



Catalyst effects on the ring-opening polymerization of 1,3-benzoxazine and on the polymer structure

Chao Liu^a, Dongmei Shen^a, Rosa María Sebastián^{a,*}, Jordi Marquet^{a,*}, Rainer Schönfeld^b

^a *Departament de Química, Universitat Autònoma de Barcelona, 08193 Bellaterra (Cerdanyola del Vallès), Barcelona, Spain*

^b *Adhesive Technologies-R&D, Henkel AG & Co. KGaA, Henkelstrasse 67, 40191 Düsseldorf, Germany*

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ABSTRACT

The effect of various catalysts on the ring-opening polymerization of a simple model of 1,3-benzoxazine has been examined in order to compare their catalytic activities and the catalyst effects on the structure of the final polymer. The catalytic activity has been estimated by the conversion of *p*-cresol-aniline-based benzoxazine and dynamic Differential Scanning Calorimetry analysis of the curing process. The ratio of phenolic to phenoxy structures (which is representative of the rate of phenoxy-phenolic rearrangement), in each case has been determined by ¹H NMR analysis of the corresponding cured mixture. Analysis of the ¹H NMR spectra of the phenolic final polymer has been also performed, thus establishing the effects of the used catalyst on the structure of the final phenolic polymer.

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1. Introduction

A new type of phenolic resins, polybenzoxazines [1], has been developed in recent years as an alternative to traditional phenolic resins that have been widely applied in our common life due to their good thermal, mechanical and dielectric properties and low cost [2]. They not only retain the aforementioned advantages traditional phenolic resins possess, but also overcome many drawbacks that traditional phenolic resins have, such as the use of strong acids or bases as catalysts and the developing of volatile by-products during processing. The classical method to make polybenzoxazines is to polymerize the benzoxazine monomer at high temperature (typically >180 °C) without an added catalyst. However, the high temperature required may lead in certain cases to destruction and degradation of the corresponding polymer [3–5]. Moreover, a lower temperature would also be a significant advantage from the processing point of view. To address this issue, catalysts have been employed to promote the ring-opening polymerization, involving Lewis acids [6–13] and nucleophilic catalysts [10–13]. For example, Ishida et al. examined many typical metal halides and phosphorus halides under solvent conditions and found that they showed good catalytic activities [6]. Endo and co-workers suggested that a combination of Lewis acid and nucleophilic catalyst effectively promotes the polymerization [12]. And

recently, they reported that acetylacetonato complexes of transition metals of the 4th period are highly efficient catalysts [13]. Despite these considerable efforts, there is still room for improvement, being a further reduction of polymerization temperature highly desirable. Another important question to address would be how a specific polymerization catalyst affects the structure of the final polymer, which is a crucial point for its final usefulness. It is well known that the polymer structure can have a great influence in its properties [1].

We recently illustrated the mechanism of the ring-opening polymerization of benzoxazine based on a detailed investigation of the polymerization behavior of a model *p*-cresol-aniline-based benzoxazine under various conditions [14]; work that combined also previously reported mechanistic studies [1,5,6,9,12,15,16]. With a better understanding of the mechanism, a patent was granted for new curable compositions [17]. In the present study, we have established the catalytic activities of a number of different catalysts and their effects on the structure of the final polymer. On the basis of these findings, a further understanding of the ring-opening polymerization process and the catalytic effects has been achieved, allowing, in principle, the tailoring of a particular structure, and therefore the polymer final properties.

2. Experimental section

2.1. Materials

All reagents and solvents were purchased from Aldrich Chemical Co. and used as received. Benzoxazine **1** was prepared according to

* Corresponding authors.

E-mail addresses: rosamaria.sebastian@uab.es (R.M. Sebastián), jordi.marquet@uab.es (J. Marquet).

the reported procedure [18] and the purity is >95% as determined by ^1H NMR.

2.2. Measurements

^1H 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 ($\delta_{\text{TMS}} = 0$) for ^1H NMR spectra. The solvent for NMR measurement was deuterated DMSO. 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 $10^\circ\text{C}/\text{min}$. About 5 mg of samples were tested in high-pressure closed aluminum pans.

2.3. General procedure for ring-opening polymerization of benzoxazine 1

In a test tube, benzoxazine **1** (113 mg, 0.5 mmol) and a catalyst (1 mol %) were dissolved in acetone (~ 0.2 mL). The mixture was dried at room temperature under high vacuum for ~ 1 h and heated in the conditions tabulated in Table 1 (columns 3 and 4, “conversion” and “ratio”). Then the resulting mixture was subjected to routine analysis.

2.4. Calculation of conversion of benzoxazine 1 and the ratio of phenolic to phenoxy CH_2 units

- (1) Calculation of conversion of **1**: As shown in Fig. 1a, the signals around 5.4 and 4.6 ppm are due to the CH_2 units of oxazine ring of benzoxazine **1**, while the signals at 6.0–3.5 ppm are attributed to all the CH_2 units of polymer and starting benzoxazine. If x represents the signal integration intensity of the CH_2 unit of benzoxazine **1** and y represents the signal integration intensity of all the CH_2 units of polymer and starting benzoxazine, the conversion of **1** was then calculated according to the following equation: $[(y - 2x)/y] \times 100\%$.
- (2) Calculation of the ratio of phenolic to phenoxy CH_2 units: As shown in Fig. 1b, the signal at 4.7–4.0 ppm was ascribed to phenoxy CH_2 units and the signal at 4.0–3.5 ppm was because of phenolic CH_2 units. If m and n represent the signal integration intensity of phenolic and phenoxy CH_2 units respectively, the ratio of phenolic to phenoxy CH_2 units is m/n .

3. Results and discussion

3.1. Comparison of the catalytic activities of various catalysts

Previous studies [1,5,6,9,12–16] on the polymerization mechanism of benzoxazine (Scheme 1) indicate that ring-opening polymerization of benzoxazine might include three main different ring-opening patterns, resulting in different intermediates. *O*-attack, *N*-attack and *Aryl*-attack can be involved in subsequent electrophilic reactions of the intermediates, and various phenoxy CH_2 units (true + general phenoxy CH_2 units) and phenolic CH_2 units (true + general phenolic CH_2 units) can be produced. Phenoxy CH_2 units are labile and finally rearrange into relatively stable phenolic CH_2 units. The ring-opening and electrophilic reactions are fast, while the rearrangement proceeds in relatively slower rate.

With this knowledge in hand, we decided to use the *p*-cresol-aniline-based benzoxazine **1** as a monomer. The thermally accelerated polymerization reactions were carried out in the presence of 1 mol % catalyst at 150°C for different times. The rate of ring-opening was estimated by the conversion of **1** (150°C , 0.5 h) and the rate of rearrangement by the ratio of phenolic to phenoxy CH_2 units (150°C , 5 h), which were determined by ^1H NMR analysis of

the cured mixture in deuterated DMSO (Table 1). The use of deuterated DMSO as ^1H NMR solvent instead of deuterated chloroform provides higher resolution and allows for a better analysis of the spectra. For details, see experimental part.

3.1.1. The rate of ring-opening under various catalysts

As it is described in Table 1, no ring-opening occurred in the absence of a catalyst at 150°C for 0.5 h (Table 1, entry 1). The monomer was completely consumed in the presence of Lil, shown to be a very active catalyst (Table 1, entry 2), confirming the results previously described by us [14]. Next, we tested a variety of lithium-based Lewis acids and found a very significant effect of the anion part on the catalyst activity. In the case of LiClO_4 and LiSCN , the monomer was efficiently consumed (Table 1, entries 3 and 4). Lower conversions were observed for LiBr , LiOPh and LiSPh (Table 1, entries 5–7). Utilization of LiCl , LiOAc , and LiOTf as a catalyst resulted in almost no conversion (Table 1, entries 8–10). An interesting result was that observed by using LiOTf or NaI separately as catalyst; in both cases almost no ring-opening occurred, but their combination led to significant conversion (Table 1, 10–12). These results suggest that the activity of lithium cation is affected by the anion partner, showing a cooperative effect between the active electrophile (Li^+) and the active nucleophile (I^-).

As a general trend, we observe that anions with high nucleophilicity and good leaving group ability facilitate the polymerization. This trend is followed in the series $\text{I}^- > \text{Br}^- > \text{Cl}^-$ or $\text{PhO}^- > \text{AcO}^- \approx \text{TfO}^-$. However, some exceptions exist, such as ClO_4^- that shows a good performance in spite of its low nucleophilicity. We attribute this behavior to a third effect, the structure of the catalyst in the medium. In the case of LiClO_4 , the lithium cation, being relatively free, probably shows higher activity.

We also checked some other catalysts. High conversions were achieved by using $\text{Zn}(\text{OTf})_2$ or FeCl_3 as catalyst (Table 1, entries 13 and 14), but in all cases lower than the obtained with Lil or LiClO_4 . Moderate conversions were observed for $\text{PTS}\cdot\text{H}_2\text{O}$ (*p*-toluenesulfonic acid), NH_4I , ZnCl_2 and CuCl_2 (Table 1, entries 15–18). $\text{Al}(\text{OTf})_3$ and NH_4SCN provided lower conversions (Table 1, entries 19 and 20) and AgOTf , CoCl_2 and NaSCN very low ones (Table 1, entries 21–23). Basic catalysts where also tested in our conditions without success since DMAP (4-dimethylaminopyridine), EMI (2-ethyl-4-methylimidazole), 4-hydroxypyridine, 3-hydroxypyridine and 2-hydroxypyridine gave very low conversions (Table 1, entries 24–28). On the basis of these latest results, it seems that basic catalysts are not efficient for the polymerization of benzoxazine.

The dynamic DSC for the reactions of the above monomer mixtures were carried out and the results are also listed in Table 1 (see DSC thermograms in the Supporting Information). In general the DSC results show a good relation with the conversion of monomer, the higher the onset or maximum temperature, the lower the conversion observed (Table 1, 150°C and 0.5 h). To this general correlation, two exceptions appear, and both have the SCN^- anion as a protagonist. In these cases (entries 4 and 20), the activity of the catalyst, measured through the conversion of the starting monomer is significantly higher than what would be expected, according to the DSC results. The explanation to these behaviors calls for further investigation, but they could be associated to the bidentate nature of the thiocyanate anion.

3.1.2. Catalyst effects on the structure of the polymer

3.1.2.1. The rate of rearrangement of phenoxy to phenolic structure (ratio phenolic/phenoxy, Table 1, column 4, 150° , 5 h). The properties of the polybenzoxazine polymers are determined by their structure [1], being, for instance, the surface energy very dependent on the availability of hydrogen bonding and coordination sites. Indeed, OH groups present in the phenolic units in the polymer produce a

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