# Asymmetric Group Transfer Polymerization of N-Cyclohexylmaleimide with Lewis Acid and Chiral Ligand Complexes

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ABSTRACT: Asymmetric group transfer polymerization (AGTP) of N-cyclohexylmaleimide (CHMI) was carried out using ketene silyl acetal as initiator in the presence of Lewis acid–chiral ligand complexes to afford optically active poly-(CHMI) ($[\alpha]_{435}^{25}$ −6.6° to +31.0°). Lewis acids used as GTP catalyst, probably activating the monomer by coordination, were zinc iodide, zinc bromide, zinc triflate, titanium tetrachloride, aluminum chloride and copper bromide. The zinc catalysts tended to accelerate the polymerization. The addition of trimethylsilyl iodide to the system accelerated the polymerization in spite of low temperature. Poly(CHMI) obtained in a poor yield with zinc triflate as Lewis acid and chiral bisoxazoline (Bnbox) showed low specific optical rotation and had the highest degree of polymerization (DP=421, $\overline{M}_n$=75400).

KEY WORDS    N-Cyclohexylmaleimide / Asymmetric Polymerization / Group Transfer Polymerization / Optically Active Polymer / Lewis Acid / Chiral Ligand /

Group transfer polymerization (GTP) is a useful for obtaining "living nature" in the polymerization of vinyl monomers.[1] GTP proceeds in the presence of Lewis acids[2,3] or basic catalysts as fluoride.[4] Ute and Hatada *et al.* reported a GTP of methyl crotonate catalyzed by HgI$_2$ and ZnI$_2$.[5-8] Asymmetric catalysts (chiral Lewis acid) with combinations of Lewis acid and chiral organic ligands have been studied extensively.[9] Mukaiyama and co-worker reported asymmetric aldol reaction using trimethylsilyl ketene acetal derivatives and Lewis acid.[10] Asymmetric reactions using chiral bisoxazoline and metal complexes have been reported.[11] Bisoxaoline–Zn(II) complexes have been increasingly utilized in catalytic asymmetric carbon–carbon bond forming-reaction.[12] However, polymers obtained by GTP using chiral Lewis acid have not been described so far. Monomers for GTP are 1- or 1,1-substituted vinyl monomers such as acrylate or methacrylate derivatives. GTP of N-substituted maleimide (RMI) was investigated with tetrabutylammonium bibenzoate (TBAB) as catalyst.[13,14] Polymerizations of RMI form two chiral centers in the polymer main chain. The synthesis of optically active poly-(RMI) have been reported.[15-21] Recently the authors reported briefly that chiral complexes of organometal with optically active ligand were very efficient catalysts for asymmetric polymerizations of RMI.[18-21] In particular, poly(cyclohexylmaleimide) (poly(CHMI)) initiated by n-butyllithium (BuLi)–3,3′-bis-[2-((4S)-4-benzyl-1,3-oxazolinyl)]pentane (Bnbox)[22] complex showed the highest specific rotation ($[\alpha]_{435}^{25}$ +111.4°).[18] But poly(CHMI)s had broad molecular-weight distribution ($\overline{M}_w/\overline{M}_n$=1.2—2.6). A most characteristic of GTP is "living" polymerization, that is, molecular weight can be controlled. This paper reports asymmetric group transfer polymerization (AGTP) of CHMI initiated by complexes of Lewis acid–

chiral ligand as catalyst (Scheme 1).

## EXPERIMENTAL

### Materials

CHMI was prepared from maleic anhydride and cyclohexylamine by usual methods. Melting point of CHMI is 89°C.

*Solvents and Reagents.* CH$_2$Cl$_2$, tetrahydrofuran (THF), toluene and methanol were purified by usual methods. Sp (Sigma) was distilled under reduced pressure. Methylene-bridged bisoxazolines (Bnbox) were synthesized by the published procedure[22] $[\alpha]_{435}^{25}$ = −150.7°(c 1.0 g dL$^{-1}$, THF). (+)-(2S, 3S)-2,3-Dimethoxy-1,4-bis-(dimethylamino)butane (DDB) and (+)-(2S, 3S)-2,3-isopropylidenedioxy-1,4-bis(dimethylamino)butane (IPDB) were synthesized by Seebach's method[23]; DDB: $[\alpha]_{435}^{25}$ = +19.8°(c 1.0 g dL$^{-1}$, THF), IPDB: $[\alpha]_{435}^{25}$ = +6.8°(c 1.0 g



Chiral Ligands
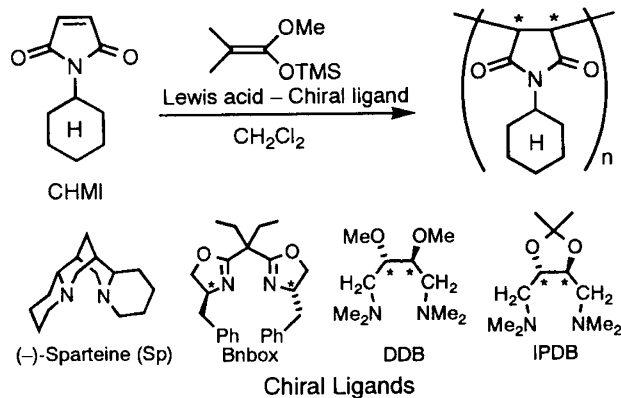
**Scheme 1.**

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**Table I.** Group transfer polymerizations with Lewis acid–MTDA for 24 h [a]

| Entry | Monomer mol L$^{-1}$ | Lewis acid [b] mol% | Solvent | Temp. ℃ | Yield [c] % | $\overline{M}_n$ [d] ×10$^{-3}$ | $\overline{M}_w/\overline{M}_n$ [d] |
|---|---|---|---|---|---|---|---|
| 1 | CHMI (0.56) | AlCl$_3$(10) | CH$_2$Cl$_2$ | rt | 0 | — | — |
| 2 | CHMI (0.56) | TiCl$_4$(10) | Toluene | 0 | 0 | — | — |
| 3 | CHMI (0.56) | CuBr$_2$(10) | CH$_2$Cl$_2$ | 0 | 0 | — | — |
| 4 | CHMI (0.56) | ZnBr$_2$(5) | CH$_2$Cl$_2$ | rt | Trace | — | — |
| 5 | CHMI (0.56) | ZnBr$_2$(10) | CH$_2$Cl$_2$ | 0 | 9.8 (49.5) [e] | 1.4 (0.8) [e] | 1.3 (1.4) [e] |
| 6 | CHMI (0.56) | ZnI$_2$(10) | CH$_2$Cl$_2$ | rt | 74.1 | 2.5 | 1.4 |
| 7 | CHMI (0.56) | ZnI$_2$(10) | THF | rt | 7.2 | 2.5 | 1.3 |
| 8 | CHMI (0.56) | ZnI$_2$(10) | Toluene | rt | 7.3 | 1.3 | 1.3 |
| 9 | CHMI (0.56) | Zn(OTf)$_2$(10) | CH$_2$Cl$_2$ | rt | 0 | — | — |
| 10 | CHMI (0.56) | Zn(OTf)$_2$(10) | CH$_2$Cl$_2$ | -35 | 0 | — | — |
| 11 | CHMI (0.56) | Zn(OTf)$_2$–TMSI(10) | CH$_2$Cl$_2$ | -35 | 29.1 [f] | 0.5 [f] | 0.5 [f] |

[a] MTDA: 10 mol%, Entry 1; 5 mol%. [b] [Lewis acid]/[TMSI] = 1.0/1.0. [c] MeOH-insoluble part. [d] By GPC. [e] Parentheses indicate MeOH : H$_2$O-insoluble part. [f] MeOH : H$_2$O-insoluble part.

dL$^{-1}$, THF). Methyl trimethylsilyl dimethylketene acetal (MTDA) (Aldrich) and trimthylsilyl iodide (TMSI) (Tokyo Chemical Industry Co., Ltd.) were used as received. MTDA was distilled under reduced pressure. Titanium tetrachloride (TiCl$_4$) was distilled under nitrogen atmosphere. Aluminum chloride (AlCl$_3$) was sublimed several times. Zinc iodide (ZnI$_2$), zinc bromide (ZnBr$_2$), zinc triflate (Zn(OTf)$_2$), and copper bromide (CuBr$_2$) were dried under reduced pressure at 270℃.

*Polymerization Procedure*

Typical experimental procedure is as follows: AGTP of CHMI was carried out in CH$_2$Cl$_2$ under dry nitrogen. Chiral ligand and Lewis acid complexes were mixed in CH$_2$Cl$_2$ at room temperature immediately before use. The solution was added to a solution of CHMI and TMSI in CH$_2$Cl$_2$ in a dry Schlenk tube *via* a cannula. The initiator (MTDA) of GTP was added to the mixture using a syringe and the mixture was stirred for 24 h. The polymerization was quenched by adding a few drops of methanol. The mixture was poured into water and extracted with CH$_2$Cl$_2$. The extracts were washed with saturated aqueous sodium thiosulfate to remove iodine, dried over MgSO$_4$, and evaporated *in vacuo*. A solution of the residue in CH$_2$Cl$_2$ was poured into excess MeOH–H$_2$O = 3/1 (v/v). The precipitate was collected by filtration, purified by reprecipitation from CH$_2$Cl$_2$–MeOH–H$_2$O systems twice, then filtered, followed by vacuum drying for 2 days.

*Measurements*

Gel permeation chromatography (GPC) measurement of the polymer was done on a LC-10AS (Shimadzu) equipped with a UV detector SPD-10A (Shimadzu) and polarimetric detector OR-990 (Japan Spectroscopic Co.) using THF as the eluent. Four GPC columns HSG-10, 15, 20, and 40H (Shimadzu) were connected in series and molecular weight was calibrated with standard polystyrene. Hg-line specific rotations were measured with a Jasco DIP-140 (Japan Spectroscopic Co.) at 25℃ (quartz cell length ($l$), 10 cm; concentration ($c$) 1.0 g dL$^{-1}$ in THF). $^1$H and $^{13}$C NMR spectra of the polymers were measured in chloroform-$d$ at room temperature in the presence of tetramethylsilane (TMS) as internal standard using a JEOL EX-270 ($^1$H, 270 MHz; $^{13}$C, 68.7 MHz) spectrometer.

## RESULTS AND DISCUSSION

*Group Transfer Polymerization*

First, GTP of CHMI using Lewis acid without chiral ligands was examined (Table I). No polymerization occurred by Lewis acids such as TiCl$_4$, AlCl$_3$, CuBr$_2$ (Entries 1, 2, and 3). GTP of CHMI initiated by MTDA under ZnBr$_2$ was carried out to give poly(CHMI) in 9.8% (MeOH-insoluble part) and 49.5% yield (MeOH–H$_2$O (3 : 1, v/v)-insoluble part) (Entry 5). Zinc catalysis was insoluble in organic solvents (CH$_2$Cl$_2$, THF, and toluene). But zinc catalysis was soluble in the presence of chiral ligand and monomer under the same polymerization conditions. When ZnI$_2$ was used as catalyst instead of ZnBr$_2$, the yield of poly(CHMI) increased to 74.1% (Entry 6). Using THF and toluene as polymerization solvent, yields decreased to about 7% (Entries 7,8). No poly(CHMI) could be obtained in the presence of a strong Lewis acid such as Zn(OTf)$_2$ (Entry 9) and at low temperature ( $-$35 ℃) (Entry 10). Müller *et al.* reported GTP of acrylate derivatives to be activated by the addition of TMSI.[24,25] Poly(CHMI) of MeOH–H$_2$O-insoluble part was obtained in the presence of TMSI (Entry 11). Acceleration of the GTP of CHMI was accomplished by the addition of TMSI.

AGTP of CHMI was examined in the presence of various chiral ligands and Lewis acids. Table II shows the conditions and results of AGTP. Bnbox or Sp inhibited GTP (Entries 1, 2, and 3), possibly due to reduction of Lewis acidity of zinc moiety by the coordination of ligands, which could not activate monomers. AGTP in the presence of TMSI afforded optically active poly(CHMI) in low yields (Entries 4 and 5). The polymer prepared with ZnI$_2$–TMSI system was insoluble in general organic solvents (Entry 5). Although no AGTP occurred in the presence of the complexes of ZnBr$_2$ or ZnI$_2$ with amine ligands in the absence of TMSI, Zn(OTf)$_2$ was effective for polymerization even in the presence of chiral ligands (Entries 6 and 8). Zn(OTf)$_2$–chiral ligands complexes have Lewis acidity enough to activate monomers. Poly(CHMI) was obtained with Zn(OTf)$_2$–Bnbox in poor yield. The polymer but showed the highest molecular weight ($\overline{M}_n$ = 75400, Entry 8). Specific rotations of poly(CHMI) were scarcely affected by solvents such as THF and CHCl$_3$. AGTP using DDB derived from ($R$, $R$)-tartaric acid afforded poly(CHMI) with low levorotation

**Table II.** Asymmetric group transfer polymerization of CHMI with chiral Lewis acid–MTDA for 24 h in $CH_2Cl_2$ [a]

| Entry | Lewis acid [b] mol% | | Chiral ligand [c] | Temp. °C | Yield [d] % | $\overline{M}_n$ [e] $\times 10^{-3}$ | $\overline{M}_w/\overline{M}_n$ [e] | $[\alpha]_{435}^{25}$ [f] degree |
|---|---|---|---|---|---|---|---|---|
| 1 | ZnBr$_2$ | (10) | Bnbox | rt | 0 | — | — | — |
| 2 | ZnI$_2$ | (10) | Sp | −35 | 0 | — | — | — |
| 3 | ZnI$_2$ | (10) | Bnbox | rt | 0 | — | — | — |
| 4 | ZnI$_2$–TMSI | (10) | Sp | −35 | 12.4 [g] | 0.6 | 1.5 | +2.3 |
| 5 | ZnI$_2$–TMSI | (10) | Bnbox | rt | 8.7 [h] | nd [i] | nd [i] | nd [i] |
| 6 | Zn(OTf)$_2$ | (10) | Sp | rt | 7.0 [h] | nd [i] | nd [i] | −6.2 [j] |
| 7 | Zn(OTf)$_2$–TMSI(10) | | Sp | −35 | 32.0 | 0.7 | 1.4 | −6.6 |
| 8 | Zn(OTf)$_2$ | (10) | Bnbox | rt | 6.3 | 75.4 | 6.3 | +11.7 |
| 9 | Zn(OTf)$_2$–TMSI(10) | | Bnbox | −35 | 5.9 | nd [i] | nd [i] | −1.1 [j] |
| 10 | Zn(OTf)$_2$–TMSI(10) | | DDB | −35 | 7.1 | 1.0 | 1.2 | −2.3 |
| 11 | Zn(OTf)$_2$–TMSI(10) | | IPDB | −35 | 5.9 | 0.9 | 1.3 | +31.0 |

[a] CHMI: 0.56 mol L$^{-1}$, MTDA: 10 mol%. [b] [Lewis acid]/[TMSI] = 1.0/1.0. [c] [Lewis acid]/[Ligand] = 1.0/1.0. [d] MeOH: H$_2$O-insoluble part. [e] By GPC. [f] in THF; error: ±0.2°. [g] MeOH-insoluble part. [h] THF-insoluble part. [i] Not determined. [j] in CHCl$_3$; error: ±0.2°.
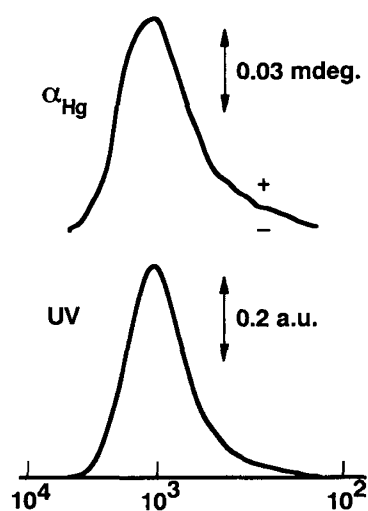


**Figure 1.** GPC curves of poly(CHMI) obtained with ZnI$_2$–TMSI–Sp (Entry 4 in Table II). The top chromatogram was obtained by polarimetric detection ($\alpha_{Hg}$) and the bottom, by UV detection (254 nm).

($[\alpha]_{435}^{25}$ −2.3°, Entry 10). When IPDB was used as chiral ligand, the obtained poly(CHMI) showed the highest dextrorotation ($[\alpha]_{435}^{25}$ +31.0°, Entry 11).

*Structures of Polymers and Mechanism*

Optically active polymers were analyzed by GPC and NMR. But poly(CHMI) could not be analyzed in detail because of low yield (Entries 8 and 11 in Table II).

GPC of the poly(CHMI) obtained with ZnI$_2$–Sp (Entry 2 in Table II) using UV and polarimetric detectors gave additional information on the chiral structure of the polymer (Figure 1). The polarimeric detector demonstrated a positive peak with pattern quite similar to the UV curve. This suggests that chiroptical properties of poly(CHMI) may be attributed not only to homogeneous chirality of main chain but local chirality by optically active groups. Other polymers provided analogous results by GPC.

Figure 2 depicts the $^{13}$C NMR spectra of poly(CHMI) initiated by (A) MTDA–ZnI$_2$ (Table I, Entry 7), (B) MTDA–Zn(OTf)$_2$–TMSI–Sp (Table II, Entry 6; $[\alpha]_{435}^{25}$ = −6.6°), (C) AIBN, (D) n-BuLi–Bnbox ($[\alpha]_{435}^{25}$ = +111.4°).[18] The methine carbon of the main chain of poly(CHMI) initiated by MTDA–ZnI$_2$ showed a peak at about 44 ppm.
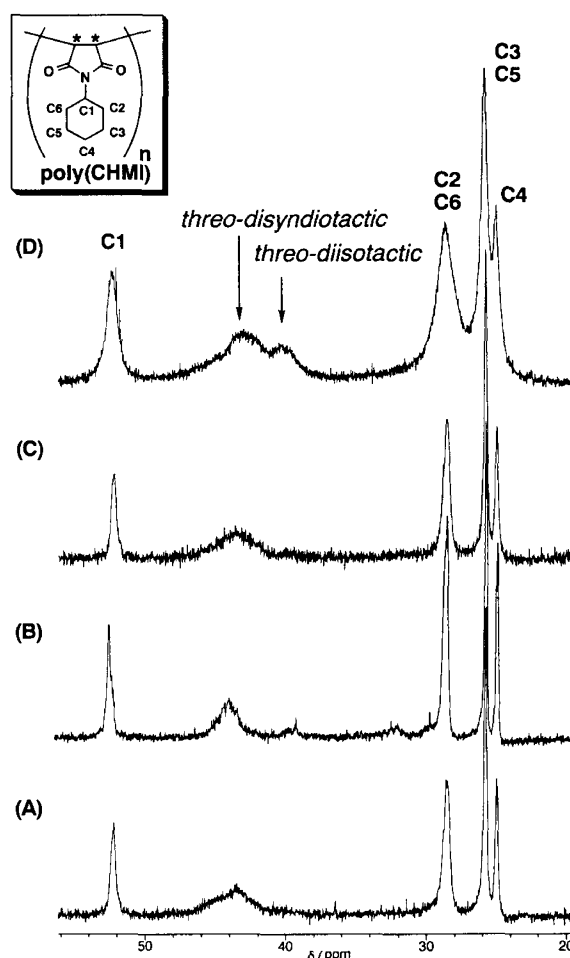


**Figure 2.** $^{13}$C NMR spectra of the poly(CHMI) initiated by (A) MTDA–ZnI$_2$ (Entry 6 in Table I), (B) MTDA–Zn(OTf)$_2$–TMSI–Sp (Entry 7 in Table II), (C) AIBN, (D) n-BuLi–Bnbox in CDCl$_3$.

Spectrum (A) was similar to that (C) of poly(CHMI) obtained with AIBN. The $^{13}$C NMR spectrum of poly-(CHMI) obtained with MTDA–Zn(OTf)$_2$–TMSI–Sp showed peaks at about 40 and 44 ppm. According to $^{13}$C NMR spectra of the poly(CHMI) obtained by asymmetric anionic polymerization,[18,20] peaks at the higher and lower magnetic field were assigned to methine carbon of threo-diisotactic and threo-disyndiotactic structures, respectively. The intensity of methine carbon for two structures was scarcely related to specific rotations of

**Scheme 2.**
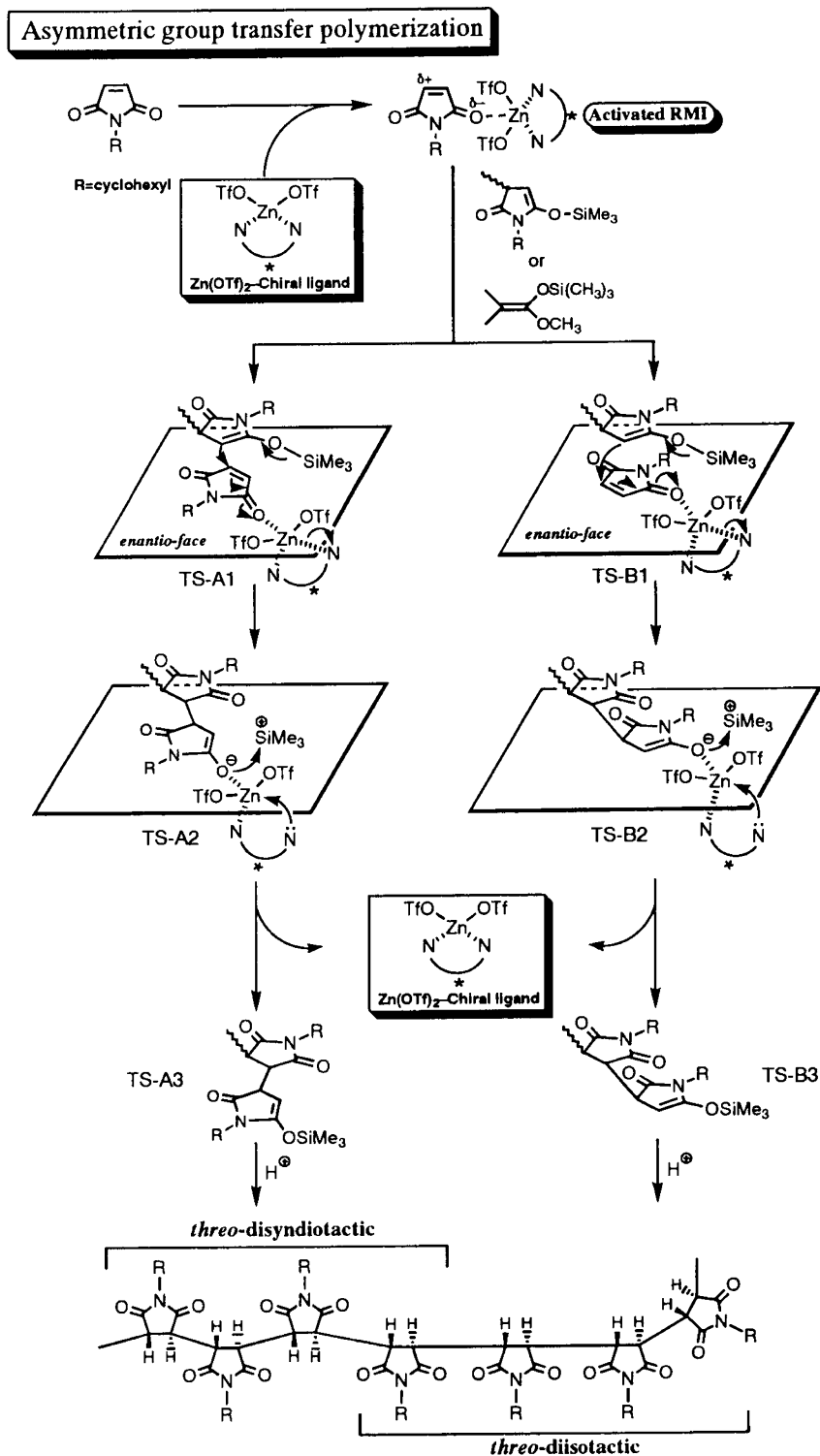
the polymer.[17,18]

Polymerization of CHMI has been reported to proceed mainly through stereoregularity of *trans*-addition of monomer because *cis* structure should incur larger steric hindrance than *trans*-structure.[26] In the case of poly(CHMI) having a $C_2$ symmetry axis, chiroptical properties of the polymers may be attributable to following: (1) helical structures of *threo*-diisotactic CHMI, (2) asymmetry of terminal groups, and (3) excess chiral stereogenic centers $(S, S)$ or $(R, R)$ of the main chain

(Scheme 2). Chiroptical properties of poly(CHMI) obtained with Lewis acid–chiral ligand complexes may be attributed to excessive chiral stereogenic centers $(S, S)$ or $(R, R)$ in the main chain of *threo*-diisotactic structure.

Although the mechanism of asymmetric induction is not clear, AGTP catalyzed by chiral Lewis acids may involve at least three steps: (1) activation of CHMI by coordination with Lewis acid, (2) nucleophilic addition of silyl enol ether in the propagating chain end to activated C=C bonds, and transfer of a trimethylsilyl group (TS-A
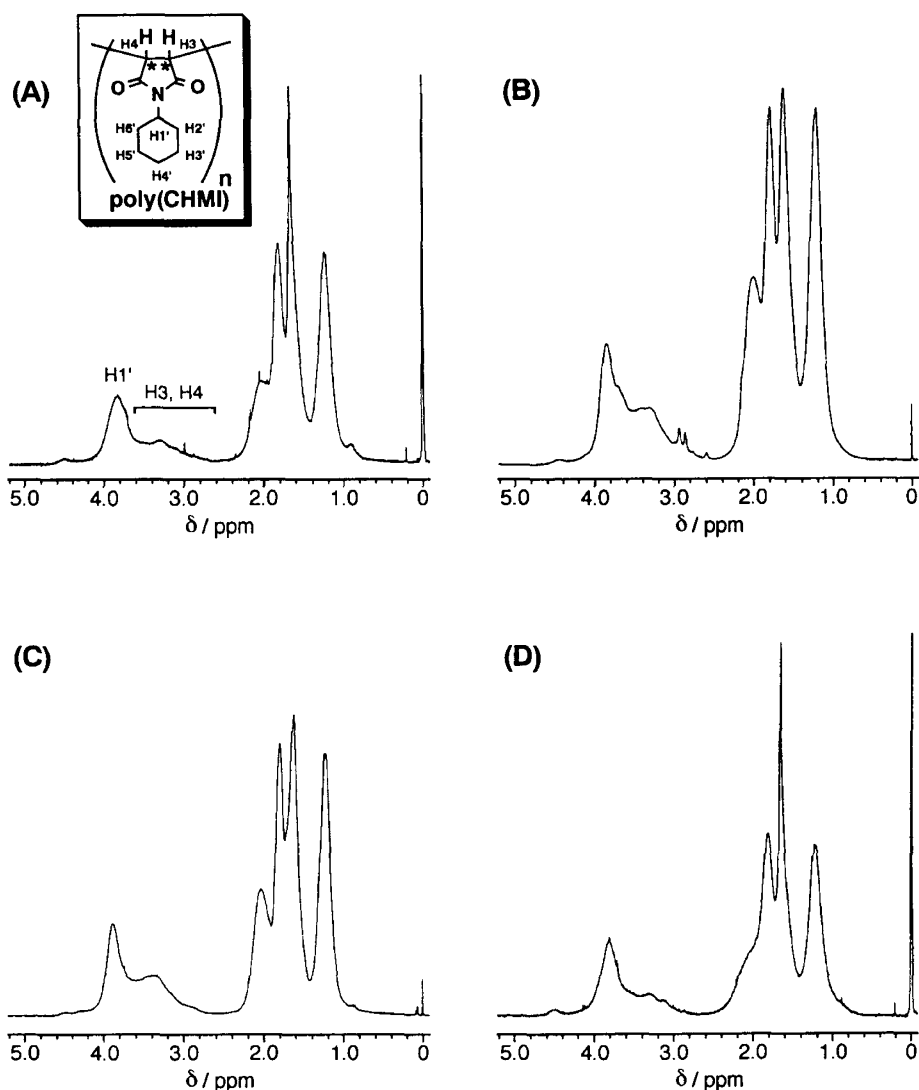
Figure 3. ¹H NMR spectra of the poly(CHMI) initiated by (A) MTDA–Zn(OTf)₂–Sp (Entry 6 in Table II), (B) MTDA–Zn(OTf)₂–TMSI–Sp (Entry 7 in Table II), (C) AIBN, (D) n-BuLi–Bnbox in CDCl₃.

1 and TS-B1), (3) ligand exchange reaction on zinc (TS-A2 and TS-B2), followed by regeneration of silyl enol ether (TS-A3 and TS-B3), and (3) recycled Lewis acid as depicted in Scheme 2. When polymerization was quenched by adding a proton, transition models TS-A3 and TS-B3 were transformed into threo-disyndiotactic and threo-diisotactic structures, respectively. The driving force of regeneration of chiral Lewis acid may be following: [27, 28] (1) conversion of structurally unstable mono-coordinated diamine ligand–zinc complex into stable bidentate diamine ligand–zinc complex (a ligand exchange reaction), (2) transfer of an anionic oxygen from Lewis acid to trimethylsilyl cation (an intermolecular metal-exchange reaction). Acceleration effects of TMSI on the GTP may support the regeneration of silyl enol ether.

Figure 3 depicts ¹H NMR spectra of poly(CHMI) initiated by (A) MTDA–Zn(OTf)₂–Sp (Table II, Entry 6; $[\alpha]_{435}^{25}$ = −6.2°), (B) MTDA–Zn(OTf)₂–TMSI–Sp (Table II, Entry 7; $[\alpha]_{435}^{25}$ = −6.6°), (C) AIBN, (D) n-BuLi–Bnbox ($[\alpha]_{435}^{25}$ = +111.4°).[18] Methine protons (H3 and H4) of the main chain for four polymers were different. Poly-(CHMI), insoluble in THF, obtained with MTDA–Zn(OTf)₂–Sp (A), exhibited a wider peak due to methine

protons than poly(CHMI) obtained with MTDA–Zn-(OTf)₂–TMSI–Sp. Spectrum (A) was similar to that of polymer obtained with n-BuLi–Bnbox (D). Spectrum (B) was similar to that of poly(CHMI) prepared by radical polymerization (C). AGTP in the presence of TMSI may thus proceed via radical like polymerization, i.e., non-chelation transition state (Scheme 3A). A GTP initiated by MTDA–Lewis acid in the absence of TMSI proceeds via transition state (Scheme 3B) such as anionic polymerization (Scheme 3C).

Figure 4 shows the ¹H NMR specta of mixture of Bnbox, Zn(OTf)₂, and CHMI in CDCl₃; (A) Bnbox, (B) Bnbox–Zn(OTf)₂, (C) Bnbox–Zn(OTf)₂–CHMI, (D) Zn-(OTf)₂–CHMI, and (E) CHMI. Signals for protons at benzyl, 4–and 5–position in the oxazoline group shifted to a low magnetic field in the presence of Zn(OTf)₂ (Figure 4 B). But signals of CHMI did not shift in the presence of Zn(OTf)₂ (Figure 4C, 4D). Bnbox may thus be coordinated to Zn(OTf)₂ through the nitrogen at bisoxazoline ring. But ¹H NMR (270 MHz) could not be clearly distinguish for CHMI activated by Zn(OTf)₂ and free CHMI. Because no polymerization of CHMI initiated by MTDA proceeds in the absence of Lewis acid, only the monomer

**Scheme 3.**
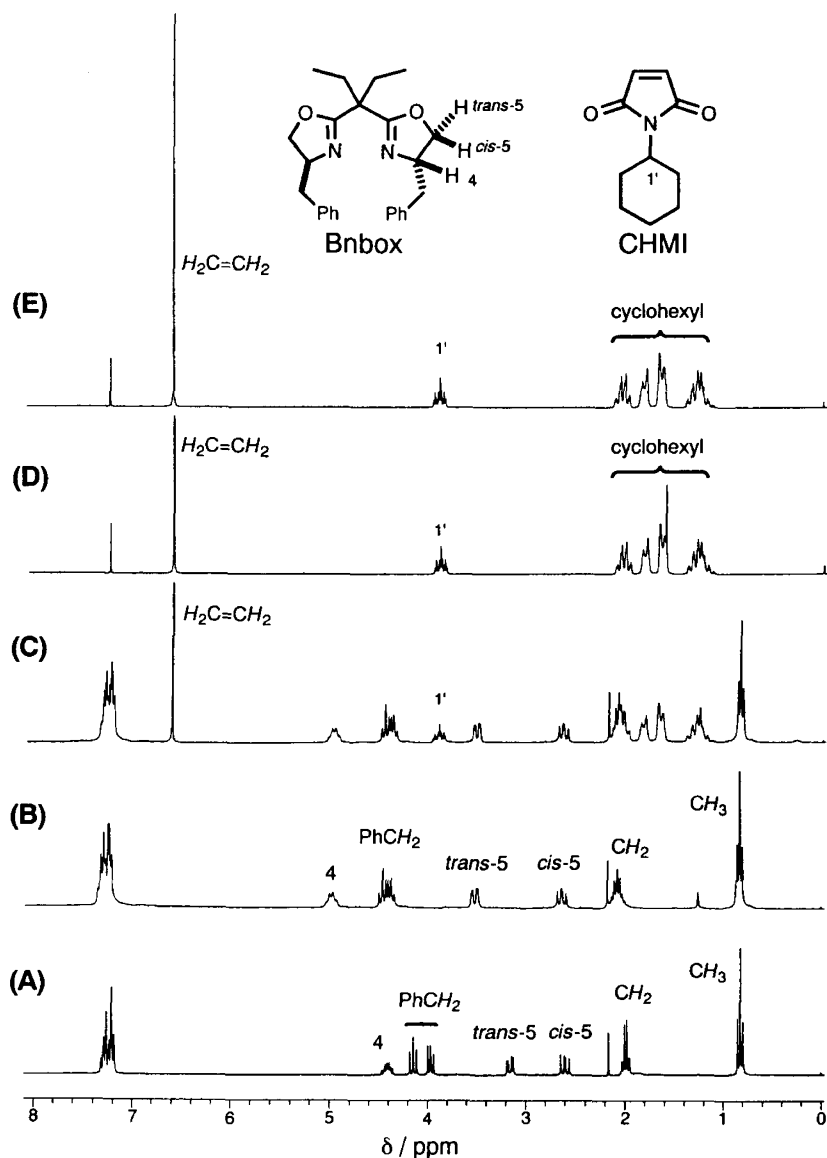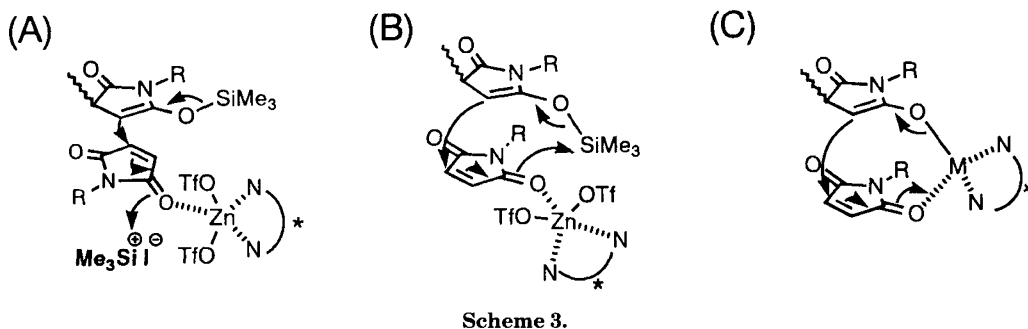


**Figure 4.** ¹H NMR spectra of mixture of Bnbox, Zn(OTf)₂, and CHMI in CDCl₃; (A) Bnbox, (B) Bnbox–Zn(OTf)₂, (C) Bnbox–Zn(OTf)₂–CHMI, (D) Zn(OTf)₂–CHMI, and (E) CHMI.

activated by Zn(OTf)₂-chiral ligand is concerned with AGTP. Chirality may consequently be induced in the polymer main chain.

AGTP is shown a method for the synthesis of optically active poly(RMI).

## CONCLUSIONS

(1) Asymmetric group transfer polymerizations of achi-

ral and $C_2$ symmetrical N-cyclohexylmaleimide (CHMI) was carried out in CH₂Cl₂ with complexes of Lewis acid and chiral ligands.

(2) The obtained poly(CHMI) showed optical activity, having specific rotation ($[\alpha]_{435}^{25}$) of $-6.6°$ to $+31.0°$. The Zn(OTf)₂–IPDB complex afforded optically active poly(CHMI) having the highest value ($[\alpha]_{435}^{25}$ $+31.0°$).

(3) The poly(CHMI) obtained Zn(OTf)₂/Bnbox complex exhibited the highest degree of polymerization

(DP$=421$, $\overline{M}_n=75400$). Poly(CHMI)s had narrow molecular-weight distribution ($\overline{M}_w/\overline{M}_n=1.2$—$1.5$) except for poly(CHMI) initiated by $Zn(OTf)_2$-Bnbox.

(4) Main-chain signals of the polymer exhibited two peaks at 40 ppm (*threo*-diisotactic) and 44 ppm (*threo*-disyndiotactic) in their $^{13}C$ NMR spectra. The higher magnetic field peak was smaller, compared with that initiated by *n*-BuLi-Bnbox complex.

(5) Chirality of the CHMI polymer was attributed to differences in $(S, S)$ and $(R, R)$ configurations in *threo*-diisotactic structures.

## REFERENCES AND NOTES

1. O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham, and T. V. RajanBaub, *J. Am. Chem. Soc.*, **105**, 5703 (1983).

2. W. R. Hertler, D. Y. Sogah, O. W. Webster, and B. M. Trost, *Macromolecules*, **17**, 1415 (1984).

3. M. T. Reetz and R. Ostarek, *Angew. Chem. Int. Ed. Engl.*, **25**, 1108 (1986).

4. W. J. Brittain and I. B. Dicker, *Macromolecules*, **22**, 1054 (1989).

5. K. Ute, T. Asada, Y. Nabeshima, and K. Hatada, *Macromolecules*, **26**, 7086 (1993).

6. K. Ute, T. Asada, and K. Hatada, *Macromolecules*, **29**, 1904 (1996).

7. K. Ute, T. Tarao, and K. Hatada, *Polym. J.*, **29**, 957 (1997).

8. K. Ute, T. Tarao, S. Hongo, H. Ohmura, K. Hatada, and T. Kitayama, *Polym. J.*, **31**, 177 (1999).

9. R. Noyori, "ASYMMETRIC CATALYSIS IN ORGANIC SYNTHESIS", John Wiley & Sons, New York, N.Y., 1994; J.-Seyden-Penne, "CHIRAL AUXILIARIES AND LIGANDS IN ASYMMETRIC SYNTHSIS", John Wiley & Sons, New York, N.Y., 1994; E. N. Jacobsen, A. Pfaltz, and H. Yamamoto, Ed., "Comprehensive Asymmetric Catalysis, Vol. I—III",

Springer-Verlag, Berlin, 1999.

10. T. Mukaiyama, K. Banno, and K. Narasaka, *Chem. Lett.*, 1001 (1973); S. Kobayashi and T. Mukaiyama, *Chem. Lett.*, 297 (1989); T. Mukaiyama, S. Kobayashi, H. Uchiro, and I. Shiina, *Chem. Lett.*, 129 (1990); S. Kobayashi, Y. Fujishita, and T. Mukaiyama, *Chem. Lett.*, 1455 (1990); S. Kobayashi, H. Uchiro, Y. Fujishita, I. Shiina, and T. Mukaiyama, *J. Am. Chem. Soc.*, **113**, 4247 (1991).

11. Review: A. K. Ghosh, P. Mathivanan, and J. Cappiello, *Tetrahedron: Asymmetry*, **9**, 1 (1998) and reference cited therein.

12. E. J. Corey and K. Ishihara, *Tetrahedron Lett.*, **33**, 6807 (1992); J. H. Wu, R. Radinov, and N. A. Porter, *J. Am. Chem. Soc.*, **117**, 11029 (1995); M. P. Sibi, J. Ji, J. H. Wu, S. Gurter, and N. A. Porter, *J. Am. Chem. Soc.*, **118**, 9200 (1996); P. G. Cozzi, P. Orioli, E. Tagliavini, and A. Umani-Ronchi, *Tetrahedron Lett.*, **38**, 145 (1997).

13. A. Saito and D. A. Tirrell, *Polym. J.*, **26**, 169 (1994).

14. K.-T. Lim, H. J. Lee, and S.-K. Choi, *Polym. Bull.*, **37**, 699 (1996).

15. Y. Okamoto, T. Nakano, H. Kobayashi, and K. Hatada, *Polym. Bull.*, **25**, 5 (1991).

16. T. Oishi, H. Yamasaki, and M. Fujimoto, *Polym. J.*, **23**, 795 (1991).

17. K. Onimura, H. Tsutsumi, and T. Oishi, *Polym. Bull.*, **39**, 437 (1997).

18. K. Onimura, H. Tsutsumi, and T. Oishi, *Macromolecules*, **31**, 5971 (1998).

19. K. Onimura, H. Tsutsumi, and T. Oishi, *Chem. Lett.*, 791 (1998).

20. T. Oishi, K. Onimura, K. Tanaka, W. Horimoto, and H. Tsutsumi, *J. Polym. Sci., Part A, Polym. Chem.*, **37**, 473 (1999).

21. K. Onimura, H. Tsutsumi, and T. Oishi, *Polym. Prepr., Jpn.*, **47**, 1151 (1998).

22. S. E. Denmark, N. Nakajima, O. J.-C. Nicaise, A.-M. Faucher, and J. P. Edwards, *J. Org. Chem.*, **60**, 4884 (1995).

23. D. Seebach, H.-O. Kalinowski, W. Langer, G. Crass, and E.-M. Wilka, *Org. Synth. Col. Vol. VII*, 41 (1990).

24. R. Zhuang and A. H. E. Müller, *Macromolecules*, **28**, 8035 (1995).

25. R. Zhuang and A. H. E. Müller, *Macromolecules*, **28**, 8043 (1995).

26. R. C. P. Cubbon, *Polymer*, **6**, 419 (1965).

27. S. Kiyooka, Y. Kaneko, M. Komura, H. Matsuo, and M. Nakano, *J. Org. Chem.*, **56**, 2276 (1991).

28. E. R. Parmee, O. Tempkin, and S. Masamune, *J. Am. Chem. Soc.*, **113**, 9365 (1991).