Selective Formation of Poly(*N*,*O*-acetal) by Polymerization of 1,3-Benzoxazine and Its Main Chain Rearrangement

Atsushi Sudo, Ryoichi Kudoh, Hiroshi Nakayama, Kazuya Arima, and Takeshi Endo*

Molecular Engineering Institute, Kinki University, Kayanomori, Iizuka, 820-8555, Japan

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ABSTRACT: Polymerization behavior of *N*-phenylbenzoxazine in bulk was studies in detail to discover new reaction pathways: (1) formation of an intermediary polymer having *N*,*O*-acetal-type linkage in the main chain and (2) its rearrangement into Mannich-type linkage in the solid state. Efficient promotion of the main chain rearrangement was achieved by using a dual system composed of imidazole and sulfonic acid.

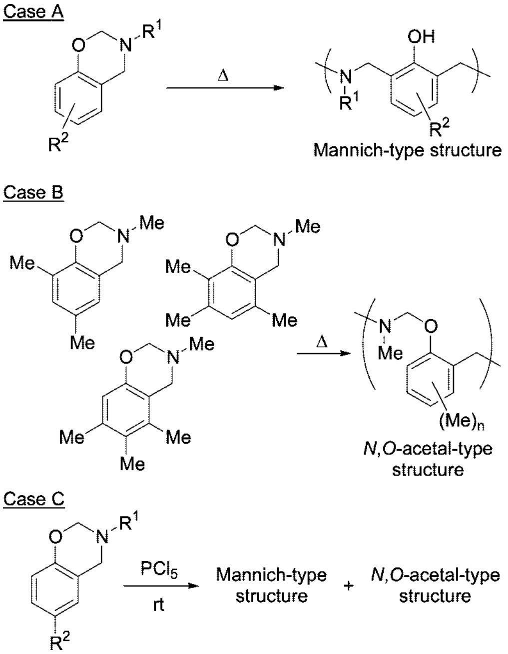
Introduction

Benzoxazine is a class of heterocyclic compounds capable of undergoing ring-opening polymerization to give the corresponding polymers, which surpass conventional materials in mechanical strength,[1] thermal stability[2] and durability under humid environment.[3] Benzoxazine can be easily synthesized by heating a solution of the corresponding phenolic compound, amine, and formaldehyde.[4] This simple and versatile synthetic method has supported development of a wide range of benzoxazine-type monomers involving curable multifunctional ones.[5−10] Recently, various benzoxazines having functional groups have been developed and applied to unique polymer systems.[11−15]

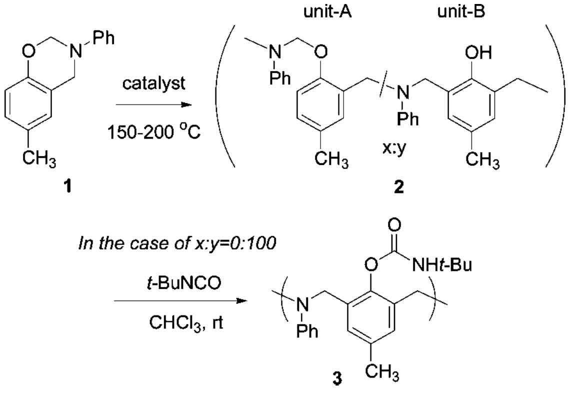
In general, the thermally induced polymerization of benzoxazines gives the corresponding polymers having phenolic moiety bridged by Mannich-type linkage ($-CH_2-NR-CH_2-$) (case A in Scheme 1).[16] The presence of the acidic phenol and basic amino groups allows the polymer chains to interact strongly with each other via hydrogen-bonding, giving rise to the excellent properties described above.[17−19] Besides this Mannich-type linkage, there has been reported another type of linkage, *N*,*O*-acetal, which can be formed under limited conditions: Ishida et al. have reported that the polymerizations of benzoxazines derived from phenols having two and three methyl groups gave the corresponding polymers having *N*,*O*-acetal-type structure (case B in Scheme 1).[20] In this case, the ortho position of the phenol moiety is blocked or sterically hindered to prevent formation of Mannich-type structure. They have also reported that the cationic polymerization with using PCl_5 at low temperature gave poly(benzoxazine) having both linkages in the main chain (case C in Scheme 1).[21]

Herein, we report our detailed investigation on a process for the formation of the phenolic poly(benzoxazine) having Mannich-type linkage in the main chain. We investigated a ring-opening polymerization of a cresol-derived *N*-phenylbenzoxazine **1**[22] to find that the polymerization does not directly afford the Mannich-type polymer, but affords a intermediary labile polymer having *N*,*O*-acetal linkage, which underwent a rearrangement reaction in the polymer main chain to give the Mannich-type linkage with generation of phenolic moiety (Scheme 2). Effects of several promoters on the main chain rearrangement are also described.

Scheme 1



Scheme 2



Results and Discussion

1. Imidazole-Promoted Polymerization. A bulk polymerization of **1** was performed in the presence of 1.0 mol % 2-ethyl-4-methylimidazole (EMI), which has been known as an effective promoter for the polymerization of a wide range of benzoxazine monomers.[23] Upon heating the system at 200 °C, **1** underwent rapid polymerization and was completely consumed within 1 h. ^{1}H NMR analysis of the resulting polymer **2** revealed that it was a phenolic polymer having Mannich-type linkage as was reported in various literatures.[20,21,24] In this polymer structure,

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* To whom correspondence should be addressed. Telephone and Fax: +81-948-22-7210. E-mail: tendo@me-henkel.fuk.kindai.ac.jp.

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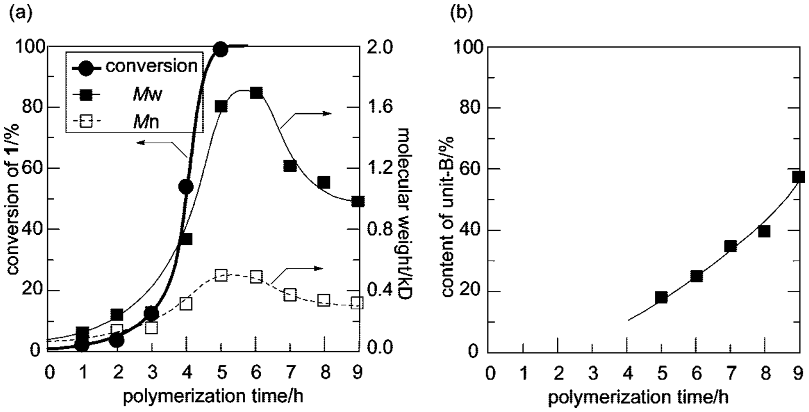


Figure 1. Time-dependences of conversion of **1** and molecular weights (a) and that of the polymer structure (b), for the polymerizations in the presence of 1 mol % 2-ethyl-4-methylimidzole (EMI) at 150 °C.

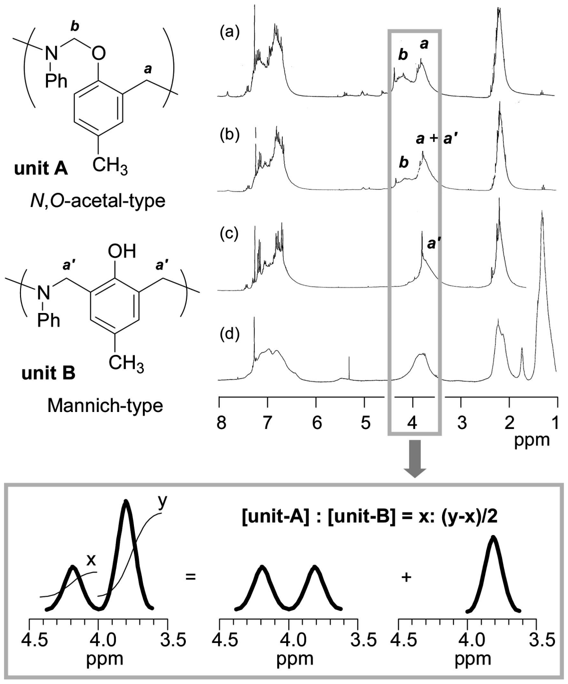


Figure 2. ^{1}H NMR spectra: (a) the polymer $\mathbf{2}_{t=5}$ obtained after heating for 5 h at 150 °C in the presence of 1 mol % EMI, (b) the polymer $\mathbf{2}_{t=9}$ obtained after heating for 9 h at 150 °C in the presence of 1 mol % EMI, (c) the polymer $\mathbf{2}_{200}$ obtained by heating $\mathbf{2}_{t=9}$ (isolated by precipitation with ether) at 200 °C for 1 h, and (d) the polymer **3** obtained by the reaction of the polymer $\mathbf{2}_{200}$ and *tert*-butylisocyanate.

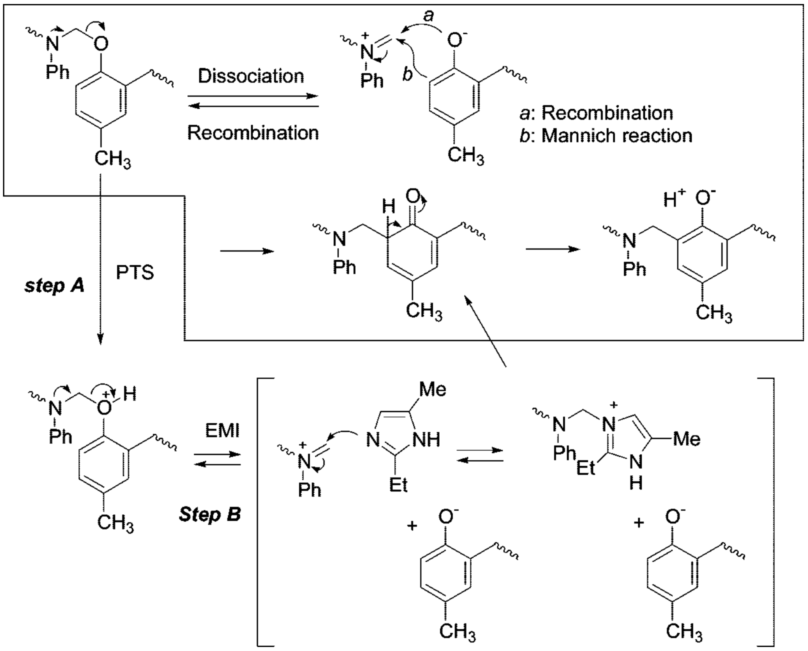
the phenolic moiety is located between two Mannich-type linkages symmetrically.

We next carried out the polymerization at 150 °C, with expectation that the polymerization would proceed much slower to permit us to follow it with more detailed structural analysis. In fact, **1** was gradually consumed and it took 5 h for its complete consumption (Figure 1a). Accordingly, the weight average molecular weight (M_w) of the resulting polymer estimated by size exclusion chromatography (SEC) increased. An interesting phenomenon was observed after the complete consumption of **1**: M_w started decreasing and became nearly half a t 8 h, which let us to suspect that the scission of the main chain might proceed at 150 °C in the presence of EMI. To clarify this issue, the polymer obtained at 5 h (represented as $\mathbf{2}_{t=5}$) and that obtained at 9 h (represented as $\mathbf{2}_{t=9}$) were studied by ^{1}H NMR (Figure 2). The spectrum for $\mathbf{2}_{t=5}$ indicated two broad signals around 3.8 ppm and 4.2 ppm, both of which should be attributable to methylene groups (Figure 2a). This spectroscopic feature was contradictory to the Mannich-type structure, which has a symmetric structure that permits two methylene groups to be equivalent and thus their signals should appear at the same position. The actual spectrum indicated lack of symmetry in the polymer structure, which made us to postulate that the main chain of $\mathbf{2}_{t=5}$ contained a significant amount of a repeating unit-A containing an *N*,*O*-acetal-type linkage. Due to the electron withdrawing nature of nitrogen and oxygen atoms, the ^{1}H NMR signal of the methylene group in the *N*,*O*-acetal-type linkage should appear at lower magnetic field than that of the another methylene group in the Mannich-type linkage. Another important feature of the spectrum was that the ratio in the signal intensity between the aromatic protons and the methylene protons was approximately 3:4. This ratio was constituent with the polymer structure predominantly consisted of the unit-A, but was contradictory to that exclusively consisted of unit-B, of which both of the ortho positions of the phenol moiety are substituted by methylene group and thus the ratio should be 2:4.

The ^{1}H NMR spectrum for the polymer $\mathbf{2}_{t=9}$ is shown in Figure 2b. The largest difference was observed in the methylene proton region, *i.e.*, the signal at 4.7 ppm weakened and that at 4.2 ppm gained its intensity. This means that the *N*,*O*-acetal linkage in the unit-A was labile and transformed into the Mannich-type structure. Based on the ratio in signal intensity between the two methylene signals, the content ratio [unit-A]:[unit-B] was calculated (for the details, see Experimental Section). As shown in Figure 1b, from 5 to 9 h, the content of unit-B gradually increased from 20% to 60%. It should be noted that this calculation was done based on the assumption that the obtained polymers had sufficiently large molecular weights enough to allow us to neglect possible errors caused by the ambiguity of the terminal structures. In reality, the polymers obtained in this work had relatively low molecular weights and thus clarification of the terminal structures should be necessary for more precise quantification. In addition, in the region 3.5−4 ppm in ^{1}H NMR, a signal for another structure can appear: Ishida and Sanders have reported that the polymerization of benzoxazine at high temperature gives the corresponding polymer being contaminated by the traditional phenolic structure without Mannich linkage, which can be formed by the main chain scission of the Mannich-type polymer with releasing a certain fragment, followed by recombination of the polymer chains.[16] However, this rearrangement can occur “after” the formation of the Mannch-type polymer, and it has no significant effect on the evaluation of the main chain rearrangement from the *N*,*O*-acetal-type polymer to the Mannich-type polymer.

The increase in the unit-B content can be eventually correlated with the decrease in the average molecular weights of the

Scheme 3



polymers estimated by SEC: The higher the unit-B content was, the lower molecular weights were estimated, to suggest the presence of hydrogen bonding between the phenolic moiety and the tertiary amino group in the unit-B that could allow the polymer to have a somewhat compact structure, leading to a longer retention time in SEC-analysis and consequent underestimation of molecular weights. This point will be discussed again (*vide infra*).

The polymer $\mathbf{2}_{t=9}$ was isolated by reprecipitation with diethyl ether. Then, this polymer was heated at 200 °C for 1 h. The SEC-estimated molecular weights of the resulting polymer (represented as $\mathbf{2}_{200}$) became smaller ($M_n = 200$, $M_w = 300$), but the weight loss during the reaction was negligible, suggesting that uncontrolled decomposition of the polymer into volatile fragments was negligible. As shown in the ^{1}H NMR spectrum for $\mathbf{2}_{200}$ (Figure 2c), the signal attributable to the *N*,*O*-acetal-type structure disappeared completely, to suggest that it underwent rearrangement to give the polymer exclusively consisted of unit-B. Based on the assumption that the polarity of the phenol moiety would cause significant deviation of the SEC-estimated molecular weights from the real ones, the polymer $\mathbf{2}_{200}$ was treated with *tert*-butylisocyanate to move its phenolic OH into the bulky and nonpolar *tert*-butylurethane moiety. As shown in the ^{1}H NMR spectrum for it (Figure 2d), polymer **3** was endowed with a *tert*-butyl group in its side chain and it inherited the Mannich-type structure from the polymer $\mathbf{2}_{200}$. A comparison of the signal intensity for the *tert*-butyl group with that for the methyl group confirmed the quantitative transformation of the phenolic OH in $\mathbf{2}_{200}$ into the corresponding *tert*-butyl urethane in **3**. SEC-analysis of **3** revealed that its M_n and M_w were 3300 and 4400, respectively, which were much higher than the SEC-estimated molecular weights of $\mathbf{2}_{200}$. These results suggested that the decrease in molecular weights during heating the polymer was not caused by its main chain scission, but was caused by the formation of a highly polar phenolic moiety by the rearrangement reaction of the *N*,*O*-acetal structure in the main chain into the Mannch-type structure.

Possible reaction pathways involved in the main chain rearrangement is shown in Scheme 3. The *N*,*O*-acetal would undergo heterolysis into the corresponding phenoxide and imminium moieties. The phenoxide can undergo not only recombination with the imminium moiety into the original *N*,*O*-acetal, but also another reaction at its ortho position. The resulting adduct can be aromatized into the thermodynamically more stable Mannich-type structure.

The main chain rearrangement was observed not only specifically at 150 °C but also at other temperatures. When **1** was heated at 180 °C in the presence of 1 mol % EMI, it reacted faster than at 150 °C and was completely consumed within 2 h (Figure 3a). At this point, the resulting polymer predominantly consisted of *N*,*O*-acetal-type repeating unit (Figure 3b). By continuous heating, the polymer underwent the main chain rearrangement smoothly to give the polymer completely consisted of the unit-B. We studied the polymerization at 200 °C again, to find that it was accompanied by the formation of the *N*,*O*-acetal-type structure and its main chain rearrangement (see Table S-2 in Supporting Information): Monomer **1** was completely consumed within 45 min, and the main chain rearrangement completed within 1.75 h.

2. Sulfonic Acid Promoted Polymerization. Polymerization of **1** was carried out at 150 °C in the presence of 1 mol % *p*-toluenesulfonic acid (PTS). As shown in Figure 4a, PTS was a much better promoter than EMI, in terms of consumption rate of **1**. However, its effect on the main chain rearrangement was comparable with that of EMI. At 180 °C, both of the monomer consumption and the main chain rearrangement were significantly accelerated (Figure 5).

3. Utilization of Dual System. On the basis of the results described above, our interest was focused on development of an efficient method to promote the main chain rearrangement at 150 °C. We examined a dual-promoter system comprising of PTS and EMI, and found that it promoted the rearrangement more efficiently than the single-promoter systems (Figure 6): First, we examined a PTS-promoted system with an increased amount of it. When the amount of PTS was increased from 1 mol % to 2 mol %, the monomer consumption was further accelerated but the main chain rearrangement was not. On the other hand, the dual-promoter system (1 mol % PTS + 1 mol % EMI) exhibited efficient promoting effect on the monomer consumption, although the consumption rate was lower than in the PTS-promoted polymerization. Furthermore, it promoted the main chain rearrangement more efficiently than the PTS-promoted system. Just after the complete monomer

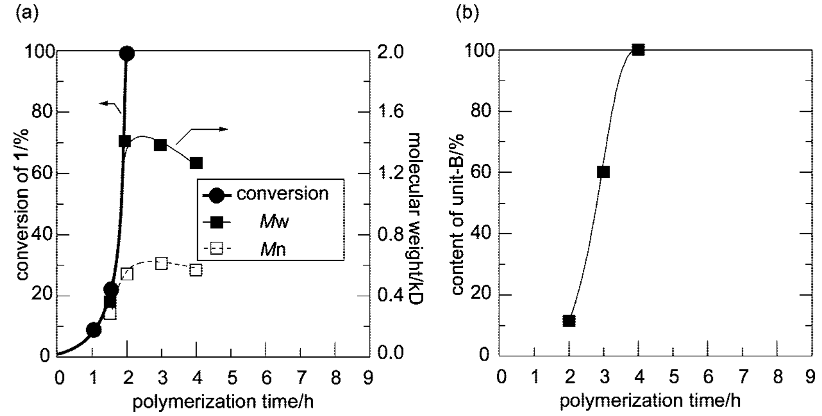


Figure 3. Time-dependences of conversion of **1** and molecular weights (a) and that of the polymer structure (b), for the polymerizations in the presence of 1 mol % 2-ethyl-4-methylimidzole (EMI) at 180 °C.

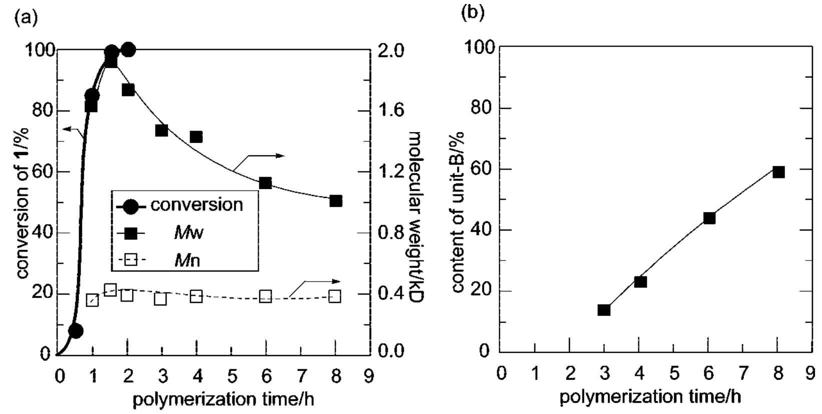


Figure 4. Time-dependences of conversion of **1** and molecular weights (a) and that of the polymer structure (b), for the polymerization in the presence of 1 mol % p-toluenesulfonic acid (PTS) at 150 °C.

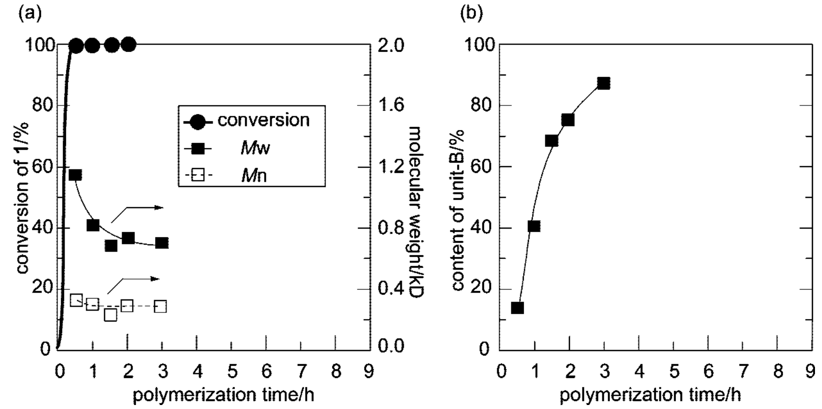


Figure 5. Time-dependences of conversion of **1** and molecular weights (a) and that of the polymer structure (b), for the polymerization in the presence of 1 mol % *p*-toluenesulfonic acid (PTS) at 180 °C.

consumption, the polymer already had more than 30% of the *N*,*O*-acetal-type units. This fast rearrangement in the early stages indicated potentially high activity of the dual-promoter system; however, in the middle to latter stages, it was decelerated significantly and the percentage of the unit-B content at 18 h was 78%, which was only slightly higher than that achieved in the PTS-promoted system. This deceleration would be caused by decreased freedom in motion of the polymer in solid state due to development of a hydrogen-bonding network between the Mannich-type units.

As is postulated by the discussion with using Scheme 3, successful main chain rearrangement would be achieved by (1) efficient dissociation of the *N*,*O*-acetal structure and (2) efficient prevention of the recombination of the ionic species into the original *N*,*O*-acetal structure. The former demand can be satisfied by addition of PTS, which can protonate the oxygen atom to promote the dissociation into the imminium and phenolic species. The latter demand would be satisfied by addition of EMI, which can react with the imminium moiety reversibly to prevent its rapid recombination with the phenolic OH. In other words, imidazole can wedge itself between the two species to avoid their recombination. By this efficient suppression of the recombination, the iminium species would be given an enough period that allows its motion to the position suitable for reacting with the ortho-position of the phenol moiety, *i.e.*, the Mannich reaction.

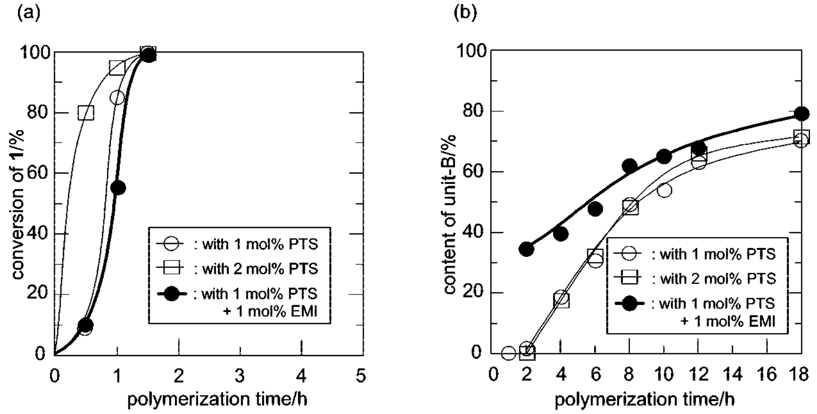


Figure 6. Time-dependences of conversion of **1** (a) and those of the polymer structure (b), for the polymerizations at 150 °C in the presence of 2 mol % PTS, 1 mol % PTS, and 1 mol % PTS + 1 mol % EMI.

Summary

Polymerization of *N*-phenylbenzoxazine afforded the corresponding Mannich-type structure via formation of intermediary poly(*N*,*O*-acetal) and its rearrangement in the polymer main chain. Development of a more efficient method to promote the rearrangement reaction at lower temperature is our next target.

Experimental Section

Materials. All reagents and solvents were used as received. Aniline, 35% aqueous solution of formaldehyde, and *p*-cresol were purchased from Wako Pure Chemical Industries and used for the synthesis of benzoxazine **1** according to the reported procedure.[22] 2-Ethyl-4-methylimidazole (EMI), *p*-toluenesulfonic acid, and *tert*-butylisocyanate were purchased from Wako Pure Chemical Industries.

Measurements. ^{1}H NMR spectra were recorded in chloroform-*d* ($CDCl_3$) on a JEOL EX-300 (^{1}H, 300 MHz) spectrometer, with tetramethylsilane (TMS) as an internal standard, acquisition period = 5.45 s; pulse delay = 1.55 s; accumulation times = 32. IR spectra were recorded with a JASCO FT/IR-460 Plus and the values were given in cm^{-1}. Number- and weight-average molecular weights (M_n and M_w) and polydispersity index (M_w/M_n) were estimated by size exclusion column chromatography (SEC) on a Tosoh HPLC HLC-8120 system, equipped with two consecutive polystyrene gel columns (G2500HXL, and G5000HXL) and refractive index (RI) and ultraviolet (UV, 254 nm) detectors, using THF as a eluent flow rate 1.0 mL/min, calibrated with polystyrene standards.

Polymerization of Benzoxazine 1. *General Procedure.* In a glass vessel, benzoxazine **1** (9.98 g; 44.0 mmol), *p*-toluenesulfonic acid (84 mg; 0.44 mmol), and 2-ethyl-4-methylimidazole (49 mg, 0.44 mmol) were placed and degassed. The mixture was heated at 70 °C under argon for approximately 30 min until it became homogeneous. From the resulting homogeneous viscous liquid, 13 portions (750 mg each) were taken and each of them was placed in a test tube. Argon inlets were attached to the resulting 13 test tubes and then they were heated in an oil bath at 150 °C. From time to time, these test tubes were taken away from the oil bath one-by-one, and each of the mixture was analyzed by ^{1}H NMR to determine conversions of **1** and the unit ratio. It was also analyzed by SEC to estimate M_n and M_w of the formed polymer.

Calculation of Unit Ratio [unit-A]:[unit-B]. As shown in Figure 2, the ^{1}H NMR spectra of the polymer **2** indicated two broad signals in the range from 3.5 to 4.5 ppm. The signal around 4.2 ppm was attributable to the *N*,*O*-acetal structure in unit-A, while the signal around 3.8 ppm was attributable to the Mannich structure in unit-A and unit-B. Based on this consideration, the unit ratio was calculated according to the following equation: [unit-A]:[unit-B] = x:(y − x)/2, where x:y is the signal intensity ratio for the two signals.

Reaction of the Polymer $\mathbf{2}_{200}$ *with tert-Butylisocyanate.* The Mannich-type polymer $\mathbf{2}_{200}$ (240 mg) was dissolved in chloroform (3 mL). The amount of phenolic OH group was calculated to be 1.0 mmol, based on the mass number of the Mannich-type repeating unit (=239). To this solution, *tert*-butylisocyanate (990 mg, 10 mmol) was added dropwise. The resulting homogeneous solution was stirred at ambient temperature for 24 h. The volatiles were removed under vacuum, and the residue was dissolved in 1 mL of chloroform and was poured into diethyl ether (10 mL). The resulting precipitate was collected by filtration with suction to isolate the polymer **3** (207 mg). On the basis of the mass number of its repeating unit (=324), the yield of **3** was calculated to be 63%.

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Supporting Information Available: The information available herein are tables summarizing the data obtained by polymerizations of **1**(time-dependences of conversion, molecular weights, and unit ratio) under various conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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