

Synthesis of Temperature-Responsive Organic-Inorganic Hybrid Hydrogel by Free-Radical Polymerization of Methacrylamide Using Water-Soluble Rigid Polysiloxane Having Acrylamido Side-Chains as a Cross-linking Agent

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(Received May 1, 2007; Accepted June 23, 2007; Published August 7, 2007)

KEY WORDS Organic-Inorganic Hybrid / Temperature-Response / Hydrogel / Water-Soluble
Polysiloxane / Polymethacrylamide / Free-Radical Polymerization /
[doi:10.1295/polymj.PJ2007028]

Polymeric hydrogels are three-dimensional polymer networks containing a large amount of water, which have been used in a variety of applications, *e.g.*, soft contact lenses, absorbents, and cosmetics, due to their high water contents and soft touchness.¹ In particular, a considerable number of researches have been focused on stimuli-responsive hydrogels, in which they can change their properties in response to environmental stimuli such as pH, temperature, ionic strength, and electric field.^{2,3} The stimuli-responsive hydrogels have been investigated for many biomedical and pharmaceutical applications, *e.g.*, drug delivery system (DDS).^{2,3} As familiar examples, it has been reported that the hydrogels composed of poly(*N*-isopropylacrylamide), poly(*N,N*-diethylacrylamide), and poly(ethylene oxide)-poly(propylene oxide) block copolymer have exhibited temperature-response.^{2–6}

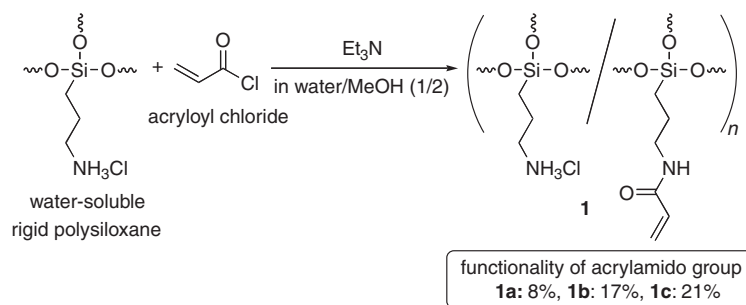
On the other hand, the hydrogels had some serious disadvantages such as brittleness and lack of mechanical toughness. So far, to solve these disadvantages of the hydrogels, synthesis of organic-inorganic nanocomposite (hybrid) hydrogels have been reported,^{7,8} which are composed of organic polymer as a main-chain and inorganic dispersed clay as a cross-linking agent. A clay has two-dimensional rigid sheet structure forming regular higher-ordered structure (lamellar phase) and can disperse in the water. These properties of the clay would contribute to the superior characteristics such as high mechanical strength, elongation, and transparency of the hydrogels. However, since other inorganic materials, which have rigid structure and dispersion behavior, have hardly ever been known, the variety of the organic-inorganic hybrid hydrogels has been restricted. The availability

of new inorganic cross-linking agents promisingly introduces additional development of new functions and applications of novel high-performance hybrid hydrogels.

So far, water-soluble polysiloxanes having alkylammonium groups were synthesized by the sol-gel reaction of aminoalkyltrialkoxysilane in strong acid aqueous solution.^{9,10} In the solid state, these polysiloxanes were stacked to form the hexagonal phase, implying their rigid-rod structures. The polysiloxanes have inspired us to use them for the development of a new hybrid hydrogel, because of their comparable water-dispersibility and rigidity to those of a clay. Accordingly, we prepared a polysiloxane-based multifunctional cross-linking agent for a new organic-inorganic hybrid hydrogel.¹¹ The cross-linking agent was synthesized by reaction of the rigid polysiloxane with acryloyl chloride. Then, the organic-inorganic hybrid hydrogels were obtained by free-radical polymerization of an acrylamide (AAM) monomer using the cross-linking agent. The compressive properties of the obtained hydrogels were more superior than those of conventional poly(AAM) (PAAm) hydrogels. Based on the backgrounds described above, development of novel temperature-responsive organic-inorganic hybrid hydrogels would be a promising topic in the material research fields.

In a series of the study, we prepared a polymethacrylamide (PMAAm)-type organic-inorganic hybrid hydrogel using the cross-linking agent mentioned above. We found that the new organic-inorganic hybrid hydrogel appeared temperature-responsive property, although PMAAm does not generally exhibit temperature-responsive behavior. Appropriate balance

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Scheme 1. Synthesis of cross-linking agents **1** using water-soluble rigid polysiloxane.

between methacrylamide (MAAm) monomer and the polysiloxane-based cross-linking agent probably affects such a behavior. In this paper, we report synthesis, temperature-responsive behavior, and mechanical property of the new organic-inorganic hybrid hydrogel.

EXPERIMENTAL

Materials

The water-soluble rigid polysiloxane was prepared according to the literature procedure.⁹ Its molecular weight (M_n) was evaluated to be 10,300 g/mol by GPC analysis with water as the eluent using pullulan standards.¹² The cross-linking agents (**1a-c**) were prepared using this water-soluble polysiloxane according to a literature procedure,¹¹ which were achieved by reaction of amino groups of the polysiloxane with acryloyl chloride. The functionalities of acrylamido groups determined by ¹H NMR spectra were 8% (**1a**), 17% (**1b**), and 21% (**1c**). Other reagents and solvents were used as received.

Synthesis of Temperature-Responsive Organic-Inorganic Hybrid Hydrogels (**2**)

A typical experimental procedure for synthesis of temperature-responsive organic-inorganic hybrid hydrogel (**2a**) was as follows. A cross-linking agent **1a** (0.059 g, 0.40 mmol unit), MAAm (0.681 g, 8.0 mmol) and potassium persulfate (KPS) (0.022 g, 0.080 mmol) were dissolved in degassed water (4.0 mL), and then oxygen was excluded from the reaction system by substitution of argon. Free-radical polymerization of this mixture was carried out by heating at 60 °C for 5 h to obtain **2a**.

Synthesis of PMAAm Hydrogels (**3**) Using Conventional Organic Cross-Linking Agent

A typical experimental procedure for preparation of PMAAm hydrogel (**3a**) using conventional organic cross-linking agent was as follows. *N,N'*-Methylene-bisacrylamide (BisAAm) (0.006 g, 0.040 mmol) as a cross-linking agent, MAAm (0.681 g, 8.0 mmol) and

KPS (0.022 g, 0.080 mmol) were dissolved in degassed water (4.0 mL), and the following procedures were same as those for synthesis of **2a**.

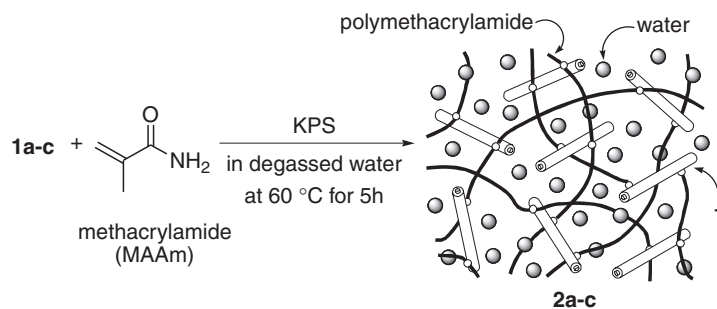
Measurements

The transmittances of the products were measured using a UV-160A spectrometer (Shimadzu Co., Ltd.) at the scanning rate of 400 nm/min. A cell containing water was used for the reference. The fracture stresses and strains were determined by compressive stress-strain measurements using a tensile-compressive tester (Little Senstar LSC-1/30, Tokyo Testing Machine Co.). The samples were water-swollen cylindrical gels with a diameter of 13 mm and a height of 15 mm. The compressive strain rate was 1.0 mm/min.

RESULTS AND DISCUSSION

The multifunctional cross-linking agents (**1a-c**) were prepared according to a literature procedure,¹¹ which were achieved by reaction of amino groups of the water-soluble rigid polysiloxane with acryloyl chloride (Scheme 1). Hybrid hydrogels (**2**) were synthesized by free-radical polymerization of MAAm using **1** initiated with KPS in degassed water under argon atmosphere at 60 °C for 5 h (Scheme 2). For the present study, we employed three cross-linking agents (**1a-c**) with different functionalities of acrylamido groups; 8%, 17%, 21%. Because 5 mol unit % of **1a-c** for MAAm were employed, the ratios of acrylamido groups in **1a-c** to MAAm were calculated to be 0.4, 0.85, and 1.05%, respectively. The obtained hydrogels **2a-c** contained water weighting more than 80% of the materials (**2a**; 82%, **2b**; 81%, **2c**; 80%). Use of the original water-soluble rigid polysiloxane instead of **1** did not afford a hydrogel, indicating the necessity of a chemical cross-linking agent in this study.

Influences of temperature on the transmittances in visible light (wavelength; 500 nm) of hybrid hydrogels **2** and conventional hydrogels **3** during heating-cooling cycles between 25 °C and 80 °C are shown in Figure 1. The hybrid hydrogel **2a** obtained using **1a** (functionality of acrylamido group; 8%) was turbid



Scheme 2. Synthesis of temperature-responsive organic-inorganic hybrid hydrogels **2**.

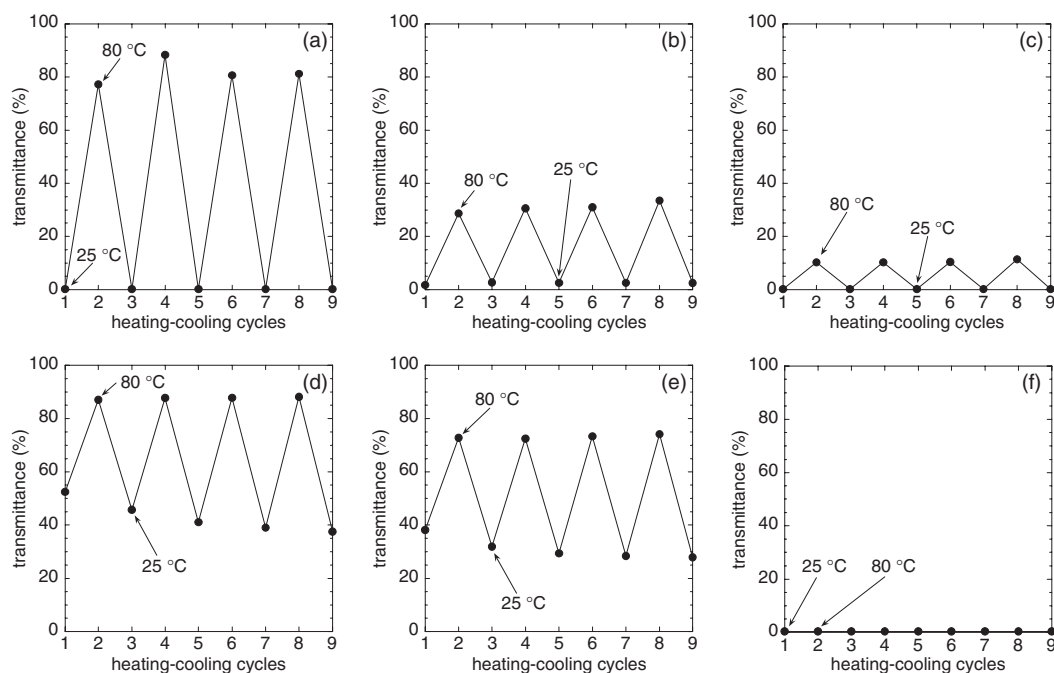


Figure 1. Transmittances in visible light (wavelength; 500 nm) of hybrid hydrogel **2a** (a), **2b** (b), **2c** (c) and hydrogels **3a** (d), **3b** (e), **3c** (f) during heating-cooling cycles between 25 °C and 80 °C.

at 25 °C (transmittance; 0%), while **2a** at 80 °C was almost transparent (transmittance; *ca.* 80%) (Figure 1a). Such behaviors were observed repeatedly during heating-cooling cycles. Photographs as shown in Figure 2 also demonstrate that **2a** has temperature-responsive property. The temperature-responsive property is probably attributed to aggregation at lower temperature and dispersion at higher temperature of the polymer chains in the hydrogels.

When **1b** or **1c**, which had higher functionality of acrylamido groups (17% and 21%) than that of **1a**, was used, the obtained hybrid hydrogels **2b**, **c** did not exhibit drastic changes of transmittances between 25 °C and 80 °C (Figure 1b and 1c). Because the motion of the polymer chains in **2b**, **c** was restricted due to high contents of cross-linking points, they could not freely change between aggregation and dispersion states in hydrogels depending on temperatures as those were observed in **2a**. These results indicate that

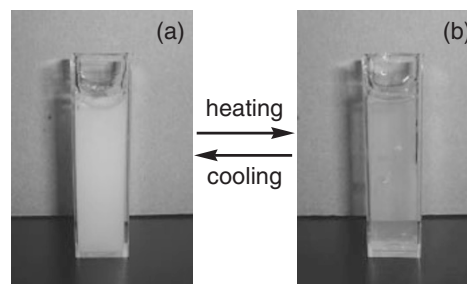


Figure 2. Photographs of **2a** at 25 °C (a) and 80 °C (b).

the chemical cross-linking densities in the hybrid hydrogels are important factor for their temperature-response. Furthermore, the hydrogels **3a-c**, which were synthesized using BisAAm as a conventional organic cross-linking agent and MAAm with different feed molar ratios ($[\text{BisAAm}]/[\text{MAAm}] = 0.5$ (**3a**), 1.0 (**3b**), and 3.0% (**3c**)), did not exhibit drastic tem-

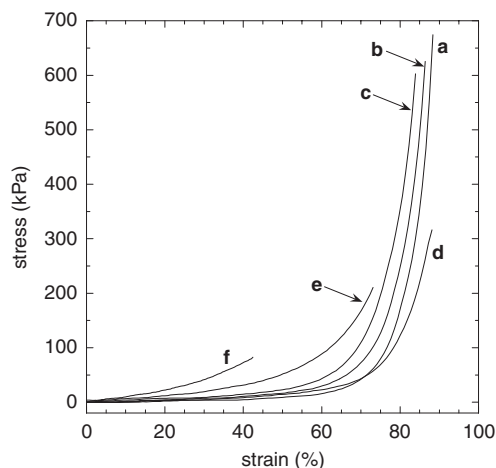


Figure 3. Stress-strain curves under compression for hybrid hydrogels **2a** (a), **2b** (b), **2c** (c) and hydrogels **3a** (d), **3b** (e), **3c** (f).

perature-response (Figure 1d–1f). These results probably indicate that the polysiloxane-based cross-linking agent **1** specifically affected the temperature-responsive behavior of PMAAm hydrogel.

Figure 3 shows stress-strain curves under compression of the hybrid hydrogels **2** and PMAAm hydrogels **3**. The hydrogels **3** broke at stresses in the range of 83–317 kPa (Figure 3d–3f), while the hybrid hydrogels **2** sustained the stresses in the range of 603–675 kPa and fracture strains of **2** were 84–88% (Figure 3a–3c). These results indicate that the compressive properties of the hybrid hydrogels **2** are more superior than those of the hydrogels **3** obtained using conventional organic cross-linking agent, probably because that the cross-linking points were dispersed well in the hydrogel **2**. Such a tendency was also observed with the hydrogels obtained using AAm monomer in our previous study.¹¹

CONCLUSION

We have prepared temperature-responsive hybrid

hydrogels by free-radical polymerization of MAAm using water-soluble rigid polysiloxane having acrylamido side-chains as a cross-linking agent. The hybrid hydrogel obtained using the polysiloxane-based cross-linking agent with relative low functionality of acrylamido group showed obvious temperature-response, *i.e.*, it was turbid at 25 °C and almost transparent at 80 °C. The compressive properties of the hybrid hydrogels were more superior than those of PMAAm hydrogels obtained using conventional organic cross-linking agent.

Acknowledgment. Y.K. acknowledges financial support from The Asahi Glass Foundation.

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