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A Highly Reactive Benzoxazine Monomer, 1-(2-Hydroxyethyl)-1,3-Benzoxazine: Activation of Benzoxazine by Neighboring Group Participation of Hydroxyl Group

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Introduction. Benzoxazines have received considerable attention because their ring-opening polymerizations afford the corresponding polymers having excellent properties such as high mechanical strength,[1] thermal stability,[2] and durability under a humid environment.[3] Benzoxazine monomers can be easily synthesized from various phenols, amines, and formaldehyde.[4] This versatile synthetic method has allowed development of various benzoxazines having functional groups[5] such as allyl,[6] propargyl,[7,8] diacetylene,[9] nitrile,[10,11] furyl,[12] epoxide,[13] amino,[14] and siloxy,[15] which were effectively used for various chemical modifications of the benzoxazine monomers and the corresponding polymers including cross-linking reactions. In addition, several benzoxazines[16,17] and its naphthalene-containing analogue (naphthoxazine)[18] having hydroxyl group have been developed. These literatures described convenient use of hydroxyl group for polycondensation and initiation of ring-opening polymerization of lactone. Recently, thermally induced polymerizations of benzoxazines having a 2-(2-hydroxyethoxy)ethyl group (=$CH_2CH_2OCH_2CH_2OH$) have been reported:[19] Because of the presence of OH group, the polymerizations of these monomers proceeded smoothly at relatively low temperature. Hydrogen bonding offered by OH may be a reason for it.

Herein, we report polymerization behavior of 3-(2-hydroxyethyl)-1,3-benzoxazine, a benzoxazine having a hydroxyl group. Our discovery of its high reactivity and the role of hydroxyl group in activating benzoxazine are described.

Experimental Section. *Synthesis of 1,3-Benzoxazine Having Hydroxyl Group **1a**.* **1a** was synthesized from *p*-cresol, 2-aminoethanol, and formaldehyde (Scheme S-1 in the Supporting Information). Alcohols were suitable solvents for the synthesis, and particularly, 2-methoxyethanol was the most suitable one because of its high boiling point that allowed the operation of the reaction at higher temperature (Table S-1 and Figure S-1 in the Supporting Information). The ^{1}H and ^{13}C NMR spectra of **1a** are shown in Figure 1.

*Thermally Induced Polymerization of **1a**.* Thermally induced polymerization of benzoxazine having hydroxyl group **1a** was carried out at 150 °C (Scheme 1). ^{1}H NMR analysis of the resulting mixture revealed that more than 90% of **1a** was consumed within 1 h, indicating that the reactivity of **1a** was remarkably higher than other *N*-alkylbenzoxazines **1b** (*N*-methyl-1,3-benzoxazine) and **1c** (*N*-*n*-propyl-1,3-benzoxazine) (Figure 2a). The formed polymer **2a** was isolated as diethyl ether-insoluble parts in 58% yield. ^{1}H and ^{13}C NMR spectra of **2a** revealed that it was a phenolic polymer having Mannich linkage (−aromatic−CH_2−NR−CH_2−aromatic−) (Figure 1).

The obtained polymer **2a** was treated with *tert*-butyl isocyanate to transform the hydroxyl groups into the corresponding urethanes for the purpose of estimation of the number- and weight-average molecular weights (M_n and M_w) of the resulting polymer **3a** by size exclusion chromatography (SEC). Previously, we reported that M_n and M_w of poly(*N*-phenyl-1,3-benzoxazine) were significantly underestimated by SEC due to the polarity of phenolic OH group, and its transformation into less polar *tert*-butylurethane permitted more reasonable estimation of M_n and M_w.[20] Similarly to these previous observations, SEC-estimated M_n and M_w of **2a** having free OH groups were estimated to be 130 and 210, respectively, while those of **3a** having *tert*-butylurethane moieties were 2300 and 3600.

Results. *Effect of Hydroxyl Group on the Polymerization Behavior of **1a**.* As shown in Figure 2a, the polymerization of **1a** was much faster than that of *N*-*n*-propylbenzoxazine (**1c**). Since the bulkiness of the *n*-propyl group (−$CH_2CH_2CH_3$) is comparable to that of 2-hydroxylethyl group (−CH_2CH_2-OH), the remarkably high reactivity of **1a** would be caused by participation of polar and potentially nucleophilic hydroxyl group in the polymerization mechanism (vide infra). *N*-Methylbenzoxazine (**1b**), which has a sterically less hindered methyl group, was more reactive than **1c**; however, **1b** was less reactive than **1a** to imply that a certain role of the hydroxyl group dominated the polymerization over the steric factor. In comparison with the hydroxyl group in **1a**, the 2-methoxyethyl group in benzoxazine **1d** had no effect to enhance reactivity. By masking OH as methyl ether, its polarity and nucleophilicity were lost, and at the same time, bulkiness was increased to result in the slow polymerization of **1d**.

The difference in reactivity between **1a** and *N*-methylbenzoxazine (**1b**) was more clearly observed when their polymerizations were performed at lower temperature, 120 °C. As shown in Figure 2b, **1a** was smoothly consumed and its conversion reached 90% at 6 h, while **1b** was consumed only in 20% in 6 h.

Next, polymerization of **1b** was performed with adding an equimolar amount of 2-(*N*,*N*-dimethylamino)ethanol (DMAE) to clarify whether such an amino alcohol can accelerate polymerization of benzoxazine in an intermolecular manner or not. As shown in Figure 2b, by adding DMAE, the polymerization of **1b** was accelerated effectively; however, it was still slower than the polymerization of **1a**, to suggest that hydroxyl group in **1a** would activate the benzoxazine moiety in an intramolecular manner.

Mechanism. The remarkable difference in reactivity between **1a** and **1b** let us postulate a mechanism where the hydroxyl group has an important role to promote the ring-opening reaction of **1a** (Scheme 2): First, **1a** would come to equilibrium with the corresponding zwitter ionic intermediate (ZI-1) having an iminium moiety and a phenoxide via reversible heterolytic bond scission of the cyclic *N*,*O*-acetal moiety.[21−23] Another type of zwitterionic intermediate is a carbocationic one (ZI-2), which is a tautomer of ZI-1. At this stage, the hydroxyl group would react with the imminium

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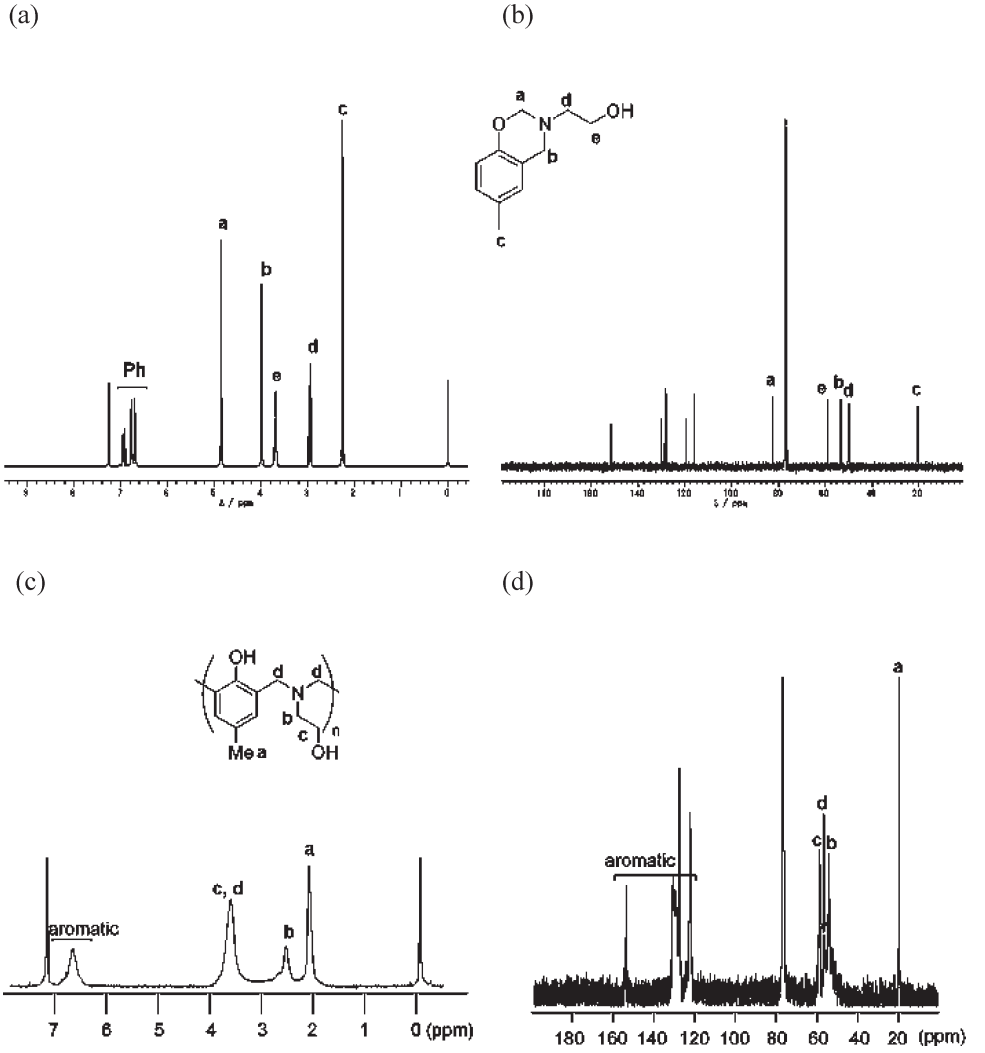
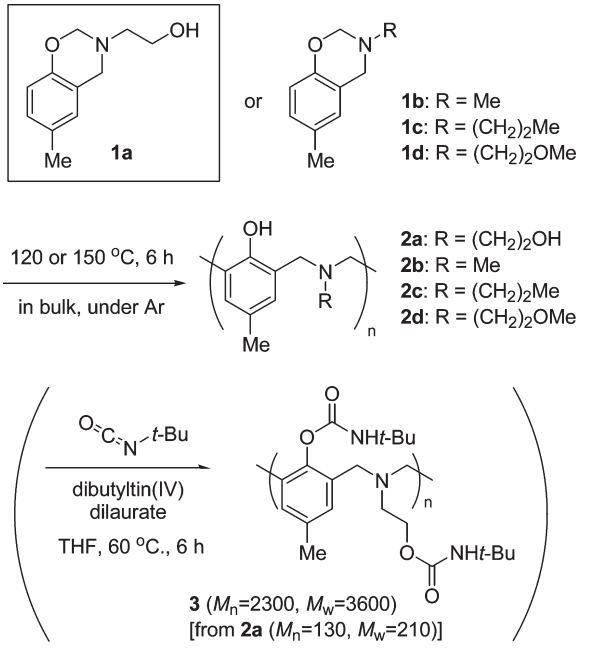


Figure 1. (a) ^{1}H NMR and (b) ^{13}C NMR spectra of **1a** and (c) ^{1}H NMR and (d) ^{13}C NMR spectra of **2a**.

Scheme 1. Thermally Induced Ring-Opening Polymerizations of Monofunctional Benzoxazines 1



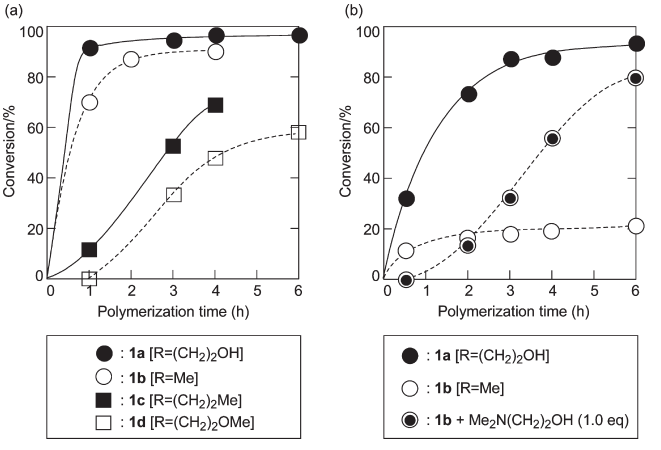
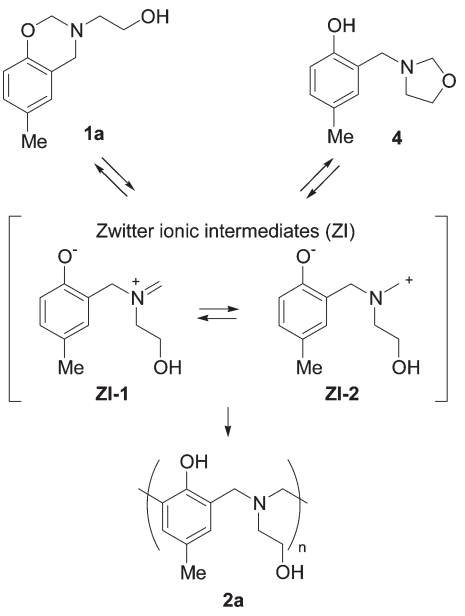


Figure 2. Time−conversion relationships for (a) the polymerizations of benzoxazines **1a**−**1d** at 150 °C and (b) those of **1a** and **1b** at 120 °C.

moiety of ZI intramolecularly to give oxazolidine **4**. Galià et al. have reported synthesis and isolation of an analogous oxazolidine, which was eventually obtained by their attempt to synthesize 3-[1,3-dihydroxy-2-methyl-2-propyl]-1,3-benzoxazine from *p*-cresol, paraformaldehyde, and 2-amino-2-methylpropane-1,3-diol.[24] The cyclization of ZI into **4** would be reversible,

Scheme 2. Reactions Involved in the Ring-Opening Polymerization of 1a



and the equilibrium nature between **1a** and **4** would result in high probability in formation of ZI, the proposed active species in the polymerization. In other words, the ring-opening reaction of **1a** into ZI was assisted by such a "neighboring group participation of hydroxyl group". Possible reactions of ZI toward the formation of poly(benzoxazine) are shown in Scheme S-2 (in the Supporting Information), which explains the importance of the rapid formation of ZI for the efficient progress of the polymerization. Another factor for the acceleration phenomenon would be the presence of phenol in **4**, which can act as an acidic catalyst to promote the ring-opening reaction of benzoxazine.

The equilibrium between **1a** and **4** was successfully observed by NMR spectroscopic analyses. The ^{1}H and ^{13}C NMR spectra shown in Figure 1 were measured just after dissolving **1a** (10 mg) in $CDCl_3$ (0.6 mL). The same solution was kept at room temperature for 24 h, and its ^{1}H NMR, ^{13}C NMR, and CH-COSY spectra were measured to confirm the formation of **4** (Figures S-2, S-3, and S-4 in the Supporting Information). Figure S-5a shows the time dependence of the ratio [**1a**]:[**4**] in the $CDCl_3$ solution. The content of **4** gradually increased, and the system reached the equilibrium after 12 h, where [**1a**]:[**4**] was 62:38. In another experiment, the solution was kept at room temperature for 6 h to obtain a mixture of **1a** and **4**, and then $CDCl_3$ was removed by evaporation to obtain a white crystalline solid (Figure S-5b). This solid was redissolved into $CDCl_3$, and its ^{1}H NMR was measured immediately to find that the solid was pure **1a**. When this solution was left at room temperature, a gradual increase of the amount of **4** was observed again.

Summary. *N*-(2-Hydroxyethyl)-1,3-benzoxazine (**1a**) underwent the polymerization much faster than other *N*-alkylbenzoxazines. The origin of this high reactivity would be the "neighboring group participation" of hydroxyl group, i.e., intramolecular reaction of hydroxyl group with cationic moieties of the zwitterionic intermediates formed by the ring-opening reaction of benzoxazine, affording a 5-membered cyclic *N*,*O*-acetal **4**. **1a** and **4** were in equilibrium through the zwitterionic intermediates, and this equilibrium increased the probability of presence of the intermediates in the system to promote the polymerization. The present concept of the "acceleration of the polymerization of benzoxazine by neighboring group participation of nucleophilic moiety" would contribute to effective molecular designs of highly reactive benzoxazine monomers.

Supporting Information Available: Experimental details and NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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