.)	(deg.)	$\times 10^{-3}$	
1	(<i>R</i>)-MPGMI	<i>n</i> -BuLi	THF (5)	0	72	86.3	+41.9	+33.5	5.3	2.1
2	(<i>R</i>)-MPGMI	<i>n</i> -BuLi	Tol. (5)	0	72	62.6	+63.7	+10.2	3.2	1.6
3	(<i>R</i>)-MPGMI	<i>n</i> -BuLi/Bnbox (1/1.2)	THF (5)	0	72	84.8	+47.9	+37.2	5.5	2.3
4	(<i>R</i>)-MPGMI	<i>n</i> -BuLi/Bnbox (1/1.2)	Tol. (5)	0	72	78.6	+33.4	+26.9	4.0	1.8
5	(<i>R</i>)-MPGMI	<i>n</i> -BuLi/Sp (1/1.2)	THF (5)	0	72	89.5	+11.2	+8.5	5.5	2.3
6	(<i>R</i>)-MPGMI	<i>n</i> -BuLi/Sp (1/1.2)	Tol. (5)	0	72	83.3	+28.3	+6.3	4.5	1.6
7	(<i>R</i>)-BnPGMI	<i>n</i> -BuLi	THF(5)	0	24	71.4	+14.9	+9.5	3.0	1.9
8	(<i>R</i>)-BnPGMI	<i>n</i> -BuLi/Bnbox(1/1.2)	THF(5)	0	24	67.3	+15.9	+8.2	2.6	1.6
9	(<i>R</i>)-BnPGMI	<i>n</i> -BuLi/Bnbox(1/1.2)	Tol. (5)	0	24	69.8	−7.1	−15.1	3.5	1.8
10	(<i>R</i>)-BnPGMI	<i>n</i> -BuLi/Sp (1/1.2)	THF(5)	0	24	66.4	+14.8	+11.9	2.8	1.5
11	(<i>R</i>)-BnPGMI	<i>n</i> -BuLi/Sp (1/1.2)	Tol. (5)	0	24	80.4	+11.8	−13.4	4.4	1.8

^a(*R*)-RPGMI, 0.5 g; ^b[organometal]/[(*R*)-RPGMI] = 0.1; ^cMethanol-insoluble part; ^d $c = 1.0$ g/dL, $l = 10$ cm, THF; ^e $c = 1.0$ g/dL, $l = 10$ cm, CHCl₃; ^fBy GPC in THF.

Table II. Anionic polymerizations of (*R*)-MPGMI^a or (*R*)-BnPGMI^a with Et₂Zn or Et₂Zn/ligand as initiators

Run	RMI	Initiator ^b	Polym. Solv.	Polym. Temp.	Polym. Time	Yield ^c	[α] ₄₃₅ ^d (THF)	[α] ₄₃₅ ^e (CHCl ₃)	M_n^f (CHCl ₃)	M_w/M_n^f (CHCl ₃)
			(mL)	(°C)	(h)	(%)	(deg.)	(deg.)	$\times 10^{-3}$	
1	(<i>R</i>)-MPGMI	Et ₂ Zn	THF (5)	20	72	66.9	+6.7	−85.9	3.2	2.0
2	(<i>R</i>)-MPGMI	Et ₂ Zn/Bnbox(1/0.5)	THF (5)	20	72	100	+333.2	+231.5	7.2	2.3
3	(<i>R</i>)-MPGMI	Et ₂ Zn/Bnbox (1/0.5)	THF (5)	0	72	99.7	—	+325.6	7.9	2.2
4	(<i>R</i>)-MPGMI	Et ₂ Zn/Bnbox (1/0.5)	THF (5)	−40	72	99.7	—	+388.2	6.9	1.9
5	(<i>R</i>)-MPGMI	Et ₂ Zn/Bnbox (1/1.2)	THF (5)	0	72	99.5	+342.6	+271.6	9.1	2.4
6	(<i>R</i>)-MPGMI	Et ₂ Zn/Bnbox (1/1.2)	THF (5)	−40	72	98.4	+445.0	+305.2	13.7	2.8
7	(<i>R</i>)-MPGMI	Et ₂ Zn/Sp (1/1.2)	THF (5)	0	72	91.4	+69.8	+50.1	6.5	2.2
8	(<i>R</i>)-MPGMI	Et ₂ Zn/Sp (1/1.2)	Tol. (5)	0	72	89.5	+16.2	+10.0	6.6	2.9
9	(<i>R</i>)-BnPGMI	Et ₂ Zn/Bnbox(1/0.5)	THF (5)	0	72	62.8	+66.5	+31.6	6.7	2.0
10	(<i>R</i>)-BnPGMI	Et ₂ Zn/Bnbox(1/0.5)	Tol. (5)	0	72	50.5	+73.5	+49.1	5.0	2.1
11	(<i>R</i>)-BnPGMI	Et ₂ Zn/Sp (1/1.2)	THF (5)	0	72	84.6	−10.2	−9.1	4.8	2.0
12	(<i>R</i>)-BnPGMI	Et ₂ Zn/Sp (1/1.2)	Tol. (5)	0	72	63.9	−4.3	−8.0	4.3	2.3

^a(*R*)-RPGMI, 0.5 g; ^b[organometal]/[(*R*)-RPGMI] = 0.1; ^cMethanol-insoluble part; ^d $c = 1.0$ g/dL, $l = 10$ cm, THF; ^e $c = 1.0$ g/dL, $l = 10$ cm, CHCl₃; ^fBy GPC in CHCl₃.

(Shimadzu), two CHROMATOPAC C-R8A (Shimadzu), a SPD-10A UV detector (254 nm) (Shimadzu), and a JASCO-OR 2090 polarimetric detector (350–900 nm) using the mixed solvent systems of *n*-hexane/2-propanol (normal-phase) or methanol/H₂O (reverse-phase) at a flow rate of 0.5 mL/min at room temperature. Capacity factors (k_1 and k_2), separation factor (α), and resolution (R_s) were estimated by the following equations: $k_1 = (t_1 - t_0)/t_0$; $k_2 = (t_2 - t_0)/t_0$; $\alpha = k_2/k_1$; $R_s = 2(t_2 - t_1)/(w_1 + w_2)$. Where t_1 and t_2 are retention times of the first- and second-eluted enantiomers, respectively, t_0 is the dead time determined with 1,3,5-tri-*tert*-butylbenzene, w_1 and w_2 are peak widths of the first- and second-eluted enantiomers, respectively.

RESULTS AND DISCUSSION

Asymmetric Anionic Polymerizations of (*R*)-MPGMI and (*R*)-BnPGMI

The results of asymmetric anionic polymerizations of (*R*)-MPGMI and (*R*)-BnPGMI with *n*-BuLi or *n*-BuLi/ligand are shown in Table I. The yields of poly((*R*)-MPGMI)s were higher than those of poly((*R*)-BnPGMI)s when they were obtained by same initiator in THF, the one reason is probably from the longer polymerization time.

Table II shows the results of polymerizations of (*R*)-MPGMI and (*R*)-BnPGMI using Et₂Zn or Et₂Zn/ligand as initiators. In this series, the yields and M_n s of poly((*R*)-MPGMI)s were higher than those of the

Table III. Anionic polymerizations of (*R*)-MPGMI^a or (*R*)-BnPGMI^a with Me₂Zn or Me₂Zn/ligand as initiators

Run	RMI	Initiator ^b	Polym. Solv.	Polym. Temp.	Polym. Time	Yield ^c	[α] ₄₃₅ ^d (THF)	[α] ₄₃₅ ^e (CHCl ₃)	M_n^f (THF)	M_w/M_n^f (THF)
			(mL)	(°C)	(h)	(%)	(deg.)	(deg.)	$\times 10^{-3}$	
1	(<i>R</i>)-MPGMI	Me ₂ Zn/Bnbox(1/0.5)	THF (5)	20	72	96.9	+288.2	+193.1	14.4	2.4
2	(<i>R</i>)-MPGMI	Me ₂ Zn/Bnbox(1/0.5)	Tol. (5)	20	72	97.2	+66.4	+2.3	13.0	2.2
3	(<i>R</i>)-MPGMI	Me ₂ Zn/Bnbox(1/0.5)	THF (5)	0	72	100	+480.7	+329.6	33.9	4.5
4	(<i>R</i>)-MPGMI	Me ₂ Zn/Bnbox(1/0.5)	Tol. (5)	0	72	96.0	+159.3	+64.2	6.7	1.5
5	(<i>R</i>)-MPGMI	Me ₂ Zn/Bnbox(1/0.5)	THF (5)	−40	72	70.4	—	+396.3	11.9	3.0
6	(<i>R</i>)-MPGMI	Me ₂ Zn/Sp (1/1.2)	THF (5)	0	72	100	+14.9	+10.3	17.4	2.2
7	(<i>R</i>)-MPGMI	Me ₂ Zn/Sp (1/1.2)	Tol. (5)	0	72	95.9	+41.3	+20.0	9.3	1.8
8	(<i>R</i>)-BnPGMI	Me ₂ Zn/Bnbox (1/0.5)	THF (5)	0	72	71.0	+52.0	+23.4	8.8	2.0
9	(<i>R</i>)-BnPGMI	Me ₂ Zn/Bnbox (1/0.5)	Tol. (5)	0	72	37.4	−19.0	−39.4	8.5	1.8
10	(<i>R</i>)-BnPGMI	Me ₂ Zn/Bnbox (1/0.5)	THF (5)	20	72	79.0	+49.5	+36.6	7.3	1.8
11	(<i>R</i>)-BnPGMI	Me ₂ Zn/Bnbox (1/0.5)	Tol. (5)	20	72	92.3	−81.9	−87.9	12.6	2.2
12	(<i>R</i>)-BnPGMI	Me ₂ Zn/Sp (1/1.2)	THF (5)	0	72	90.0	−10.0	−9.7	8.7	2.0
13	(<i>R</i>)-BnPGMI	Me ₂ Zn/Sp (1/1.2)	Tol. (5)	0	72	84.3	−0.3	−6.6	9.5	2.4

^a(*R*)-RPGMI, 0.5 g; ^b[organometal]/[(*R*)-RPGMI] = 0.1; ^cMethanol-insoluble part; ^d $c = 1.0$ g/dL, $l = 10$ cm, THF; ^e $c = 1.0$ g/dL, $l = 10$ cm, CHCl₃; ^fBy GPC in THF.

Table IV. Radical polymerizations of (*R*)-MPGMI^a or (*R*)-BnPGMI^a with AIBN as initiator

Run	Initiator ^b	Polym. Solv.	Polym. Temp.	Polym. Time	Yield ^c	[α] ₄₃₅ ^d (THF)	[α] ₄₃₅ ^e (CHCl ₃)	M_n^f (THF)	M_w/M_n^f (THF)
		(mL)	(°C)	(h)	(%)	(deg.)	(deg.)	$\times 10^{-3}$	
1	(<i>R</i>)-MPGMI	THF (2)	60	24	14.0	+76.8	−25.6	1.2	1.5
2	(<i>R</i>)-MPGMI	Tol. (2)	60	24	62.0	−10.1	−89.8	6.7	2.0
3	(<i>R</i>)-BnPGMI	THF (2)	60	24	36.9	+62.1	−3.6	0.9	1.4
4	(<i>R</i>)-BnPGMI	Tol. (2)	60	24	89.2	+5.9	−30.1	4.1	2.4

^a(*R*)-RPGMI, 0.5 g; ^b[AIBN]/[(*R*)-RPGMI] = 0.01; ^cMethanol-insoluble part; ^d $c = 1.0$ g/dL, $l = 10$ cm, THF; ^e $c = 1.0$ g/dL, $l = 10$ cm, CHCl₃; ^fBy GPC in THF.

poly((*R*)-BnPGMI)s because of the bulkier substituent in the ester group of the latter. The chiral ligand Bnbox is favorable for increasing the yield and M_n of poly((*R*)-MPGMI) than Sp (Runs 5 and 7 Table II) in this series of polymerizations while solvents have no great influence on these aspects (Runs 7 and 8 in Table II). For poly((*R*)-BnPGMI)s obtained with the complex of Et₂Zn and ligand, the higher yields and M_n s were obtained in polar solvent THF, manifesting that solvent had an effect on the polymerization process and the propagation rate was affected at the growing end of polymer by the polarity of solvent and the π – π effect of phenyl group or benzyl group of the side chain and toluene.

In Table III, the results of polymerizations of (*R*)-MPGMI and (*R*)-BnPGMI using Me₂Zn/ligand as initiators are presented. The solvents had distinct effect on M_n s of poly((*R*)-MPGMI)s and slight influence on yields of these polymerizations obtained at 0 °C with the both chiral ligands of Bnbox and Sp (Runs 3, 4, 6 and 7 in Table III) where the higher M_n s and yields were also obtained in polar THF. With the increase of

polymerization temperature to 20 °C, the M_n of poly((*R*)-MPGMI) (Run 1 in Table III) decreased to about 42% of the M_n obtained at 0 °C (Run 3 in Table III) in THF. While in toluene, the M_n of the poly((*R*)-MPGMI) obtained at 20 °C (Run 2 in Table III) increased to about 200% of the M_n of poly((*R*)-MPGMI) obtained at 0 °C (Run 4 in Table III). The yield and M_n of poly((*R*)-BnPGMI) obtained with Me₂Zn/Bnbox at 0 °C in THF (Run 8 in Table III) were higher than the poly((*R*)-BnPGMI) obtained in toluene (Run 9 in Table III). However, the yield and M_n of poly((*R*)-BnPGMI) obtained at 20 °C in toluene (Run 11 in Table III) with the same initiator were very higher than the poly((*R*)-BnPGMI) obtained in THF (Run 10 in Table III). The effect of temperature on polymerization in toluene is probably resulted from the increase of propagation rate with the increase in temperature.

In radical polymerizations, both poly((*R*)-MPGMI) and poly((*R*)-BnPGMI) obtained in THF (Runs 1 and 3 in Table IV) had very lower yields and M_n s than those obtained in toluene (Runs 2 and 4 in Table IV).

Figure 1. CD and UV spectra (measured in THF, $c = 0.2$ g/L, $l = 1$ mm) of (a) (*R*)-MPGMI ($[\alpha]_{435} = -167.7^\circ$), and (b) (*R*)-MPGSI ($[\alpha]_{435} = -3.4^\circ$); CD and UV spectra of poly((*R*)-MPGMI) obtained with (c) *n*-BuLi in THF at 0°C ($[\alpha]_{435} = +33.5^\circ$), (d) Et_2Zn in THF at 0°C ($[\alpha]_{435} = -85.9^\circ$), (e) AIBN in THF ($[\alpha]_{435} = -25.6^\circ$), and (f) AIBN in Tol. ($[\alpha]_{435} = -89.8^\circ$).

Although the effect from solvent in radical polymerization is small, the yields of radical polymerizations of (*R*)-MPGMI and (*R*)-BnPGMI were higher in toluene, suggesting that the polymerization processes of polar monomers RPGMIs of five-member imide ring were affected in polar solvent such as THF.

Chiroptical Properties and Structures of Poly((R)-MPGMI) and Poly((R)-BnPGMI)

In all polymerizations obtained in the three series of using organometal/ligand as initiators, poly((*R*)-MPGMI)s of less bulky substituent in the ester group of monomer unit generally had higher dextrorotations than poly((*R*)-BnPGMI)s obtained in the same experimental conditions. The configurational chirality of levorotation was induced in poly((*R*)-BnPGMI)s because of the effect of chirality of *N*-substituent of side chain and ligand, thus they had smaller absolute values of specific rotation after counteracted with the devorotation of their polymer unit—model compound (*R*)-BnPGSI. Bnbox gave distinguished effect on obtaining high optically active poly((*R*)-MPGMI)s and poly((*R*)-BnPGMI)s than Sp by virtue of the chirality of bisoxazoline ring of Bnbox through affecting the additional direction of monomer in the growing end of polymer. Both two organometal dialkylzincs were of benefit to increase the optical activity of the polymers, as shown in Tables II and III, compared with the polymers obtained in *n*-BuLi series.

The CD and UV spectra of (*R*)-MPGMI, its model compound, and the poly((*R*)-MPGMI)s obtained with only organometal *n*-BuLi or Et_2Zn in anionic polymerizations and AIBN in radical polymerizations are shown in Figure 1. The positive Cotton effect due to the $\pi\text{--}\pi^*$ transition of the phenyl in the side chain and the double bond of maleimide ring, and the $n\text{--}\pi^*$ transition of carbonyl groups of maleimide ring appeared in the wide range of UV absorbance area at 270 to 350 nm for the monomer. For its model compound, the negative Cotton effect due to the $\pi\text{--}\pi^*$ transition of phenyl in the side chain and the $n\text{--}\pi^*$ transition of carbonyl groups of succimide ring was shown in the range of 240 to 270 nm. According to the different CD spectra of poly((*R*)-MPGMI)s compared with that of model compound (*R*)-MPGSI, it is known that the asymmetric induction occurred in the main chains of these polymers. The poly((*R*)-MPGMI) obtained with only *n*-BuLi (c in Figure 1) or Et_2Zn (d in Figure 1) showed positive Cotton effect and negative Cotton effect, respectively, at 250 nm, suggesting that the content differences of (*S,S*) configurational pair and (*R,R*) configurational pair in the main chains of these two polymers are opposite. In the CD spectra of poly((*R*)-MPGMI)s obtained with Et_2Zn /Bnbox at different temperatures of polymerization (Figure 2), great positive Cotton effects appeared at 220 and 250 nm, suggesting chiral ligand made an effective asymmetric induction in the main chains of

Figure 2. CD and UV spectra (measured in CHCl_3 , $c = 0.2 \text{ g/L}$, $l = 0.2 \text{ mm}$) of poly((*R*)-MPGMI) obtained with $\text{Et}_2\text{Zn/Bnbox}$ (1.0/0.5) in THF at: (a) -40°C ($[\alpha]_{435} = +388.2^\circ$), (b) 0°C ($[\alpha]_{435} = +325.6^\circ$), and (c) 20°C ($[\alpha]_{435} = +231.5^\circ$).

these polymers. Furthermore, the intensities of these effects corresponded to the specific rotations of these polymers, it is discernible that the lower temperature of polymerization is more advantageous for the asymmetric induction in the main chain of poly((*R*)-MPGMI).

The expanded ^{13}C NMR spectra of poly((*R*)-MPGMI)s for main chain (36–48 ppm), carbonyl of side chain (166–167 ppm), and carbonyl of imide ring (174–176 ppm) are shown in Figure 3. The poly((*R*)-MPGMI) obtained with AIBN showed a peak at about 43.5 ppm for its main chain, but the poly((*R*)-MPGMI) obtained in anionic polymerizations with only *n*-BuLi, Et_2Zn , and organometal/chiral ligand had the apex of this peak at about 42.5 ppm. This is probably ascribed to the unshielding effect between monomer units of polymer obtained from anionic polymerization, in which the monomer units were not very adjacent because of its stereoregular *threo*-diisotactic structure. The peak assigned to carbonyl group of imide ring (175 ppm) of poly((*R*)-MPGMI)s obtained with anionic polymerization was sharper than that of those obtained by radical polymerization, but the peak of the carbonyl group of side chain (165 ppm) had no great difference among the polymers obtained from different polymerizations due to farther from the main chain

Figure 3. Expanded ^{13}C NMR spectra of poly((*R*)-MPGMI)s obtained by radical or anionic polymerization: (A) AIBN in THF at 60°C ($[\alpha]_{435} = -25.6^\circ$), (B) *n*-BuLi in THF at 0°C ($[\alpha]_{435} = +33.5^\circ$), (C) Et_2Zn in THF at 0°C ($[\alpha]_{435} = -85.9^\circ$), (D) $\text{Me}_2\text{Zn/Bnbox}$ (1.0/0.5) in THF at 0°C ($[\alpha]_{435} = +329.6^\circ$), (E) $\text{Et}_2\text{Zn/Bnbox}$ (1.0/0.5) in THF at -40°C ($[\alpha]_{435} = +388.2^\circ$), and (F) $\text{Me}_2\text{Zn/Bnbox}$ (1.0/0.5) in THF at -40°C ($[\alpha]_{435} = +396.3^\circ$).

of polymer. This confirmed the polymers obtained in anionic polymerizations had much more stereoregular structure in main chain than the polymer obtained by radical polymerization.

X-Ray diffraction (XRD) spectra were measured to study the structure of the poly((*R*)-MPGMI)s (Run 1 in Table I, Run 1 and 4 in Table II, Run 5 and 6 in Table III). The crystallization peak could not be observed in the XRD spectra of poly((*R*)-MPGMI)s although the crystallization degree of poly((*S*)-methylbenzylmaleimide)s (poly((*S*)-MBZMI)s) was observed increasing in proportion to their specific rotation,³³ poly((*R*)-MPGMI) probably formed the stereoregular structure without crystallizability because of its bulkier ester group than the methyl of *N*-substituent of poly((*S*)-MBZMI).

Optical Resolution

The preparation conditions for CSPs from poly((*R*)-MPGMI)s are shown in Table V. The 30 racemates

Table V. Preparations of poly((*R*)-MPGMI)s or poly((*R*)-BnPGMI)s-coated-silica gel column^a

Column No.	Polymer	Specific Rotation of Polymer ^b	Silica-Gel	Dispersant ^c	Flow Rate	$P_{\max}$ ^e	N^d
	(wt %)	(deg.)			(mL/min)	(kg/cm ²)	
1 ^f	Poly((<i>R</i>)-MPGMI) (5)	+396.3	Si-100	2-PrOH	1.25	388	798
2 ^f	Poly((<i>R</i>)-MPGMI) (5)	+396.3	Si-100ODS	2-PrOH	0.60	391	954
3 ^g	Poly((<i>R</i>)-MPGMI) (5)	+33.5	Si-100	2-PrOH	0.93	399	1010
4 ^h	Poly((<i>R</i>)-BnPGMI) (5)	−87.9	Si-100	2-PrOH	1.08	398	565

^aColumn size: 150 × 2.0 mm I.D. ^b $c = 1.0$ g/dL, $l = 10$ cm, CHCl₃. ^c2-PrOH: 2-propanol. ^d N : Theoretical plate number, $N = 5.54 \times (t_r/W_{1/2})^2$. ^eHighest pressure to pack CSP into column. ^fPoly((*R*)-MPGMI) obtained with Me₂Zn/Bnbox (1/0.5) in THF at −40 °C. ^gPoly((*R*)-MPGMI) obtained with *n*-BuLi in THF at 0 °C. ^hPoly((*R*)-BnPGMI) obtained with Me₂Zn/Bnbox (1/0.5) in Tol. at 20 °C.

Chart 1.

tried in HPLC analyses with these CSPs are listed in Chart 1. Table VI shows the results of optical resolution with the CSPs prepared from poly((*R*)-MPGMI)s. When used column 1, in which the poly((*R*)-MPGMI) was coated on the surface of silica gel, six racemates in normal-phase analyses of HPLC and two racemates in reverse-phase analyses were resolved with high separation factors as showed in Table VI. While used column 2, five racemates were resolved in reverse-phase with higher separation factors and resolutions besides the same six racemates resolved in normal-phase analyses. The reason is that the surface of silica gel in Si-100ODS was end-capped by hydrophobic octadecyl, which decreased the H–H combination of silica gel with the eluent and racemate, therefore, increased the interactions between the polymer and racemate. The interactions between racemate and poly((*R*)-MPGMI) may include bipolar-bipolar effect due to carbonyl of imide ring and side chain, the π – π^* effect ascribed to phenyl, H–H combination in nor-

mal-phase, hydrophobic interaction in reverse-phase, and the interaction of ions. The high resolution ability showed in normal-phase may primarily be ascribed to the H–H combination of molecular interaction.

When used the column 3 that coated with the poly((*R*)-MPGMI) of specific rotation of +33.5°, the racemates resolved by column 1 could not be resolved by this CSP. Because this poly((*R*)-MPGMI) was obtained with only *n*-BuLi and had no large difference in specific rotation with its model compound, it probably had no stereoregular structure, which is supposed to be an important factor for the discrimination ability of poly((*R*)-MPGMI) to racemates.

The poly((*R*)-BnPGMI) of specific rotation −87.9° (Run 11 in Table III) was used to prepare the column 4 as the CSP of HPLC, its preparation method and result are shown in Table V. There are no racemates resolved by this column judged from UV and polarimetric detectors. Because of the differences of the specific rotations between poly(RPGMI)s and their

Table VI. Optical resolution results using column 1 (Run 1–8) and column 2 (Run 9–19)

Run	Racemate	Mobile Phase ^a	Flow Rate	Injected Volume	t_1	t_2	k_1	k_2	α	R_s
			(mL/min)	(μ L)						
1	1	Hex/2-PrOH (9/1)	0.10	1.0	7.14	13.4	0.48	1.79	3.69	2.42
2	2	Hex/2-PrOH (9/1)	0.10	1.0	5.32	6.34	0.11	0.32	3.02	0.53
3	3	Hex/2-PrOH (9/1)	0.10	1.0	5.98	9.50	0.24	0.97	4.02	2.68
4	4	Hex/2-PrOH (9/1)	0.10	1.0	6.14	9.98	0.28	1.07	3.88	2.35
5	6	Hex/2-PrOH (9/1)	0.50	1.0	6.65	8.28	5.17	6.68	1.29	0.94
6	13	Hex/2-PrOH (9/1)	0.50	1.0	1.92	5.42	1.03	4.71	4.59	1.91
7	1	MeOH/H ₂ O (7/3)	0.10	1.0	9.43	15.9	1.49	3.00	2.01	1.66
8	2	MeOH/H ₂ O (7/3)	0.10	1.0	5.90	7.36	0.72	1.20	1.66	0.84
9	1	Hex/2-PrOH (9/1)	0.50	1.0	1.47	2.75	0.66	2.13	3.22	1.85
10	2	Hex/2-PrOH (9/1)	0.50	1.0	0.95	1.27	0.08	0.43	5.53	1.28
11	3	Hex/2-PrOH (9/1)	0.50	1.0	1.25	1.59	0.19	0.80	4.16	1.60
12	4	Hex/2-PrOH (9/1)	0.50	1.0	1.08	1.69	0.23	0.79	3.48	1.65
13	6	Hex/2-PrOH (9/1)	0.50	1.0	3.85	5.00	3.37	4.69	1.39	0.77
14	13	Hex/2-PrOH (9/1)	0.50	1.0	1.73	4.29	0.96	3.88	4.03	2.03
15	1	MeOH/H ₂ O (7/3)	0.50	1.0	3.89	5.78	4.26	6.83	1.60	1.62
16	2	MeOH/H ₂ O (7/3)	0.50	1.0	3.14	3.83	3.25	4.19	1.29	1.03
17	3	MeOH/H ₂ O (7/3)	0.50	1.0	2.95	3.89	3.00	4.27	1.42	1.45
18	4	MeOH/H ₂ O (7/3)	0.50	1.0	2.82	3.92	2.82	4.31	1.53	1.57
19	13	MeOH/H ₂ O (7/3)	0.50	1.0	6.74	12.4	8.13	15.9	1.95	2.11

^aHex: *n*-Hexane, 2-PrOH: 2-Propanol, MeOH: Methanol, H₂O: Water. **Figure 4.** HPLC resolution chromatograms of poly((*R*)-MPGMI) coated Si-100 column (column 1, Table V) listed in Table VI: (a) Run 2, (b) Run 3, (c) Run 4, and (d) Run 5. The top chromatograms were measured by polarimetric detector (α_{Hg}) and bottom by UV detector (254 nm).

model compounds, it is considered that (*S,S*) configurational pairs are rich in the main chains of poly((*R*)-MPGMI)s and (*R,R*) configurational pairs are rich in the main chains of poly((*R*)-BnPGMI)s.⁴² The discrimination ability to racemates is under the influences of the configurational *N*-substituent of the side chain and the (*S,S*) or (*R,R*) configurational pairs of the main chain of poly(RPGMI) as a whole, therefore even the poly((*R*)-BnPGMI) of stereoregular structure did not show good optical resolution ability because of their unbefitting stereochemical structures between racemate and poly((*R*)-BnPGMI).

Their chromatograms of HPLC are shown in Figure 4. The (–) enantiomers of racemates were eluted at first because (+) enantiomers were absorbed by the CSP prepared from the poly((*R*)-MPGMI) of higher dextro-rotation. This phenomenon is different from the results reported by Oishi and co-workers that the CSPs prepared from poly(*N*-1-anthrylmaleimide) and poly(*N*-1-phenylmaleimide) of positive specific rotations selectively interacted with (*S*)-BINOL.^{30,43} The reason may result from the consideration that the chiral discriminability of poly(RMI) to various racemates is mainly due to their structural suitability for prompting the interaction between them.

SUMMARY

Optically active polymers could be obtained by anionic and radical polymerizations of chiral monomers (*R*)-MPGMI and (*R*)-BnPGMI with achiral initiators. The polymers of high specific rotations were obtained by asymmetric anionic polymerizations with organometal/chiral ligand complex as initiators because of the engendering of stereoregular *threo*-diisotactic structure. Therefore the optical activity of polymers is ascribed not only to the chirality of *N*-substituent but also the new asymmetric induction in the main chain of the polymers. The obtained poly((*R*)-BnPGMI) had lower polymerizability and optical rotation compared with poly((*R*)-MPGMI) because of the bulkiness of its ester group in side chain.

The good optical resolution ability of poly((*R*)-MPGMI) to varieties of racemates is mainly resulted from the stereoregularity of main chain of the polymer, and the asymmetric atmosphere of side chain probably makes contribution to the optical resolution.

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