Asymmetric Anionic Polymerization of (S)-(–)-N-Maleoyl-L-Valine Methyl Ester

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(Received May 6, 2004; Accepted September 2, 2004; Published November 15, 2004)

ABSTRACT: A kind of *N*-substituted maleimide (RMI), chiral (S)-(–)-*N*-maleoyl-L-valine methyl ester ((S)-(–)-MVMI) was synthesized successfully from L-valine and maleic anhydride with a specific rotation of $[\alpha]_{435} = -102.2^\circ$. The polymers of high specific rotations of $[\alpha]_{435} = -340.4^\circ$ and $[\alpha]_{435} = -292.2^\circ$ were obtained by the asymmetric anionic polymerizations of (S)-(–)-MVMI with diethylzinc (Et_2Zn)/(*S,S*)-(1-ethylpropylidene)bis(4-benzyl-2-oxazoline) ((*S,S*)-Bnbox) (1.0/1.2) and Et_2Zn /(-)-sparteine (Sp) (1.0/1.2) initiators, respectively. Asymmetric inductions in the main chains of polymers with *threo*-diisotactic structures were investigated by the measurements of gel permeation chromatography (GPC), circular dichroisms (CD), and ^{13}C NMR. [DOI 10.1295/polymj.36.878]

KEY WORDS *N*-substituted Maleimide / Optically Active Polymer / Asymmetric Anionic Polymerization /

Intensive interest is focused on syntheses of optically active polymers in recent years because of their expected applications to chiral stationary phase of high performance liquid chromatography (HPLC), chiral catalysts and adsorbents.^{1–11} Asymmetric synthesis polymerization is one of the ways available for synthesizing optically active polymers. In this way, *N*-substituted maleimides were paid great attention because their polymers can be *threo*-diisotactic structure by *trans*-opening reaction of a carbon–carbon double bond. As early as in 1982, Okamoto and co-workers reported asymmetric polymerizations of PhMI at the 28th Meeting of Polymer Science (Kobe, Japan). In 1991, they systematically reported asymmetric polymerizations of PhMI with various chiral anionic initiators, the highest specific rotation of $[\alpha]_{25}^D = -23.7^\circ$ was obtained using a *n*-BuLi–Sp–CuI complex.² The research on asymmetric anionic polymerizations of eleven types of achiral RMIs [*N*-substituent: R = *n*-propyl (PMI), isopropyl (IPMI), *n*-butyl (nBMI), isobutyl (IBMI), *s*-butyl (SBMI), *t*-butyl (TBMI), cyclohexyl (CHMI), benzyl (BZMI), phenyl (PhMI), 1-naphthyl (1-NMI), and 2-fluorenyl (FMI)] with a *n*-BuLi/Sp complex as initiator was also reported by Oishi *et al.*¹² Recently, a new attempt for the anionic polymerizations of achiral RMIs by using chiral bisoxazoline derivatives as chiral ligands were carried out by Oishi *et al.* Methylene bridged chiral bisoxazoline derivatives were found effective chiral ligands in anionic polymerizations of achiral RMIs.^{13–17} Although the polymers of high specific rotations were obtained by asymmetric anionic polymerizations of chiral RMI with organometal and chiral ligand such

as Sp or Bnbox,^{18,19} the reported most chiral RMIs were carried out mainly by radical polymerizations, *i.e.*, *N*-maleoyl-L-alanine (AMI) and *N*-maleoyl-L-phenylalanine (PAMI) were radically polymerized in several solvents to obtain optically active polymers, their specific rotations were $[\alpha]_{25}^D = -32^\circ$ to -42° and $[\alpha]_{25}^D = -144^\circ$ to -164° for AMIs and PAMIs, respectively.²⁰ Further from the results, the radical polymerizations of *N*-maleoyl-L-phenylalanine cyclohexyl ester (CHPAM) and other four types of *N*-maleoyl-L-phenylalanine alkyl ester (RPAM) (alkyl: ethyl (EPAM), butyl (BPAM), dodecyl (DPAM), and benzyl (BZPA)) were performed.^{21–23} It was known from these researches that the bulkiness of ester group decreased polymerizability but was favorable to asymmetric induction in the main chain of the homopolymer. From the above results, the asymmetric anionic polymerizations of chiral RMIs bearing an amino acid residue with interesting initiators like organometal/(*S,S*)-Bnbox complexes may give polymers of high specific rotation and stereoregular structure, thus the research is in a strong desire.

In this work (S)-(–)-*N*-maleoyl-L-valine methyl ester was synthesized from maleic anhydride, methanol, and a low cost aliphatic amino acid L-valine (Scheme 1), its specific rotation was -102.2° . Anionic polymerizations were conducted with organometal or organometal and chiral ligand complex as initiators (Scheme 2). The highest specific rotation of $[\alpha]_{435} = -340.4^\circ$ of polymer was obtained using $\text{Et}_2\text{Zn}/(\textit{S,S})\text{-Bnbox}(1.0/1.2)$. Chiroptical properties and structures of these polymers were investigated by GPC, CD, and ^{13}C NMR measurements.

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Scheme 1. Synthesis of (*S*)-(-)-MVMI. **Scheme 2.** Polymerization of (*S*)-(-)-MVMI.

EXPERIMENTAL

Reagents

Solvents used in the reactions and polymerizations were purified by the usual methods.²⁴ Commercially available *n*-butyllithium (*n*-BuLi) (in *n*-hexane solution, 1.55 mol/L), diethylzinc (Et₂Zn) (in *n*-hexane solution, 0.819 mol/L) and dimethylzinc (Me₂Zn) (in *n*-hexane solution, 1.00 mol/L) (Kanto Chemical Co., Inc.) were used without further purification.

Commercially available (-)-sparteine (Sp) (Tokyo Kasei Kogyo Co., Ltd.) was used after purified by distillation under reduced pressure ([α]₄₃₅ = -10.3°

(*c* = 1.0 g/dL, *l* = 10 cm, THF)).

(*S,S*)-(1-Ethylpropylidene)bis(4-benzyl-2-oxazoline) was prepared as reported previously.²⁵ ([α]₄₃₅ = -150.7° (*c* = 1.0 g/dL, *l* = 10 cm, THF)).

Radical initiator, 2,2'-azobisisobutyronitrile (AIBN) (Ishizu Seiyaku, Ltd.) was used after recrystallized from methanol.

Synthesis of Monomer (S)-(-)-MVMI

Thionyl chloride (SOCl₂) (15.5 mL, 210 mmol) was added dropwise to methanol (60 mL) of -10 °C in a three-neck flask which was cooled by ice and NaCl. L-Valine (10.0 g, 85.4 mmol) was added slowly to this

Scheme 3. Synthesis of model compound (S)-(-)-MVSI.

solution at room temperature, and the mixture was stirred for 24 h. After reaction, methanol and SOCl_2 were removed by distillation under reduced pressure. (S)-(-)-Valine methyl ester hydrochloride was obtained by washing the slurry with Et_2O , followed by filtering and drying.

(S)-(-)-Valine methyl ester hydrochloride (10.2 g, 60.7 mmol) was suspended into ethyl acetate (65 mL) at 0°C , triethylamine (Et_3N) (8.0 mL, 58 mmol) was dropwise added into the mixture. After stirred over 10 min, it was collected by suction filtration. Maleic anhydride (5.9 g, 61 mmol) was dissolved into ethyl acetate (55 mL), and then added into the above filtrate at 0°C , followed with stirring for 2 h at room temperature. (S)-(-)-Maleamic acid-L-valine methyl ester ((S)-(-)-MVMA) was obtained by concentrating the above solution with a rotary evaporator.

(S)-(-)-MVMA (5.1 g, 20 mmol) was dissolved in toluene (200 mL) and put into a three-neck flask. Celite 545 (5.0 g) was added into the solution. After the solution was heated to 50°C , ZnBr_2 (4.5 g, 20 mmol) was added. The solution of 1,1,1,3,3,3-hexamethyldisilazane (HMDS) (6.3 mL, 30 mmol) in toluene (40 mL) was added dropwise into it at 80°C , and kept at this temperature for 48 h with stirring. The insoluble part in toluene was filtered off, and filtrate was concentrated. Obtained product was dissolved into ethyl acetate, then washed and separated by a funnel in a sequence of 0.1 N HCl, H_2O , saturated NaHCO_3 , and saturated NaCl solution. After dried over Na_2SO_4 , filtered, and concentrated by a rotary evaporator, crude (S)-(-)-MVMI was obtained, then purified further by column chromatography (solvent: *n*-hexane/ EtOAc = 6:1) (yield, 0.8 g (19%); colorless prism; mp $70\text{--}71^\circ\text{C}$; $[\alpha]_{435} = -102.2^\circ$ ($c = 1.0 \text{ g/dL}$, $l = 10 \text{ cm}$, in THF)). ^1H NMR (δ in ppm from TMS in CDCl_3): 0.86–0.89 (d, 3H, $-\text{CH}_3$), 1.07–1.10 (d, 3H, $-\text{CH}_3$), 4.38–4.41 (d, 1H, $-\text{CH}$), 6.79 (s, 2H, $-\text{CH}=\text{CH}-$). ^{13}C NMR (δ in ppm from TMS in CDCl_3): 19.09, 20.47 (CH_3), 28.25 (CH), 52.15 ($-\text{OCH}_3$), 57.29 ($-\text{NCH}$), 133.98 ($-\text{CH}=\text{CH}-$), 168.93, 169.93 (C=O). *Anal.* (%), Calc.: C, 56.86; H, 6.20; N, 6.63; Found: C, 57.01; H, 6.17; N, 6.62.

Synthesis of Model Compound (S)-(-)-N-Succinoyl-L-valine Methyl Ester ((S)-(-)-MVSI)

(S)-(-)-MVMI (0.30 g, 1.4 mmol) was dissolved in ethyl acetate (20 mL) in a Schlenk reaction tube, 10% palladium-activated carbon (Wako Pure Chemical Industries, Ltd., 0.030 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 ((S)-(-)-MVSI) (Scheme 3) (yield, 0.30 g (quant); white solid; $[\alpha]_{435} = -195.5^\circ$ ($c = 1.0 \text{ g/dL}$, $l = 10 \text{ cm}$, THF)). ^1H NMR (δ in ppm from TMS in CDCl_3): 1.92 (d, 3H, CH_3), 2.60 (s, 4H, $-\text{CH}_2-\text{CH}_2-$), 6.17 (q, 1H, CH). *Anal.* (%), Calc.: C, 56.33; H, 7.09; N, 6.57; Found: C, 56.25; H, 7.29; N, 6.48.

Polymerization

For anionic polymerization, monomer and chiral ligand were put in a Schlenk reaction tube and a pear-shaped flask, respectively. They were 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*-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 two 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

Table I. Asymmetric anionic polymerizations of (S)-(-)-MVMI^a with only organometal

Run	Initiator ^b	Polym. Solvent ^c (mL)	Polym. Temp. (°C)	Polym. Time (h)	Yield ^d (%)	M_n^e ($\times 10^{-3}$)	M_w/M_n^e	$[\alpha]_{435}^f$ (deg)
1	<i>n</i> -BuLi	Tol.(5)	0	24	17.3	12.6	1.2	-208.7
2	<i>n</i> -BuLi	THF(3)	0	24	48.6	16.4	3.6	-59.0
3	<i>n</i> -BuLi	Tol.(3)	0	24	19.0	11.2	1.2	-186.7
4	Et ₂ Zn	THF(3)	0	72	64.8	10.8	1.3	-150.2
5	Et ₂ Zn	Tol.(3)	0	72	2.2	—	—	—

^aMonomer: 0.5 g. ^b[Organometal]/[Monomer] = 0.1. ^cTol.: Toluene, THF: Tetrahydrofuran. ^dMethanol insoluble part. ^eBy GPC. ^f $c = 1.0$ g/dL, $l = 10$ cm, THF.

Table II. Asymmetric anionic polymerizations of (S)-(-)-MVMI^a with organometal/(-)-sparteine complexes

Run	Initiator ^b	Polym. Solvent ^c (mL)	Polym. Temp. (°C)	Polym. Time (h)	Yield ^d (%)	M_n^e ($\times 10^{-3}$)	M_w/M_n^e	$[\alpha]_{435}^f$ (deg)
1	<i>n</i> -BuLi/Sp(1.0/1.2)	THF(3)	0	24	33.6	15.7	1.3	-185.1
2	<i>n</i> -BuLi/Sp(1.0/1.2)	Tol.(3)	0	24	40.0	12.1	1.3	-245.4
3	Et ₂ Zn/Sp(1.0/1.2)	THF(3)	0	72	55.6	11.9	1.3	-229.8
4	Et ₂ Zn/Sp(1.0/1.2)	Tol.(3)	0	72	40.5	12.5	1.7	-292.2
5	Me ₂ Zn/Sp(1.0/1.2)	THF(3)	0	72	88.1	19.9	1.5	-254.2
6	Me ₂ Zn/Sp(1.0/1.2)	Tol.(3)	0	72	29.5	22.2	1.7	-266.3
7	Et ₂ Zn/Sp(1.0/0.5)	THF(3)	0	72	51.1	10.6	1.3	-231.5
8	Et ₂ Zn/Sp(1.0/0.5)	Tol.(3)	0	72	7.3	—	—	—

^aMonomer: 0.5 g. ^b[Organometal]/[Monomer] = 0.1. ^cTol.: Toluene, THF: Tetrahydrofuran. ^dMethanol insoluble part. ^eBy GPC. ^f $c = 1.0$ g/dL, $l = 10$ cm, THF.

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.

Measurements

Specific rotations were measured on concentration of 1.0 g/dL in THF at 25 °C using a quartz cell (10 cm) with a JASCO P-1030 polarimeter (JASCO Co., Ltd.). CD spectra were measured on concentration of 1.0 g/dL in THF at 25 °C using a quartz cell of 0.2 mm with a JASCO J-805 spectropolarimeter. Number-average molecular weights (M_n s) of polymers were measured with gel permeation chromatography (GPC) using THF as an eluent and polystyrene as a standard at 50 °C by the Shimadzu LC-10A instrument equipped with a UV-vis detector SPD-10A, a polarimetric detector (JASCO OR-990), and a data processor. ¹H and ¹³C NMR spectra were obtained with a JEOL-EX270 apparatus (JEOL, Ltd.). Elementary Analyses were carried out with a Perkin-Elmer Series II CHNS10 analyzer 2400 (PerkinElmer, Ltd, Japan).

RESULTS AND DISCUSSION

Polymerizations of (S)-(-)-MVMI

The polymerization conditions and results of (S)-(-)-MVMI with only organometal are shown in Table I. When used only *n*-BuLi or Et₂Zn, the yields of polymerizations were lower in toluene than in THF (Runs 2 to 5). That is, polar solvent was beneficial to obtain higher yields in these polymerizations. In THF, the yield of polymer obtained by Et₂Zn was higher than that used *n*-BuLi, but its M_n was lower than the latter. Table II shows the results of polymerizations initiated by organometal/Sp. With the using of Sp, the yields of polymerizations in toluene increased but decreased in THF when compared to the yields of polymerizations using only organometals *n*-BuLi and Et₂Zn respectively in Table I. Among three kinds of organometals, the highest yield of polymerization was obtained by using Et₂Zn/Sp in toluene, but in THF the highest yield was obtained by using Me₂Zn/Sp.

A chiral ligand of (S,S)-Bnbox was used in this work because it showed great effectiveness for obtaining optically active poly(RMI)s reported previously.^{13–19} Compared with the polymerizations used only organometal Et₂Zn (Runs 4 and 5 in Table I), the

Table III. Asymmetric anionic polymerizations of (*S*)-(-)-MVMI^a with organometal/(*S,S*)-Bnbox complexes

Run	Initiator ^b	Polym. Solvent ^c (mL)	Polym. Temp. (°C)	Polym. Time (h)	Yield ^d (%)	M_n^e ($\times 10^{-3}$)	M_w/M_n^e	$[\alpha]_{435}^f$ (deg)
1	Et ₂ Zn/(<i>S,S</i>)-Bnbox(1.0/0.5)	THF(3)	0	72	57.7	11.1	1.5	-163.6
2	Me ₂ Zn/(<i>S,S</i>)-Bnbox(1.0/0.5)	THF(3)	0	72	66.9	27.0	1.7	-127.8
3	Et ₂ Zn/(<i>S,S</i>)-Bnbox(1.0/0.5)	Tol.(3)	0	72	49.3	9.0	1.4	-189.4
4	Me ₂ Zn/(<i>S,S</i>)-Bnbox(1.0/0.5)	Tol.(3)	0	72	59.9	22.6	1.6	-172.4
5	Et ₂ Zn/(<i>S,S</i>)-Bnbox(1.0/1.2)	Tol.(3)	0	72	54.8	11.8	1.3	-340.4
6	Me ₂ Zn/(<i>S,S</i>)-Bnbox(1.0/1.2)	Tol.(3)	0	72	69.5	21.9	1.6	-202.9

^aMonomer: 0.5 g. ^b[Organometal]/[Monomer] = 0.1. ^cTol.: Toluene, THF: Tetrahydrofuran. ^dMethanol insoluble part. ^eBy GPC. ^f $c = 1.0$ g/dL, $l = 10$ cm, THF.

Table IV. Radical polymerizations of (*S*)-(-)-MVMI^a

Run	Initiator ^b	Polym. Solvent ^c (mL)	Polym. Temp. (°C)	Polym. Time (h)	Yield ^d (%)	M_n^e ($\times 10^{-3}$)	M_w/M_n^e	$[\alpha]_{435}^f$ (deg)
1	AIBN	THF(3)	0	24	trace	—	—	—
2	AIBN	Tol.(3)	0	24	56.0	10.5	1.6	-181.4

^aMonomer: 0.5 g. ^b[AIBN]/[Monomer] = 0.05. ^cTol.: Toluene, THF: Tetrahydrofuran. ^dMethanol insoluble part. ^eBy GPC. ^f $c = 1.0$ g/dL, $l = 10$ cm, THF.

yields of polymerizations using Et₂Zn/(*S,S*)-Bnbox (Runs 1 and 3 in Table III) increased in toluene greatly but decreased slightly in THF, it is the same phenomenon with the using of Et₂Zn/Sp (Runs 7 and 8 in Table II). The reason may be as follows: when used only Et₂Zn without ligand, with the increasing of *p* character of zinc atom coordinated by THF, its nucleophilicity increased in THF, but in toluene, the initiation ability of polymerization was lower because Et₂Zn formed binuclear complex, thus the yield of polymerization in THF was higher than in toluene. On the other side, when used Et₂Zn with ligand, the zinc atom was activated by the coordination of nitrogen atom of ligand because the nitrogen atom has higher basicity than the oxygen atom of THF, therefore the yields of polymerizations were almost the same wherever in THF or in toluene. The yields and M_n s of polymers obtained by Me₂Zn/(*S,S*)-Bnbox both in THF and toluene were higher than that used Et₂Zn/(*S,S*)-Bnbox. This is probably from the complex of Me₂Zn/(*S,S*)-Bnbox has higher nucleophilicity to prompt the growing of ion pairs than the complex of Et₂Zn/(*S,S*)-Bnbox, therefore the yield of its polymerization was increased by higher initiation rate. Moreover, the methyl or ethyl affected the additional direction of monomer in polymerization process because of their steric hindrance when Zn⁺-Me or Zn⁺-Et coordinated in the growing end of polymer. The M_n of polymer would be greater because of its higher propagation rate when used less bulky Me₂Zn in polymerization. Table IV shows the results of radi-

cal polymerizations of (*S*)-(-)-MVMI with AIBN as initiator. The yield of polymerization in toluene was 56%, but in THF the insoluble part of polymer in methanol could not be obtained.

Chiroptical Properties and Structures of Poly((*S*)-(-)-MVMI)s

The specific rotation of (*S*)-(-)-MVMI was -102.2° ($c = 1.0$ g/dL, $l = 10$ cm, THF), and its model compound ((*S*)-(-)-MVSI) had a specific rotation of -195.5° . All specific rotations of the polymers obtained by asymmetric anionic polymerizations and radical polymerization were levorotatory ($[\alpha]_{435} = -59.0^\circ$ to -340.4°). Most of the polymers had higher specific rotations than model compound. It showed asymmetric inductions in main chains of these polymers occurred. All polymers obtained in anionic polymerizations in toluene had higher specific rotations than that obtained in THF in the same conditions except for two runs (Run 5 in Table I and Run 8 in Table II) whose specific rotations could not be determined because of very low yields.

Polymers obtained with organometal/Sp complexes (Table II) had higher specific rotations than that used only organometal (Table I) both in THF and in toluene. These results confirmed that the better asymmetric fields were formed by using the complexes of chiral ligand and organometal in these anionic polymerizations. The specific rotation of polymer obtained with Me₂Zn/Sp was the highest among the polymers obtained with three kinds of organometal

Figure 1. CD and UV spectra of (S)-(-)-MVMI, model compound, and poly((S)-(-)-MVMI)s: 1. (S)-(-)-MVMI ($[\alpha]_{435} = -102.2^\circ$); 2. model compound ($[\alpha]_{435} = -195.5^\circ$); 3. Run 5 in Table III ($[\alpha]_{435} = -340.4^\circ$); 4. Run 4 in Table II ($[\alpha]_{435} = -292.2^\circ$); 5. Run 2 in Table I ($[\alpha]_{435} = -59.0^\circ$); and 6. Run 2 in Table IV ($[\alpha]_{435} = -181.4^\circ$). The top sub-figures were CD spectra and bottom sub-figures were UV spectra.

and Sp complexes in THF. While in toluene the highest specific rotation of polymer was obtained with $\text{Et}_2\text{Zn}/\text{Sp}$.

The specific rotation of polymer obtained with $\text{Et}_2\text{Zn}/(S,S)\text{-Bnbox}(1.0/1.2)$ in toluene (Run 5 in Table III) increased when compared with the polymer obtained using $\text{Et}_2\text{Zn}/\text{Sp}(1.0/1.2)$, and it was the highest among all polymers. But the polymer obtained with $\text{Me}_2\text{Zn}/(S,S)\text{-Bnbox}(1.0/1.2)$ had lower specific rotation than that obtained with $\text{Me}_2\text{Zn}/\text{Sp}(1.0/1.2)$.

Both in THF and toluene the polymers obtained with $\text{Et}_2\text{Zn}/(S,S)\text{-Bnbox}$ had higher specific rotations than the polymers obtained with $\text{Me}_2\text{Zn}/(S,S)\text{-Bnbox}$ in spite of the ratio of chiral ligand to organometal. This phenomenon differed from the polymers obtained with organometal/Sp. When increased the ratio of (S,S)-Bnbox to organometal, the specific rotations of polymers obtained both with $\text{Et}_2\text{Zn}/(S,S)\text{-Bnbox}$ and $\text{Me}_2\text{Zn}/(S,S)\text{-Bnbox}$, respectively, increased greatly, which was also contrary to the polymerizations used

Figure 2. GPC chromatograms of poly((*S*)-(-)-MVMI): (A) Run 5 in Table III ($[\alpha]_{435} = -340.4^\circ$), and (B) Run 2 in Table IV ($[\alpha]_{435} = -181.4^\circ$). The top curves (solid line) were obtained by UV detector and bottom curves (dash line) were obtained by polarimetric detector.

organometal/Sp.

For radical polymerizations, the polymer obtained in toluene (Run 2 in Table IV) had specific rotation of a little lower than model compound and lower than all other polymers in toluene, which manifested the difficulty to construct stereoregular polymer in radical polymerization than in anionic polymerization.

CD spectral patterns of poly((*S*)-(-)-MVMI)s obtained with organometal or organometal/chiral ligand complexes even with radical initiator AIBN were almost similar (Figure 1), which suggests that these polymers have similar structures. Figure 1 indicates that the larger the specific rotation of polymer, the higher is the peak at 220 nm, suggesting asymmetric induction took place in the main chains of polymers more effectively in the runs of higher specific rotations. Another point needs to be paid attention is that for the polymers with higher specific rotations (Run 5 in Table III and Run 4 in Table II) there was a small negative peak at about 264 nm. The reason may be ascribed to that helical conformations were formed in main chains of these polymers because there was no peak appeared in CD spectrum of model compound (*S*)-(-)-MVSI around this range.

In UV curves of GPC measurements of poly((*S*)-(-)-MVMI)s (Figure 2), the polymers showed only one high molecular weight fraction, suggesting that whole polymer main chains are optically active. The intensities of peaks of polarimetric curves were in correspondence with the magnitudes and signs of the specific rotations of polymers. The relationship between optical activities and molecular weights can be known from GPC chromatograms monitored by both UV and polarimetric detectors simultaneously. The shapes

of two curves were almost similar, indicating that the poly((*S*)-(-)-MVMI)s with different molecular weights possess equivalent optical rotations. This means the optical activities of these polymers are independent of molecular weights and mainly ascribed to chiral stereogenicity of the whole main chain.

^{13}C NMR spectra of poly((*S*)-(-)-MVMI)s were measured to investigate the relationships between optical activities and structures of poly((*S*)-(-)-MVMI)s. On the basis of previous works reported by Oishi and coworkers, the peaks at lower and higher magnetic field around 43 ppm were assigned to *threo*-disyndiotactic and *threo*-diisotactic structure, respectively.^{20–22} In this work the main chain signals of poly((*S*)-(-)-MVMI)s with higher specific rotations ((A) and (B) in Figure 3) within 40–46 ppm ((A) and (B) in Figure 4, the expanded ^{13}C NMR spectra) were sharper than that of the polymer obtained from radical polymerization ((D) in Figure 4) and the polymer of lower specific rotation ((C) in Figure 4). This indicates the polymers obtained by asymmetric anionic polymerization with organometal/ligand complex have more stereoregular structures than that obtained by radical polymerization or anionic polymerization with only organometal *n*-BuLi as initiator. Furthermore, from expanded ^{13}C NMR spectra of the latter two polymers, *threo*-disyndiotactic and *threo*-diisotactic structure in the main chains of these polymers are showed clearly around 40–46 ppm. That means optically inactive *threo*-disyndiotactic structure formed simultaneously with the optically active *threo*-diisotactic structure in the main chains of these polymers in polymerization processes, which is the reason why these polymers had lower specific rota-

Figure 3. ^{13}C NMR spectra of poly((*S*)-(-)-MVMI)s: (A) Run 5 in Table III ($[\alpha]_{435} = -340.4^\circ$), (B) Run 4 in Table II ($[\alpha]_{435} = -292.2^\circ$), (C) Run 2 in Table I ($[\alpha]_{435} = -59.0^\circ$), and (D) Run 2 in Table IV ($[\alpha]_{435} = -181.4^\circ$).

tions. The polymer obtained by radical polymerization mainly had *threo*-disyndiotactic structure was judged by the peak at about 44 ppm in ^{13}C NMR spectrum.^{12,21} The *threo*-diisotactic structure of polymer obtained by anionic polymerization showed peak at about 40–43 ppm in ^{13}C NMR spectrum, and the polymer of high specific rotation mainly had *threo*-diiso-

tactic structure was also recognized.¹⁸ In this work, the peaks at about 43 ppm in ^{13}C NMR of (A) and (B) polymers in Figure 4 are considered as from *threo*-diisotactic structure because of their high specific rotations obtained by anionic polymerizations. In addition, the polymers which mainly have *threo*-diisotactic structure will be rigid because they may

Figure 4. Expanded ^{13}C NMR spectra of poly((*S*)-(-)-MVMI)s: (A) Run 5 in Table III ($[\alpha]_{435} = -340.4^\circ$), (B) Run 4 in Table II ($[\alpha]_{435} = -292.2^\circ$), (C) Run 2 in Table I ($[\alpha]_{435} = -59.0^\circ$), and (D) Run 2 in Table IV ($[\alpha]_{435} = -181.4^\circ$).

contain stereoregular helical structure. Thus their peaks of *threo*-diisotactic structure shifted a little to lower magnetic field at about 43 ppm because of the unshielding effect of carbonyl of succimide and carbonyl of ester neighbored to the carbon atoms of main chain. Another distinguishing point in expanded ^{13}C NMR spectra of the polymers with higher specific rotations ((A) and (B) in Figure 3) was that their peaks ascribed to carbonyl carbon (around 176 ppm), methyl carbon (around 19 ppm) and methine carbon (around 27 ppm) were split into two parts. While the polymer obtained from radical polymerization ((C) in Figure 3) did not show this phenomenon. This may also support that the polymers of higher specific rotations obtained from asymmetric anionic polymerizations have more stereoregular *threo*-diisotactic structures when compared with the polymer obtained from radical polymerization.

SUMMARY

A kind of chiral monomer of (*S*)-(-)-*N*-maleoyl-L-valine methyl ester with a specific rotation of $[\alpha]_{435} = -102.2^\circ$ was synthesized successfully from an aliphatic amino acid L-valine and maleic anhydride.

Asymmetric anionic polymerizations were carried out with organometal or organometal and chiral ligand complex as initiators, the polymer with highest specific rotation ($[\alpha]_{435} = -340.4^\circ$) was obtained using $\text{Et}_2\text{Zn}/(S,S)\text{-Bnbox}(1.0/1.2)$.

Chiral ligands are effective for asymmetric anionic polymerizations to prepare optically active polymers, and asymmetric inductions in main chains of the polymers were confirmed by ^{13}C NMR and CD, GPC measurements.

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