Asymmetric Polymerization of *N*-Substituted Maleimide

Tsutomu OISHI, Hiroko YAMASAKI, and Minoru FUJIMOTO

*Department of Industrial Chemistry, Technical College, Yamaguchi University,
2557 Tokiwadai, Ube, Yamaguchi 755, Japan*

(Received September 25, 1990)

ABSTRACT: Homopolymerizations of non-chiral *N*-substituted maleimide (RMI, *N*-substituent(R) = *N*-*n*-propyl, *N*-isopropyl, *N*-*n*-butyl, *N*-isobutyl, *N*-*s*-butyl, *N*-*t*-butyl, *N*-cyclohexyl (CHMI), *N*-benzyl, *N*-phenyl, *N*-1-naphthyl, and *N*-2-fluorenyl) were performed with *n*-butyllithium (*n*-BuLi)/(–)-sparteine (Sp) in toluene to obtain chiral homopolymers with considerably high specific rotation. The specific rotation $[\alpha]_D$ and mean residue ellipticity for CHMI polymer were the largest in the polymers ($[\alpha]_D = ca. -40^\circ$ in $CHCl_3$). The polymerization of CHMI and the chiroptical property of the polymers were investigated in detail. Optical rotation could be attributed to a three-diisotactic structure of RMI polymer main chains.

KEY WORDS *N*-Substituted Maleimide / Asymmetric Polymerization /
Optically Active Polymer / Sparteine / Butyllithium /

There have been many reports¹ on polymerization and copolymerization of optically active *N*-substituted maleimide (RMI). Radical copolymerizations of non-chiral RMI with styrene (ST) in chiral solvents, *i.e.*, 1-menthol² and lecithin³ micell were also reported. In these cases, optical rotation was attributed to asymmetric induction to the copolymer main chain and specific rotation of the copolymers obtained was generally low. Okamoto and coworkers⁴ reported that anionic polymerizations of triphenylmethyl methacrylate (TrMA) were carried out with *n*-butyllithium (*n*-BuLi)/(–)-sparteine (Sp) as catalyst to obtain polymers with abnormally high specific rotation ($[\alpha]_D > 300^\circ$). It was thought that chirality was ascribed to a helical conformation of TrMA polymer main chain. Okamoto *et al.*⁵ also reported that the asymmetric polymerization of *N*-phenyl maleimide (PhMI) was performed with *n*-BuLi/(–)-Sp catalyst to yield the chiral PhMI polymer having 12° of the specific rotation.

We report here that homopolymerizations of non-chiral RMI [*N*-substituent(R) = *N*-*n*-

propyl (PMI), *N*-isopropyl (IPMI), *N*-*n*-butyl (*n*BMI), *N*-isobutyl (IBMI), *N*-*s*-butyl (SBMI), *N*-*t*-butyl (TBMI), *N*-cyclohexyl (CHMI), *N*-benzyl (BZMI), *N*-phenyl (PhMI), *N*-1-naphthyl (NMI), and *N*-2-fluorenyl (FMI)] were performed with BuLi/(–)-Sp in toluene, and that the obtained polymers have considerably high specific rotation. In addition, since CHMI polymer has the greatest specific rotation in the RMI polymers, the polymerization of CHMI and the chiral property of the polymers obtained are studied in detail.

EXPERIMENTAL

RMI Monomers

Eleven types of RMI were prepared from maleic anhydride and the corresponding primary amine by the usual methods.⁶ Boiling points and melting points of RMI are as follows: *n*PMI bp 100°C/24 mmHg, IPMI bp 89°C/20 mmHg, *n*BMI bp 105°C/20 mmHg, IBMI bp 60°C/8.5 × 10^{–2} mmHg, SBMI bp 60°C/2 mmHg, TBMI bp 55°C/2 mmHg, CHMI mp 89°C, BZMI mp 70°C, PhMI mp

90–91°C, NMI mp 117°C, and FMI mp 182°C. RMI monomers were identified by IR, NMR spectra, and elemental analyses.

Catalyst and Solvents

Commercially available *n*-BuLi and *t*-butyllithium (*t*-BuLi) in hexane solutions were used without further purification. Solvents; toluene (Tol), tetrahydrofuran (THF), and methanol were purified by the usual methods. (–)-Sp was purified by distillation under reduced pressure: bp 93–94°C/5 × 10^{−2} mmHg; $[\alpha]_D^{20} = -17.5^\circ$ (*c* = 1.0 g dl^{−1}, ethanol). (–)-Sp and BuLi were mixed at room temperature just before use.

Polymerization

Anionic homopolymerizations of RMI were attained with BuLi/(–)-Sp as initiator in toluene or THF at several temperatures. A constant volume of toluene and RMI monomer were placed in a dry glass ampule under nitrogen. The solution was cooled to about −180°C (liquid nitrogen) and then degassed under vacuum by the ordinary freeze-thaw technique. After this procedure was repeated three times, the catalyst solution was then added with a syringe to the monomer solution cooled to the temperature of polymerization. The reaction was terminated by the addition of a few drops of methanol. The polymer was precipitated in a large amount of methanol, separated by filtration, and purified by reprecipitation from chloroform–methanol system three times.

Measurements

D-line specific rotations, optical rotatory dispersion (ORD) and circular dichroism (CD) spectra were obtained with the same instruments as reported previously.⁷

199.5 MHz ¹H NMR and 50.1 MHz ¹³C NMR spectra were measured in deuterium chloroform at room temperature with a JEOL FX-200. In ¹H NMR measurement, tetramethylsilane was used as a standard.

RESULTS AND DISCUSSION

Homopolymerization of RMI

The results of anionic homopolymerizations of RMI by use of *n*-BuLi/(–)-Sp in toluene are shown in Table I. All the polymers obtained in toluene were optically active, but the specific rotations $[\alpha]_D$ of FMI and NMI polymers were very small. The obtained polymers revealed obvious CD peaks, as shown in Figure 1. The magnitude of the mean residue ellipticity $[\theta]$ corresponded each to $[\alpha]_D$. In addition, the specific rotations of RMI polymers were plotted against the polar substituent constants or the steric substituent constants of the Taft's equation.⁸ However, the relation was not linear, and the chirality of RMI polymers could not be correlated to steric and polar character of *N*-substituents of RMI.

In particular, the specific rotation ($[\alpha]_D = ca. -40$) and the mean residue ellipticity ($[\theta] = -2800 \text{ deg cm}^2 \text{ dmol}^{-1}$) for CHMI polymer were the largest in the polymers. The polymerization of CHMI and chiroptical property of the CHMI polymers were investigated in detail. The effects of the molar ratios

Figure 1. CD curves for RMI polymers: (1) CHMI, (2) *n*BMI, (3) PhMI, (4) *n*PMI, (5) SBMI, (6) IBMI, (7) IPMI, (8) TBMI, (9) BZMI, and (10) FMI, NMI polymers.

Table I. Anionic polymerization of *N*-substituted maleimide with *n*-BuLi/(–)-sparteine system in toluene^a

	RMI	Toluene	Temp	Catalyst	Polymeri- zation time	Yield	$[\alpha]_D^b$	$\overline{M}_n^c$	$\overline{DP}$	$[\theta]^d$
	mol l ⁻¹	ml	°C	$\times 10^2$ mol l ⁻¹	h	%	deg.	$\times 10^{-3}$		
CHMI	0.14	20	0	1.2	19	73.4	–39.5	3.3	18	–2880
CHMI	0.28	20	0	1.2	17	75.8	–37.0	3.4	19	–2410
CHMI	0.14	20	–17	1.2	1	77.7	–38.2	3.2	18	–2640
<i>n</i> PMI	0.72	10	0	1.2	18	9.8	–4.9	6.7	48	–880
IPMI	1.33	6	0	4.0	16	18.8	–18.7	12.6	99	–440
<i>n</i> BMI	0.65	10	0	1.2	18	10.2	–7.1	9.6	62	–1060
IBMI	0.65	10	0	1.2	18	5.8	–13.4	14.8	96	–490
SBMI	1.64	4	6	9.3	17	52.7	–21.0	9.3	61	–760
TBMI	1.19	6	0	4.0	16	9.9	+2.8	—	—	+130 ^e
BZMI	0.90	6	0	3.6	17	94.9	+11.3	3.2	17	+650
PhMI	0.29	20	0	1.9	17	33.2	–15.4	2.3	13	–980 ^e
FMI	0.09	30	0	1.2	17	63.5	–0.4	1.8	7	~0
NMI	0.11	20	0	1.2	17	55.7	+0.9	2.0	9	~0

^a [BuLi]/[(–)-Sp] = 1.0/1.2.^b *C* = 0.5 to 1.0%; *l* = 10 cm; CHCl₃ or THF.^c By GPC.^d λ = 246 ± 3 nm; deg · cm² dmol⁻¹; *C* = 0.3 to 1.0%; *l* = 1.0 mm; in CHCl₃ or THF.^e λ = 255 ± 1 nm.

of *n*-BuLi and (–)-Sp on the polymerization and the specific rotations of the CHMI polymers obtained are summarized in Table II. The magnitude of $[\alpha]_D$ for CHMI polymer was the best when the ratio of *n*-BuLi/(–)-Sp was 1.2.

In order to clarify the effects of the polymerization solvents on the specific rotation of the polymers obtained, polymerizations of CHMI were performed with *n*-BuLi/(–)-Sp in the mixture solvents of toluene and THF at –78°C. The results are shown in Figure 2. The specific rotation of the polymers obtained only in THF was zero. Yields, the rate of polymerization, and molecular weight ($\overline{M}_n$) increased with THF amount in the mixture, but the specific rotations decreased. When THF exists, an ionic pair at the growing chain end is solvated by THF, which inhibits the co-ordination of a RMI monomer with the ionic pair.⁹ Accordingly, the increase of a THF amount enhances the free ion, which may

Figure 2. Effects of polymerization solvent (mixture of THF and toluene) on polymerization yields and specific rotations ($[\alpha]_D$) of CHMI polymers obtained with *n*-BuLi/(–)-Sp at –78°C.

hinder asymmetric polymerization by the catalyst.

The dependence of concentrations of *n*-BuLi

Table II. Dependence of $[n\text{-BuLi}]/[(-)\text{-Sp}]$ ratios on specific rotations of CHMI polymers obtained at 0 °C^a

Run	Monomer CHMI	$[n\text{-BuLi}]$	Cat.	Polym. time	Yield	$[\alpha]_D^b$
	mol l ⁻¹	$[(-)\text{-Sp}]$	$\times 10^2 \text{ mol l}^{-1}$	h	%	deg.
2-1	0.28	1.0/0.4	1.2	16	40.6	-32.91
2-2	0.28	1.0/0.8	1.2	16	73.8	-35.37
2-3	0.28	1.0/1.2	1.2	17	75.8	-36.96
2-4	0.28	1.0/1.6	1.2	16	38.4	-33.96

^a Solvent: toluene 20 ml.^b In CHCl_3 , $l = 10 \text{ cm}$, $C = 1.0\%$. **Figure 3.** Dependence of concentrations of $n\text{-BuLi}$ and CHMI on polymerization yields and specific rotations ($[\alpha]_D$) of CHMI polymers obtained. **Figure 4.** Dependence of polymerization time on conversions and specific rotations ($[\alpha]_D$) of CHMI polymers obtained with $n\text{-BuLi}/(-)\text{-Sp}$ at (1) 0, (2) -17, and (3) -78°C.

Figure 5. Dependence of polymerizations time on conversions and specific rotations ($[\alpha]_D$) of CHMI polymers obtained with *t*-BuLi/(–)-Sp at 0°C.

Figure 6. CD spectra for CHMI polymers in solvents: (1) THF, (2) CHCl₃, and (3) CH₂Cl₂.

and CHMI on conversions and specific rotations of RMI polymer is shown in Figure 3. Specific rotations could not be affected by the concentration of the catalyst but were almost constant. The specific rotations slightly decreased with increasing RMI monomer concentration. It can be seen from Figure 4 that yields of polymers obtained at 0°C were quantitative in about 5 h, but that polymers

Figure 7. Effects of measurement temperatures on CD spectra of CHMI polymers in solvents: (1) THF, (2) chloroform, and (3) dichloromethane.

obtained at –17°C and –78°C were about 50 and 20% yields. Both specific rotations and $\bar{M}_n$ of the polymers obtained at 0 and –17°C were constant, and not correlated with polymerization time. A part of the polymer obtained at –78°C was insoluble in THF, and the specific rotations of the soluble polymer were –10 to –14°.

The results of the polymerization of CHMI with *t*-BuLi/(–)-Sp at 0°C are summarized in Figure 5. The specific rotations of the polymers obtained were constant, and could not be affected by polymerization time, as well as

Figure 8. Relationships between specific rotations of (●) CHMI, (○) SBMI polymers and dielectric constants of solvents: (1) C_6H_6 , (2) $CHCl_3$, (3) C_6H_5Br , (4) C_6H_5Cl , (5) THF, (6) CH_2Cl_2 , (7) $CHCl_2CHCl_2$, (8) CH_2ClCH_2Cl , (9) *o*-dichlorobenzene.

n-BuLi/(–)-Sp. The specific rotations $[\alpha]_D$ of the polymers obtained with *n*-BuLi/(–)-Sp were almost equal to those obtained with *t*-BuLi/(–)-Sp. The specific rotation of the polymers was thus not influenced by the difference of steric character between *t*-butyl and *n*-butyl groups.

Solvent effects of CHMI polymers on CD spectra are shown in Figure 6. The CD patterns in THF, chloroform and dichloromethane were slightly different. It can be seen from Figure 7 that the magnitude of the molecular ellipticity $[\theta]$ decreased with rise of temperature and increased with fall of temperature. Optical rotations and heights of CD peaks were reproducible. Relationships between dielectric constants, ϵ_r , of the measurement solvents and specific rotations $[\alpha]_D$ of CHMI or SBMI polymers are shown in Figure 8. It was found that the specific rotations of polymers were not correlated with the dielectric constants of solvents.

Cubbon¹⁰ reported that eight RMI monomers were polymerized by free radical and *n*-BuLi and that both types of initiator gave rise to polymers which have a predominantly threo-diisotactic polymer based on only X-ray

Figure 9. 1H NMR spectra for CHMI polymers obtained with (a) *n*-BuLi/(–)-Sp, (b) *n*-BuLi, and (c) AIBN in toluene.

analysis. According to his paper,¹⁰ RMI polymers may not be completely stereoregular and predominantly threo-diisotactic with occasional threo-disyndiotactic placements which disrupt the crystallinity to some extent. In addition, the stereospecificity of RMI polymers arises as a result of the geometry of the monomer unit, which requires trans opening of the double bonds and leads to the formation of a helix. Inspection of models indicates that there is little freedom of rotation of the helix, and so when there is threo-diisotactic sequence, the polymer will probably take the helical conformation in solution.

In order to confirm the existence of threo-

Figure 10(A).

Figure 10(B).

diisotactic sequence, IR, ^1H and ^{13}C NMR spectra of some CHMI polymers were measured.

Three kinds of CHMI polymers obtained in toluene from different initiators, that is, a (a) polymer obtained with $n\text{-BuLi}/(-)\text{-Sp}$; a (b) polymer obtained with $n\text{-BuLi}$; and a (c) polymer obtained with AIBN, indicated different ^1H and ^{13}C NMR spectra in deuterium chloroform, as shown in Figures 9 and 10. The ^1H NMR spectra for three polymers were slightly different. That is, the signal pattern at about 3.3 ppm, assigned to H1 and H2 for the (c) polymer was different from those for (a) and (b) polymers, as shown in Figure 9. This suggests that H1 and H2 for the (a) and (b) polymer exist in the region of complicated structure. The signal assigned to $\text{H}3_a$, (subscript a means an axial H), at 3.9 ppm shifted to the higher magnetic field in the following order: the (c) < (b) < (a) polymer. This indicates that $\text{H}3_a$ for the (a) polymer exists in the vertical area of the plane of the carbonyl group containing the maleimide ring. Accordingly, the (a) polymers may contain more helical configuration than (b) and (c) polymers. The signals assigned to $\text{H}4_e$ and $\text{H}5_e$, (subscript e means an equatorial H), at about 2.1 ppm became lacking in the following order: the (c) < (b) < (a) polymer. This indicates that the signals due to $\text{H}4_e$ and $\text{H}5_e$ also shifted to the higher magnetic field in the same order, and that $\text{H}4_e$ and $\text{H}5_e$ for the (a) polymer are located in the vertical region of the carbonyl group as well as $\text{H}3_a$. This suggests that the (a) polymer has the most threo-diisotactic sequences, *i.e.*, helical configuration. The (c) polymer may contain more threo-disyndiotactic sequence than the (a) or (b) polymers.

In ^{13}C NMR spectra, the signal patterns at about 177, 43, 29 ppm were slightly different among the three polymers. That is, the signal

Figure 10. ^{13}C NMR spectra for CHMI polymers obtained with (a) $n\text{-BuLi}/(-)\text{-Sp}$, (b) $n\text{-BuLi}$, and (c) AIBN in toluene.

Figure 11. IR spectra for CHMI polymers obtained with (a) *n*-BuLi/(–)-Sp in toluene, (b) *n*-BuLi in toluene, (c) AIBN in toluene, (d) *n*-BuLi/(–)-Sp in THF, and (e) AIBN in THF.

Scheme 1.

Scheme 2.

pattern due to the carbonyl group (C1, C2) at about 177 ppm became complicated in the order of (a), (b), and (c) polymers, as shown in Figure 10(A). This suggests that the (c) polymer contains the most threo-disyndiotactic and/or atactic sequence besides the threo-diisotactic one. The signals due to the cyclohexyl group (C6 and C7) at about 28 ppm became sharp in the order of (a), (b), and (c) polymers, as shown in Figure 10(B). This suggests that the C6 and C7 carbons of the (a) polymer exist in the area of intricate structure, *i.e.*, helical configuration. In addition, signals due to the main chain (C3, C4) in the range of about 42 to 44 ppm revealed narrow splitting and shifted to the low magnetic field in the same order, as shown in Figure 10(B). This suggests that the C3 and C4 carbons in the (a) polymer exist in the vertical area of the plane of the carbonyl group containing the maleimide ring, and that the (a) polymer includes the most threo-diisotactic sequences.

IR spectra for a (d) polymer with zero specific rotation, which was obtained by polymerization with *n*-BuLi/(–)-Sp in THF, and a (e) polymer with zero specific rotation obtained by photopolymerization in THF, besides (a), (b), and (c) polymers are shown in Figure 11. Three IR peaks at 890, 740, and 630 cm^{-1} were characteristic among five CHMI polymers. The

ratio of IR peaks at 890, 740, and 630 for (b) polymer was similar to that for the (d) polymer, and the ratio for (c) polymer was the same as that for the (e) polymer. The ratio for the (a) polymer was 1:1:1 and different from the other polymers, which suggests that only the (a) polymer takes a different structure.

It seems that the chirality of the RMI polymer can be attributed to the three types shown in Scheme 2 (A), (B), and (C). That is, the (A) type is that the chirality of the RMI polymers may be attributable to a helical structure of the threo-diisotactic RMI polymer main chain, as shown in Scheme 2(A). In addition, the (B) type is that the asymmetric induction around both the terminal RMI units of the polymer becomes important because of low molecular weight, as shown in Scheme 2(B). However, the magnitudes of the optical rotations of the polymers are too large, compared with those for the asymmetric induction obtained previously.^{2,3} Accordingly, there is little possibility of asymmetric induction shown in Scheme 2(B).

Farina¹¹ reported that polymerizations of cycloalkene derivatives can yield two trans-additions, *i.e.*, chiral centers of (S, S) and (R, R), and that if one is produced more than the other, the obtained polymer can be optically active. Accordingly, the chirality of the polymer is not necessarily a helical structure. This is the (C) type. According to this concept, the RMI polymers are represented diagrammatically in Scheme 2(C). The concept that chirality is attributable to excessive chiral center of (R, R) or (S, S), is very convenient to explain the chirality of the RMI polymers. That is, the RMI Polymers can be expected to contain more chiral centers of (S, S) than (R, R), because the specific rotations of the polymers are negative, except for BZMI and TBMI, as shown in Table I.

Cubbon¹⁰ reported that inspection of RMI polymer model indicates that threo-diisotactic polymers can form the 3_1 helix in which the repeat distance is 4.7 Å, and that the diameter

of the helix with no substituents on the nitrogen is about 10 Å. As shown in Table I, both specific rotations $[\alpha]_D$ of FMI and NMI polymers were almost zero, indicating that polymerization degrees ($\overline{DP}$) of FMI ($\overline{DP}=7$) and NMI ($\overline{DP}=9$) may not be enough to form a helical structure. On the other hand, according to the concept of the (C) type, FMI and NMI polymers may contain the chiral centers of (S, S) almost similar to those of (R, R).

It cannot definitely be concluded that the chirality of the RMI polymer is attributable only to the helical structure (Scheme 2(A)) or to the excessive chiral center of (S, S) or (R, R); in this case, the polymers is not necessarily a helix (Scheme 2(C)). The RMI polymers may not be completely stereoregular but predominantly threo-diisotactic with occasional threo-disyndiotactic, as described above. Accordingly, only the helical structure of the RMI polymer may not be independently formed, and the polymer may contain some threo-disyndiotactic sequence. The threo-disyndiotactic sequences can yield not helical but linear structures. Therefore, the chirality of the RMI polymers may be ascribed not only to the helical structure but also to the excessive chiral centers of (S, S) or (R, R).

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

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