

# Imidazole Derivatives with an Intramolecular Hydrogen Bond as Thermal Latent Curing Agents for Thermosetting Resins

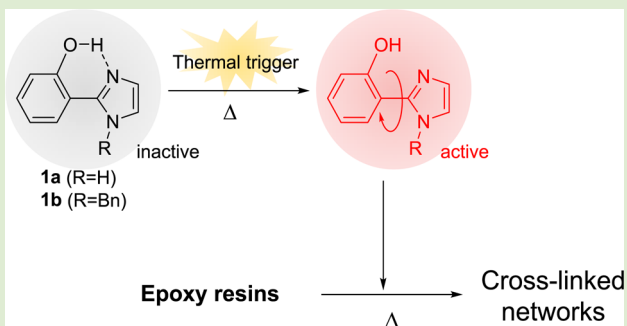
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## S Supporting Information

**ABSTRACT:** Epoxy resins are important thermosetting resins widely used in industrial applications. Though imidazoles as curing agents have attracted particular attention because of their high reactivity in chain polymerizations with epoxides, polymerization of a liquid epoxy resin containing imidazoles proceeds gradually even at room temperature. This makes it difficult to use such mixtures as one-component materials for industrial applications. To improve the shelf life of the mixtures, we have developed a very simple and powerful thermal latent curing agent, a 2-(2-hydroxyphenyl)imidazole derivative (**1**), having an intramolecular hydrogen bond between the phenolic hydroxyl group and the nitrogen atom of the imidazole ring, leading to suppression of reactivity of **1** toward epoxy resins at room temperature. It was confirmed that high reactivity of **1** toward epoxy resins at 150 °C was based on breakage of the intramolecular hydrogen, whereas the epoxy resin composition showed long-term storage stability at room temperature.



In general, epoxy resins have high thermal and electric resistances. They are important thermosetting resins widely used in industrial applications, such as in adhesives, structural materials, and coatings. To date, many types of chemical compounds have been used to cure epoxy resins;<sup>1–9</sup> however, imidazoles have only recently attracted particular attention because of their high reactivity in chain polymerizations with epoxides.<sup>10</sup> Both nucleophilic and base-catalyzed processes take place in the polymerization reactions,<sup>4</sup> and these processes can be altered by introducing substituents on the imidazole rings.<sup>11</sup>

However, it is difficult to control the intrinsic high reactivity of imidazoles toward epoxy resins. Indeed, a liquid mixture consisting of imidazoles and epoxy resins is gradually converted to form an insoluble solid of cross-linked polymer networks even at room temperature. This makes it difficult to use such mixtures as one-component materials for industrial applications such as the fabrication of electronic and fine parts. To improve the storage stability, latent curing agents have been developed.

Hamerton and co-workers proposed the use of metal cation–imidazole salt complexes as thermal latent curing agents.<sup>12,13</sup> Shin and co-workers prepared polycaprolactone microcapsules containing imidazole derivatives to achieve one-component epoxy resin materials with long shelf life at 20 °C.<sup>14,15</sup> However, these curing agents are powder-like materials, and they present a serious problem of heterogeneous dispersion in resins. These agents aggregate and do not permeate into fine spaces in resins. This leads to inadequate curing in micrometer- or submicrometer-sized narrow spaces. Recently, Szychaj and co-

workers reported that imidazolium salt ionic liquids can act as homogeneous thermal latent curing agents for epoxy resins. The ionic liquids have long-term storage stability and good curability around 150 °C, while somewhat complicated synthetic processes are required, and some of them need to be activated above 200 °C.<sup>16</sup>

In this communication, we feature a 2-(2-hydroxyphenyl)imidazole derivative (**1**),<sup>17</sup> which has an intramolecular hydrogen bond between the phenolic hydroxyl group and the nitrogen atom of the imidazole ring (Scheme 1). It is expected that the intramolecular hydrogen bond in **1** would restrain the nucleophilicity of the imidazole moiety and that the curability of **1** toward epoxy resins would be shown by breaking the intramolecular hydrogen bond with heat. Herein, we have applied **1** as a thermal latent curing agent, to our knowledge for the first time, and evaluated its reactivity and storage stability, in an epoxy resin.

Imidazole derivatives **1a** and **1b** were synthesized from glyoxal, salicylaldehyde, and amines in a few reaction steps (see Supporting Information (SI)).<sup>18</sup> To examine the intramolecular hydrogen bonding of **1a** and **1b** at various temperatures, <sup>1</sup>H NMR spectral measurements were performed in DMSO-*d*<sub>6</sub>. In the case of **1a**, it is difficult to confirm the breaking of the intramolecular hydrogen bond because of the overlapping of

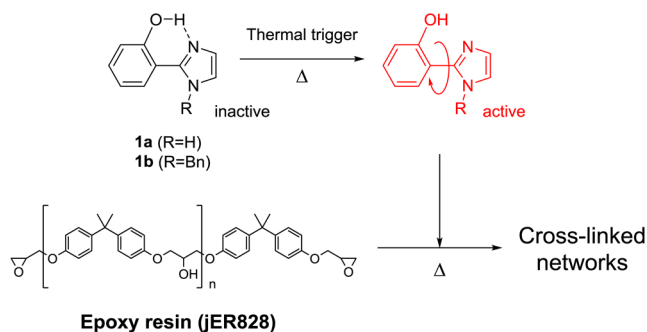
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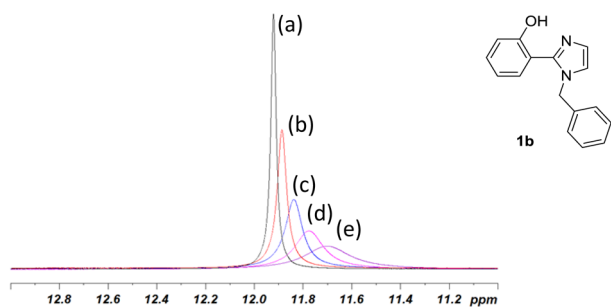
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### Scheme 1. One-Component Thermal Latent Curing System Consisting of an Epoxy Resin (jER828) and an Imidazole Derivative 1 with an Intramolecular Hydrogen Bond

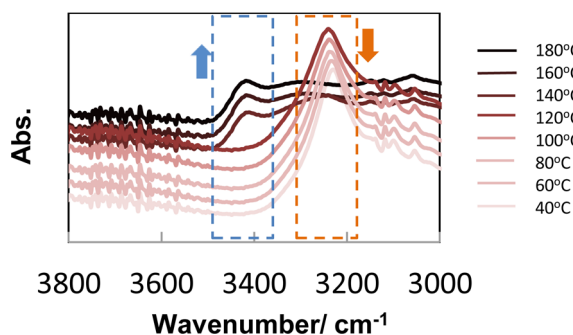


the peaks of protons on the heteroatoms (see SI). However, the phenolic proton of **1b** was clearly observed at 11.9 ppm as a sharp singlet peak at 23 °C (Figure 1a). Upon increasing the



**Figure 1.** Peak shift of the phenolic proton of **1b** in  $^1\text{H}$  NMR spectral measurements with  $\text{DMSO-}d_6$  at (a) 23 °C, (b) 40 °C, (c) 60 °C, (d) 80 °C, and (e) 100 °C.

temperature, the peak shifted to a higher magnetic field region and broadened, suggesting that the intramolecular hydrogen bond was partially unlocked (Figure 1b–e).<sup>19</sup> Furthermore, FT-IR measurements of **1a** showed a clear spectral change upon heating (Figure 2). Above 140 °C, a broad peak at 3230

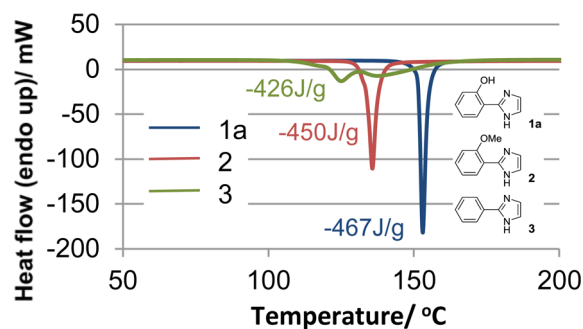


**Figure 2.** FT-IR spectral changes of **1a** upon heating, over the temperature range 40–180 °C.

$\text{cm}^{-1}$  disappeared, whereas another peak at 3417  $\text{cm}^{-1}$  appeared. Both peaks are assigned to the stretching vibration of hydroxyl groups. The spectral change indicated that the hydroxyl group of **1a** becomes free from intramolecular hydrogen bonding. FT-IR spectra also suggested that the phenolic benzene ring is fixed pointing toward the imidazole ring at a lower temperature because of intramolecular hydrogen bonding, which is then broken by thermal treatment to become

the activated state. These NMR and FT-IR spectral changes caused by a change in temperature prompted us to use **1a** as a thermal latent curing agent for a bifunctional epoxy resin, jER828 (Mitsubishi Corporation, Japan).

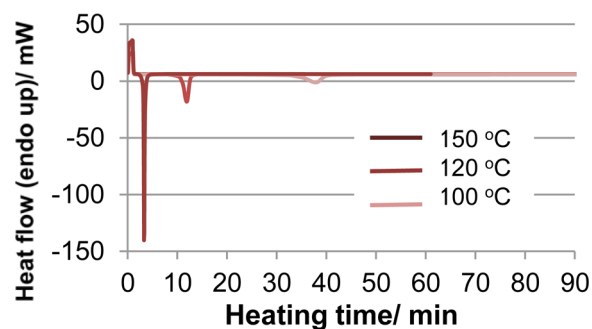
We evaluated the curability using differential scanning calorimetry (DSC) with jER828 compositions containing 11 mol % of **1a** (Figure 3). Although **1a** remains a powdery



**Figure 3.** DSC curves of jER828 compositions containing 11 mol % of **1a**, **2**, or **3**.

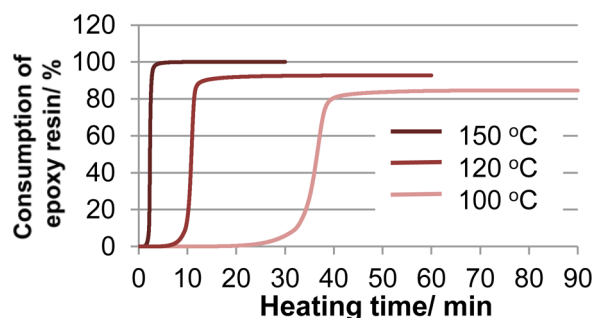
material, it was compatible with the epoxy resins. It is noteworthy that jER828 and **1a** mixed homogeneously and that a clear composition was obtained after mixing with a three-roll mill. As control samples, compositions containing the same molar quantity of 2-(2-methoxyphenyl)imidazole (**2**) or 2-phenylimidazole (**3**) were also prepared. Mixtures of the resin with **2** or **3** were heterogeneous even after mixing them. The compatibility of **1a** with the resin arises from its intramolecular hydrogen bonding, which inhibits intermolecular hydrogen bonding between curing agents. These three compositions were then heated from 50 to 250 °C under an atmosphere of nitrogen. A scan rate of 10 °C/min was used. The curing process of each sample was observed in situ. The curing exotherms of these epoxy mixtures were approximately 450 J/g, which indicated that the imidazole derivatives **1a**, **2**, and **3** have similar curability. However, the temperatures required to initiate the different curing reactions clearly differed. The epoxy composition of **1a** (jER828/**1a**) had a sharp exothermic peak above 150 °C. However, the peak of the composition of **2** (jER828/**2**) was largely shifted to the lower temperature region, while **3** (jER828/**3**) had broad exothermic peaks. These results indicated that **1a** has high reactivity toward epoxy resins, as well as toward the other control imidazole derivatives, and that the intramolecular hydrogen bond of **1a** contributes to restraining the reactivity in the lower temperature region.

The reactivity of **1a** toward the epoxy resin at various temperatures (150, 120, and 100 °C) was then investigated using an isothermal DSC method. The results of a heat flow analysis of a jER828/**1a** composition are shown in Figure 4. A sharp exothermic peak was observed after 3 min of heating at 150 °C. However, isothermal peaks observed upon heating at 120 or 100 °C were rather broad; this became even more pronounced at lower temperature. This peak broadening may result from diffusion control because of an increase in viscosity during the polymerization. Samples of jER828/**2** and jER828/**3** were also subjected to isothermal DSC analysis (see SI). A similar tendency was observed for these compositions; however, the exothermic peaks appeared earlier than in the case of the jER828/**1a** composition.



**Figure 4.** Isothermal DSC scans of a composition of jER828 and **1a** (jER828/1a) at 150, 120, and 100 °C.

To discuss the reactivity of these imidazole derivatives, it is useful to convert the obtained exothermic peaks to the consumption rate of epoxy resins, which provides an indication of the curing speed (Figure 5). We found that the jER828/1a

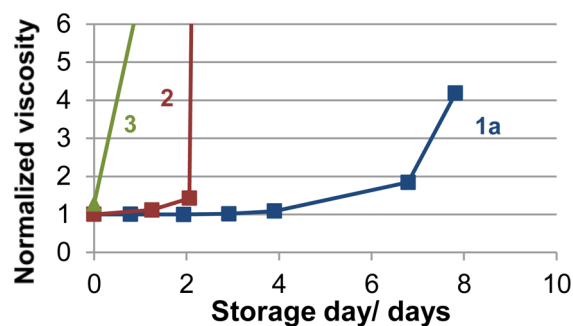


**Figure 5.** Consumption of epoxy resins in isothermal DSC analysis of the jER828/1a composition at 150, 120, and 100 °C.

composition cured rapidly at 150 °C, with almost 100% consumption of the epoxy resins. However, when heating at 120 or 100 °C, the composition showed no marked heat flow change. In these cases, induction periods (7 min at 120 °C and 24 min at 100 °C) were observed. These results indicated the suitability of **1a** as a thermal latent curing agent, and it is expected that the jER828/1a composition could be used as a one-component thermosetting resin.

The jER828/2 composition exhibited shorter induction periods than the jER828/1a composition (see SI). Furthermore, the jER828/3 composition showed no induction period at any of the temperatures considered here. These results indicate that the jER828/1a composition has better storage stability than the compositions of **2** or **3**. All had high curability. We confirmed that the intramolecular hydrogen bond of **1a** is important for the storage stability of jER828 compositions.

The storage stability of these compositions was further evaluated by measuring their changes in viscosity at 23 °C (Figure 6). We consider that the composition can be stored without a decrease in stability if the numerical value of the normalized viscosity is not >2. In the cases where jER828 compositions contained **2** or **3**, which have no intramolecular hydrogen bonding, the viscosity increased rapidly after mixing, and the product solidified within 2 days. However, the viscosity of the jER828/1a composition did not increase at all over a period of 3 days, but thereafter it slowly increased for up to a week. These findings demonstrated that the nucleophilicity of the imidazole ring of **1a** is well restrained at 23 °C by intramolecular hydrogen bonding.



**Figure 6.** Storage stability of jER828 compositions containing **1a**, **2**, or **3**.

In summary, we described a new thermal latent curing agent **1a** having an intramolecular hydrogen bond. This simple organic compound was easily synthesized and mixed homogeneously with epoxy resins. NMR and FT-IR spectral measurements suggest that heating induces breakage of the intramolecular hydrogen bonds. Its high reactivity toward epoxy resins at 150 °C was confirmed. The epoxy resin composition has long-term storage stability at room temperature. In conclusion, our results indicate a new and simple strategy for the development of both thermal latent curing agents and one-component thermosetting resins for application in various fields in the chemical industry.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsmacrolett.5b00601.

Materials, measurements, synthesis of latent curing agents, and experimental methods (PDF)

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### Notes

The authors declare no competing financial interest.

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