

# Theoretical Study on Mechanism of Asymmetric Anionic Polymerization of *N*-Substituted Maleimide by using a Zn Complex with a Chiral Bisoxazoline ligand

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*N*-Substituted maleimides (RMIs) are polymerized to form optically active polymers by using asymmetric catalysts prepared from optically active bisoxazoline (Rbox) derivatives and dialkylzinc. In the present study, the mechanism of the initiation reaction for an anionic polymerization of HMI (maleimide) as a model monomer was investigated by use of the Density Functional Theory (DFT) calculations. HMI does not coordinate to Zn<sup>2+</sup> during the initiation reaction, which proceeds via a mechanism similar to S<sub>N</sub>2 reactions.

Key words: polymerization, maleimide, chiral ligand, density functional theory

## 1. INTRODUCTION

*N*-Substituted maleimides (RMIs) are prochiral molecules, so it is possible to synthesize optically active polymers. Oishi and his co-workers have been produced many optically active RMIs polymers<sup>1</sup> by using the technique that RMIs were polymerized with catalysts consisting of Rbox and metal ion such as Li<sup>+</sup> or Zn<sup>2+</sup> (Eq. 1).

According to the experimental results listed in Table I,<sup>1</sup> the magnitude of specific optical rotation of poly(RMI)s at 25 °C, [α]<sub>435</sub><sup>25</sup>, were proved to be depending not only on the metal ion but on the chiral ligand in the catalyst. The *N*-substituent in RMI is also one of the important factors for determining the optical property of the polymers. In order to design a new asymmetric catalyst, it is important to understand why the factors such as

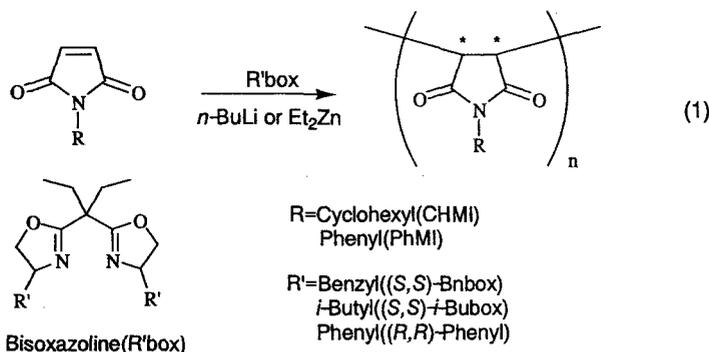
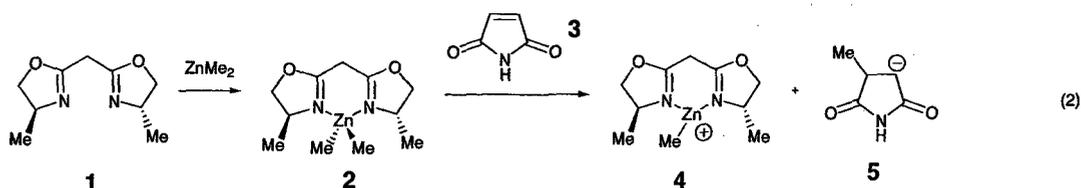


Table I Physical parameters of poly(RMI) in experiments by using Rboxes as the chiral ligand in the catalysts<sup>1</sup>

RMI	R'box	Et <sub>2</sub> Zn			<i>n</i> -BuLi		
		yield %	DP <sup>1)</sup>	[α] <sub>435</sub> <sup>25</sup> 2) deg	yield %	DP <sup>1)</sup>	[α] <sub>435</sub> <sup>25</sup> 2) deg
CHMI	( <i>S,S</i> )-Bnbox <sup>3)</sup>	99	45.3	+117.5	97	23.2	+111.4
	( <i>S,S</i> )- <i>i</i> -Bubox <sup>3)</sup>	20	128.8	+72.3	89	19.2	+84.1
	( <i>R,R</i> )-Phbox <sup>3)</sup>	6	36.0	-32.4	99	16.9	-49.4
PhMI	( <i>S,S</i> )-Bnbox <sup>3)</sup>	92	13.3	+94.6	83	9.2	+0.9
	( <i>S,S</i> )- <i>i</i> -Bubox <sup>3)</sup>	49	16.3	+28.5	99	16.1	+8.7
	( <i>R,R</i> )-Phbox <sup>3)</sup>	20	18.0	-37.6	99	9.2	-18.3
( <i>S</i> )-NEMI	( <i>S,S</i> )-Bnbox <sup>4)</sup>	48	123.7	+119.5			

1) Degrees of polymerization by GPC, 2) c=0.4–1.0 g dL<sup>-1</sup>, CHCl<sub>3</sub>, 3) 24h in toluene, 4) 48h in tetrahydrofuran.



the metal ion, substituents on RMIs and the chiral ligand induce such differences.

We investigated the polymerization mechanism of RMI for catalyst of 2,2'-ethylpropylidene-bis((4*S*)-4-benzyl-2-oxazoline) (Bbox) with alkyl lithium<sup>2</sup> since details of the polymerization mechanism of RMIs have not been understood. It was confirmed that the initiation reaction is closely related to the optical property of the polymers and the propagation reaction proceeds to form chiral carbons with the same configuration which is produced in the initiation reaction. Asymmetry in the catalyst has little effects for inducing the optical activity in the propagation reaction. In these catalysts, RMI as a monomer can coordinate to Li<sup>+</sup> during polymerization because the Li<sup>+</sup> in the catalyst has an empty coordination site for RMI. RMI coordinates to the empty site, followed by a transfer of the alkyl group from Li<sup>+</sup> to the coordinated RMI. A similar mechanism is confirmed for polymerization of RMIs by using the catalyst consisting of *N*-diphenylmethyl-1-benzyl-2-pyrrolidinoethanamine and diethylzinc. Zn<sup>2+</sup> in the catalyst is also has an empty site for a monomer coordination.<sup>3</sup>

The polymerization of RMIs using a catalyst of Bbox with dialkylzinc produced the optically active polymers as discussed above though Zn<sup>2+</sup> has a tetrahedral coordination geometry as shown in Eq. 2 of the model reaction investigated here. It was confirmed that no maleimides (HMIs) can coordinate to Zn<sup>2+</sup> of 2 to form a complex with a trigonal bipyramid geometry at the B3LYP/6-31G(d) level of theory. The results mean that Zn<sup>2+</sup> has no empty coordination sites for HMI. It is, therefore, unlikely that the reaction shown in Eq. 2 proceeds through the mechanism similar to that using the catalyst with the empty coordination site.

In the present study, the initiation mechanism of the HMI polymerization with Me<sub>2</sub>Zn-Mebox (2,2'-methylidene-bis((4*S*)-4-methyl-2-oxazoline)) model complexes was investigated by use of the Density Functional Theory (DFT) calculations. We also compare the mechanism with those

previously investigated for the Li as well as Zn<sup>2+</sup> complex. As will be discussed later, the present mechanism for the initiation reaction is very similar to the, so-called, S<sub>N</sub>2 mechanism accompanying the inversion of the methyl group.

## 2. METHOD OF CALCULATIONS

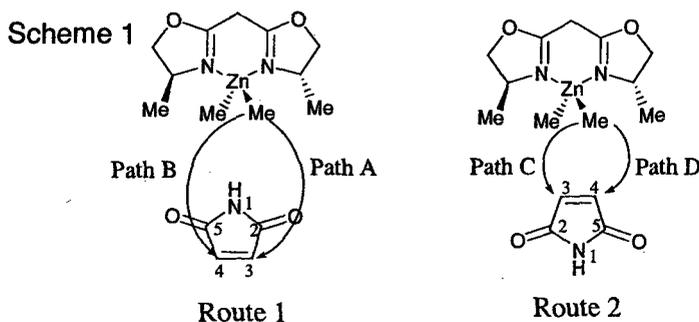
The DFT calculations were adopted to investigate the initiation mechanism for polymerization of HMI by using a model catalyst 2 with Mebox. Semiempirical calculations were carried out by using the MOPAC program<sup>4</sup> included in the WinMOPAC program<sup>5</sup> to obtain all the transition states (TS), reactants and products at the PM3<sup>6</sup> level of theory. The geometries obtained were used for initial structures for the DFT calculations which were performed by using the Gaussian 98 program<sup>7</sup> at the B3LYP/LANL2DZ<sup>8</sup> level of theory. HMI was used as the model monomer in the present study.

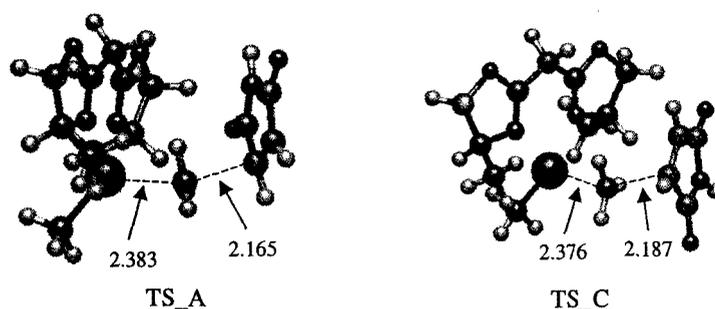
## 3. RESULTS AND DISCUSSIONS

### 3.1 Mechanisms of the initiation reaction

The coordination of a monomer to a central metal such as Ti<sup>4+</sup> in metallocene catalysts is essential to alkyl transfers seen in many catalytic reactions.<sup>9</sup> However, we have to consider a mechanism without coordination of HMI to the Zn<sup>2+</sup> since the metal ion has no empty sites for the coordination. Moreover, we could not optimize any complexes with Zn<sup>2+</sup> having the five coordination geometry. For the present initiation reaction, we found a mechanism shown in Scheme 1 where the HMI directly attacks one of the methyl groups on Zn<sup>2+</sup> to form 4 and an anionic intermediate 5.

As HMI has a prochiral molecular plane, the methyl transfer from Zn<sup>2+</sup> produces two types of intermediates with a carbon having the *S* or *R* configuration. They are called the *S*- or *R*-intermediate. According to the direction of the substituent of HMI, Paths A and C in Scheme 1 produce the *S* intermediate *S*-5, and the rest paths, Path B and D, produce the *R* intermediate *R*-5. The NH fragment in HMI directs upper in Route 1

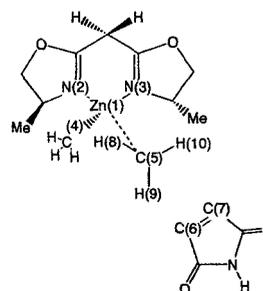




**Figure 1** TS structures in Path A and C at the B3LYP/LANL2DZ level of theory. Values in the figure are distances in Å.

**Table II** Optimized bond lengths (in Å) and dihedral angle (in degree) for TSs of all the paths.

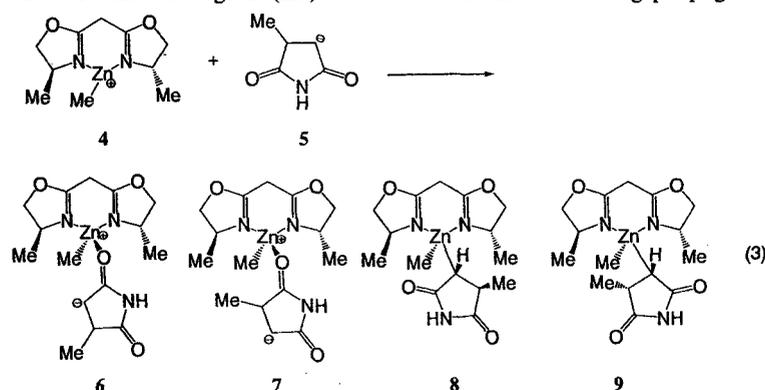
	Path A	Path B	Path C	Path D
Zn(1)-N(2)	2.177	2.177	2.178	2.180
Zn(1)-N(3)	2.170	2.179	2.173	2.170
Zn(1)-C(4)	2.048	2.048	2.048	2.048
Zn(1)-C(5)	2.383	2.392	2.376	2.398
C(5)-C(6) or C(7)	2.165	2.177	2.187	2.126
H(8)-H(9)-H(10)-C(5)	3.4	3.0	2.5	5.3



while that in Route 2 does lower in the Scheme.

TSs in Paths A-D were optimized at the B3LYP/ LANL2DZ level of theory. TS structures for Paths A and C (TS\_A and TS\_C, respectively) producing the *S*-intermediates were displayed in Figure 1. Their geometrical parameters are listed in Table II. The dihedral angles of the central methyl group turned out to be 2.5-5.3 degree. The distances between Zn<sup>2+</sup> and the methyl carbon Zn(1)-C(5) were calculated to be ca. 2.4 Å for all the paths. These values are larger by ca. 0.35 Å than those in **2**. The distances between the C(5)-C(6) or C(7) were calculated to be 2.126-2.187 Å. Therefore, it has to be emphasized that the central methyl group, which has a tetrahedral geometry in **2**, takes a typical sp<sup>2</sup> geometry in the TS geometries for all the paths. As the methyl group in the anion intermediate **5** takes a tetrahedral geometry, the initiation reaction proceeds via a mechanism similar to the S<sub>N</sub>2 reaction although the reaction of neutral molecules produces two charged molecules, **4** and **5**.

The magnitude of activation energies (E<sub>a</sub>) is



critical to whether or not the reaction proceeds via the mechanism obtained. E<sub>a</sub>'s are defined as the energy difference between the total energy for the TS of each path and sum of the energies for **2** and **3**. Path A was confirmed to be the route with the lowest barrier in the four paths and the barrier was calculated to be 10.7 kcal mol<sup>-1</sup>. All the values were calculated to be less than 13 kcal mol<sup>-1</sup>, i.e., those for Path B, C and D were calculated to be 11.6, 12.6 and 12.5 kcal mol<sup>-1</sup>, respectively. These values are consistent with the experimental results that the polymerization is initiated at 0 °C. Energies relative to E<sub>a</sub> of Path A turned out to be 0.9-1.9 kcal mol<sup>-1</sup>. The very small value leads to equally form the *R*- and *S*-intermediates.

### 3.2 Formation of complexes for propagation reactions

The initiation reaction produces two ions, **4** and **5** as discussed above. The former ion has an empty coordination site. It is easily considered that these ions react to form a complex which is used for succeeding propagation reactions. As the

**Table III** Stabilization energies (Es) and relative energies ( $\Delta$ Es) by the complexation (in kcal mol<sup>-1</sup>)

	Es <sup>1)</sup>	$\Delta$ Es <sup>2)</sup>
6	-49.2	0.0
7	-32.5	16.7
8	-45.9	3.3
9	-45.7	3.5

1)Energies differences from 2 and 3, 2)Energies relative to 6.

enolate ion 5 has three sites which can coordinate to Zn<sup>2+</sup>, there are four plausible complexes such as 6, 7, 8 and 9 in Eq. 3. While the enolate oxygen coordinates to Zn<sup>2+</sup> in 6, 7 uses the carbonyl oxygen to make a coordination bond with Zn<sup>2+</sup>. As the enolate oxygen is more negative than the carbonyl oxygen, the former complex is expected to be more stable than the latter. Table III lists stabilization energies due to complex formation and energy differences from that of 6 which is the most stable in the four complexes. 7 is less stable by 16.7 kcal mol<sup>-1</sup> than 6.

Both 8 and 9 use the anionic carbons to coordinate to the central metal. The anionic carbon is sterically crowded in comparison with the oxygens, these complexes are expected to be less stable than the 6. As 6 was calculated to be more stable than 8 and 9 by 3.3 and 3.5 kcal mol<sup>-1</sup>, the complex with the coordinated enolate oxygen should be the main species in the reaction conditions. Moreover, the anionic carbon on the five-membered ring easily reacts with one of the olefinic carbon in the second HMI for the propagation reaction. Therefore, 6 is considered to be the plausible reactant for propagations. A mechanistic investigation for the propagation reaction is in progress.

#### 4. CONCLUDING REMARKS

In the present study, we investigated the initiation mechanism of the HMI polymerization by using the model catalyst of Zn<sup>2+</sup>-Mebox. We can summarize the findings of our theoretical study as follows.

- (1) The polymerization is initiated by transfer of the alkyl group from Zn<sup>2+</sup> to the HMI. As the methyl group in the TS is planar derived from the sp<sup>2</sup> hybridization, the initiation reaction proceeds via the mechanism similar to the S<sub>N</sub>2 reactions. This result is completely different from that previous investigated for the reaction using metal ions with an empty coordination site and from those for metallocene catalysts.
- (2) The product 4 and 5 in the initiation reaction react to make the complex for succeeding propagation reactions. 6, the complex with the enolate oxygen coordinating to Zn<sup>2+</sup>, is the most stable and is used for the propagation reaction.

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