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Polymerization–Depolymerization System Based on Reversible Addition-Dissociation Reaction of 1,3-Benzoxazine with Thiol

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Supporting Information

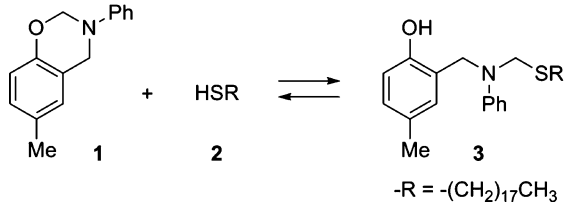
ABSTRACT: The reversible nature of the addition reaction of 1,3-benzoxazine and thiol at ambient temperature was discovered by investigating the reaction with using *p*-cresol-derived *N*-phenyl benzoxazine **1** and 1-octadecanethiol **2**. The reaction was performed in several deuteriated media involving $CDCl_3$ and $CDCl_3$ + CD_3OD, for monitoring their reaction by ^1H NMR spectrometry. $CDCl_3$ was a favorable solvent for the efficient progress of the reaction, and its combination with CD_3OD allowed further acceleration of the reaction. In both cases, the reaction proceeded until conversion of **1** reached a certain ceiling value, to suggest that the reaction was reversible. This reversible nature was concretely confirmed by finding a dissociation reaction of isolated **3** into **1** and **2** in $CDCl_3$. Analogously, a bisphenol A-derived bifunctional benzoxazine **4** and 1,6-hexanedithiol **5** underwent the polyaddition in $CDCl_3$ + CD_3OD at ambient temperature to afford the corresponding polymer **6**. Successful depolymerization of **6** into small fragments was achieved by dissolving **6** in $CDCl_3$.

One of the currently evolving topics in the field of polymer chemistry is the development of polymer materials with using covalent bonds that can be reversibly formed and dissociated.[1−4] Incorporation of such dissociable covalent bonds into polymers allows (1) depolymerization into the corresponding monomers and (2) de-cross-linking of three dimensionally networked polymers into the corresponding linear ones, which can be cross-linked again on demand. These systems have been extensively investigated from the viewpoint of chemical recycling of polymer materials.[1,5] In addition, potential applicability of those systems to the design and development of dissociable adhesives[6−8] and self-healable polymer materials[2,4,9−11] is of recent expanding interest. The reversible reactions that have been employed therein involve (1) equilibrium polymerizations,[1,12−17] (2) the Diels–Alder and retro Diels–Alder reactions,[7,8,18−20] (3) the reversible ring-opening reaction of azalactones with phenols,[21−23] (4) olefin metathesis,[24−29] and (5) the thermal or photolytic homolysis of covalent bonds into stabilized radicals and their recombination to recover the covalent bonds.[6,10,11,30]

Herein, we report our discovery of the reversible nature of the addition reaction of 1,3-benzoxazines and thiols and its application to a new polyaddition–depolymerization system. So far, 1,3-benzoxazines have been investigated as a class of cyclic monomers that undergo the ring-opening polymerization to afford the corresponding polymers possessing excellent thermal and mechanical properties.[31−33] Besides this main focus of interest, ring-opening addition reactions of benzoxazines with nucleophilic reactants into the corresponding adducts have become another important target of exploring because some of them proceed at ambient temperature and, thus, are applicable to polymer synthesis, free from energy consumption. One of the examples is the reaction with resorcinol that has been reported by us,[34] and another one is that, with thiols, which have been successfully applied to highly efficient curing systems by Gorodisher et al.[35] and Yagci et al.[36] Independently, we have focused our attention on the fundamental aspects of the reaction behaviors of benzoxazines with thiols to discover the reversible nature of the reaction that is the highlight of the present contribution. A model system consisted of a monofunctional benzoxazine and a monothiol as well as its development to the corresponding polyaddition–depolymerization system consisted of a bifunctional benzoxazine and dithiol are described.

The addition reaction of a monofunctional benzoxazine and monothiol was investigated as a model for polyaddition (Scheme 1). As the components, *N*-phenylbenzoxazine **1** derived from *p*-cresol and 1-octadecanethiol **2** were employed. These components were mixed in several deuteriated solvents, and the progress of the reaction at room temperature was monitored by ^1H NMR. The initial concentration of these components was 0.1 M in all the cases. For the detection of **1**, its characteristic singlet signals at around 5.3 and 4.6 ppm attributable to the two methylene groups in the oxazine ring

Scheme 1. Reversible Addition-Dissociation System Composed of Benzoxazine 1 and Thiol 2



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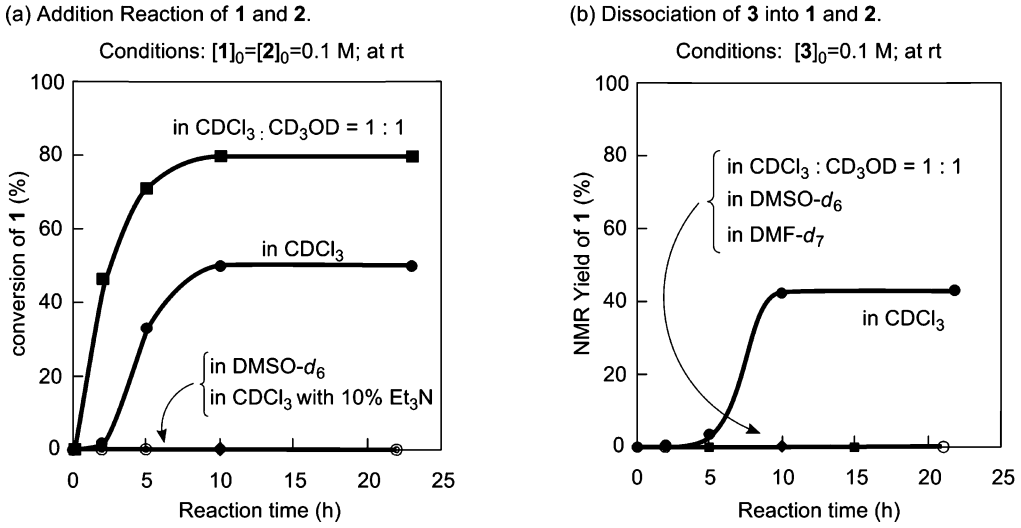
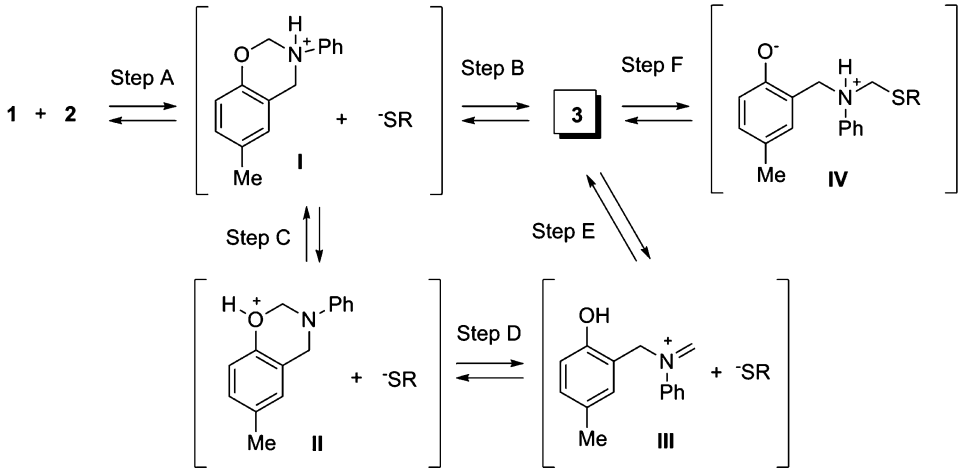


Figure 1. Time-dependences of (a) NMR yield of the adduct **3** formed by the addition reaction of benzoxazine **1** and thiol **2** and (b) NMR yield of **1** formed by the dissociation reaction of the adduct **3**.

Scheme 2. Possible Reaction Steps Involved in the Reversible System Consisted of Benzoxazine and Thiol



were used. The signal intensity of the former one was compared with that of the singlet signal for the methyl group on the aromatic ring to calculate the conversion of **1**. Figure 1a shows the resulting time−conversion relationships for the reaction investigated under four different conditions: In $CDCl_3$, the addition reaction of **1** and **2** proceeded smoothly until 10 h later from the starting point of the reaction, where conversion of **1** reached 50%. An interesting behavior of the reaction was observed after that. Conversion of **1** did not increase anymore, suggesting that the reaction attained equilibrium. In a 1:1 mixture of $CDCl_3$ and CD_3OD, the reaction proceeded faster to achieve a higher conversion of **1** at the equilibrium. Higher contents of CD_3OD would allow more efficient addition reaction; however, the poor solubility of thiol **2** avoided the relevant experiments. In contrast, in DMSO-d_6, the reaction did not proceed at all. Furthermore, addition of triethylamine inhibited the reaction completely.

Upon finding that the addition reaction of **1** and **2** proceeded most efficiently in a mixture of $CDCl_3$ and CD_3OD, the reaction was upscaled with using a 1:1 mixture of chloroform and methanol for the purpose of isolation of the corresponding adduct **3**. In this reaction medium, benzoxazine **1** and thiol **2** were mixed in a 1:0.6 molar ratio. The mixture was poured into an excess amount of methanol to precipitate the resulting adduct **3**. Benzoxazine **1** was soluble in methanol and, thus, easily removed from **3** by washing with methanol. On the other hand, thiol **2**, with a long alkyl chain, was insoluble and, thus, difficult to be washed by methanol; however, this issue was avoided by minimizing the amount of **2** to 0.6 equiv to **1**, otherwise adduct **3** was not successfully separated from unconsumed **2**. The chemical structure of **3** was confirmed by ^1H and ^{13}C NMR (Figures S1 and S2 in Supporting Information). The chemical shifts of the ^1H NMR signals depended significantly on solvent used for NMR measurement: The signals attributable to (1) the phenolic OH, (2) CH_2 in the Mannich bridge, (3) CH_2 located between nitrogen and sulfur atoms, and (4) the other CH_2 adjacent to sulfur atom shifted by changing $CDCl_3$ to DMSO-d_6, to imply that polarity of solvent influenced on the interaction between the phenolic and the amino groups. Later in the manuscript, the influence of the solvents on the NMR analyses of **3** is correlated with its dissociation behaviors in these solvents. During the ^1H NMR analysis of the adduct **3** in $CDCl_3$, its dissociation into benzoxazine **1** and thiol **2** was observed: Intensity of the signals at 5.3 and 4.6 ppm attributable to the methylene groups in the cyclic *N,O*-acetal moiety of **1** increased gradually, to suggest

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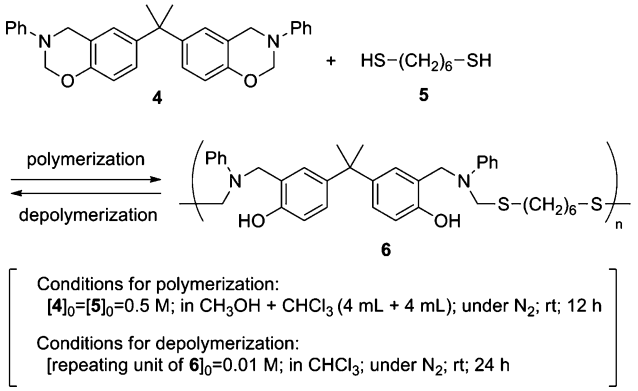
that the reactants **1** and **2** were in an equilibrium with the adduct **3**. Any signals attributable to byproducts and reaction intermediates were not observed. Figure 1b shows the time-dependences of the amount of **1** formed by the dissociation of four different media, which clarified the dissociation of **3** proceeded specifically in $CDCl_3$, while **3** was stabilized somehow in the other solvents.

The solvent effects observed herein are summarized as follows: (1) For the addition reaction, protic media was favorable, while polar but aprotic solvents were not suitable. Addition of triethylamine inhibited the reaction. (2) For the dissociation reaction, less polar media was favorable, while polar ones were not favorable. These tendencies can be correlated with the reaction mechanisms depicted in Scheme 2: As has been reported by Golodisher et al.,[35] the initial step of the addition reaction would be proton transfer from thiol to the nitrogen atom of benzoxazine (in step A). Protic solvents such as methanol can promote this step, while proton acceptors such as DMSO and triethylamine can interfere with it. The resulting species **I** activated by protonation would undergo the S_N2-type nucleophilic attack of thiolate (in step B), leading to the formation of the corresponding adduct **3**. Another possible route from **I** to **3** involves proton transfer from the nitrogen atom to the oxygen atom in the benzoxazine ring (in step C). The protonated benzoxazine **II** can undergo the ring-opening reaction into an acyclic species **III** bearing iminium moiety (in step D), to which thiolate can attack to give the adduct **3** (in step E). In highly polar media, the adduct **3** can be transformed into **IV** with a zwitter ionic structure (in step F). On the other hand, the rate determining step of the dissociation of **3** would be the spontaneous dissociation of **3** into the species **III** and thiolate, which is enabled by delocalization of the lone pair on the nitrogen atom into the carbon−sulfur σ^* bond. This spontaneous dissociation would be inhibited by protonation on the nitrogen atom that gives **IV** (in step E). This highly polar form can be stabilized in highly polar media such as DMSO-d_6, DMF-d_7, and a mixture of $CDCl_3$ and CD_3OD, to reduce the concentration of **3** and, thus, would be responsible for the inhibition of the dissociation of **3**. Coincidently, this hypothesis is in good accordance with the observation in the NMR analyses of **3**, that is, the chemical shifts depended on solvent significantly. This dependence would have been caused by influence of polarity of solvent on degree of proton transfer from the phenolic moiety to the amino groups in **3**.

The discovery of the reversible nature of the reaction of benzoxazine and thiol prompted us to exploit it for developing a reversible polymerization−depolymerization system composed of bifunctional benzoxazine **4** and dithiol **5** (Scheme 3). First, **4** and **5** were mixed in a 1:1 mixture of chloroform and methanol, the media that maximized the yield of the benzoxazine-thiol adduct in the model system. As a result, the corresponding polymer **6** was formed and isolated. Figure 2 shows the SEC profile of **6**, from which M_n and M_w of **6** were estimated to be 3900 and 6200, respectively. These values suggested that the chain extension in the polyaddition system was not efficient to obtain high molecular weight polymers due to the low efficiency in the addition reaction of benzoxazine and thiol, and this consideration is in good accordance with the reversible nature of the model system in which the maximum conversion of benzoxazine at the equilibrium was 80%. In fact, the residual benzoxazine was detected by ^1H NMR analysis of **6** (Figure S3 in Supporting Information). The spectrum indicated a singlet at 5.4 ppm attributable to the methylene protons in

Scheme 3. Reversible Polyaddition−Depolymerization System Composed of Bifunctional Benzoxazine 4 and Dithiol 5



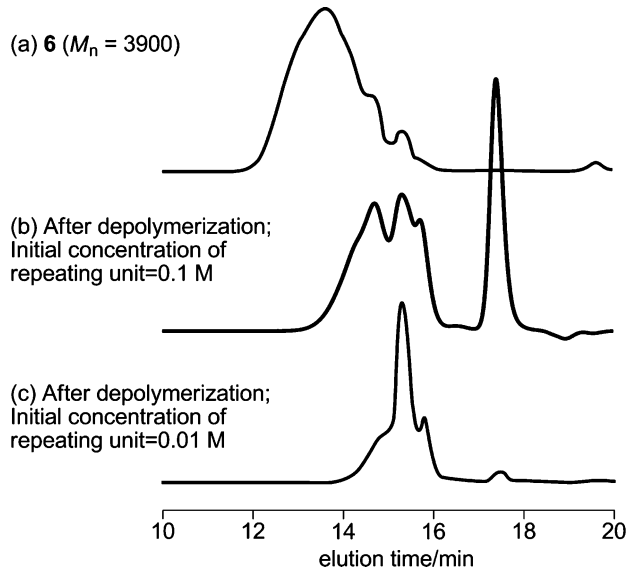


Figure 2. SEC profiles of (a) polymer **6**; (b) a mixture of products obtained by the depolymerization of **6** with setting the initial concentration of the repeating unit to be 0.1 M; (c) a mixture of products obtained by the depolymerization of **6** with setting the initial concentration of the repeating unit to be 0.01 M.

the benzoxazine ring. With using this signal, the conversion of benzoxazine in the present polyaddition system was roughly estimated to be 88%. Comparison of the spectrum of **6** with that of the model compound **3** clarified their structural similarity, that is, in both the spectra, signals that appeared at 4.4 and 4.7 ppm implied that both of the compounds bear -N−CH_2-S- and -aryl-CH_2−N- linkages.

Finally, the polymer **6** was dissolved in $CDCl_3$ at room temperature with expecting its depolymerization, since the benzoxazine-thiol adduct **3** dissociated into benzoxazine **1** and thiol **2** under the same conditions. The initial concentration of the repeating unit was adjusted to 0.1 M. After 24 h, the solution was analyzed by ^1H NMR. The resulting spectrum is shown in Figure S3 in Supporting Information. Formation of the benzoxazine moiety by depolymerization was confirmed by observing two singlet signals at 5.3 and 4.6 ppm attributable to the two methylene groups in the cyclic *N,O*-acetal moiety of benzoxazine moiety. From the relative signal intensities, conversion of the repeating unit into benzoxazine moiety was

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calculated to be 41%. As shown in Figure 2, the SEC profile of the resulting mixture shifted from that of the polymer **6** to a lower molecular weight region, implying that the polymer **6** underwent the depolymerization. Concentrations of **4** and **5** at the equilibrium were increased significantly by reducing the initial concentration of the repeating unit of the polymer **6** to 0.01 M.

Figure S3 shows the ^{1}H NMR spectrum measured after 24 h. The conversion of the repeating unit into benzoxazine moiety estimated by the NMR analysis was 75%. SEC analysis of the solution confirmed successful depolymerization of the polymer **6** into fragments with low molecular weights (Figure 2).

In summary, we established a new polymerization−depolymerization system based on a newly discovered reversible nature of the addition reaction of benzoxazine and thiol. The system can be operated under ambient conditions, and the direction of the system, toward polymerization or toward depolymerization, is controllable by choosing appropriate solvent specifically. Future studies will focus on its potential applicability to chemical recycling, dissociable adhesives, and self-healable materials, with designing the polymer structures appropriately for specific demands.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details and the ^{1}H and ^{13}C NMR spectra used for the present study are given. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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