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Mechanistic Studies on Ring-Opening Polymerization of Benzoxazines: A Mechanistically Based Catalyst Design

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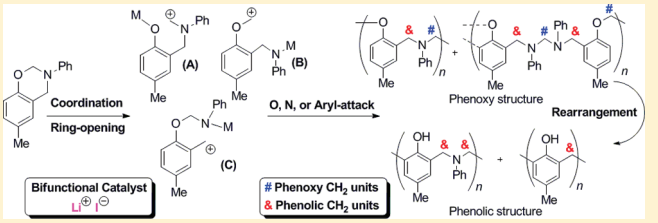
ABSTRACT: Ring-opening polymerization behavior of a model *p*-cresol−aniline-based benzoxazine under various conditions was investigated in detail by ^{1}H NMR analysis in deuterated DMSO. An improved mechanistic scheme was proposed to explain the observed experimental results. In light of this mechanistic scheme, several bifunctional catalysts were studied, and lithium iodide was found to be a very active and effective catalyst. Lithium cation is the Lewis acid part and effectively coordinates with oxygen or nitrogen atoms and promotes ring-opening of benzoxazines. Iodide ion is the nucleophilic part with good leaving ability and can react with the ring-opened imminium intermediates to prevent its rapid recombination with the phenolate.



INTRODUCTION

Polybenzoxazines attract much attention recently as good phenolic resins due to their attractive and useful properties: excellent static and dynamic mechanical properties, low water absorption and flammability, no liberation of byproducts, near-zero shrinkage or volumetric expansion upon curing, high UV and chemical retardence, and considerable molecule-design flexibility.[1] They have showed high potential to be applied as composite materials to many economically important fields, such as aerospace and automotive industries. It has been reported that the inner hydrogen-bonding networks mainly derived from the Mannich bridge structure may be responsible for these good properties considering the relatively low cross-linking density.[2] In order to achieve a good molecular understanding of the polymer and the structure−property relationships, it is of great importance to understand the curing mechanistic pathways.

Polybenzoxazines typically are made from high-temperature (typically >180 °C) bulk curing/ring-opening polymerization of benzoxazine monomers without an added catalyst, and the monomers are prepared from inexpensive raw materials including phenols, primary amines, and formaldehyde. However, the high temperature required for the ring-opening polymerization is one of the main shortcomings, since the high temperature may destroy the inner hydrogen-bonding interactions and result in degradation of the polymer.[3] So a low curing temperature is highly needed and attempts to reduce the curing temperature have been carried out, with different degree of success, by using various catalysts.[4−9] Moreover, the presence of a catalyst accelerates the reaction rate and reduces the curing time, which is also important and valuable for industrial production. To this end, a need exists for better understanding the polymerization mechanism in order to design more efficient catalysts.

Burke and co-workers[10] first reported the ring-opening reaction of benzoxazine, indicating that aminoalkylation preferred to occur at the free ortho position rather than at the free para position of the phenol in the reaction of 1,3-dihydrobenzoxazine with a phenol. Riese et al.[11] also observed this ortho preference during the investigation of the kinetics of monofunctional benzoxazines in the presence of catalytic amounts of 2,4-di-tert-butylphenol. They proposed that the ortho preference derived from the intermediate formed by intermolecular hydrogen-bonding coordination of phenolic hydroxyl group with oxygen atom of oxazine ring and iminium species resulting from ring-opening of oxazine ring via protonation by the phenol may be responsible for the para reaction. In 1968, McDonagh and Smith[12] suggested that ring chain tautomerism may exist in protonated benzoxazine. In recent years, the Ishida group has done a lot of extensive work on polybenzoxazine chemisty.[1−4] On the basis of comprehensive survey and studies of various cationic, anionic and radical initiators,[4] they have proposed that ring-opening polymerization of the benzoxazine proceeds through a cationic mechanism. A simplified mechanistic scheme is shown in Scheme 1.[4e] It is considered that there are two main steps involved in the polymerization. The first one is the ring-opening step and the second the electrophilic substitution step. Depending on the polymerization conditions, the final polymer may have phenolic structure,[3c] phenoxy structure,[4e] or both.[4b]

Yagci and co-workers[8] studied the photoinitiated cationic polymerization of a monofunctional benzoxazine at room temperature and found the structure of the as-synthesized polymers were quite complex. They suggested that it was due to different

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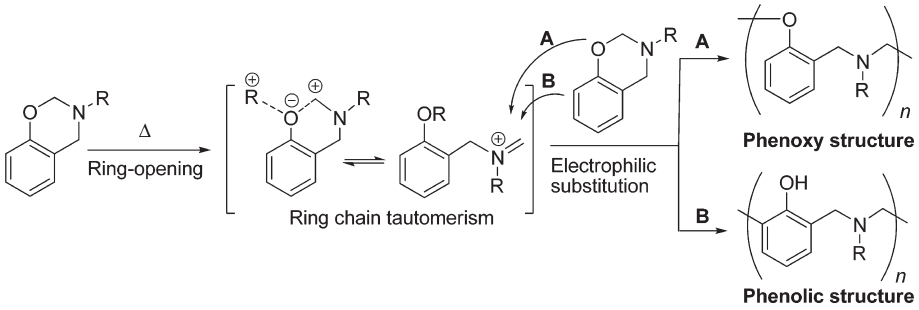
Scheme 1. Simplified Mechanistic Scheme for Ring-Opening Polymerization of Benzoxazines



ring-opening processes of the protonated monomer either at the oxygen or nitrogen atoms. The Ueda group[13] investigated the model condensation reaction of 3,4-dihydro-6,8-dimethyl-3-phenyl-2*H*-1,3-benzoxazine and 2,4-xylenol in the absence and presence of various acid catalysts and proposed some possible pathways at the initial curing stage. Recently, Endo and colleagues[6a] discovered new reaction pathways for the thermal polymerization of a benzoxazine in bulk. The polymerization affords an intermediary labile phenoxy structure in the main chain, which was first reported by Ishida group.[4b] Its following rearrangement finishes phenolic structure. During the preparation of this paper, Chutayothin and Ishida[14] reported an investigation on the polymerization initiation mechanism of benzoxazine by analyzing and comparing the rude products of model benzoxazine dimerization reactions with a large number of pure model compounds prepared based on the hypothesized initiation mechanism. They proposed that oxygen and nitrogen protonated species can be involved in the protonation initiation step, the oxygen protonated species is reactive and the nitrogen one is stable, and the Mannich bridge structure is less stable than methylene bridge structure and can be rearranged to it.

Much progress has been lately achieved on the mechanistic studies of ring-opening polymerization of benzoxazines, and it seems that the whole and detailed picture of the mechanism is in the way of being established. In this paper we report an investigation on the thermal ring-opening polymerization of a *p*-cresol−aniline-based benzoxazine **1**, based on the ^{1}H NMR analysis of thermally cured mixtures under different conditions in deuterated DMSO. The obtained results, which complement well the ones very recently reported by Ishida,[14] have led us to propose a modified and more comprehensive mechanism. In the light of this improved mechanistic scheme, our finding that lithium iodide is a very active bifunctional catalyst for the thermal ring-opening polymerization of benzoxazines is justified.

RESULTS AND DISCUSSION

3,4-Dihydro-6-methyl-3-phenyl-2*H*-1,3-benzoxazine (**1**) stands out to be the model benzoxazine for this study because one reaction site (6-position) on the phenolic ring is blocked by a methyl group to avoid the formation of highly cross-linked polymer, the structure of the polymer obtained is relatively simple, and its solubility in common organic solvents is quite good, which allows us to follow and characterize the reaction easily and efficiently in all the conditions tested. Since the signals of methylene units of the polybenzoxazine in ^{1}H NMR spectra are most characteristic and easily recognized, the following analysis is focused on the methylene proton region (5.0−3.5 ppm). ^{13}C NMR spectra did not give useful information.

Initially, benzoxazine **1** was cured in the absence of a catalyst at 200 °C at different times. The as-synthesized polymers were used as standards. As outlined in Figure 1, after heating for 2 h, the polymer consisted of true phenoxy and true phenolic structure, showing two broad overlapped signals at 4.5−4.0 and 4.0−3.5 ppm (due to methylene units) in the ^{1}H NMR spectra in deuterated chloroform (Figure 1a). After another 2 h, only true phenolic structure existed, exhibiting one broad signal at 4.0−3.5 ppm in the ^{1}H NMR spectra in deuterated chloroform (Figure 1b). These results are consistent with the report of the Endo group.[6a] It is worth to note that we can better differentiate the peaks in the ^{1}H NMR spectra when changing the NMR solvent from deuterated chloroform to deuterated DMSO (Figure 1c,d), which is of great importance for the following analysis.

Many catalysts have been reported to be effective promoters for the thermal ring-opening polymerization of benzoxazines thus far.[4−9] We then tested two typical catalysts *p*-toluenesulfonic acid (PTS) and 2-ethyl-4-methylimidazole (EMI) (5 mol %) on the model benzoxazine **1** at 150 °C for 5 h.[6a,7] As shown in Figure 2, ^{1}H NMR analysis in deuterated DMSO demonstrates that although PTS can effectively promote the polymerization and almost no phenoxy structure exists, the inner structure of the polymer is quite different and complicated, and only a part of the structure is true phenolic structure (Figure 2c). It should be mentioned that in deuterated chloroform we only observe one broad signal (Figure 2d). In the case of EMI, in the ^{1}H NMR spectra in deuterated chloroform, two overlapped broad peaks are observed, and the left signal at 4.4−4.0 ppm is clearly bigger than the right one at 4.0−3.5 ppm, which is contradictory to the above explanation (Figure 1) that the structure of thermally cured polymer mainly consist of true phenoxy and true phenolic structure, because in that case the left signal at 4.4−4.0 ppm should be always less than or equal to the right one at 4.0−3.5 ppm. As a sharp comparison, in the ^{1}H NMR spectrum of the same polymer in deuterated DMSO besides the signals due to true phenoxy and true phenolic structure, there is a downfield signal located at 4.7−4.4 ppm, which might be attributed to similar phenoxy structure. All these results reveal that the curing chemistry of benzoxazines is rather complicated and the inner structure of polybenzoxazine depends to a great degree on the curing conditions, which promotes us to reconsider the mechanism carefully.

On the basis of the above experimental facts and the literature,[4e,6a,8,13,14] we propose a detailed mechanism, as depicted in Scheme 2. The mechanism is divided into three main steps: coordination ring-opening, electrophilic attack, and rearrangement. First, the catalyst coordinates with an

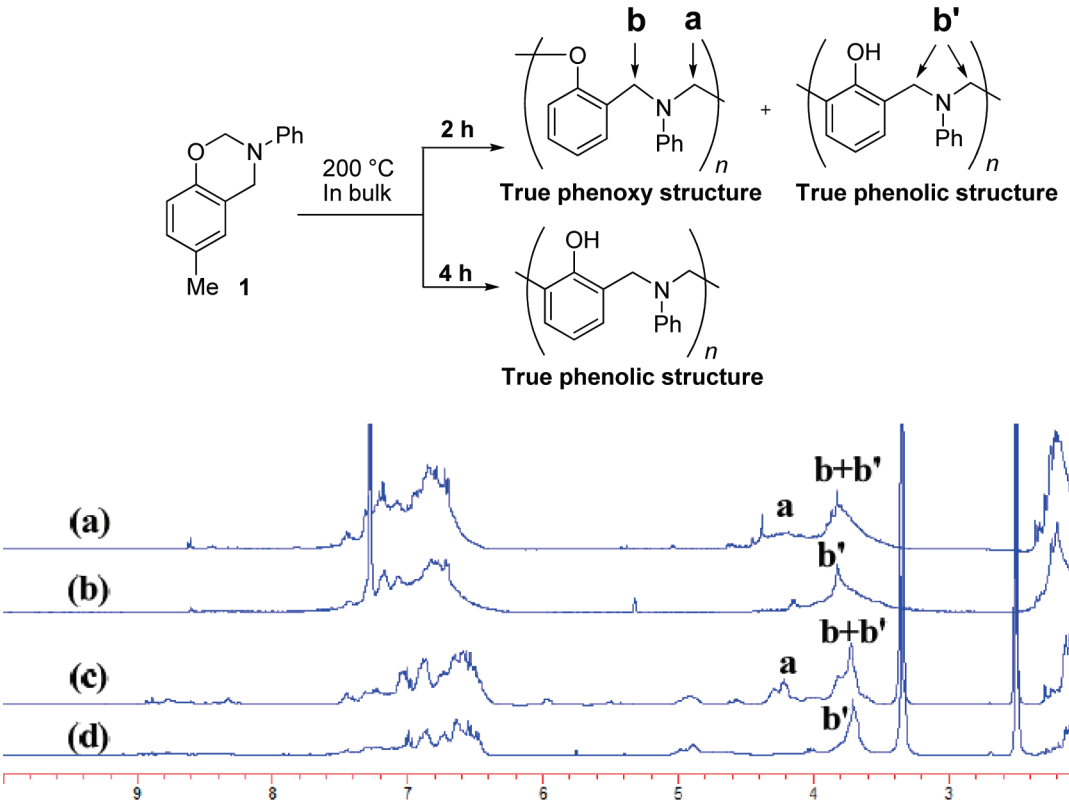


Figure 1. ^{1}H NMR spectra of thermally cured benzoxazine **1** at 200 °C for 2 h in deuterated chloroform (a) or deuterated DMSO (c) and for 4 h in deuterated chloroform (b) or deuterated DMSO (d). The benzoxazine monomer spectrum is shown in Figure 5a.

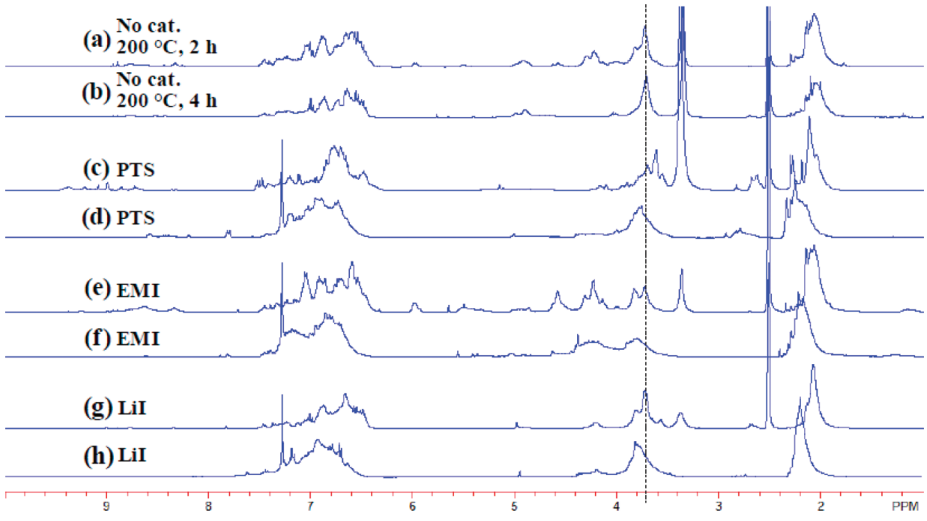
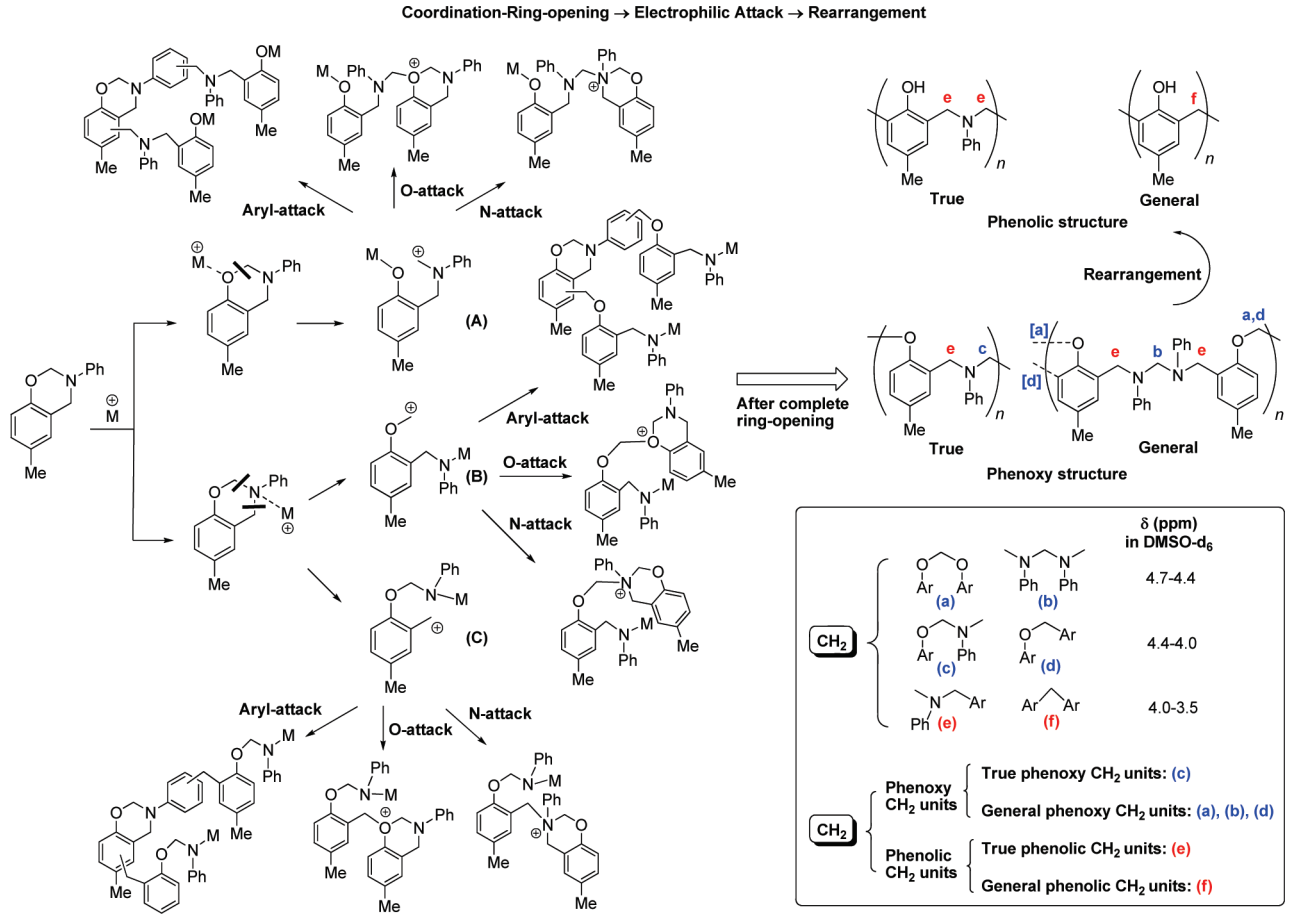


Figure 2. ^{1}H NMR spectra of thermally cured benzoxazine **1** (a) at 200 °C for 2 h in deuterated DMSO, (b) at 200 °C for 4 h in deuterated DMSO, (c) in the presence of 5 mol % PTS at 150 °C for 5 h in deuterated DMSO, (d) in the presence of 5 mol % PTS at 150 °C for 5 h in deuterated chloroform, (e) in the presence of 5 mol % EMI at 150 °C for 5 h in deuterated DMSO, (f) in the presence of 5 mol % EMI at 150 °C for 5 h in deuterated chloroform, (g) in the presence of 5 mol % LiI at 150 °C for 5 h in deuterated DMSO, and (h) in the presence of 5 mol % LiI at 150 °C for 5 h in deuterated chloroform.

oxygen or nitrogen atom and generates three possible cationic intermediates **A**, **B**, and **C** by different heterolysis patterns. For each intermediate, the following electrophilic reactions may involve O-attack, N-attack, and Aryl-attack. As a result, the polymer obtained may contain phenoxy structure (true + general phenoxy structure) and phenolic structure (true + general phenolic structure) represented in Scheme 2. Finally, phenoxy structure is transformed into phenolic structure by rearrangement.

Considering structure complexity of the polymer and to simplify the analysis, we decided to focus on the CH_2 units in the polymer. During the polymerization, six different types of CH_2 units can exist (Scheme 2): ArO−CH_2−OAr (a), −(Ph)N−CH_2−N(Ph)− (b), ArO−CH_2−N(Ph)− (c),

Scheme 2. Improved Mechanism for the Ring-Opening Polymerization of Benzoxazines



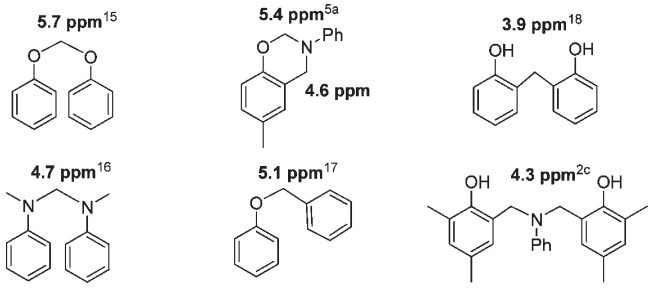


Figure 3. ^{1}H NMR chemical shifts of methylene groups of model compounds for the estimation of chemical shifts of CH_2 units in the polymer.

ArO−CH_2−Ar (d), −(Ph)N−CH_2−Ar (e), and Ar−CH_2−Ar (f). We call $\mathbf{CH_2}$(a−d) phenoxy CH_2 units [$\mathbf{CH_2}$(c) true phenoxy CH_2 units + $\mathbf{CH_2}$(a,b,d) general phenoxy CH_2 units] and $\mathbf{CH_2}$(e,f) phenolic CH_2 units [$\mathbf{CH_2}$(e) true phenolic CH_2 units + $\mathbf{CH_2}$(f) general phenolic CH_2 units]. It is very difficult to exactly distinguish the contributions of every type of CH_2 units on the signals in the ^{1}H NMR spectrum as different vicinities of the CH_2 units can influence their chemical shifts in the spectrum. In Figure 3, we list some known compounds with the chemical shifts of methylene groups. They are used as the reference to chemical shifts of the above CH_2 units in the polymer. In combination of ^{1}H NMR spectra of polybenzoxazines obtained above (Figure 2), the possible chemical shift ranges of various CH_2 units are estimated and indicated in Scheme 2. From the chemical point of view, phenoxy CH_2 units $\mathbf{CH_2}$(a−d) are labile and finally are transformed into relatively stable phenolic CH_2 units $\mathbf{CH_2}$(e,f). For example, the benzyl phenyl ether rearrangement, i.e., $\mathbf{CH_2}$(d) → $\mathbf{CH_2}$(f), has been extensively studied and used for synthetic purposes.[19] To further support this point, the standard polymer obtained by curing benzoxazine **1** at 200 °C for 4 h which exhibits almost total phenolic CH_2 units was heated for 2 h more at 200 °C. Their ^{1}H NMR, IR, and T_g (74.9 °C, determined by DSC)[5d] did not change, indicating the stability of phenolic CH_2 units.

With this mechanistic scheme in mind, the above experimental facts (Figure 2) can be reasonably explained. At a high temperature (~200 °C) and without a catalyst, O−CH_2 bonds of the benzoxazine monomers are in complete or partial dissociation state and ring-opening of the benzoxazines mainly produces the thermodynamically more stable intermediate **A** (Scheme 2). The following electrophilic reactions mainly are O-attack or Aryl-attack type electrophilic reactions at the phenolic rings of benzoxazines, providing the corresponding true phenoxy and phenolic CH_2 units. Consequent rearrangement furnishes the complete true phenolic CH_2 units. As a result, in the corresponding ^{1}H NMR spectrum only one sharp peak is observed for the true phenolic CH_2 units (Figure 2b). However, at a lower temperature and in the presence of a catalyst, more ring-opening

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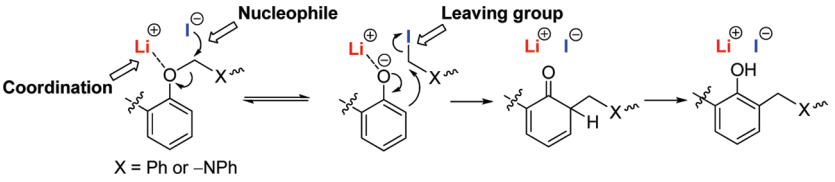
Scheme 3. Proposed LiI-Promoted Rearrangement Model



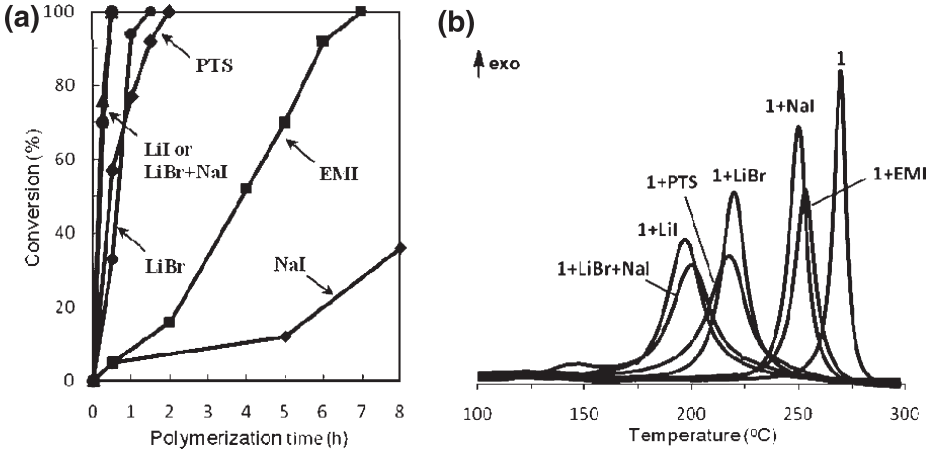


Figure 4. (a) Time dependences of conversion of benzoxazine **1** for the polymerizations with 1 mol % various catalysts at 150 °C. (b) Differential scanning calorimetry (DSC) plots of pure benzoxazine **1** and mixtures of **1** with 1 mol % various catalysts.

patterns seem to be available, resulting in three main intermediates **A**, **B**, and **C**. The selectivity of the following electrophilic reactions seems to be lower and O-attack, N-attack, and Aryl-attack type electrophilic reactions operate, affording various phenoxy and phenolic CH_2 units. Phenoxy CH_2 units finally are transformed into phenolic CH_2 units by rearrangement. In Figure 2c, the more complicated signal at 4.0−3.5 ppm is probably due to the existence of various phenolic CH_2 units. In Figure 2e, the signal at 4.7−4.4 ppm may be attributed to general phenoxy CH_2 units $\mathbf{CH_2}$(b) or even $\mathbf{CH_2}$(a). The signal at 4.4−4.0 ppm can be due to true phenoxy CH_2 units $\mathbf{CH_2}$(c) and general phenoxy CH_2 units $\mathbf{CH_2}$(d). The signal at 4.0−3.5 ppm probably suggests the existence of true phenolic CH_2 units $\mathbf{CH_2}$(e) and general phenolic CH_2 units $\mathbf{CH_2}$(f). In brief, our results can perfectly justify the reports in the literature[4−9] about the different properties of the polymers obtained by thermal curing or by catalyzed curing.

Next, we attempted to design some good catalysts for the ring-opening polymerization of benzoxazines. In light of the further understanding of the mechanism, a catalyst should be able to prefer coordinating with oxygen than to nitrogen atoms and mainly produce intermediate **A** and effectively promote the rearrangement in order to obtain higher percentage of true phenolic CH_2 units (Mannich structure). Recently, the Endo group[6a] has reported that a dual system composed of PTS and EMI effectively promotes the rearrangement. PTS is advantageous to C−O dissociation and EMI serves as a nucleophile to prevent its recombination. Inspired by these results, we speculated that a bifunctional catalyst (acid part + nucleophilic part with leaving group ability) might be a suitable effective promoter. Lithium iodide was expected to fulfill the requirements (Scheme 3). Lithium cation is the acid part and known to have a very high affinity toward oxygen atom. Iodide ion serves as the nucleophilic part and in addition has good leaving group properties. Lithium iodide resulted to be a very good catalyst, mainly furnishing phenolic CH_2 units with high percentage of true phenolic CH_2 units (Figure 2g) (T_g = 90 °C determined by DSC of the resulting polybenzoxazine).[20] As a comparison, under similar conditions PTS provided phenolic CH_2 units with more amounts of general phenolic CH_2 units and EMI mainly afforded phenoxy CH_2 units (Figure 2c,e).

To better understand effects of the bifunctional catalyst, LiBr, NaI, and LiBr + NaI were then tested. We carried out the polymerization in the presence of 1 mol % catalyst in order to reduce the polymerization rate and allow us to follow the reactions with more detailed information. As we can see in Figure 4a, LiI is a very active catalyst, in terms of conversion rate of **1**. In 0.5 h, the monomer is consumed completely. PTS only achieves 57% conversion, and in the case of EMI almost no monomer is consumed. When LiBr was used, the conversion decreases to 33%. NaI almost does not show catalytic effect. Nevertheless, the combination of LiBr + NaI indicates nearly same catalytic effect as that of LiI. The differential scanning calorimetry DSC results are in line with these outcomes (Figure 4b). Pure **1** reacts with a maximum temperature of 269 °C. In the presence of 1 mol % LiI, the maximum temperature considerably decreases to 197 °C. The maximum temperature of the reaction with 1 mol % PTS as a catalyst is 218 °C, and when EMI is used, the maximum temperature (253 °C) is just slightly lower than that observed with pure **1**. LiBr gives a maximum temperature at 220 °C, whereas the use of NaI leads to a maximum temperature at 250 °C. However, the combination of LiBr + NaI results in a very similar maximum temperature as that of LiI. All these results show that the acid part

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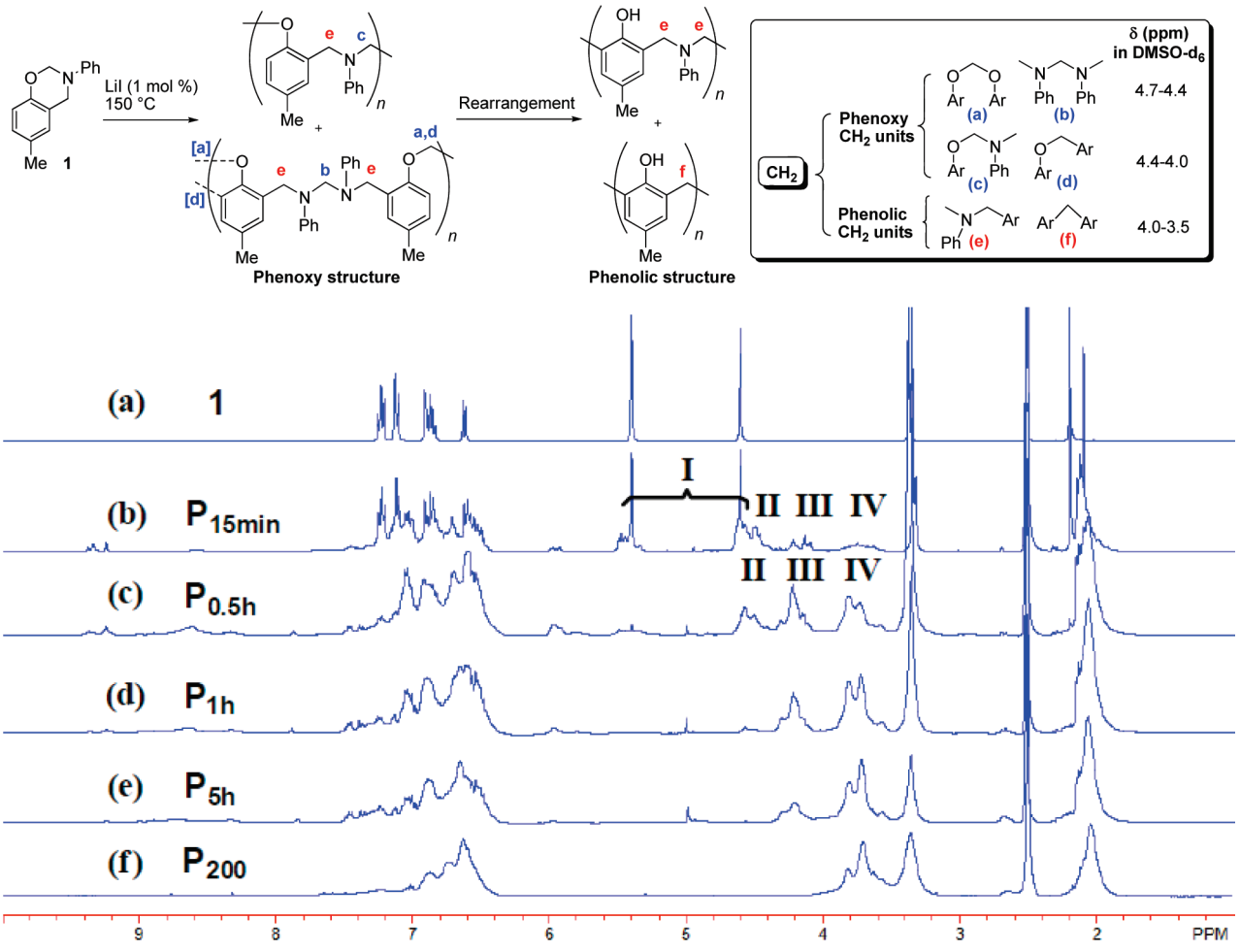

Figure 5. ^{1}H NMR spectra in deuterated DMSO of (a) benzoxazine monomer **1**, (b) the polymer $\mathbf{P}_{15\,min}$ obtained by heating **1** in the presence of 1 mol % LiI at 150 °C for 15 min, (c) the polymer $\mathbf{P}_{0.5\,h}$ obtained by heating **1** in the presence of 1 mol % LiI at 150 °C for 0.5 h, (d) the polymer $\mathbf{P}_{1\,h}$ obtained by heating **1** in the presence of 1 mol % LiI at 150 °C for 1 h, (e) the polymer $\mathbf{P}_{5\,h}$ obtained by heating **1** in the presence of 1 mol % LiI at 150 °C for 5 h, (f) the polymer $\mathbf{P}_{200}$ obtained by heating polymer $\mathbf{P}_{5\,h}$ at 200 °C for 2 h. Note: signal I = CH_2 (residual oxazine rings of the structure formed by Aryl-attack of various intermediates, (Scheme 2), signal II = $\mathbf{CH_2}$(a,b), and signal III = $\mathbf{CH^2}$(c,d), signal IV = $\mathbf{CH^2}$(e,f).

plays a key role in the curing and nucleophilic part with leaving group ability is beneficial and can greatly influence and adjust catalytic activity of the catalyst.

The above conclusions are further supported by the ^{1}H NMR spectra of thermally cured mixtures of **1** in the presence of 1 mol % LiI at different times in deuterated DMSO. In Figure 5, ^{1}H NMR spectra of thermally cured mixtures of **1** in the presence of LiI at 150 or 200 °C for different times are shown. As can be seen in Figure 5b, ^{1}H NMR spectrum of polymer $\mathbf{P}_{15\,min}$ presents five main signals due to different types of CH_2 units at δ 5.5−5.3, 4.7−4.5 ppm (I), 4.7−4.4 ppm (II), 4.4−4.0 ppm (III), and 4.0−3.5 ppm (IV). Signal I, apart from the peaks at 5.4 and 4.6 ppm due to the starting benzoxazine **1**, may be ascribed to the residual oxazine rings in the structure formed by Aryl-attack of intermediates **A**, **B**, or **C** (Scheme 2). Signal II can be due to general phenoxy CH_2 units $\mathbf{CH_2}$(b) or even $\mathbf{CH_2}$(a). Signal III probably indicates the presence of true phenoxy CH_2 units $\mathbf{CH_2}$(c) and general phenoxy CH_2 units $\mathbf{CH_2}$(d). Signal IV may be due to true phenolic CH_2 units $\mathbf{CH_2}$(e) and general phenolic CH_2 units $\mathbf{CH_2}$(f). It is shown in Figure 5c that after 0.5 h all the oxazine rings in the mixture undergo ring-opening and three main signals II, III, and IV are produced, indicating a fast ring-opening step. After 1 h, signal II almost disappears and is transformed into signal III or IV by rearrangement (Figure 5d), which reveals the relative unstability of the ketal-type general phenoxy CH_2 units $\mathbf{CH_2}$(a,b). As comparison, after 5 h signal III does not disappear and displays quite a number of phenoxy CH_2 units $\mathbf{CH_2}$(c) or $\mathbf{CH_2}$(d) (Figure 5e). We surmise that due to their ketal-type structure general phenoxy CH_2 units $\mathbf{CH_2}$(b) are transformed into true phenolic CH_2 units $\mathbf{CH_2}$(e), whereas general phenoxy CH_2 units $\mathbf{CH_2}$(a) are converted to phenoxy CH_2 units $\mathbf{CH_2}$(d). These results suggest that phenoxy CH_2 units $\mathbf{CH_2}$(c,d) are more difficult to undergo rearrangement. In the ^{1}H NMR spectrum of polymer $\mathbf{P}_{200}$ obtained by heating polymer $\mathbf{P}_{5\,h}$ at 200 °C for 2 h, signal III attributable to phenoxy CH_2 units $\mathbf{CH_2}$(c,d) completely disappears and finally is changed to peak IV due to phenolic CH_2 units $\mathbf{CH_2}$(e,f) (Figure 5f), demonstrating that phenoxy CH_2 units are labile and phenolic CH_2 units are the final stable structure in the polymer.

CONCLUSIONS

An improved mechanistic scheme for ring-opening polymerization of benzoxazines has been proposed on the basis of ^{1}H

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NMR analysis of various thermally cured mixtures of benzoxazine **1** in deuterated DMSO. The use of deuterated DMSO for the ^{1}H NMR analysis allows us to recognize and characterize the inner structure of the model polybenzoxazine, and it is anticipated that this work could serve as the basis for developing effective and good initiators for the ring-opening polymerization of benzoxazines. In the light of this mechanism, the ring-opening polymerization of benzoxazines under various conditions can be explained, and lithium iodide was proposed and found to be a very active bifunctional catalyst. Our next target will be to screen more catalysts and to study the detailed effects of the catalyst on the inner structure and properties of polybenzoxazines.

EXPERIMENTAL SECTION

Materials. All reagents and solvents were purchased from Aldrich Chemical Co. and used as received. Benzoxazine **1** was prepared according to the reported procedure,[5c] and the purity is >95% as determined by ^{1}H NMR.

Measurements. ^{1}H NMR spectra were taken on a Bruker AM-360 (360 MHz). Chemical shifts were reported in parts per million relative to TMS as an internal standard ($\delta_{TMS} = 0$) for ^{1}H NMR spectra. The solvent for NMR measurement was deuterated DMSO or deuterated chloroform. DSC studies were done on a DSC-Q20 thermal analyzer from TA Instruments with N_2 as a purge gas at a scanning rate of 10 °C/min. About 5 mg of samples was tested in high-pressure closed aluminum pans.

General Procedures for Ring-Opening Polymerization of Benzoxazine 1. In a test tube, benzoxazine **1** (113 mg, 0.5 mmol) and a catalyst (1 or 5 mol %) were dissolved in acetone (~0.2 mL). The mixture was dried at room temperature under high vacuum for ~1 h and heated under the conditions showed above. Then the resulting mixture was subjected to routine analysis.

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