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Accelerating the dehydrogenation reaction of alcohols by introducing them into poly(allylamine)^{†‡}

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A novel quaternized polymer was synthesized by introducing butanediol into poly(allylamine) and converting the remaining amino groups into quaternary ammonium cations. The polymer accelerated the dehydrogenation of butanediol due to high hydrophilicity and electrostatic repulsion. The reaction rate was higher by one order of magnitude than that in single molecules.

Hydrogen gas is indispensable for industrial applications such as manufacturing key chemical products, manufacturing steel, and oil refining. Furthermore, it has received significant attention as a next-generation source of renewable energy because of its high energy density and environmental friendliness.^{1–3} However, for its utilization, mature technologies for hydrogen production,^{4,5} storage and transportation,^{6–8} and utilization^{9,10} are required. Among them, hydrogen storage materials capable of safely transporting hydrogen are still under development.^{11–14}

Polymer materials with high-density substitution of molecules capable of storing hydrogen gas through chemical bonding can safely store hydrogen gas even under ambient conditions without being volatile, toxic, or combustible.^{15–18} Moreover, they exhibit high moldability and handleability that are unique to polymeric materials.^{15,17–19} As molecules that can store hydrogen are densely packed in the polymer bulk, hydrogen (or proton) transfer reactions efficiently occur between these molecules.^{16,20–29} The dehydrogenation reaction of these polymer materials including a small amount of solvent, even in the solid state, proceeds with complete conversion by a metal complex catalyst.^{21,30–35} However, the aggregation of polymer chains significantly inhibits the reaction of molecules capable of storing hydrogen; hence, the reaction

rate of functional molecules is lower in macromolecules than in single molecules.^{36–38}

This study aimed to substantially increase the reaction rate of dehydrogenation by introducing molecules capable of storing hydrogen into quaternized polymers to inhibit the aggregation between polymer units and chains based on electrostatic repulsion. A novel quaternized polymer with molecules that can store hydrogen was synthesized by introducing butanediol, which was expected to rapidly dehydrogenate, into poly(allylamine) and converting the remaining amino groups into quaternary ammonium cations with iodomethane.

To date, molecules that can reversibly store hydrogen through chemical bonds have been extensively investigated as organic hydrides. Among them, secondary alcohols exhibit a small difference in the standard Gibbs energy of formation with the dehydrogenated product (ketone);^{21,35} further, the dehydrogenation reaction proceeds under relatively mild conditions in the presence of an iridium complex catalyst that considerably reduces the activation energy because of a unique catalytic cycle.^{34,35,39} Recently, butanediol, which can be partly produced from biomass, was reported to undergo cyclization and dehydrogenation to produce γ -butyrolactone in an organic solvent in the presence of an iridium catalyst.³²

In this study, we aimed to identify alcohol molecules that can be rapidly dehydrogenated in the presence of aqua(2,2'-bipyridine-6,6'-dionato)(pentamethylcyclopentadienyl)iridium (iii) (**Ir cat.**), an iridium catalyst. Upon screening, we selected 9-fluoreno1; phenylethyl alcohol, which undergoes rapid dehydrogenation;^{15,21,35} and 1,4-butanediol, which is dehydrogenated with cyclization.³² These three alcohols were dehydrogenated at 150 °C in anisole in the presence of **Ir cat.** (0.1 mol%) (Table 1). The conversion was determined by ¹H-NMR spectroscopy (Table 1 and Fig. S1[†]) and was found to be consistent with the results of gas chromatography in terms of the amount of hydrogen gas generated. The dehydrogenation of the three alcohols followed first-order kinetics (Fig. S2[†]), enabling the estimation of the dehydrogenation rate constants (*k*). As shown in Table 1, the dehydrogenation rate

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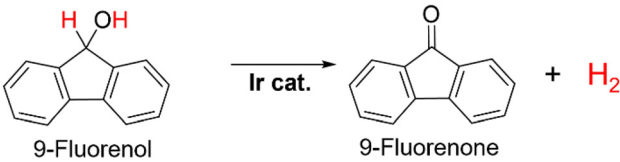
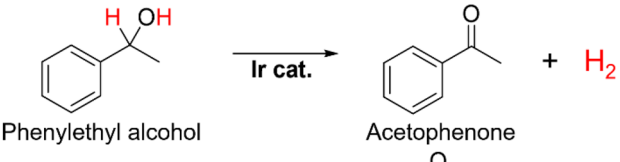
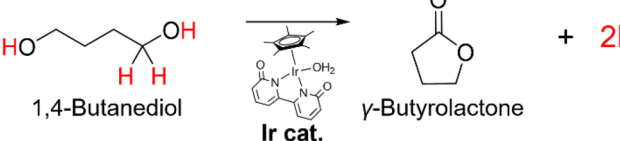
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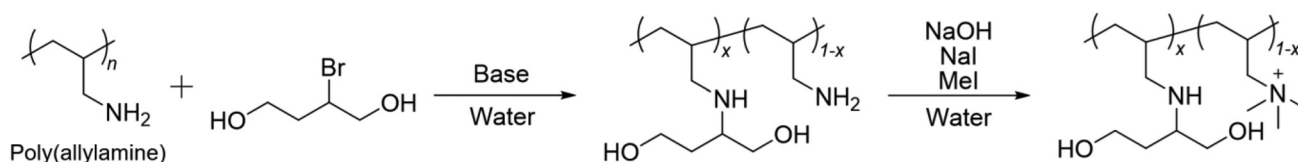
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Table 1 Dehydrogenation of 9-fluoreno, 1-phenylethyl alcohol, and 1,4-butanediol

Scheme of the dehydrogenation reaction	Reaction rate constant in anisole ($\times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$)
 <p>9-Fluoreno $\xrightarrow{\text{Ir cat.}}$ 9-Fluorenone + H_2</p>	0.32
 <p>Phenylethyl alcohol $\xrightarrow{\text{Ir cat.}}$ Acetophenone + H_2</p>	0.27
 <p>1,4-Butanediol $\xrightarrow{\text{Ir cat.}}$ γ-Butyrolactone + 2H_2</p>	1.2

Calculated by $^1\text{H-NMR}$. As a representative example, $^1\text{H-NMR}$ spectra in the case of 1,4-butanediol/ γ -butyrolactone are shown in Fig. S1.† Ir-catalyzed dehydrogenation of 9-fluoreno,⁶ phenylethyl alcohol,¹³ and 1,4-butanediol¹⁴ has been already reported, but a comparison of reaction kinetics in the same solvent was not achieved.

**Scheme 1** Synthesis of 1,4-butanediol-substituted poly(allylamine).

constant of 1,4-butanediol ($1.2 \text{ M}^{-1} \text{ s}^{-1}$) was one order of magnitude higher than those of 9-fluoreno ($0.32 \text{ M}^{-1} \text{ s}^{-1}$) and phenylethyl alcohol ($0.27 \text{ M}^{-1} \text{ s}^{-1}$), indicating that 1,4-butanediol is more favourable for rapid dehydrogenation. Subsequently, we introduced 1,4-butanediol into poly(allylamine) at high density.

Herein, 1,4-butanediol was introduced to poly(allylamine) to avoid the aggregation of polymer units and polymer chains. The introduction of 1,4-butanediol into poly(allylamine) has the following four advantages for dehydrogenation reactions in water: (1) highly hydrophilic amino groups can maintain or improve the hydrophilicity of the polymer. (2) pK_a of poly(allylamine) is 9.5, which allows the 1,4-butanediol-substituted poly(allylamine) to be cationic in aqueous solution; furthermore, the 1,4-butanediol-substituted poly(allylamine) can convert the remaining amino groups to quaternary ammonium cations *via* reaction with methyl iodide. (3) Since the molecular weight of the polymer backbone is not high, the mass hydrogen density is not significantly lowered by the introduction of molecules that can reversibly store hydrogen through chemical bonds. (4) Poly(allylamine)s of suitable molecular weights ($M_w = 1600$ to $50\,000$) are commercially available.

1,4-Butanediol-substituted poly(allylamine) was prepared *via* nucleophilic substitution of poly(allylamine) with 2-bromo-

1,4-butanediol in water (Scheme 1), following the procedure reported in our previous paper²⁸ (details are in the ESI†). The introduction degree was significantly improved by introducing bases such as K_2CO_3 and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), which act as proton scavengers during the reaction, and by using lower molecular weight poly(allylamine); this rate was adjustable between 17% and 76% (Table 2). The resulting 1,4-butanediol-substituted poly(allylamine) was found to not change in $^1\text{H-NMR}$ even after being subjected to 100°C (which is the highest temperature in the dehydrogenation experiments in the current work) in air for more than 24 h, thereby demonstrating excellent heat resistance.

Subsequently, the remaining amino groups of 1,4-butanediol-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 76%) were quaternized with iodomethane to form quaternary ammonium cations. By adding 8 equivalents of iodomethane to 1,4-butanediol-substituted poly(allylamine), all the remaining amino groups were successfully quaternized (Fig. S3c†). Similar to 1,4-butanediol-substituted poly(allylamine), the obtained quaternized polymer showed no change in the $^1\text{H-NMR}$ spectra even after being subjected to 100°C in air for 24 h, thus indicating adequate heat resistance for dehydrogenation. Furthermore, for analysis of the conversion rate after dehydrogenation, γ -butyrolactone-substituted poly(allylamine)



Table 2 Preparation of 1,4-butanediol-substituted poly(allylamine)

Entry	Poly(allylamine) M_w ($\times 10^3$)	2-Bromo-1,4-butanediol (M)	Base	Base (M)	Temperature ($^{\circ}\text{C}$)	Introduction degree ^a (%)
1	25	1.0	—	—	25	17
2	25	4.0	—	—	25	19
3	25	4.0	K_2CO_3	4.0	25	31
4	5.0	4.0	K_2CO_3	4.0	25	59
5	5.0	4.0	DBU	4.0	25	70
6	5.0	4.0	DBU	4.0	80	76

^a Determined by $^1\text{H-NMR}$.

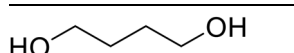
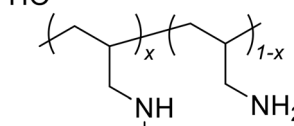
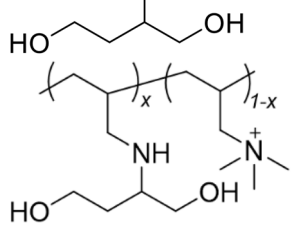
and its quaternized polymer were also prepared using the same procedure (details are in ESI†). For the preparation of γ -butyrolactone-substituted poly(allylamine), the introduction degree was significantly improved by increasing the reaction temperature; this rate was adjustable between 21% and 70% (Table S1†). Similarly, the remaining amino groups of γ -butyrolactone-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 70%) were completely quaternized with excessive iodomethane to form quaternary ammonium cations.

1,4-Butanediol, 1,4-butanediol-substituted poly(allylamine) (introduction degree: 76%), and the quaternized polymer were dehydrogenated in water at 0.5 M at 90 $^{\circ}\text{C}$ in the presence of **Ir cat.** (20 mol%) (Table 3 and Fig. S8†) for analyzing their dehydrogenation kinetics. For all three compounds, we plotted $\ln(1-x)$ (x : conversion) against time t from the integral rate equation, and obtained straight lines passing through the origin, supporting the first-order reaction (Fig. S8†). In addition, since dehydrogenation using **Ir cat.** is a pseudo-first-order reaction with respect to **Ir cat.**, it is assumed that the concentration of **Ir cat.** does not change during the reaction; subsequently, the apparent reaction rate constant k' was calcu-

lated and the actual reaction rate constant k was calculated using k' . Surprisingly, the reaction rate constants for dehydrogenation of 1,4-butanediol-substituted poly(allylamine) ($1.7 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) and its quaternized polymer ($1.9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) were higher than that of 1,4-butanediol ($0.16 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$) (Table 3). This is contradictory to the existing knowledge that the reaction rate of functional molecules in macromolecules is lower than that in single molecules. This is presumably because the presence of an amino group or a quaternary ammonium cation improves the hydrophilicity, and aggregation between polymer units and chains is inhibited the electrostatic repulsion accompanying quaternization.

In addition, the quaternized polymer was dehydrogenated under the same experimental conditions while the temperature was changed. $\ln k$ was plotted against the temperature $1/T$ (K^{-1}), and a straight line was obtained from the Arrhenius plot, showing the activation energy, which was calculated to be 48 kJ mol^{-1} (Fig. S9 and Table S2†). This value is smaller than 62 kJ mol^{-1} , which is the difference in the standard enthalpy of formation between 1,4-butanediol and γ -butyrolactone.⁴⁰ Similar to the conventional 9-fluoreno-¹⁸ and 2-propanol-substituted polymers,⁴¹ the catalytic cycle peculiar to the Ir catalyst dramatically lowers the activation energy of the cyclization reaction (dehydrogenation reaction) of the 1,4-butanediol-substituted polymer.

Table 3 Dehydrogenation of 1,4-butanediol, 1,4-butanediol-substituted poly(allylamine) ($M_w = 5000$, introduction degree: 76%), and its quaternized polymer

Chemical Structure of alcohols for dehydrogenation	Reaction rate constant in water ($\times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$)
	0.16
	1.7
	1.9

Alcohols were dehydrogenated in water (0.5 mol L^{-1}) with **Ir cat.** (20 mol%) at 90 $^{\circ}\text{C}$. As a representative example, $^1\text{H-NMR}$ spectra in the case of quaternized 1,4-butanediol-substituted poly(allylamine)/quaternized γ -butyrolactone-substituted poly(allylamine) are shown in Fig. S7.†

Conclusions

In this study, we found that the Ir-catalyzed dehydrogenation of 1,4-butanediol was faster than that of other alcohols by one order of magnitude in water. A novel quaternized polymer was prepared by introducing 1,4-butanediol into poly(allylamine) and cationizing the remaining amino group with iodomethane. Owing to the high hydrophilicity derived from the quaternary ammonium cation and the repulsion between polymer chains, the quaternized polymer accelerated the dehydrogenation reaction of butanediol; moreover, the reaction rate was one order of magnitude higher than that of the single molecule (1,4-butanediol). A demonstration of a phenomenon, which reverses the general tendency that the reaction rate of functional molecules decreases by being a macromolecule, will significantly accelerate further research on hydrogen storage using polymer materials to improve the reaction rate of molecules that can reversibly store hydrogen through chemical bonds.



Conflicts of interest

There are no conflicts to declare.

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