

FOCUS REVIEW

Polymers for carrying and storing hydrogen

Ryo Kato and Hiroyuki Nishide

Safe and efficient hydrogen-carrying and -storing materials are in high demand for future hydrogen-based energy systems. Series of hydrogen carriers have been studied and examined, such as organic hydrides, metal hydrides and metal-organic frameworks; however, these carriers often suffer from safety issues and usually fix and store hydrogen at energy-consuming high pressures and/or temperatures. Here, we review organic polymers and their molecular design for hydrogen storage. Porous organic polymers, hypercrosslinked polymers and polymers with intrinsic microporosity reversibly stored and released hydrogen through hydrogen physisorption on their highly porous structures. Ketone and *N*-heterocycle polymers fixed and stored hydrogen at atmospheric pressure through the formation of chemical bonds to form the corresponding alcohol and hydrogenated *N*-heterocycle polymers, respectively. Electrochemical hydrogenation using water as a hydrogen source was also effective, in which the polymer worked as a scaffold for hydrogenation. The hydrogenated polymers released hydrogen in the presence of catalysts at mild conditions. The potential of using organic polymers in the quest for finding new types of hydrogen-carrying and -storing materials that are very safe and portable is suggested.

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INTRODUCTION

Hydrogen is the lightest molecule, and the chemical energy per mass of hydrogen (142 kJ g^{-1}) is at least three times larger than that of other chemical fuels (e.g., the equivalent value for liquid hydrocarbons is 47 kJ g^{-1}).¹ The combustion of hydrogen, as well as its use in electricity-producing fuel cells, is not associated with carbon dioxide emission. Hydrogen is produced at chemical facilities and from a great variety of potential sources. Even though the majority of hydrogen used today still comes from fossil fuels, it can also be produced using renewable energy sources, such as biomass and solar or wind power.^{2,3} One of the lowest carbon-intensive approaches is the electrolytic production of hydrogen using sustainable sources of electricity. The flexible grid-power systems currently in production enable the storage of intermittent electricity in the form of hydrogen fuel during times of low demand but high supply.⁴ Despite these clear merits, the widespread use of hydrogen, which is a gas under ambient conditions, is still limited owing to the lack of technologies to store and transport it in a high-density, compact and efficient manner.

Conventional storing and transporting methods for hydrogen include using cryogenic or high-pressure tanks. However, hydrogen storage with cryogenic tanks is restricted because it requires cooling to 20 K and thermal insulation. Large amounts of energy are necessary for the liquefaction and continuous boil-off of hydrogen. Compressing gaseous hydrogen, even to 70–80 MPa, requires tank walls with a relatively high thickness to increase the hydrogen density. The tanks are accompanied by inherent safety risks, such as explosions (e.g., by collisions), the permeability of hydrogen and embrittlement of the tank walls. In terms of the costs of hydrogen storage, reports from the DOE (the Department of Energy) of United States of America and

NEDO (New Energy and Industrial Technology Development Organization) of Japan suggest that the cost of pressure vessels and compressors accounts for nearly half of the total cost; thus, the reduction of these two costs is highly recommended.^{5,6} Additionally, liquid hydrogen storage within tanks is not advantageous for relatively small-scale, dispersive and on-site hydrogen usage.

Hydrogen-storing and -carrying materials with a high gravimetric and/or volumetric density that are safe, easy to handle, low cost and have low energy losses during hydrogen storage/transport/release are highly essential for hydrogen-based energy systems. Liquid organic hydrogen carriers or organic hydrides have been researched and tested on the industrial scale to be used in existing infrastructure for oil storage.⁷ They store hydrogen by forming chemical or covalent bonds at atmospheric pressure, thus featuring high stability. This chemical bond formation is also known as hydrogen fixing. However, organic liquids are not always suitable to be examined as hydrogen storage materials for small-scale applications, for transporting hydrogen from manufacturing locations to hydrogen-using dispersion locations and storing hydrogen until using it as energy around residential areas because of their safety risks, such as toxicity, flammability and volatility.

Metal hydrides were among the first solid-state materials considered for reversible hydrogen storage.⁸ Metals, such as lithium, magnesium and aluminum, form hydrides in which hydrogen represents a significant gravimetric portion of the material. A few metal hydrides have been evaluated as hydrogen storage materials installed in high-pressure tanks. However, the recovery of hydrogen from these hydrides involves energy-inefficient endothermic processes that

require high temperatures, and the problematic issue of disposing metal hydrides currently makes them impractical.

Porous materials, such as activated carbon and metal-organic frameworks (MOFs), store hydrogen through physical adsorption on the surfaces of materials. The weak interactions between hydrogen and the material allow reversibility of the hydrogen storage and release, but they also lead to a low hydrogen density in ambient conditions. In addition, porous materials require high pressure conditions to store sufficient amounts of hydrogen. Porous organic polymers have also been studied as hydrogen storage materials because of their purely organic origins and tunable structures.

In this article, we describe organic polymer materials for hydrogen-carrying and -storing. The first approach is based on the physical adsorption of hydrogen on highly porous polymers, and the second approach is based on chemical storage through the reversible hydrogenation/dehydrogenation of polymers. Both of these types of polymers have been studied, along with their molecular design, primarily due to their inherent advantages of being lightweight, moldable, easy to handle, and safe. Although fiber-reinforced plastics have been developed as next generation materials for the walls of hydrogen tanks, less attention has been focused on using polymers for hydrogen-carrying and -storing, except for proton-conductive polymers^{9–11} and hydrogen-permeable polymer membranes.¹² We will suggest here the potential of using organic polymers to search for new types of hydrogen-carrying and -storing materials. The history of polymer hydrogenation is addressed in the concluding part of this review to enable future perspectives for polymer-based hydrogen carriers.

HYDROGEN STORAGE WITH POROUS ORGANIC POLYMERS

The physisorption of hydrogen on solids is a reversible process in which hydrogen is adsorbed and released without decomposition of the solid and unintended losses of hydrogen, based on the fundamentals of gas adsorption. Their hydrogen density is generally low at ambient atmosphere due to weak interactions between hydrogen and the material, while the hydrogen density is enhanced at very low temperatures and/or high pressures and with increases in the porosity or surface area of the solid. For example, hydrogen adsorption on activated carbon, carbon fibers and graphite has been conducted because of their high surface areas (ca. 2000 m² g⁻¹).¹³ The activated carbons adsorbed hydrogen with the capacity of ca. 5 wt% at 77 K (ca. 4 MPa) and ca. 1 wt% at room temperature (ca. 20 MPa).¹⁴ The storage capacity of single-wall and multiwall carbon nanotubes for

hydrogen was lower than 1 wt% at room temperature but ca. 6 wt% at 77 K at 10 MPa.¹⁵ The next step in the pursuit of physical hydrogen storage materials is to enhance their capability by incorporating very small and designed pores.

MOFs are crystalline solids that consist of multidentate organic ligands that connect metal ions and, similar to zeolites, often have a three-dimensional framework. Outstanding surface areas nearly reaching 5000 m² g⁻¹ and high pore volumes confer considerable potential to MOFs as prospective materials for hydrogen storage.^{16,17} A wide range of varying topologies and pore sizes from combinations of organic ligands and metal connectors has been explored. For example, highly porous cubic frameworks comprised of Zn₄O(CO₂)₆ units coordinated by an octahedral array of 1,4-benzenedicarboxylate and benzene tribenzoate groups adsorbed 1 wt% hydrogen at room temperature (2 MPa) and 4.5–7.5 wt% at 78 K (0.08 MPa).^{18–20} However, a way toward achieving hydrogen adsorption at ambient conditions has not been envisioned, even for precisely designed MOFs.

Porous organic polymers have received research interest as a physical adsorbent of hydrogen (Table 1). They are amorphous, they possess micro- or nanopores with high porosity, but with dispersed pore sizes and structures, and they are metal free and lightweight. In addition, large number of synthetic routes exist with excellent scalability for porous organic polymers.

Hypercrosslinked polymers, such as hypercrosslinked polystyrene prepared from poly(chloromethylstyrene-co-divinylbenzene) in **1** (Figure 1), have been synthesized via simple and scalable Friedel–Crafts alkylation reactions using a wide range of polymers, resulting in networks with very fine pore structures.^{21,22} The typical procedure to form hypercrosslinked polymers is as follows: The precursor is first crosslinked using an alkylation reaction where the majority of the repeat units are linked by at least three bonds. Rapid crosslinking locks the polymer chains into an expanded form. After removing the solvent, the space that the solvent had previously occupied becomes porous, and a network of intercommunicating pores are left behind. The yielded hypercrosslinked polymers can store hydrogen up to ca. 5 wt% at a high pressure of 8 MPa and a low temperature of 77 K, but they store very low amounts of hydrogen, 0.2 wt%, even at 9 MPa at room temperature.²³

Polymers of intrinsic microporosity are one class of purely organic microporous polymers that contain rigid and distorted macromolecules composed of fused-ring components. They form microporous organic frameworks with relatively high surface areas (ca. 1000 m² g⁻¹) because of their inability to pack space efficiently.²⁴ The polymer shown in **2** in Figure 1 was synthesized using a simple and efficient dioxane-forming reaction that incorporated cyclotriechylene subunits.²⁵ Polymer **3** was synthesized from triptycene subunits prepared through a dibenzodioxane formation reaction between hexahydroxytritycene and tetrafluoroterephthalonitrile.²⁶ Both polymers showed pore sizes in the range of 0.6–0.8 nm, which was indicative of ultramicroporosity. These insoluble network polymers had a high surface area and reversible hydrogen adsorption of ca. 1.5 wt% at 0.1 MPa and 3.2 wt% at 1 MPa at 77 K.^{25,26} With a similar strategy, a kind of star triptycene-based microporous polymer was synthesized via a cross-coupling reaction of trihalotriptycenes, which resulted in a surface area of ca. 2000 m² g⁻¹ and reversible hydrogen uptake of 1.93 wt% at 0.1 MPa and 77 K (**4**; Figure 1).²⁷

Porous organic polymers can reversibly and immediately store and release hydrogen and store significant amounts of hydrogen at cryogenic temperatures and/or high pressures. However, such as porous carbon and MOFs, they still achieve minimal hydrogen storage capacity in ambient conditions. Increasing the interaction energy of

Table 1 Porous polymers and their hydrogen storage capability

Polymer	Surface area (m ² g ⁻¹)	Hydrogen adsorption			Ref.
		Temperature (K)	Pressure (MPa)	Capacity (wt%)	
1	1930	77	0.1	1.5	21– 23
		77	8	5.4	
		273	9	0.2	
2	830	77	0.1	1.4	25
		77	1	1.7	
3	1760	77	0.1	1.8	26
		77	1	3.2	
4	1990	77	0.1	1.9	27

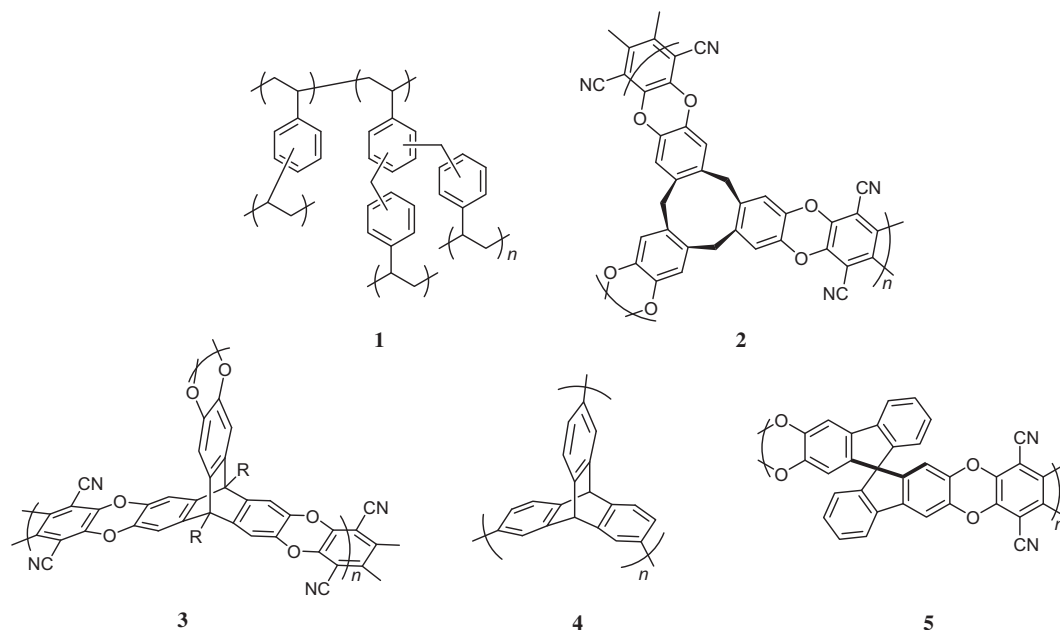


Figure 1 Structures of the hypercrosslinked polymer, **1**; the intrinsic microporous polymers, **2** and **3**; the star triptycene polymer, **4**; and the spirobifluorene polymer, **5**.

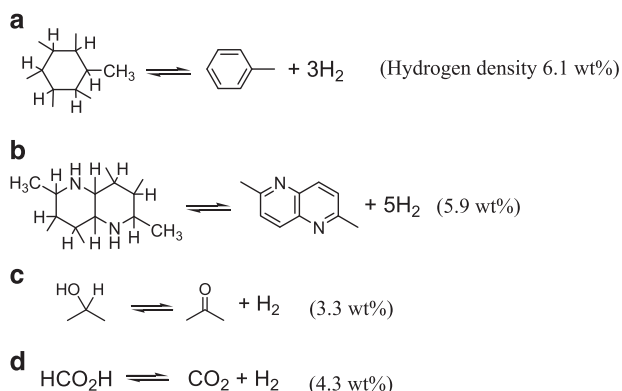
hydrogen with the polymer surface is an effective strategy for solving this limitation. The effect of pore size on adsorption enthalpy suggested both theoretically and experimentally that decreasing the pore size increases the adsorption enthalpy. Hypercrosslinked networks of aromatic rings with very small pores have been synthesized and examined. While the hydrogen capacity was not high at room temperature because of the insufficient surface area and pore volume, the resulting materials exhibited adsorption enthalpies reaching -18 kJ mol^{-1} ,²⁸ allowing for reversible hydrogen storage at room temperature. Recently, very high gas-permeable polymer membranes have been synthesized using molecular design by incorporating nanoporous structures.²⁹ One such example includes the spirobifluorene-based polymers with intrinsic microporosity shown in **5** (Figure 1).³⁰ This research could also open new possibilities for porous organic polymers with hydrogen storage capabilities at room temperature.

HYDROGEN STORAGE WITH POLYMERS BY FORMING CHEMICAL BONDS

Hydrogen storage using organics along with chemical storage approaches or hydrogen-fixing through chemical bond formation has been mostly researched by using organic liquid compounds, hydrogen carriers or so-called organic hydrides. The typical example is the hydrogenation and dehydrogenation of cycloalkanes. A combination of toluene and methylcyclohexane with a hydrogen density of 6.1 wt% was tested at a large-scale of 1 kl.³¹ Similarly, *N*-heterocycles have also been demonstrated as hydrogen carriers.³² The N–H bonds and neighboring C–H bonds are weaker than the C–H bonds of carbocycles, and hydrogenated *N*-heterocycles thermodynamically favor the release of hydrogen under relatively mild conditions.³³ Both aromatic compounds and aliphatic compounds, such as alcohol^{34,35} and formaldehyde,³⁶ have been studied, as illustrated by the acetone and 2-propanol (Scheme 1c). The reversible redox reaction pair of CO_2 /formic acid also works as a hydrogen carrier.³⁷

The chemical storage capability is accomplished by forming chemical bonds with hydrogen and features high stability and a high hydrogen storage capacity of 2–6 wt% under atmospheric pressure. However, these organic compounds are mostly liquids or used as solutions, and they suffer from safety issues; their usage is restricted by legal regulations. Furthermore, the hydrogenation of these compounds mostly proceeds at high pressures via highly energy-consuming processes. They require vessels or sealed tanks that operate at high pressures and/or temperatures and often encounter difficulties when separating the evolved hydrogen gas from the vapor of the carrier molecules.

We have recently studied chemical hydrogen carriers using polymers such as alcohol³⁸ and *N*-heterocycle³⁹ polymers (Figure 2). The carriers in the form of organic polymers are free from storage risks and from the legal regulations of liquid organic hydrogen carriers. Reversible hydrogenation and dehydrogenation or hydrogen storage and release was accomplished at mild conditions, at room temperature and 80 °C, and at atmospheric pressure using the polymeric hydrogen carriers.



Scheme 1 Hydrogen storage with organic molecules by forming chemical bonds.

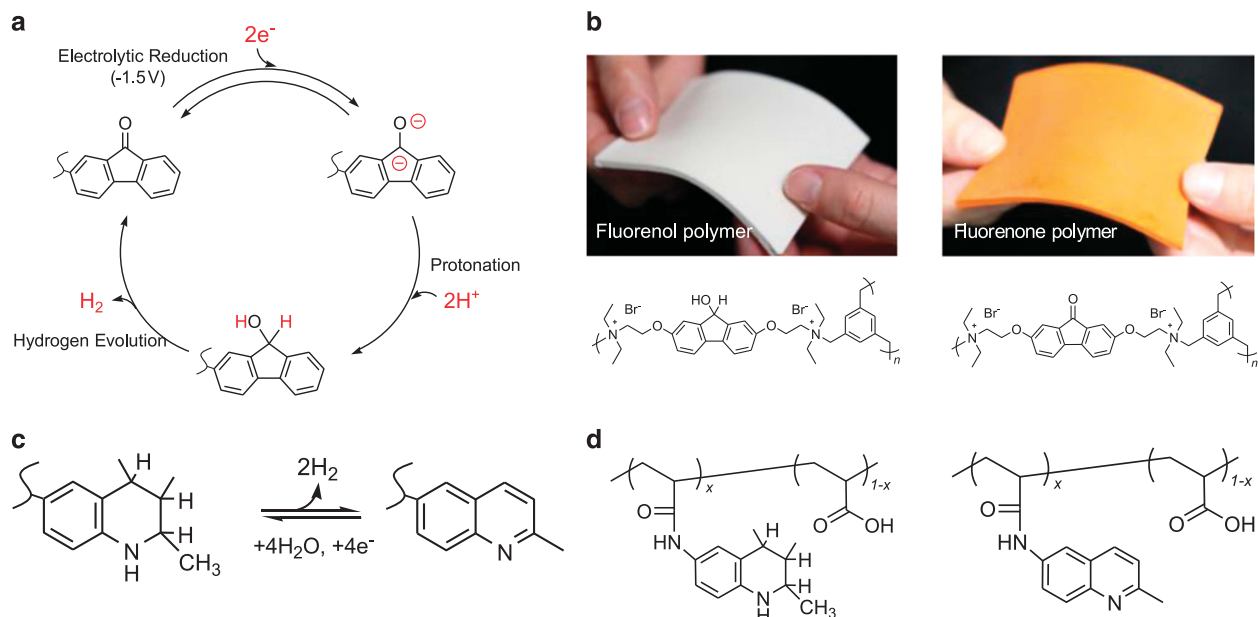


Figure 2 Hydrogen storage with organic polymers by forming chemical bonds. (a) Schematic representation of the hydrogen-fixing and -releasing cycle. (b) A sheet of the fluorenone and fluorenone polymer. (c) Hydrogen storage reactions with the quinaldine and hydroquinaldine polymers. (d) Hydroquinaldine and quinaldine-substituted poly(acrylic acid).

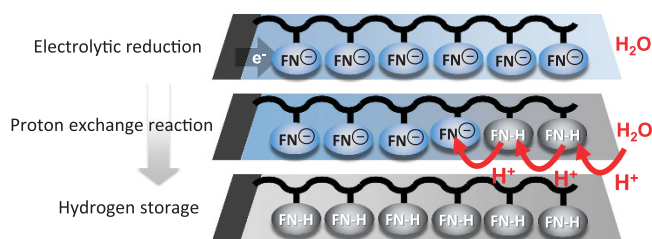


Figure 3 Schematic image of the proton or hydrogen exchanging reaction among the highly populated fluorenone units in the polymer.

Fluorenone is an alcohol derivative of fluorene that contains two hydrogen atoms with C–H and O–H chemical bonds, and it efficiently releases hydrogen in the presence of an iridium catalyst, for example, aqua (6,6'-dihydroxy-2,2'-bipyridine)(pentamethylcyclopentadienyl) iridium(III) bis (triflate),⁴⁰ under mild conditions to yield fluorenone, the corresponding ketone form of fluorenone. The fluorenone and fluorenone pair was found to reversibly store hydrogen through the catalytic dehydrogenation and electrolytic hydrogenation cycle.

The cycle effectively worked for its polymeric analogs. For example, a bendable fluorenone/fluorenone polymer sheet and fluorenone polymers quantitatively released hydrogen in the presence of a small amount of an aqueous iridium catalyst solution at 80 °C. The formed fluorenone polymer fixed hydrogen using water as a hydrogen source or extracted protons from water during electrolytic hydrogenation at room temperature.

The polymers were swelled with water to form a hydrogel with a water content of 25–35 wt%. The gel held a very high concentration (ca. 1 M) of fluorenone/fluorenone units, which was beyond the limited solubility of the monomeric fluorenone and fluorenone in water (ca. 0.2 mM). While the fluorenone/fluorenone units were immobilized in the polymer or amorphous gel, they were still highly reactive to protons or hydrogen. Proton or hydrogen exchanging reactions

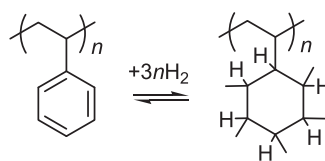


Figure 4 Hydrogenation of polystyrene.

among the highly populated fluorenone/fluorenone units occurred very efficiently,⁴¹ and the units were fully hydrogenated or dehydrogenated throughout the polymer (Figure 3). The entire bulk of the polymer with a thickness of ca. 1 μm was quantitatively hydrogenated and rapidly released hydrogen.

Fluorenone polymer composites with carbon nanofibers as a conductive additive were used to perform cycles of hydrogen-fixing and -releasing in water. The hydrogen evolution was similar to that of the neat fluorenone polymer, and the evolved pure hydrogen gas nearly reached the theoretical hydrogen capacity contained in the composite sheet. The composite sheet was then hydrogenated again after applying -1.5 V (versus Ag/AgCl), and this cycle was performed 50 times without any significant deterioration in the hydrogen evolution capacity.

Quinaldine, one of the *N*-heterocycles, has been reported to be a reversible hydrogen carrier with a hydrogen capacity of 2.7 wt%.⁴² Quinaldine and 1,2,3,4-tetrahydroquinaldine were introduced to poly(acrylic acid) (Figure 2d). The hydroquinaldine polymer evolved hydrogen by simply warming at 80 °C in the presence of an aqueous iridium complex catalyst solution. The evolved hydrogen amounted to ca. 160 ml per 1 g of polymer at room temperature after a few hours (>90% of the formulated amount). The hydrogen evolution rate from the polymer was more than 10 times larger than that from the monomeric hydroquinaldine, which could be ascribed to the highly populated hydroquinaldine units in the polymer.

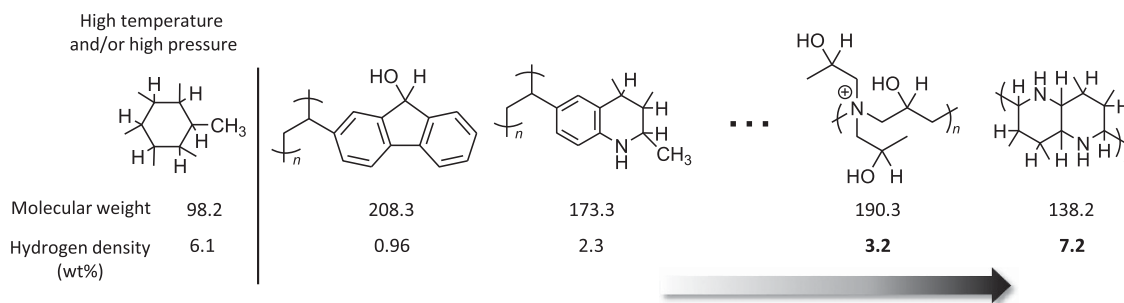


Figure 5 Hydrogen density of the polymers (including the prophetic ones).

The quinaldine polymer coated on a carbon substrate was hydrogenated after the electrodeposition of nickel microparticles in the polymer layer, and the polymer stored hydrogen by forming chemical bonds using water as a hydrogen source. Electrochemical hydrogenation using water with a hydrophilic polymer scaffold has been characterized as one of the hydrogen gas-free hydrogenation processes.

Polymers containing ketone or *N*-heterocycle groups fixed and stored hydrogen under atmospheric pressure through the formation of chemical bonds without any other vessel to store hydrogen. The advantages of these polymers enable easy handling and provide portable hydrogen-carrying materials for use in, for example, a home/on-site or pocketable hydrogen-supply system.

STAUDINGER'S EXPERIMENTS: HYDROGENATION OF POLYSTYRENE

A hundred years ago, the first experiment was performed to fix hydrogen onto polystyrene and natural rubber through hydrogenation and to prove the existence of long polymer chains (Figure 4). Staudinger *et al.*^{43–45} dissolved polystyrenes with different molecular weights of 1800, 3000 and 5000 in methylcyclohexane and hydrogenated them with nickel at 200 °C to yield hexahydrostyrene polymers or poly(cyclohexyl ethylene)s. They measured the falling times or relative viscosities of the hydrogenated polymer solutions with an Ostwald viscometer, and they were comparable with those of the solutions of the starting polystyrenes. They concluded that the solution viscosity, one of the so-called colloidal properties of polystyrene, was maintained for the fully hydrogenated or saturated polymer. This experiment provided crucial evidence to strongly support the existence of covalently bonded long-chained organic molecules and to deny the assumption that polystyrene is an assembly of low-molecular-weight aromatic subunits formed by secondary bonding forces. He substantiated his proposed relationship between the solution viscosity and the molecular weight of the polymers, with molecular weight measurements using the freezing point depression of the polystyrene solution and the hydrogenated oligomeric specimens. This experiment on polystyrene and hydrogenated samples was conducted at the dawn of macromolecular chemistry. We re-examined the hydrogen fixing on polystyrene in the presence of 10 MPa of hydrogen and a palladium catalyst at 200 °C, which yielded fully hydrogenated polystyrene or poly(cyclohexyl ethylene). A nearly quantitative evolution of hydrogen gas was produced by heating the solution of the hydrogenated polystyrene in the presence of a platinum catalyst. Thus, polystyrene works as a hydrogen-storing and -releasing polymer.

The DOE of United States of America has targeted the development of hydrogen adsorbates or hydrogen carriers with 6 wt% hydrogen.⁴⁶ The hydrogen density could be improved with the molecular design of organic polymers, such as those in Figure 5.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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Ryo Kato received his PhD in 2017 at Waseda University under the supervision of Prof Hiroyuki Nishide and joined the Department of Applied Chemistry as an Assistant Professor. He is a postdoctoral scholar in Prof Stuart Rowan's group at the University of Chicago in 2018. His research interests are synthesis and application of functional polymers (especially redox polymers), stimuli-responsive materials, nanocomposites and energy storage devices.



Hiroyuki Nishide received his PhD in 1975 at Waseda University and was Humboldt research fellow at the Free University Berlin. He returned to Waseda University as an Assistant Professor in 1978 and has been Professor at the Department of Applied Chemistry since 1987. He has conducted research in the field of syntheses and applications of functional polymers, recently focusing on the organic polymers for energy-related devices. He is past president of the Society of Polymer Science, Japan, of the Federation of Asian Polymer Societies and of Japan Union of Chemical Science and Technology. He received the award of the Society of Polymer Science, Japan (1990), SPSJ Award for Outstanding Achievement in Polymer Science and Technology (2011) and the Chemical Society of Japan Award (2014).