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Design of Latent Accelerators for Thermally Latent (Poly)addition of Epoxide with Hemiacetal Ester

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Summary: This article describes thermally latent addition of epoxides and hemiacetal esters using novel latent accelerators. As latent accelerators for the thermally-controlled (poly)addition, we desinged schiff-base zinc chloride complexes ($ZnCl_2/\mathbf{1_R}$) and salen-zinc complex (Zn/**2**). This latent reaction takes place via the reaction of epoxides and carboxylic acids produced from thermal dissociation of hemiacetal esters at moderate temperatures. Use of bifunctional monomers give the corresponding polyesters with side chains bearing acetal and hydroxyl group through the polymerization using the catalysts with tuned Lewis acidities. Zn/**2** shows a sharper temperature dependence than $ZnCl_2/\mathbf{1_H}$.

Keywords: hemiacetal ester; latent accelerator; polyaddition; schiff-base; thermally latent reaction; zinc complex

Introduction

Latent reactions (i.e., reactions inactive under ambient conditions but active only with specific external stimulation such as heating and photoirradiation) have been attracted much attention in developing adhesive, coatings, paintings, and photoresist with simple procedures.[1] In designing a latent reaction, it is important that a catalyst with precisely controllable activity/inactivity must be employed to attain both sufficient reactivity and storability.[1]

We have focused on hemiacetal esters, which are produced via the addition of carboxylic acids with vinyl ethers, as latent substrates.[2] Hemiacetal esters may thermally dissociate to their raw materials, namely carboxylic acids and vinyl ethers. The carboxylic acids thermal-latently produced from hemiacetal esters can nucleophilically react with epoxide and oxetane.[2] However, the spontaneous dissociation temperature of hemiacetal esters takes place only at high temperature (>160 °C),[2,3] although the thermal dissociation can be accelerated by Lewis acids.

In designing a catalyst for this latent reaction, moderately Lewis acidic complexes are good candidates if their acidities can be tuned by appropriate choices of metals and anionic or neutral ligands. The appropriate design makes thermally latent catalysts meet the requests for both high latency at ambient conditions and high activity at desired temperatures. We selected zinc complexes with schiff-bases and salen ligands (Figure 1), whose steric and electronic characters have wide diversities. In this article, we describe latent (poly)addition of epoxides with hemiacetal esters catalyzed by novel thermally latent catalyst, salen–zinc and schiff-base–zinc chloride complexes.

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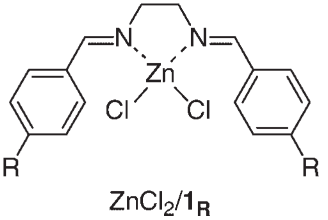


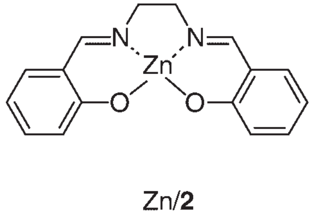


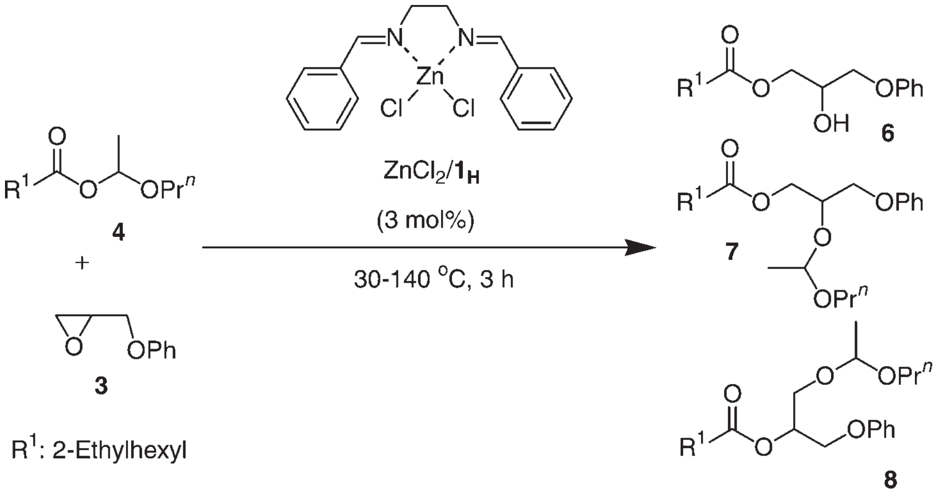
Figure 1.

Results and Discussion

Thermally Latent (Poly)Addition of Hemiacetal Ester with Epoxide Catalyzed by Schiff-base–zinc Chloride Complexes

We examined the addition of an epoxide [glycidyl phenyl ether (**3**)] with a hemiacetal ester [1-propoxyethyl-2-ethylhexanate (**4**)] (Scheme 1, Table 1). The moderate Lewis acidic complexes ($ZnCl_2/\mathbf{1_R}$) were prepared through coordination of schiff-bases ($\mathbf{1_R}$) to zinc chloride. In contrast to the reaction with bare $ZnCl_2$ at room temperature (run 5), conversions of neither epoxide (**3**) nor hemiacetal ester (**4**) were observable in the reaction with $ZnCl_2/\mathbf{1_H}$ below 80 °C (runs 1 and 2). No conversion of **3** nor **4** was observable in the prolonged reaction at 80 °C for 24 h and in the reactions with $\mathbf{1_H}$ (runs 8-9) and without additives at 140 °C (run 10). The satisfactory conversions in the reaction with $ZnCl_2/\mathbf{1_H}$ were attained at 140 °C (run 4). These results clearly indicate that $ZnCl_2/\mathbf{1_H}$ serves as a thermally latent catalyst for the addition of **3** and **4**.

The products composed of three compounds, i.e., an ester with a hydroxyl group (**6**) and esters with acetal groups (**7** and **8**). The products **7** and **8** originate from the acetalizations of **6** and its primary alcohol analogue (**9**) with cleaved *n*-propyl vinyl ether (**5**), respectively (Scheme 2). The absence of the 1,2-addition bearing a primary hydroxyl group (**9**) is attributable to the faster acetalization of **9** with **5** than the case of the 1,3-addition with a secondary hydroxyl group (**6**) due to the steric hindrance and the lower reactivity of secondary alchohol than primary alchohol. The ratio of the products depends on the temperature. Namely, the composition of the product **6** increased as the increase of



Scheme 1.

Table 1.
Thermally latent addition reaction of **3** and **4** with $ZnCl_2/\mathbf{1_H}$[a]

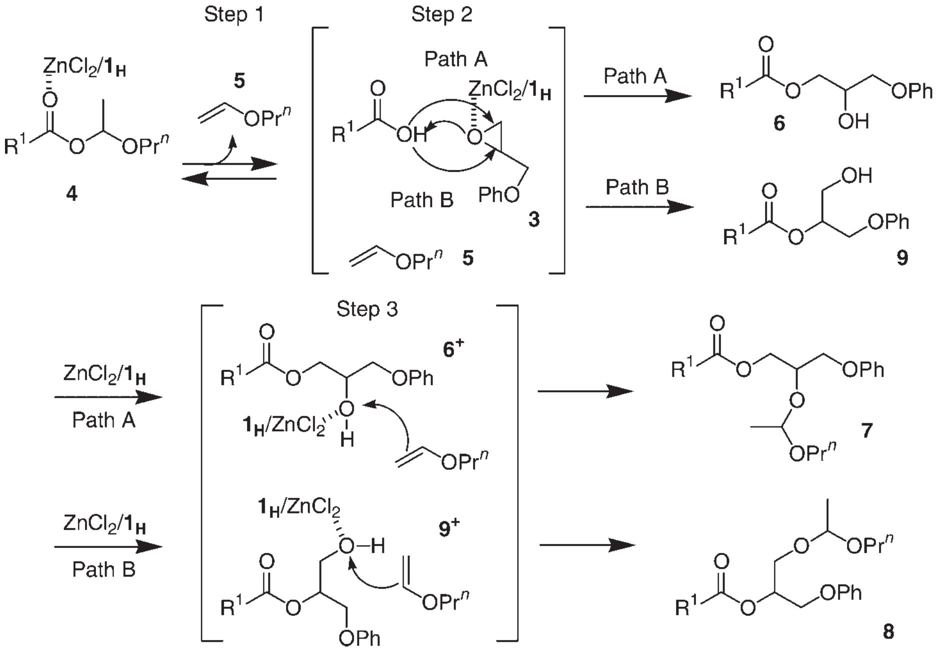
Run	Catalyst	Temperature	Conversion[b] of **3**	Conversion[b] of **4**	Product ratio[b] (**6**)/(**7**)/(**8**)
		(°C)	(%)	(%)	(%)
1	$ZnCl_2/\mathbf{1_H}$	60	0	0	–[c]
2		80	0	0	–[c]
3		100	15	12	42/33/25
4		140	99	99	41/38/21
5	$ZnCl_2$	r.t.	7	10	0/67/33
6		100	60	56	9/64/26
7		140	99	97	–[d]
8	$\mathbf{1_H}$	100	0	0	–[c]
9		140	0	0	–[c]
10	No catalyst	140	0	0	–[c]

[a] Conditions: N_2, 3 h, bulk, catalyst (3 mol%);
[b] Determined by ^1H NMR spectroscopy;
[c] No reaction;
[d] The mixture includes oligomers from **2**, and the product ratio **6**/**7**/**8** could not be calculated by ^1H NMR spectroscopy.

temperature, although the ratios of the product from the primary alcohol (**9**) to those from the secondary alcohols (**6** and **7**) are identical. This increase in the ratio of **6** is ascribed to the predominant evaporation of **5** (b.p. = 65 °C) at higher temperatures over the acetal formation through the attack of the alcohols (**6** and **9**) to **5**.

The electrophilic additions of both **6** to **5** and **9** to **5** are also catalyzed with $ZnCl_2/\mathbf{1_H}$, which activates epoxide, as well as the dissociation of **4** (Scheme 2).[4]

In order to evaluate the electronic effect of the *para*-substituents on the schiff-base ligands ($\mathbf{1_R}$) on the catalytic activity, **2** and **3** were reacted in the presence of $ZnCl_2/\mathbf{1_R}$



Scheme 2.

[R: H, OEt, and NMe_2]. $ZnCl_2/\mathbf{1_H}$ and $ZnCl_2/\mathbf{1_{OEt}}$ initiated the reaction from 90 °C. In contrast, $ZnCl_2/\mathbf{1_{NMe2}}$ initiated the reaction from 110 °C due to the lower Lewis acidity originating from the high electron donating ability of dimethyl amino group. The conversions with $ZnCl_2/\mathbf{1_H}$ and $ZnCl_2/\mathbf{1_{OEt}}$ at 140 °C reached quantitative and 70%, respectively (Figure 2). However, the conversion with $ZnCl_2/\mathbf{1_{NMe2}}$ bearing electron-donating dimethyl amino group is very low under the same conditions. The conversion in the reaction at each temperature decreases as the electron-donating ability of the substituent, and it suggest that the catalytic activity is controlled by the substituent. A plausible reason for very low activity of $ZnCl_2/\mathbf{1_{NMe2}}$ is the deactivation by the basic dimethylamino group that competes with the Lewis acidity of the zinc-center.

$ZnCl_2/\mathbf{1_H}$, which proved an excellent catalyst with both high catalytic activity and latency, was applied to thermally latent polyaddition of bisphenol A diglycidylether (**10**) and di-1-propoxyethyl adipate (**11**) at several temperatures in a similar manner with the model reaction (Scheme 3). As expected, the polyaddition did not proceed at ambient temperatures, but proceeded above 80 °C (Figure 3). The conversions of the monomers in the polyaddition for 3 h at 140 °C reached 95%, and the objective polymer was obtained in 62% yield. This result clearly indicates that the polyaddition of **10** and **11** with $ZnCl_2/\mathbf{1_H}$ requires identical temperatures with those for the model reaction.

The resulting polymer composed of three kinds of structural units [i.e., the units carrying an ester with a secondary hydroxyl group (**12**) and esters with an acetal group (**13** and **14**)]. The units **13** and **14** originate from the acetalizations of the units bearing primary and secondary alcohol structures with cleaved *n*-propyl vinyl ether, respectively, in a similar manner with the model reaction (Schemes 2 and 3). We attributed the yield significantly lower than the conversion of **10** due to the elimination of *n*-propyl vinyl ether[4]. The maximum yield for the polymer containing 40 mol% amounts of the alcohol

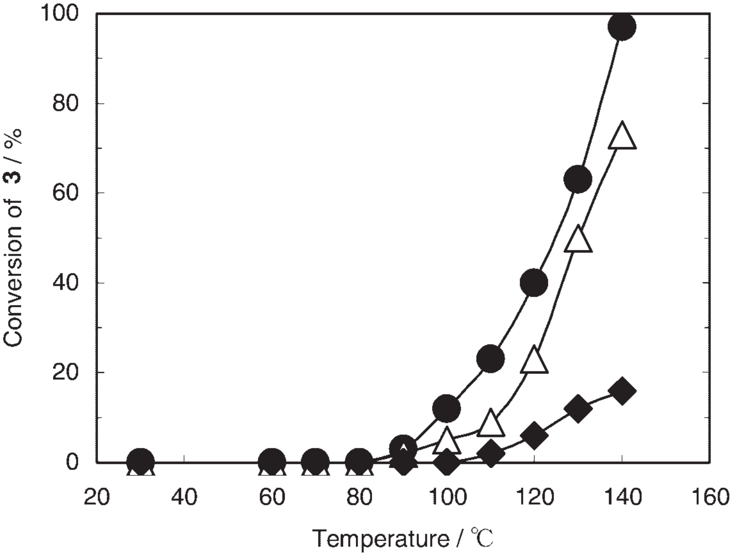
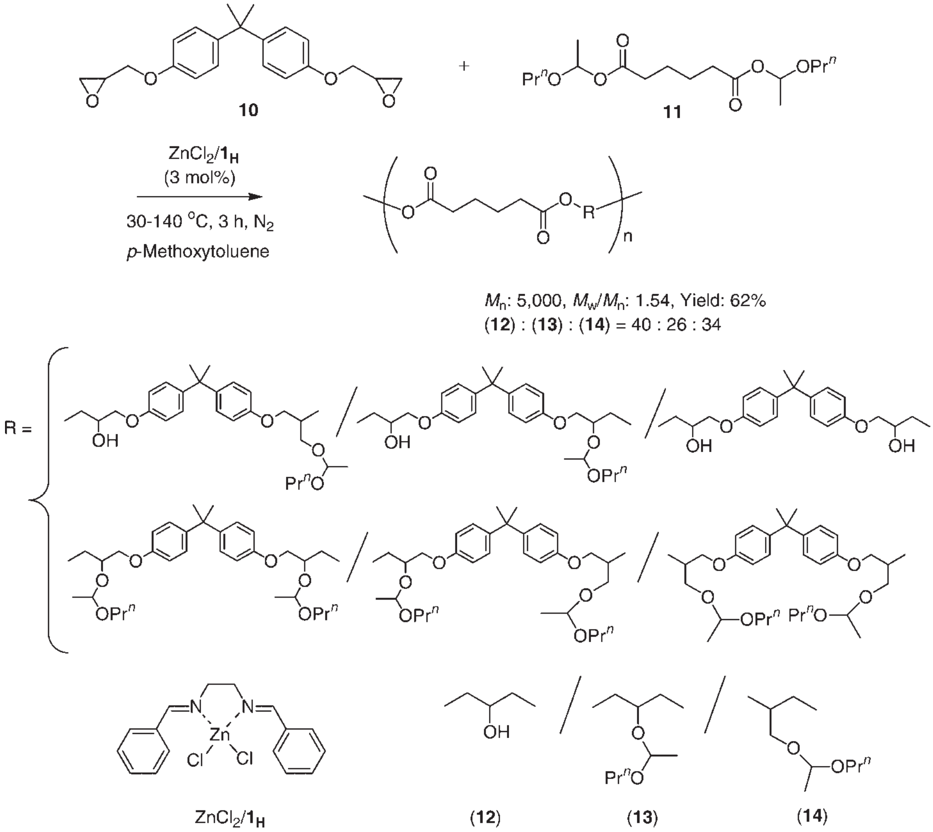


Figure 2.

Relationship between the time versus conversion of **3** in the addition of **3** and **4** with 3.0 mol% amounts of $ZnCl_2/\mathbf{1_R}$ for 3 h ($\mathbf{1_H}$; ●, $\mathbf{1_{OEt}}$; △, $\mathbf{1_{NMe2}}$; ◆) at several temperatures.



Scheme 3.

unit **12** is 88%. The number average molecular weight (M_n) of the obtained polymer estimated by SEC was ca. 5000.

Thermally Latent Polyaddition of Hemiacetal Ester with Epoxide Catalyzed by Salen-Zinc Complex

The chloride in the schiff-base–zinc complexes possibly deteriorates electronic and mechanical properties of products, if the complexes were used in curing of sealing materials for electronic devices, which is one of the most common applications of this latent polyaddition. Accordingly, we employed a salen–zinc complex (Zn/**2**), which is a halogen-free analogue of schiff-base–zinc chloride complexes.

We carried out the polyaddition of **10** and **11** with Zn/**2** (3.0 mol%) at several temperatures for 6 h as a model reaction of a novel halogen-free thermally latent curing (Scheme 4). No polyaddition of **10** and **11** proceeded at 100 °C and under ambient conditions for 24 h. The polyaddition of **10** and **11** with Zn/**2** proceeded above 110 °C and **10** was consumed quantitatively at 150 °C. These results clearly indicate that Zn/**2** served as a novel thermally latent catalyst for polyaddition of **10** and **11**. Zn/**2** required the identical temperature for enough conversion of **10** and **11**. Thermally latent polyaddition of **10** and **11** with Zn/**2** exhibits a sharper temperature dependence than that with $ZnCl_2/\mathbf{1_H}$ (Figure 3). The unit ratio of **12**, **13**, and **14** in the obtained polymer was 30/48/22 determined by ^1H NMR spectroscopy. The ratio of the 1,3-addition, which equals to the composition {([**12**]+[**13**])/[**14**]}, is higher than that in the polyaddition with $ZnCl_2/\mathbf{1_H}$. We

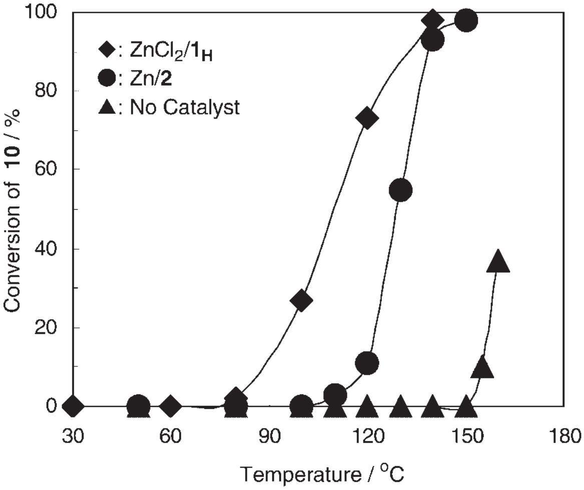
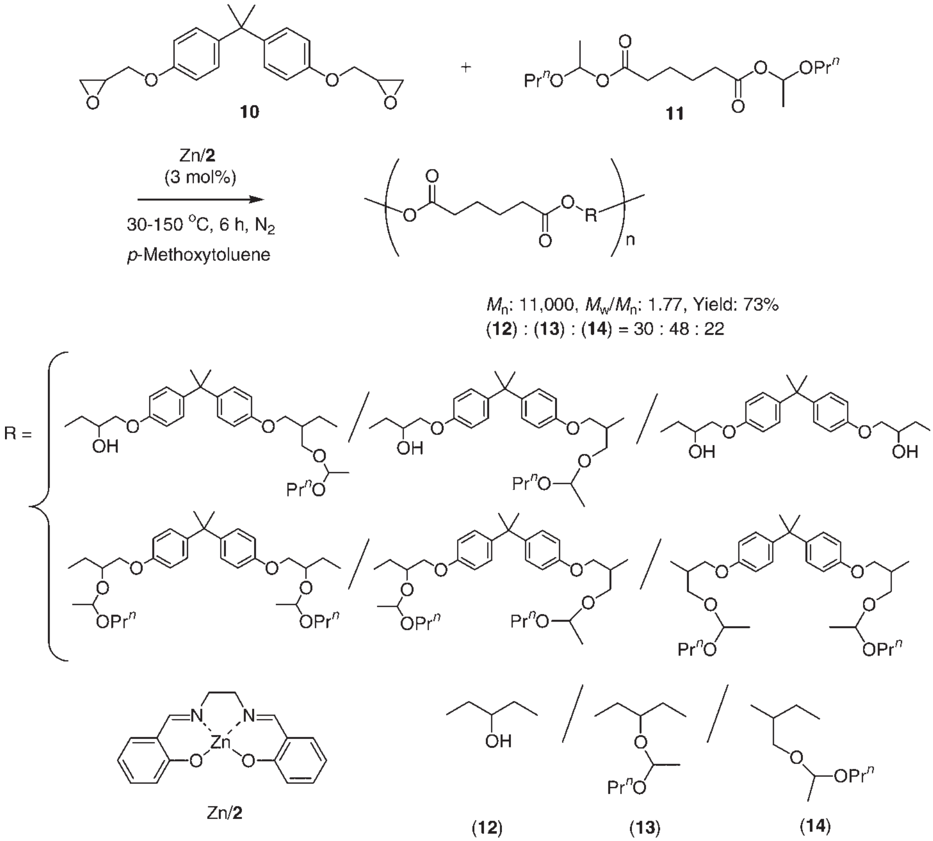


Figure 3.
Relationship between the temperature versus conversion of **10** in the polyaddition of **10** and **11** with 3.0 mol% amounts of $ZnCl_2/1_H$ and Zn/**2** and that without catalyst for 6 h at 30–160 °C.



Scheme 4.

estimated that $ZnCl_2/\mathbf{1_H}$ is more Lewis acidic than Zn/**2** by electron-withdrawing chloride, and that the higher Lewis acidity resulted in decreasing the thermodynamically stable 1,3-addition bearing secondary hydroxyl group due to the higher activation of epoxide. However, in the case of Zn/**2**, the degree of acetal formation is higher than that in the polyaddition with $ZnCl_2/\mathbf{1_H}$, and as a result, the yield is also higher. This result is peculiar to salen–metal complex in polyaddition with Zn/**2**.

Conclusions

In this article, we described latent catalysis of thermally latent (poly)addition of hemiacetal esters with epoxides using zinc complexes. Schiff-base zinc complexes ($ZnCl_2/\mathbf{1_R}$) catalyze the addition at moderately elevated temperatures, and show good latency under ambient conditions. The electronic characters of the substituents control over the Lewis acidities of the schiff–base–zinc chloride complexes that regulate both the activity and the latency of the reaction. A salen-zinc complex (Zn/**2**) also serves as an effective catalyst for the thermally latent polyaddition of a bifunctional hemiacetal ester and a diepoxide, whose temperature dependency is sharper than that of the polyadditions with the schiff-base zinc chloride complexes. As well as the sharp temperature dependence (i.e., the high activity at desired conditions and high latency under ambient conditions), the halogen-free structure is also an important feature, because halogen-containing catalysts potentially deteriorate the properties of products, especially if they were employed for curing of sealings of electron-devices. The thermally latent polyaddition of hemiacetal esters and epoxides catalyzed by these zinc complexes will find uses in construction of one-pot curing systems with longer stability and better activity than those in conventional systems.

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