# Asymmetric Anionic Polymerization of *N*-Substituted Maleimides with $Et_2Zn$ and Chiral Bisoxazolines

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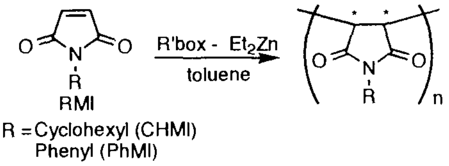
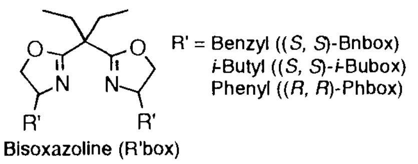
Anionic polymerizations of *N*-substituted maleimides (RMI:R= cyclohexyl (CHMI), R= phenyl (PhMI)) were achieved by chiral anionic initiator such as diethylzinc ($Et_2Zn$) – chiral bisoxazoline (R'box) to afford optically active poly(RMI). The polymerizability was enhanced by the accelerated nucleophilicity of the ethyl groups in $Et_2Zn$ due to R'box ligands. The specific rotations of poly(PhMI) ($[\alpha]_{435}^{25}$ – 28.4 to + 94.6°) were *much* improved than those initiated by *n*-BuLi - R'box.

The asymmetric synthesis polymerizations have been extensively investigated in recent years.[1] Although various polymerizations to synthesize optically active polymers were performed, most of studies were reported on the polymerizations of achiral 1- or 1,1-substituted vinyl monomers ($CH_2$=CRR') with various chiral ligands.[1] On the other hand, polymerizations and copolymerizations of optically active 1,2-disubstitued ethylene type monomers, *i.e.*, chiral RMI have been systematically studied by the authors.[2] But only a few studies on asymmetric anionic polymerizations of achiral RMI have been made.[3-6] Recently the authors have also reported briefly that chiral complexes of organolithium with optically active methylene-bridged bisoxazoline derivatives were very efficient catalysts for the asymmetric polymerizations of RMI.[6] In particular, the poly(CHMI) initiated by *n*-BuLi – 3,3'-bis-[2-((4*S*)-4-benzyl-1,3-oxazolinyl)]pentane ((*S*, *S*)-Bnbox) complex showed the highest specific rotation ($[\alpha]_{435}^{25}$ + 111.4°) in the poly(RMI) reported so far. In preceding papers,[3-6] the asymmetric anionic polymerizations of achiral RMI were initiated by organolithium, Grignard reagent, cuprate, and sodium bis(2-methoxyethoxy)aluminum hydride. However only a few studies have been reported on the polymerizations of RMI with initiator of low basicity such as diethylzinc ($Et_2Zn$). Hagiwara and Narita *et al.* reported anionic polymerizations of PhMI with organozinc compounds as initiators.[7] The polymers polymerized with $Et_2Zn$ were low yields (9%) even at 80 °C in toluene or 1,2-dimethoxyethane.

Chiral bisoxazolines have recently been employed as ligands in wide variety of metal-catalyzed asymmetric reactions.[8] But no studies have been known on asymmetric polymerization initiated by organozinc - bisoxazoline complexes yet.





Herein, the authors report acceleration effects of $Et_2Zn$ – bisoxazoline complex on the asymmetric polymerizations and chiroptical properties of the poly(RMI).

Bisoxazolines (R'box) were synthesized by the published procedure.[9] The polymerizations of RMI with $Et_2Zn$ – R'box were examined in toluene at 0 °C. The results are summarized in Table 1. No polymerizations of RMI initiated by $Et_2Zn$ proceed in the absence of R'box (Runs 5 and 10), but poly(RMI)s could be obtained on an addition of R'box at 0 °C. The obtained polymers showed optical activity. In particular, when the polymerizations of CHMI were carried out with $Et_2Zn$ – (*S*, *S*)-Bnbox complex, the polymer exhibited the highest specific rotation ($[\alpha]_{435}^{25}$ + 117.5) in an excellent yield (Run 1). The degrees of polymerization of all poly(CHMI) increased. The poly(CHMI) initiated by $Et_2Zn$ – (*S*, *S*)-*i*-Bubox had poor yield and low specific rotation (Run 2), but showed the highest degree of polymerization (DP = 128.8, $\overline{M}_n$ = 23000, $\overline{M}_w / \overline{M}_n$ = 1.93). The polymerizations of RMI initiated by $Et_2Zn$ – (*R*, *R*)-Phbox complexes were found to proceed more slowly as compared to those initiated by $Et_2Zn$ – other ligands, and the obtained poly(RMI)s exhibited poor yield and low specific rotation (Runs 3 and 8). On the other hand, specific rotations of poly(PhMI) were *much* improved than those initiated by *n*-BuLi - R'box (Runs 6 – 8). The variations of specific rotations of poly(PhMI) were larger than those of poly(CHMI). Despite the degrees of polymerization of poly(PhMI) were similar to those initiated by *n*-BuLi - R'box, the poly(PhMI) initiated by $Et_2Zn$ – (*S*, *S*)-Bnbox complex showed higher specific rotation ($[\alpha]_{435}^{25}$ + 94.6°; Run 6) than that ($[\alpha]_{435}^{25}$ + 0.9°) obtained with *n*-BuLi – (*S*, *S*)-

**Table 1.** Anionic polymerization of RMI with $Et_2Zn$ - R'box in toluene for 24 h at 0 °C

| Run | RMI | R'box[a] | Yield[b] /% | DP[c] | $[\alpha]_{435}^{25}$ [d] /deg. | DP[c] | $[\alpha]_{435}^{25}$ [d,e] /deg. |
|---|---|---|---|---|---|---|---|
| 1 | CHMI | (*S*,*S*)–Bnbox | 99 | 45.3 | + 117.5 | 23.2 | + 111.4 |
| 2 | | (*S*,*S*)–*i*-Bubox | 20 | 128.8 | + 72.3 | 19.2 | + 84.1 |
| 3 | | (*R*,*R*)–Phbox | 6 | 36.0 | – 32.4 | 16.9 | – 49.4 |
| 4 | | (*R*,*R*)–Phbox | 12[f] | 90.9 | – 13.7 | | |
| 5 | | none | 0 | – | – | | – |
| 6 | PhMI | (*S*,*S*)–Bnbox | 92 | 13.3 | + 94.6 | 9.2 | + 0.9 |
| 7 | | (*S*,*S*)–*i*-Bubox | 49 | 16.3 | + 28.5 | 16.1 | + 8.7 |
| 8 | | (*R*,*R*)–Phbox | 20 | 18.0 | – 37.6 | 9.2 | – 18.3 |
| 9 | | (*R*,*R*)–Phbox | 25[f] | 18.4 | – 28.4 | | |
| 10 | | none | 0 | – | – | | – |

[a] 10 mol%, $[Et_2Zn]/[R'box]$ = 1.0/1.2. [b] MeOH - insoluble part. [c] By GPC, calibrated with standard polystyrene. [d] c = 0.4 – 1.0 $gdl^{-1}$, *l* = 10 cm or 5 cm, $CHCl_3$ (Run 1, 2, 3, 4), THF (Run 6, 7, 8, 9). [e] Initiated by *n*-BuLi – R'box for 24 h at 0 °C, reference 6. [f] Polymerization time; 70 h.

Bnbox complex.[6] Yields of the polymers obtained with (*R*, *R*)-Phbox as chiral ligand were improved by long period of reaction, but the absolute values of specific rotation fell (Runs 4 and 9).

Thus, R'box efficiently promoted the asymmetric anionic polymerizations of RMI initiated by $Et_2Zn$. The increase of the reactivity can be explained by the following reason. Monomeric $Et_2Zn$ with *sp* hybridized linear geometry is inert to monomers such as RMI because the ethyl groups - metal bonds are rather nonpolar.[10,11] When $Et_2Zn$ complexes with electronegative substituents such as bisoxazolines, the carbon – zinc bond polarity is enhanced by creating a bent geometry in which the zinc atom used molecular orbitals of a higher *p* character. Therefore, the $Et_2Zn$ – R'box complexes have both high electron-donor ability of ethyl groups and acceptor character at the zinc atom as shown Figure 1. The yields of polymers were significantly different by the substituent at 4-position in oxazoline ring, which could be ascribed to the steric hindrance of the substituent. That is, the yield was low due to the rigid phenyl group of (*R*, *R*)-Phbox in polymerization with $Et_2Zn$–(*R*, *R*)-Phbox complex. On the other hand, the benzyl and *i*-butyl substituents of (*S*, *S*)-Bnbox and (*S*, *S*)-*i*-Bubox didn't prevent approaching RMI. Consequently, the yields and the number-average molecular weight ($\bar{M}_n$) increased markedly. The specific rotations of the polymers obtained were influenced by 4-positional substituent of the oxazoline. The reason can be explained by bulkiness of the substituent in the following order: phenyl < *i*-butyl < benzyl group. The chiral space built up by Bnbox complex is the largest. Since (*S*, *S*)-Bnbox was capable of building better asymmetric fields at the polymer growth-ends, chirality could be induced to the main chain of the poly(RMI). Further, when the polymerizations were initiated by an ethyl group on $Et_2Zn$, another ethyl group could act as a shielding group in ZnEt – R'box complex at the growing chain end. The CHMI has a bulky and an aliphatic substituent, and the PhMI has a plane and an aromatic substituent. Therefore, it can be considered that the CHMI is affected by *only* steric repulsions of the substituent at 4-position in the oxazoline ring. When the polymerization of PhMI initiated by $Et_2Zn$ – (*S*, *S*)-Bnbox, the phenyl ring of PhMI might participate in a π-stacking interaction with the benzyl group in oxazoline rings.

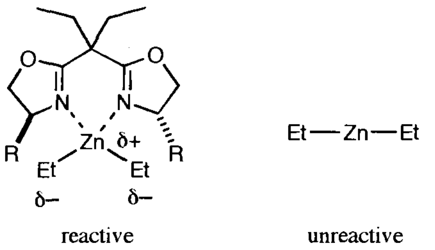


**Figure 1.** Activation of $Et_2Zn$ by bisoxazoline ligands.

Further studies on the details of the polymerization are in progress.

Typical experimental procedure is as follows: Anionic homopolymerizations of RMI were carried out in toluene under dry nitrogen. Chiral R'box and $Et_2Zn$ were mixed at 0 °C just before use. An initiator solution was added to the monomer solution cooled to 0 °C. The reaction was terminated by the addition of a few drops of methanol. The polymer was precipitated in excess methanol containing a small amount of hydrochloric acid, separated by filtration, and purified by re-precipitation from chloroform-methanol or THF-methanol systems three times, then filtered and dried *in vacuo*.

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