

Accelerating the Dehydrogenation Reaction of Alcohols by Introducing Them into Poly(allylamine)

Kouki Oka[†], Yusuke Kaiwa[†], Kazuki Kobayashi, Yuka Tobita, Kenichi Oyaizu*

Department of Applied Chemistry, and Research Institute for Science and Engineering,
Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan.

[†]K.Oka and Y.K. contributed equally to this work.

Supplementary Methods

Materials. Bromosuccinic acid was purchased from Sigma-Aldrich Co. Dimethyl sulfide borane, 1,8-diazabicyclo[5.4.0]-7-undecene (**DBU**), α -Bromo- γ -butyrolactone, and Iodomethane was purchased from Tokyo Chemical Industry Co. Poly(allylamine) was provided by Nittobo Medical Co. Sodium chloride and other chemicals were obtained from Kanto Chemical Co.

Measurements. ^1H NMR spectra were recorded on a JEOL ECX-500 spectrometer with chemical shifts downfield from tetramethylsilane as the internal standard. Infrared spectrum was obtained using a JASCO FT/IR-6100 spectrometer. Thermal analyses were performed with a TG/DTA 220 thermal analyzer at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen. The evolved hydrogen gas was characterized by gas chromatography (GC-8A, Shimadzu, MS-5A column, Ar carrier) and the resulting hydrogen peak at 1.2 min was recorded. the dehydrogenation

Preparation of 2-bromo-1,4-butanediol¹.

Under a nitrogen atmosphere, bromosuccinic acid (12 g, 60 mmol) was dissolved in THF (120 mL, 0.50 M) and was cooled in an acetone/dry ice bath. While cooling, dimethyl sulfide borane (12 mL, 0.12 mol) was added, and the solution was stirred for 60 hours. After the reaction, an excess amount of methanol was added, and the solution was then evaporated to give a yellow liquid of 2-bromo-1,4-butanediol (8.3 g, 82%): ¹H-NMR (500 MHz, Chloroform, δ (ppm)): 4.3 (m, -BrCH-, 1H), 3.8 (m, -OCH₂, 4H), 3.1-2.4 (br, OH, 2H), 2.1 (m, -CH₂-, 2H). FT-IR (ATR): ν (cm⁻¹) = 3339 (br; ν (O-H)).

Preparation of 1,4-butanediol-substituted poly(allylamine).

2-Bromo-1,4-butanediol (2.4 g, 14 mmol) was dissolved in water (28 mL) and poly(allylamine) aqueous solution ($M_w = 5,000$ or $25,000$, 20 wt%) (4.0 g, 14 mmol) was then added. Base was added if necessary (Table 2). The solution was stirred for 24-hours. After the reaction, dialysis with water, solvent removal, and vacuum drying yielded a yellowish powder, which was characterized as 1,4-butanediol-substituted poly(allylamine) (Figure S3b and S4). The polymer was soluble to water. $^1\text{H-NMR}$ (500 MHz, D_2O ; δ , ppm): 4.0–3.8 (NCH), 3.8–3.4 (OCH_2), 2.9–2.2 (NCH_2), 1.9–0.9 (Methylene and CH_2). IR (KBr, cm^{-1}): 3261 ($\nu_{\text{N-H}}$), 3061 ($\nu_{\text{O-H}}$), 2901 ($\nu_{\text{Methylene}}$).

Quaternization of 1,4-butanediol-substituted poly(allylamine).

1,4-Butanediol-substituted poly(allylamine) (introduction degree: 76%, 1.5 g, 4.0 mmol), sodium chloride (0.34 g, 8.7 mmol), sodium iodide (0.15 g, 1.0 mmol), and iodomethane (4.5 g, 32 mmol) was dissolved in water (60 mL). The mixture was stirred at 36°C for 24 hours. After the reaction, the solution was dialyzed with water for 24 hours. Then, the solution was evaporated to give a yellow powder. The polymer was soluble in water, and was characterized as the quaternized polymer, as follows (Figure S3c and S5): ¹H-NMR (500 MHz, D₂O, δ (ppm)): 4.0–3.1 (br, -NCH-, -OCH₂-, -CH₂-, -N⁺-CH₂-), 2.9–2.2 (br, -NCH₂-), 1.9-0.9 (br, Methylene and CH₂). FT-IR (KBr): ν (cm⁻¹) = 3260 (s; ν(O-H)), 2922 (s; ν(methylene)).

Preparation of γ -butyrolactone-substituted poly(allylamine).

α -Bromo- γ -butyrolactone (11 g, 64 mmol) was dissolved in methanol (32.0 mL) and poly(allylamine) aqueous solution ($M_w = 5,000$, 20 wt%) (4.6 g, 16 mmol) was then added. Base (**DBU**) was added. The solution was stirred for 24-hours. After the reaction, dialysis with water, solvent removal, and vacuum drying yielded γ -butyrolactone-substituted as a yellow powder. The reaction conditions and the introduction degree were summarized in Table S1. The polymer was soluble in water and was characterized as γ -butyrolactone-substituted poly(allylamine), as follows (Figure S6b). $^1\text{H-NMR}$ (500 MHz, D_2O ; δ , ppm): 3.7—3.5 (OCH_2), 3.2—2.9 (NCH), 2.7—2.3 (NCH_2), 2.0—1.0 (Methylene and CH_2). IR (KBr, cm^{-1}): 3285 ($\nu_{\text{N-H}}$), 2933 ($\nu_{\text{Methylene}}$), 1670 ($\nu_{\text{C=O}}$).

Quaternization of γ -butyrolactone-substituted poly(allylamine).

γ -butyrolactone-substituted poly(allylamine) (introduction degree: 70%, 0.96 g, 2.6 mmol), sodium chloride (0.34 g, 8.7 mmol), sodium iodide (0.096 g, 0.65 mmol), and iodomethane (2.9 g, 21 mmol) was dissolved in water (40 mL). The mixture was stirred at 36°C for 24 hours. After the reaction, dialysis in water, precipitation purification in acetone, and vacuum drying gave a yellow powder of the quaternized polymer. The polymer was soluble in water, and was characterized as the quaternized polymer, as follows (Figure S6c): $^1\text{H-NMR}$ (500 MHz, D_2O , δ (ppm)): 4.0–3.5 (br, -NCH-, -OCH₂-, 3H), 3.5–2.7 (br, -NCH₂-, -CH₂-, 6.8H), 2.6–0.9 (br, Methylene, -CH₂- 6H). FT-IR (KBr): ν (cm^{-1}) = 2931 (s; ν (methylene)), 2922 (s; ν (C=O)).

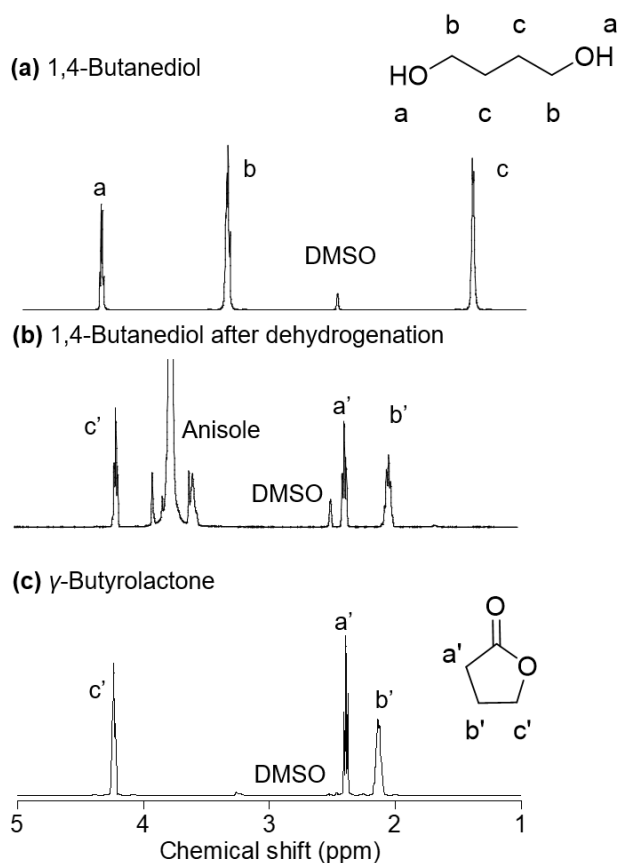


Figure S1. 500 MHz ^1H -NMR spectra (dimethyl sulfoxide- d_6) of a) 1,4-butanediol, b) 1,4-butanediol after hydrogenation, and c) γ -butyrolactone.

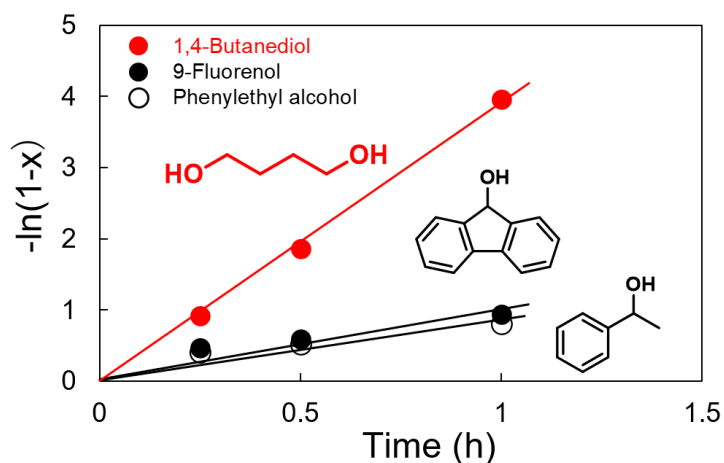


Figure S2. Conversion of dehydrogenation of 1,4- butanediol, 9-fluorenone, and phenylethyl alcohol at 150°C (x : conversion determined by ^1H -NMR and H_2 gas yield determined by gas chromatography). $\ln\{[1,4\text{-butanediol}]/[1,4\text{-butanediol}]_0\} = -kt$. k is the reaction rate constant, and t is the reaction time.

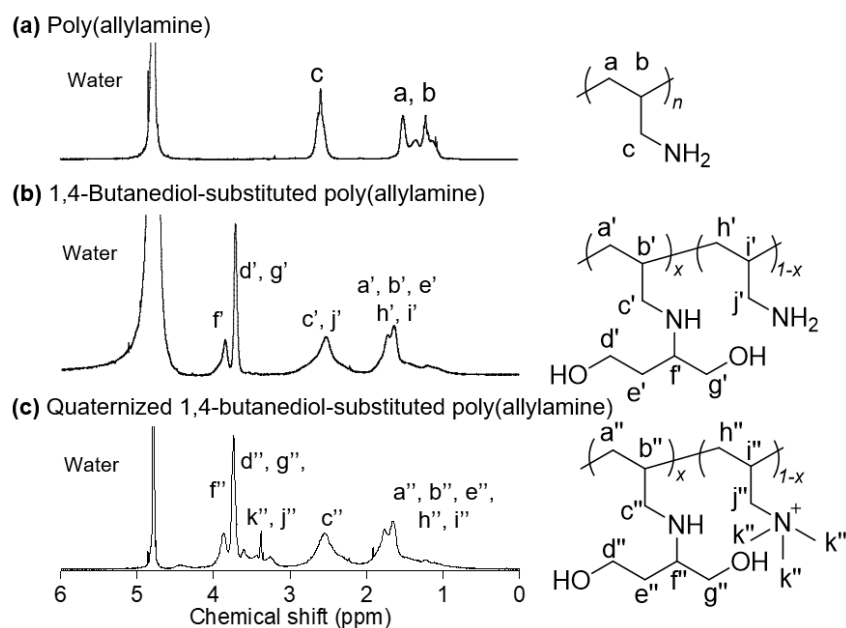


Figure S3. 500 MHz ^1H NMR spectra (D_2O) of (a) poly(allylamine) ($M_w = 5000$), (b) 1,4-butanediol-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 76%), (c) quaternized 1,4-butanediol-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 76%). NH groups (attached with butanediol) were very low basicity compared to the remaining NH_2 groups and were considered not to be quaternized. In addition, following the previous work², we confirmed that c' and c'' appeared at the similar chemical shift.

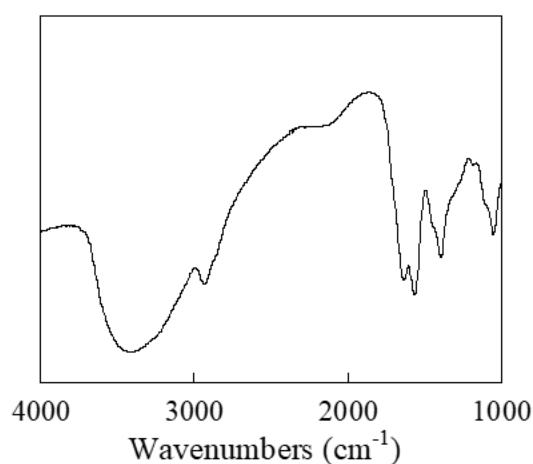


Figure S4. FT-IR spectrum of 1,4-butanediol-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 76%).

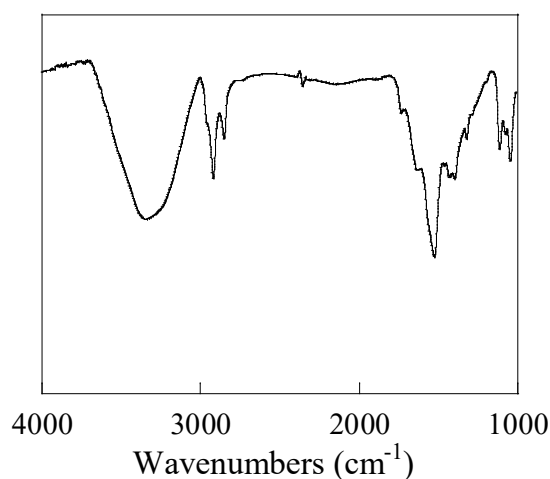


Figure S5. FT-IR spectrum of quaternized 1,4-butanediol-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 76%).

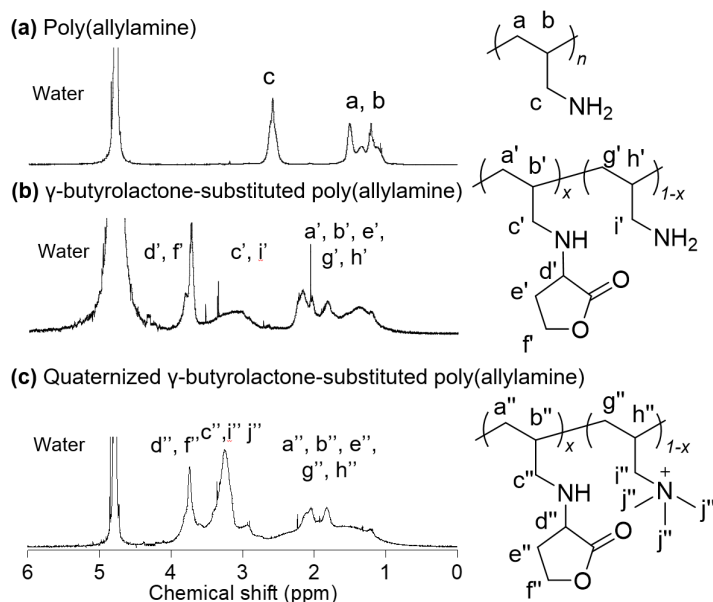


Figure S6. 500 MHz ^1H NMR spectra (D_2O) of (a) poly(allylamine), (a) γ -butyrolactone-substituted poly(allylamine), (b) quaternized γ -butyrolactone-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 70%), (c) quaternized γ -butyrolactone-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 70%).

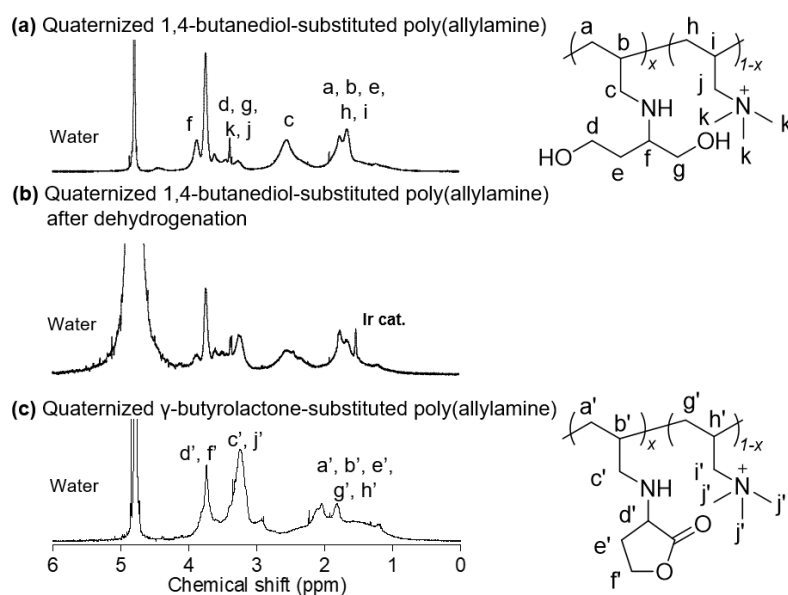


Figure S7. 500 MHz ^1H NMR spectra (D_2O) of a) quaternized 1,4-butanediol-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 76%), b) quaternized 1,4-butanediol-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 76%) after dehydrogenation, and c) quaternized γ -butyrolactone-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 70%). After dehydrogenation of quaternized 1,4-butanediol-substituted poly(allylamine), the peaks of c' j' appeared, hydrogen gas corresponding to the conversion from quaternized 1,4-butanediol-substituted poly(allylamine) to quaternized γ -butyrolactone-substituted poly(allylamine) was obtained. The conversion rate using ^1H NMR spectra was calculated from a comparison of the integrated values of the peaks from 2.3–2.7 ppm from quaternized 1,4-butanediol-substituted poly(allylamine) and 2.7–4.0 ppm from quaternized 1,4-butanediol-substituted poly(allylamine) and quaternized γ -butyrolactone-substituted poly(allylamine).

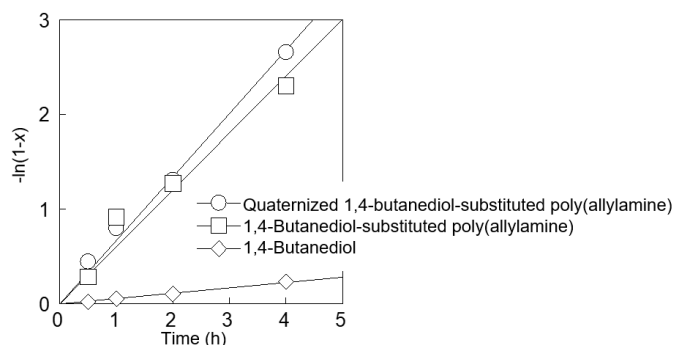


Figure S8. Dehydrogenation of quaternized 1,4-butanediol-substituted poly(allylamine) (\circ), 1,4-butanediol-substituted poly(allylamine) (\square) and 1,4-butanediol (\diamond). As shown in Figure S8, even taking into account an initial lag time or slow-down at the later stage, the overall conversion for dehydrogenation of quaternized 1,4-butanediol-substituted poly(allylamine), 1,4-butanediol-substituted poly(allylamine) and 1,4-butanediol followed the first-order reaction. Furthermore, the reproducibility of the conversion rate is confirmed within a 5% error by several identical experiments.

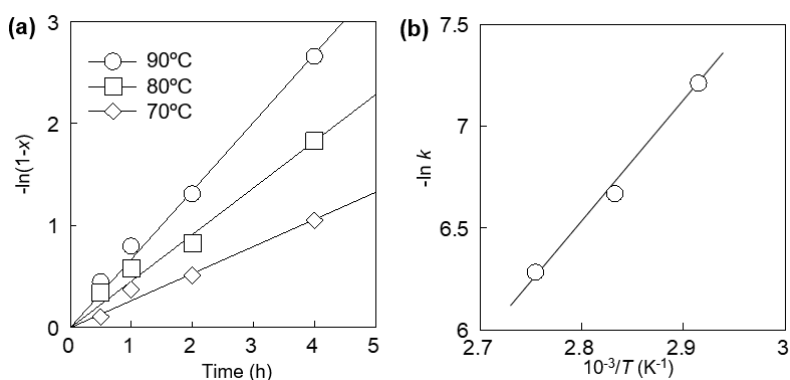


Figure S9. (a) Conversion plots for the dehydrogenation of quaternized 1,4-butanediol-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 76%) at 90, 80, and 70 °C (x : conversion). The first order reaction was observed. The first-order reaction: $\ln\{[1,4\text{-butanediol-substituted poly(allylamine)} (M_w = 5000, \text{introduction degree: } 76\%)]/[1,4\text{-butanediol-substituted poly(allylamine)} (M_w = 5000, \text{introduction degree: } 76\%)]_0\} = -kt$. k is the reaction rate constant and t represents the reaction time. (c) Arrhenius plot used to determine the activation energy for the dehydrogenation of quaternized 1,4-butanediol-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 76%).

Table S1 Synthesis of γ -butyrolactone-substituted poly(allylamine).

Entry	Temperature (°C)	Introduction degree ^{a)} (%)
1	25	21
2	60	70

^{a)} Determined by ¹H-NMR.

Table S2 Dehydrogenation of quaternized 1,4-butanediol-substituted poly(allylamine)

Temperature (°C)	Conversion ^{a)} (%)				k' ($\times 10^{-4} \text{ s}^{-1}$)	k ($\times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$)
	30 min	1 h	2 h	4 h		
90	36	58	73	91	1.9	1.9
80	29	44	56	84	1.3	1.3
70	10	32	40	65	0.74	0.74

^{a)} Determined by ¹H-NMR.

References

- (1) Saini, D.; Kumar, P.; Fernandes, R. A. Stereoselective total synthesis of obolactones and 7',8'-dihydroobolactones. *New Journal of Chemistry* **2021**, *45* (40), 18976-18982, 10.1039/D1NJ03990C. DOI: 10.1039/D1NJ03990C.
- (2) Wytrwal, M.; Koczurkiewicz, P.; Wójcik, K.; Michalik, M.; Kozik, B.; Żylewski, M.; Nowakowska, M.; Kepczynski, M. Synthesis of strong polycations with improved biological properties. *Journal of Biomedical Materials Research Part A* **2014**, *102* (3), 721-731. DOI: <https://doi.org/10.1002/jbm.a.34744>.