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Synthesis and Temperature-Responsive Properties of Novel Semi-interpenetrating Polymer Networks Consisting of a Poly(acrylamide) Polymer Network and Linear Poly(acrylic acid) Chains

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ABSTRACT: A novel semi-interpenetrating polymer network (semi-IPN) gel consisting of an AAm gel and linear PAAc chains was designed and developed. The semi-IPN gel was simply prepared by infiltrating PAAc chains into AAm gel networks from an outer PAAc solution through immersion of AAm gels in the PAAc solution. The semi-IPN gel swelled at higher temperature and shrunk at lower temperature. Swelling-ratio transition temperatures of the semi-IPN gel shifted to lower values with increasing pH of the surrounding PAAc solution. The swelling-ratio transition of the semi-IPN gel became sharper with higher-molecular-weight PAAc. These swelling-ratio changes were completely reversible. A prototype of a light modulator was fabricated utilizing semi-IPN microgel particles containing 20 wt % of carbon black pigment. The transmittance of the light modulator was altered from 63 to 8% when the light modulator was heated from 10 to 60 °C.

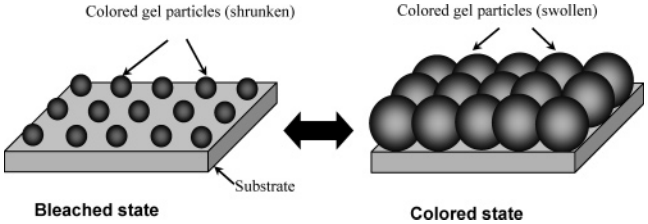
Introduction

Stimuli-responsive gels have been attracting much attention, both in fundamental fields and in practical applications, because gels are soft and respond to a wide variety of external stimuli, such as temperature, electricity, exposure to light, and chemicals.[1−10] These gels are considered appropriate for biomimetic materials. Numerous research groups around the world are developing applications for such gels in actuators, artificial muscles, drug-delivery systems, and sensors.[11−19]

Recently, we developed novel light-modulation gel materials that utilize the reversible volume-change property of stimuli-responsive gels.[20] The mechanism of the light-modulation materials emulates that of pigment cells of cephalopods such as squid and octopi,[21,22] which can rapidly change their skin color. These stimuli-responsive gels contain a high concentration of pigment as a colorant. The mechanism of the light-modulation materials is shown in Scheme 1. A light modulator made up of an array of stimuli-responsive colored gel particles changes color in synchronization with the expansion and contraction of the colored gel particles because the area covered with the colored gel particles is reversibly altered according to the volume change of the gel particles. These light-modulation materials have merit in that the color and kinds of stimuli can be designed independently of one another.

We have studied light-modulation properties of *N*-isopropylacrylamide (NIPAM) gels containing high concentrations of pigment. NIPAM gels exhibit volume phase transitions from swollen to shrunken states at its lower critical solution temperature, 34 °C, by hydrophobic interaction between NIPAM polymer chains in water. Thus, a light modulator using colored NIPAM gel particles can be expected to show a colored state below the LCST and a bleached state above the LCST. We confirmed that a light modulator using the dispersion of colored NIPAM gel particles showed excellent light-modulation performance.[20] On the other hand, when light-modulation gels showing a colored state at higher temperatures and a bleached state at lower temperatures are developed, these gels may be applied to energy-efficient “smart glass.” The smart glass alters its transmittance according to changes in the outside air temperature. More specifically, the glass becomes colored when the outside air temperature is high, and clear when the outside temperature is low. This smart glass can control the energy flow from the sun and reduce building air-conditioning loads.

Scheme 1: Schematic Drawing of the Color-Change Mechanism of a Light Modulator Utilizing Stimuli-Responsive Colored Gel Particles



To create smart glass, new types of stimuli-responsive gels must be developed with upper critical solution temperature (UCST) properties that swell at higher temperatures and shrink at lower temperatures. Several research groups have developed such gels by applying interpenetrating polymer networks (IPN).[16−18,23] These IPN gels are made of two different polymers, mostly cross-linked poly(acrylamide) (PAAm) and cross-linked poly(acrylic acid) (PAAc), which form interpolymer complexes through hydrogen bonding. Okano et al. reported a drastic swelling change in the IPN gels arising from cooperative polymer−polymer interactions (a zipperlike effect).[18] However, the swelling of IPN gels consisting only of PAAm and PAAc gradually increased and did not revert completely to their original state. Okano et al. reported that poor reversibility may be the result of too large a swelling ratio in the swollen state,

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resulting in PAAc and PAAm polymer chains that are too far apart to reform a PAAm−PAAc complex.[18] A hydrophobic unit such as a butylacrylamide moiety was introduced into the PAAm network to reduce the swelling ratio of the IPN gels at their swollen state for obtaining the reversibility of volume changes. Complete reversibility and a larger swelling ratio at the swollen state, resulting in a larger volume change, are important if the IPN gels are to be adapted to smart glass. In addition, it is desirable to prepare micrometer-size gel particles to achieve fast response time to temperature change because the response time of the volume change of gels is approximately proportional to the square of the cross-sectional diameter.[24] With IPN gel, however, preparation of such small gel particles is difficult because, when polymerization of acrylic acid in the presence of PAAm gels is carried out, formation of the second network, PAAc polymer networks, around the PAAm gels makes it difficult to separate the resulting individual IPN gels. An alternative method for preparing micrometer-size IPN gels that polymerizes AAc monomer and a cross-linker in micrometer-size PAAm gel particles independently needs complicated procedures, and the polymerization reaction for preparation of the second PAAc network is difficult to control because of the evaporation of solvent and PAAc from small PAAm gel particles.

Here, we propose a new UCST gel that can be easily prepared with micrometer size and form more stable and reproducible interpolymer complexes with a higher swelling ratio at the swelling state. The concept is a method to immerse linear PAAc polymer in PAAm network gel particles from the surrounding PAAc solution and to form semi-IPN gels. The semi-IPN gels are expected to show reversible volume change because the linear PAAc chains can be moved both in the PAAm gel network and the surrounding aqueous PAAc solution relatively freely and form polymer complexes with PAAm gel networks when the two polymer chains are far apart. The semi-IPN gels are also expected to have a larger swelling ratio at the swelling state than that of the IPN gels because PAAc chains are not cross-linked and, as a result, are more likely to absorb surrounding water. In addition, the semi-IPN gels are a suitable structure for synthesis of spherical gel particles with micrometer size, ideally shaped for light-modulation gels in terms of response time and reducing the granularity of a light modulator. The semi-IPN gel can be synthesized by immersion of PAAc polymer within micrometer-size PAAm gel particles, which can be easily prepared by inverse phase-suspension polymerization.

From this perspective, we report the development of a semi-IPN gel consisting of PAAm polymer networks containing linear PAAc polymer chains and its swelling behavior. We prepared semi-IPN gel particles by using black pigment for light modulation. The development of a prototype smart glass device that uses the black semi-IPN gel particles, and its light-modulation properties, are also described in this paper.

Experimental Section

Materials. AAm monomer, *N*,*N*′-methylenebisacrylamide (MBA, cross-linker), Ammonium persulfate (APS, radical initiator), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), and cyclohexane were purchased from Wako Pure Chemical Co., Ltd. PAAc powders with average molecular weights of 5000, 25 000, and 250 000 were also purchased from Wako Pure Chemical Co., Ltd. The molecular weights of PAAc were determined by viscosity measurements. An aqueous dispersion of carbon black pigment (model number TBK-BC3) was purchased from Taisei Chemical Industry Ltd. The average diameter of particles of carbon black pigment was approximately 130 nm. Sorbitan monostearate was purchased from Nikko Chemicals Co., Ltd. All reagents were used without further purification. Microphotographs of semi-IPN gels were taken by using an optical microscope (Nikon ECLIPSE ME600) equipped with a charge-coupled device (CCD) camera (Carl Zeiss Axio Cam HRc).

Preparation of Rod-Shaped PAAm Gel. A mixture of AAm (0.53 g), MBA (14 mg), and APS (6 mg) was dissolved in distilled water (10 mL). Nitrogen gas was bubbled through the solution for 20 min to remove dissolved oxygen. The solution was cooled at 0 °C with an ice−water bath. TMEDA (100 μl) was added, and the solution was stirred for 10 s. The solution was transferred into a sample tube with 10 glass capillaries (inner diameter 140 μm), and the sample tube was capped tightly. The sample tube was immersed in a water bath (15 °C) for 3 h to polymerize. PAAm gels were extracted by breaking the glass capillaries and immersing them in a large amount of water to remove residual chemicals. Thus, rod-shaped PAAm gels were obtained.

Preparation of Disk-Shaped PAAm Gel. A mixture of AAm (0.53 g), MBA (14 mg), and APS (6 mg) was dissolved in distilled water (10 mL). Nitrogen gas was bubbled through the solution for 20 min to remove dissolved oxygen. The solution was cooled at 0 °C with an ice−water bath. TMEDA (100 μl) was added, and the solution was stirred for 10 s. The solution was transferred between glass plates (100 mm × 100 mm × 3 mm), and the gap between the glass plates was maintained with Teflon sheets (thickness 1 mm). The glass plates were covered with a plastic bag and were immersed in a water bath (15 °C) for 3 h to polymerize. After polymerization was completed, the resulting AAm gel was peeled off the glass plate and cut into disk shapes (diameter 12 mm). The resulting disk-shaped AAm gels were immersed in a large amount of water for 1 week to remove residual chemicals. Thus, the disk-shaped PAAm gels were obtained.

Measurement of PAAc Permeation Speed into PAAm Gel. A glass tube (diameter 6 mm × 100 mm) was filled with an aqueous PAAc solution and capped with rubber septums. The glass tube was covered with a jacket in which water flowed from a constant-temperature water bath. Rod-shaped PAAm gels were immersed into the PAAc solution, and the temperature of the water in the jacket was controlled at 15 °C at a precision within 0.1 °C. The diameter change of PAAm gel over time was measured by using an optical microscope. The diameter change was expressed as (d/d_0), where d and d_0 represent the diameter of gels under certain conditions and at the preparation, respectively.

Measurement of Diameter Changes of Semi-IPN Gel. A glass tube (diameter 6 mm × 100 mm) was filled with an aqueous PAAc solution and capped with rubber septums. The glass tube was covered with a jacket in which water flowed from a constant-temperature water bath. Rod-shaped PAAm gel was immersed into PAAc solution and kept for 1 day to form semi-IPN gel. Then the temperature of water in the jacket was raised from 10 to 60 °C with temperature steps of 5 °C. At each condition, the temperature was kept for 30 min to reach the semi-IPN at equilibrium-swelling state. The diameter change as a function of temperature was measured with an optical microscope and expressed as d/d_0.

Measurement of Swelling Ratio of Semi-IPN Gel and PAAc Molar Ratio to PAAm in Semi-IPN Gel. Disc-shaped PAAm gels at the equilibrium-swelling state (15 °C) were placed onto an aluminum Petri dish, then dried on a hot plate (120 °C) for 3 h and in vacuo at 50 °C for 1 day. The weight of the dried disc-shaped PAAm gels were measured, and their average weight (w_0) was calculated.

Other disc-shaped PAAm gels synthesized under the same conditions as the PAAm gels used above were immersed into aqueous PAAc solution (110 mL). The solution was immersed into a temperature-controlled water bath (15 °C) for 3 weeks to form semi-IPN gels and to reach the equilibrium-swelling state. The weights of the semi-IPN gels at the equilibrium-swelling state (w_{wet}) were measured. Then, the semi-IPN gels were dried under the same conditions for drying PAAm gels. The weights of the dried semi-IPN gels (w_{dry}) were measured. The swelling ratio of semi-IPN gel (S) and the molar ratio of AAc to AAm in semi-IPN gel (R) were calculated as follows:

$$S = \frac{w_{\mathrm{wet}} - w_{\mathrm{dry}}}{w_{\mathrm{dry}}}$$

$$R = \frac{(w_{\mathrm{dry}} - w_0)/M_{\mathrm{AAc}}}{w_0/M_{\mathrm{AAm}}}$$

Here, M_{AAc} and M_{AAm} represent molecular weights of AAc and AAm units in PAAc and PAAm polymer chains, respectively.

Preparation of Semi-IPN Gel Particles Containing Carbon Black Pigment. A mixture of AAm (0.53 g), MBA (14 mg), and aqueous carbon black dispersion (8.5 g, pigment solid content 15.1 wt %) was dissolved in distilled water (10 mL). Nitrogen gas was bubbled through the solution for 20 min to remove dissolved oxygen. The solution was cooled at 0 °C with an ice−water bath. APS (80 mg) was added, and the solution was stirred for 30 s. The solution was suspended in cyclohexane (300 mL) and sorbitan monostearate (emulsifier) (9.0 g) in a 2 L separable round-bottom flask equipped with a mechanical stirrer and vigorously stirred for 30 min at 15 °C. TMEDA (0.5 mL) dissolved in cyclohexane (2.5 mL) was added to the above suspension to accelerate the polymerization. The suspension was polymerized at 15 °C for 3 h. Thereafter, the reaction mixture was poured into pure water (1.5 L). The mixture was stirred for 1 h and left to stand overnight; then, cyclohexane was removed by decantation. The resulting PAAm gel particles were washed with pure water (2 L × 3) to remove the emulsifier and other chemical residues. Thus, black PAAm gel particles were obtained. Black semi-IPN gel particles were prepared by immersing the black PAAm gel particles into 2 wt % of PAAc solution for 1 day to infiltrate PAAc into the PAAm gel particles. The diameter changes of the semi-IPN gel particles were measured with an optical microscope (Nikon ME600) with a calibrated scale. The amount of volume change of the gel, $dV = V/V_0 = (D/D_0)^3$, was calculated from the equilibrium diameter (D) and that of the fully shrunken state (D_0) at 10 °C. The temperature was controlled within 0.1 °C by a hot plate (Mettler FP 82HT).

Preparation and Optical Properties of a Prototype Smart Glass Using Black Semi-IPN Gel Particles. A glass plate (50 mm × 50 mm × 0.9 mm) was coated with black semi-IPN gel dispersion in 2 wt % of PAAc (gel solid content 1.5 wt %). The glass plate was laminated with another glass plate. Monodispersed polystyrene particles (110 μm in diameter) were used to maintain the space between the glass plates. The edges of the glass plates were sealed with UV-curable adhesive. Thus, a light modulator using the black semi-IPN gel particles was obtained. The spectra in the visible light region of the light modulator were measured by using a UV−vis spectrometer (HITACHI U-4000). The spectra of the light modulator with black semi-IPN gel particles at their shrunken and swollen states were measured at 10 and 60 °C, respectively.

Results and Discussion

IPN gels consisting of PAAm and PAAc double polymer networks were reported to exhibit volume changes according to temperature changes.[18] On the other hand, PAAm and PAAc are known to form complexes that have an upper critical solution temperature (UCST) and dissociate reversibly at 25 °C in aqueous PAAm−PAAc solution mixtures. These facts indicate that the IPN structure is not necessarily important to show volume change of a gel consisting of PAAm and PAAc double polymer networks because linear PAAm and PAAm can aggregate into compact shape, make a complex, and precipitate in water below the UCST. On the basis of these facts, we designed a semi-IPN gel consisting of linear PAAc dispersed in PAAm gels. The semi-IPN gels are expected to show the UCST property and complete reversibility in volume change.

We thought that linear PAAc chains might infiltrate PAAm gel networks in aqueous solution and form a semi-IPN structure, although it has been reported that polymers with larger molecular weight are difficult to penetrate into polymer gel networks.[25,26] On the basis of this assumption, PAAm gel was immersed into 2 wt % of aqueous PAAc (average molecular weight 25 000) solution. Shrinkage of the PAAm gel was observed at ambient temperature. The PAAm gel became swollen again as the temperature rose. We found that the PAAm gel in aqueous PAAc solution showed reversible volume changes according to temperature changes. In addition, the weight of the dried shrunken PAAm gel that had been immersed in PAAc solution was almost twice that before immersion in the PAAc solution. These results indicated that, by simply immersing a PAAm gel into aqueous PAAc solution, the PAAc chains can infiltrate into the PAAm gel network and form a semi-IPN that exhibits volume changes in response to temperature changes. Then, the volume-change properties of the semi-IPN were investigated in more detail.

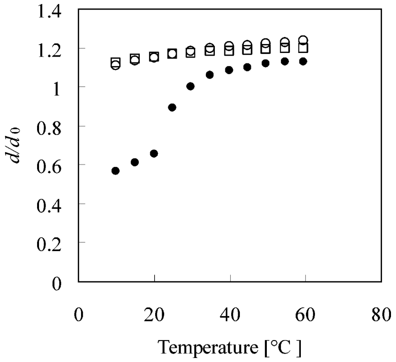

Figure 1. Temperature-dependent diameter changes of PAAm gel in various media as a function of temperature: (●) PAAc 2 wt %, (○) AAc 2 wt %, (□) distilled water.

A rod-shaped PAAm gel was synthesized by solution polymerization in a glass capillary (inner diameter 140 μm). The PAAm gel was immersed into 2 wt % of aqueous PAAc solution and left to stand for 1 day to form a semi-IPN gel. Figure 1 shows the temperature-dependent diameter change of the semi-IPN gel as a function of temperature. To confirm the volume change stemming from the semi-IPN structure, temperature-dependent diameter changes of the same PAAm gels in distilled water and 2 wt % of aqueous AAc monomer were also measured. In the case of using PAAc solution, a PAAm gel that forms a semi-IPN gel with PAAc shrank at lower temperatures and exhibited drastic changes in diameter from 25 °C to 35 °C. On the other hand, PAAm gel did not show such diameter change either in water or aqueous AAc monomer solution. The polymeric structure of AAc was important to the diameter change of the semi-IPN gel.

From these results, the following conclusions can be made: (1) PAAc with relatively high molecular weight can permeate PAAm gel networks and form a semi-IPN gel. (2) In the semi-IPN gel, PAAc chains form a polymer complex with a PAAm network at a lower temperature, which promotes shrinkage of the semi-IPN gel. (3) The semi-IPN demonstrates reversible volume change due to the reversible formation of polymer complexes between AAm gel networks and PAAc chains according to temperature changes.

In general, it is reported that permeation of polymeric compounds into gel networks is difficult. For example, Freitas et al. reported that gels can absorb low-molecular-weight polymers, but exclude high-molecular-weight polymers or proteins, a property that can be useful in the separation of various chemicals.[25] Ishidao et al. reported that poly(ethylene oxide) (PEO) and starch hardly infiltrated N-isopropylacrylamide

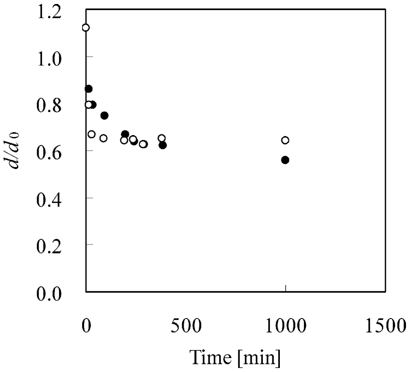

Figure 2. Time-dependent diameter changes of rod-shaped PAAm gels immersed into 2 wt % of PAAc solutions at 15 °C. Molecular weight of PAAc: (○) 5000, (●) 250 000.

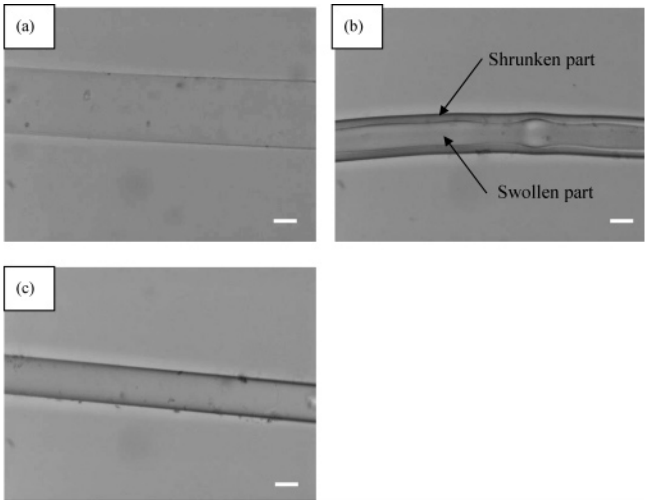

Figure 3. Contraction process of a PAAm gel in 2 wt % of aqueous PAAc250k solution to form a semi-IPN gel at 15 °C. The time courses of the pictures are (a) 0 h, (b) 3 h, and (c) 16.7 h. Scale bars in the photographs are 50 μm.

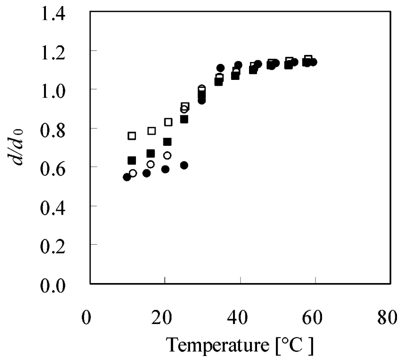

Figure 4. Diameter-change properties of semi-IPN gels in aqueous PAAc solution with various PAAc concentrations as a function of temperature. Concentration of PAAc: (●) 0.2 wt %, (○) 2.0 wt %, (■) 5.0 wt %, (□) 10 wt %. Molecular weight of PAAc: 25 000.

gel networks when the average molecular weights of these polymers were larger than several thousands.[26] Our results, however, showed that PAAc chains could penetrate and form polymer complexes with PAAm gel networks, even when the molecular weight was large. To investigate this phenomenon, time-dependent diameter changes of PAAm gel in PAAc solutions were carried out.

Figure 2 shows the time-dependent diameter change of rod-shaped PAAm gels at 15 °C just after immersion in 2 wt % of aqueous PAAc solutions of different molecular weights. PAAc with average molecular weights of 5000 (PAAc5k) and 250 000 (PAAc250k) were used for the measurement. In case of PAAc5k, the PAAm gel rapidly shrank and reached the equilibrium-shrinking state after approximately 30 min. In contrast, a PAAm gel in the PAAc250k solution showed slower shrinking speed, but reached almost the same diameter after 17 h. This phenomenon indicated that both kinds of PAAc could penetrate PAAm gel networks completely and formed a semi-IPN gel. The kinetics of the formation process of the semi-IPN gel was monitored by an optical microscope. In Figure 3, the shrinking process of the PAAm gel to form the semi-IPN gel is shown when the PAAm gel was immersed into the PAAc250k solution at 15 °C. The PAAm gel gradually shrunk from the outside, and two domains were observed after 3 h. It is known that the difference in appearance of transparent objects results from the difference in the refractive indices between the objects. Therefore, these two clear domains in the PAAm gel indicated that PAAc chains infiltrating from the outside the PAAm gel formed a shrunken semi-IPN gel that had a higher polymer concentration than the swollen PAAm gel and, therefore, had a higher refractive index.

On the basis of these observations, the permeation mechanism of PAAc into PAAm gels was assumed as follows. Free PAAc chains infiltrates PAAm networks driven by hydrogen bonding between them because PAAc can make strong hydrogen bonds between PAAm at a lower temperature. The PAAc moves forward deep inside of the PAAm networks, along the PAAm chains, by forming and dissociating hydrogen bonds. By this, PAAc chains with higher molecular weight can infiltrate a PAAm gel network relatively easily.

As described above, it was found that a wide range of molecular weights of PAAc could be used for preparing semi-IPN gel. Effects of various parameters of PAAc such as concentration, molecular weight, and pH on the properties of the semi-IPN gels were investigated in detail.

The concentration of PAAc seems to affect the volume-change properties of semi-IPN gel because the concentration alters the equilibrium distribution of PAAc to PAAm gel and/or the osmotic pressure of the PAAc solution. Temperature-dependent diameter changes of semi-IPN gels prepared in various concentrations, from 0.2 to 10 wt %, of aqueous PAAc with a molecular weight of 25 000 (PAAc25k) were measured. The pHs of PAAc25k solutions were adjusted to about 3.2 by using NaOH aq. The results are shown in Figure 4: Each semi-IPN gel shrank at a lower temperature and swelled at a higher temperature. When the concentration of PAAc solution was lower, diameters of the semi-IPN gels at a shrunken state became smaller. On the other hand, the diameters at swollen states were almost the same despite the concentration of PAAc solution. At first, the diameter of a semi-IPN gel was assumed to become smaller at higher concentrations of PAAc because of the osmotic pressure from the PAAc solution. The results, however, belied this expectation. There must be another influence from the PAAc other than osmotic pressure. Hence, the swelling ratios and PAAc/PAAm ratios of semi-IPN gels were carefully investigated for various concentrations of PAAc.

Semi-IPN gels were prepared by immersing disk-shaped PAAm gel into aqueous PAAc solutions at various concentrations for more than 3 weeks at 15 °C to reach the equilibrium-swollen state. The swelling ratio and PAAc/PAAm ratio of the semi-IPN gels were obtained by gravimetric measurement. Results are shown in Figure 5. The PAAc ratio increased when the concentration of PAAc became higher (Figure 5a). The swelling ratios of the semi-IPN gel at 15 °C were around 1.2 in all cases despite the concentration of PAAc (Figure 5b). This

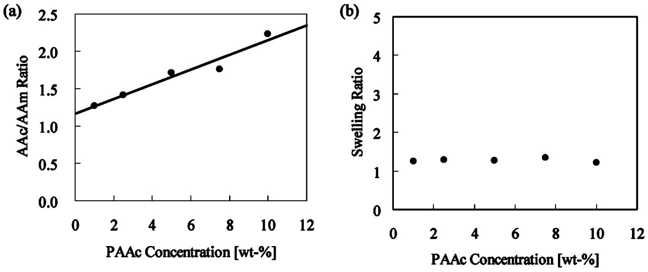

Figure 5. PAAc−concentration dependence of (a) PAAc/PAAm ratio of the semi-IPN gel and (b) water absorptivity of the semi-IPN gel at its shrunken state at 15 °C. Molecular weight of PAAc: 25 000.

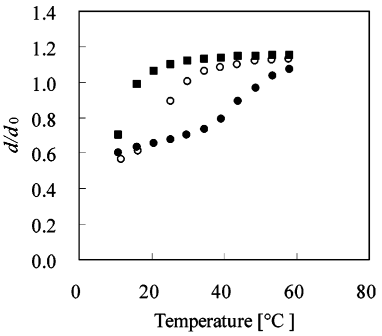

Figure 6. Effect of pH of PAAc solution on temperature dependence of the d/d_0 of the semi-IPN gel. pH of PAAc solution: (●) 2.06, (○) 3.09, (■) 3.38. Molecular weight of PAAc: 25 000.

result indicated that the semi-IPN gel in a shrunken state can hold a certain amount of water against a certain amount of polymer chain in the gel whether the PAAc forms polymer complexes with PAAm. Therefore, the difference in diameters of semi-IPN gels in various concentrations of PAAc solution is explained as follows: with higher concentration of PAAc, the amount of PAAc in the semi-IPN gel increased, while the amount of water held per unit weight of polymer remained constant. As a result, the amount of polymer and water comprising the semi-IPN gel increased and led to enlargement of the diameter of the semi-IPN gel.

Then, the pH effect of PAAc solutions is described. In aqueous solutions of PAAc25k (2 wt %) with various pHs by adding NaOH aq, PAAm gels were immersed to form semi-IPN gels. Diameter-change properties of these semi-IPN gels are shown in Figure 6. In PAAc25k solution without neutralization (pH 2.63), semi-IPN gel began to swell around 30 °C, and the diameter gradually increased with temperature change. On the other hand, semi-IPN gels in higher pH solutions began to swell at lower temperature and showed sigmoidal change in diameters. The semi-IPN gel in pH 3.09 solution showed drastic diameter change from 20 to 40 °C. In the case of pH 3.38, the semi-IPN gel had already been swelling at 10 °C. From these results, we found that diameter of the semi-IPN gels began to change more sigmoidally and began to swell at a lower temperature as the pH of the surrounding solution was increased.

The pH dependence of the diameter change can be explained as follows: increasing pH promotes the dissociation of carboxyl groups in PAAc chains. The carboxyl groups cannot contribute to the formation of the hydrogen bond with PAAm, which weakens the attraction force between the PAAc and the PAAm. In consequence, increasing the pH, which makes the polymer complexes between PAAm and PAAc readily dissociate at a lower temperature, decreases the diameter-change temperature of the semi-IPN gel. It is also reported by Tanaka et al. that volume change of gels becomes sharp when the ionic components in the gels increase.[2] Analogously, the diameter changes of the semi-IPN gels becomes sharp according to pH increase with the increase of ionic components in the semi-IPN gels caused by the dissociation of the carboxyl group.

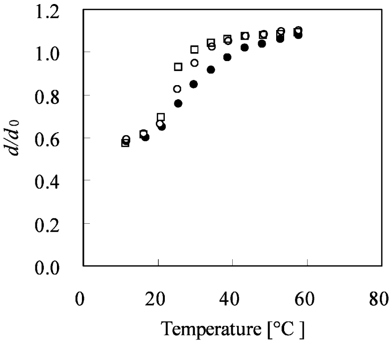

Figure 7. Effect of average molecular weight of PAAc on temperature dependence of the d/d_0 of the semi-IPN gel. Molecular weight of PAAc: (●) 5000, (○) 25 000, (□) 250 000. Concentration of PAAc solution: 2.0 wt %.

These results show that the diameter-change temperature and its profile can be adjusted by pH changes. When using these semi-IPN gels as light modulation gels, the light modulation temperature can be controlled by the pH of the surrounding solution with a certain degree of freedom. In other words, light modulation gels that respond to various temperature ranges can be prepared utilizing semi-IPN gels.

The effect of molecular weight of PAAc on semi-IPN gel was investigated. Semi-IPN gels were prepared from PAAm gels and 2.0 wt % PAAc solutions with average molecular weights of 5000, 25 000, and 250 000, respectively (pH was adjusted to 3.2 with NaOH aq.). Temperature dependence for the diameters of the semi-IPN gels was measured in the same PAAc solution. Results are shown in Figure 7. All the semi-IPN gels showed almost the same amount of diameter change: d/d_0 was 0.6 at 10 °C and 1.1 at 60 °C, respectively. In addition, the semi-IPN gels started to swell around 20 °C. One characteristic difference was the sharpness of the diameter change. The larger the molecular weight of PAAc, the sharper the diameter change of the semi-IPN. It is known that random poly(AAm−AAc) gel and IPN gel constructed from PAAm and PAAc networks show gradual and sigmoidal volume change, respectively. Okano et al. suggested that long and independent polymer chains are important for sigmoidal volume change in IPN gel.[18] Dissociation of some initial complex between PAAm and PAAc is considered to promote the cooperative dissociation of the ladderlike polymer complexes between PAAm and PAAc chains (a zipper effect). Analogously, in the case of the semi-IPN gels, the polymeric and sequential structure of PAAc was found to be important to produce the sigmoidal d/d_0 change shown in Figure 7. The effect on the profile of the d/d_0 change of molecular weight, in other words, the length of the polymeric structure, became clear for the first time using the semi-IPN structure; it had been difficult to evaluate with IPN gel.

The d/d_0 changes in response to reversible stepwise temperature change between 15 and 60 °C were evaluated by using a semi-IPN gel prepared in 2.0 wt % of aqueous PAAc25k solution. As shown in Figure 8, the d/d_0 changes were completely reversible within a constant range. Complete reversibility of the d/d_0 of the semi-IPN gel was different from that of IPN gel constructed of PAAm and PAAc reported previously. Okano et al. reported that once IPN gel consisting of PAAm and PAAc fully swelled, the IPN gel lost the ability to shrink to its initial shrunken state in response to a decrease in temperature.[18] The reason was assumed to be that PAAm

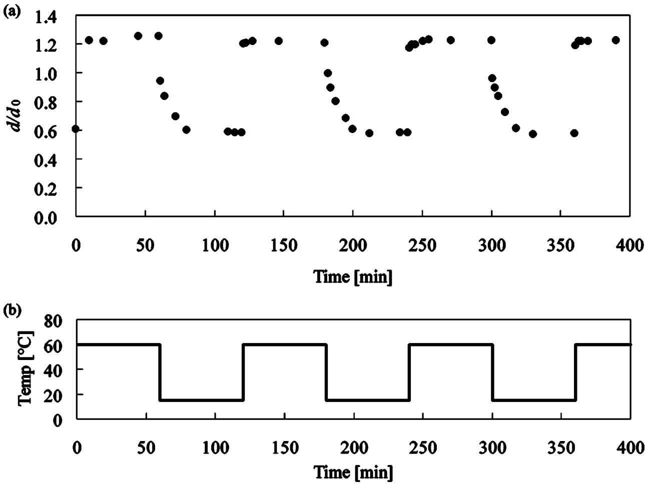

Figure 8. Reversible diameter change of the semi-IPN gel in response to stepwise temperature change between 15 and 60 °C. (a) Diameter change of the semi-IPN gel. (b) Temperature change of the surrounding PAAc solution. Molecular weight and concentration of PAAc were 25 000 and 2.0 wt %, respectively.

and PAAc chains might be separated too far in the swollen state at high temperature to reform PAAc−PAAm complexes. They also assumed that the decrease in concentration of PAAc at swelling could promote ionic dissociation of PAAc, which made it difficult for PAAc to form a polymer complex with PAAm. On the basis of these assumptions, Okano et al. introduced hydrophobic moieties such as butylacrylamide into the PAAm polymer network for reversible volume change. The hydrophobic moieties in the PAAm network reduced the water absorptivity of IPN gel and prevented PAAm chains from separating far from PAAc network chains. This IPN gel exhibited good reproducibility of volume change, while the swelling ratios were changed generally from 1−2 to 2−4 when heated (about twice change in volume).[18] On the contrary, semi-IPN gel studied here used PAAm gel and PAAc chains dissolved in aqueous media. Therefore, the PAAc chains can be moved both in the PAAm gel network and aqueous phase relatively freely and form polymer complexes with PAAm gel networks. In addition, because PAAc chains also existed at a constant concentration in outer aqueous solution, the ionic dissociation rate of PAAc was assumed to be constant after the full dissociation of PAAc−PAAm polymer complexes. Thus, even when PAAc and PAAm separate at a higher temperature, PAAc chains can reform a polymer complex with PAAm gel networks through the thermal diffusion process and reach their initial equilibrium states. In fact, when PAAm gel at the equilibrium-swelling state in aqueous media was immersed in a PAAc solution where PAAc chains were considered to be distant from PAAm gel networks, PAAc chains penetrated the PAAm gel network and reached the equilibrium-shrunken state (Figure 2). Furthermore, the diameter of shrunken gel in Figure 2 was almost as same as those of other experiments, as shown in Figures 1, 6, 7, and 8. These results indicate that the semi-IPN can always reach the same equilibrium-shrunken state. The freedom of movement of PAAc chains and a constant concentration of PAAc chains around the semi-IPN gel environment were considered to contribute to the excellent reversibility of the d/d_0 changes of the semi-IPN gel, even while achieving a larger volume change (about twice the change in diameter, eight times the change in volume). The precise comparison of reversible swelling-changes properties between the IPN gels and the semi-IPN gels is a very interesting topic in a fundamental point of view. However, it was difficult to prepare small IPN gels with micrometer-size-like rod-shaped IPN gels and IPN gel microparticles, which are important for precise measurement of the swelling ratio, because the PAAc gel networks formed around IPN gels hinder the separation of each IPN gels, as mentioned in the Introduction. We are now trying to develop a method to compare the swelling behaviors of these gels. We hope to report the results elsewhere soon.

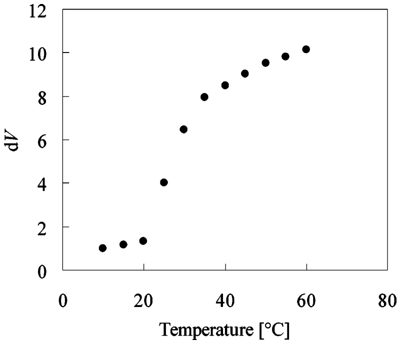

Figure 9. Volume-change property of the black semi-IPN gel containing carbon black pigment as a function of temperature. Molecular weight and concentration of PAAc were 25 000 and 2.0 wt %, respectively.

Stability of the diameter change even with repetitive temperature changes is one of the most important attributes for various applications, especially for optical devices such as smart glass. It was confirmed that the semi-IPN gel characteristics were suitable for these applications.

In Figure 8, the swelling process was faster than the shrinking process. The difference in speed between swelling and shrinking can probably be explained as follows: as discussed earlier, rapid swelling was due to the cooperative dissociation of polymer complex between PAAm and PAAc chains. In addition, the diffusion speed of polymer chains increases at higher temperatures. On the other hand, PAAm and PAAc need to approach each other and to make hydrogen bonds at lower temperatures to shrink the semi-IPN gel. It is also noted that the semi-IPN gel showed relatively fast response to temperature changes. Because the semi-IPN can be prepared by a simple procedure, it is possible to synthesize semi-IPN gel with micrometer size. Thus, this rod-shaped semi-IPN gel completes its volume change within 30 min, although complete volume changes took more than 10 h in the case of reported bulk IPN gel.[18] The difference derived from the fact that the interval required for volume change of a gel is principally governed by the collective diffusion of the polymer network of the gel.[24] The fact that fast-response UCST gel can be easily prepared by using the semi-IPN gel structure may expand the application area of the semi-IPN gels.

To investigate light modulation properties of the semi-IPN gel, black semi-IPN microgel particles were prepared by using AAm gel particles containing 20 wt % of carbon black pigment and 2.0 wt % of aqueous PAAc25k solution. Figure 9 shows the temperature-dependent volume-change profile of the black semi-IPN microgel particles. Here, we defined the amount of volume change as $dV = V/V_0$. The V and V_0 expressed the volume of the black semi-IPN gel at an equilibrium-swelling state and fully shrunken state at 10 °C. The reason we used dV here instead of d/d_0 is that it was difficult to accurately measure the initial diameter of PAAm microgel particles. It was confirmed that, even when containing a high concentration of pigment, semi-IPN gel could exhibit larger volume changes with temperature changes.

A light modulator as a prototype of smart glass was fabricated by utilizing the dispersion of the black semi-IPN microgel

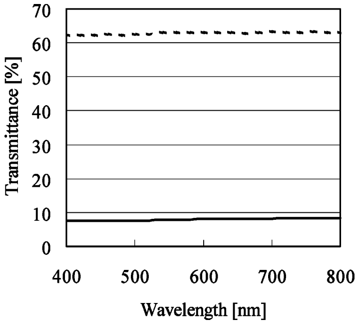

Figure 10. Transmittance change of a light modulator utilizing black semi-IPN gel particles. Colored and bleached states were measured at 10 °C (dotted line) and 60 °C (solid line), respectively. Molecular weight and concentration of PAAc were 25 000 and 2.0 wt %, respectively.

particles in 2.0 wt % of aqueous PAAc25k solution. The light modulator was almost transparent at lower temperatures and turned dark as the temperature increased. The transmittances of the light modulator at 10 and 60 °C are shown in Figure 10. After several cycles of heating and cooling, no leakage of pigment from the semi-IPN microgel particles was observed. The reason is probably that the size of the pigment particles is much larger than the mesh size of the PAAm polymer network and the pigment particles were tightly confined in the PAAm polymer networks, as we reported previously.[20] The light modulator using a simple dispersion of the black semi-IPN gel particles was not stable for a long time, because of the sedimentation and gradual aggregations of the particles in the light modulator. The aggregations among the gel particles gradually occurred because the gel particles developed a sticky surface when they shrank. However, through this experiment, we revealed that the semi-IPN colored with pigment has a strong potential as a new form of light modulation material, especially for smart glass applications. In addition, we have already reported that sedimentation and aggregation of colored gel particles in a light modulator could be solved by holding these gel particles in another polymer matrix.[27] Attempts to improve the stability of the light modulator are currently underway.

Conclusion

Through this study, we have designed a novel semi-IPN gel constructed with linear PAAc chains infiltrated into PAAm gel networks and have determined the volume-change properties of the semi-IPN gel with interaction between PAAm networks and PAAc chains. The semi-IPN gel can be synthesized simply by immersing PAAm gel into aqueous PAAc solution. The PAAc ratio and the diameter of the semi-IPN gel became larger with increased concentrations of PAAc in the outer solution. The semi-IPN gel shrank at a lower temperature and swelled at a higher temperature. The temperature range for producing volume change can be controlled by adjusting the pH of the outer PAAc solution. The higher the pH, the lower the volume-change temperature, and the diameter-change profile became sigmoidal. The semi-IPN gel containing higher-molecular-weight PAAc exhibited diameter change over a narrower temperature range. The effect of sequential length of PAAc chains on the volume-change property of the semi-IPN gels was clarified. This sharper change is considered to result from the cooperative dissociation of the PAAc−PAAm complex. The semi-IPN gel exhibited reversibility due to the free movement of linear PAAc chains between inside of the semi-IPN gel and the surrounding PAAc solution. A light modulator as a prototype of smart glass for energy conservation was also fabricated utilizing semi-IPN gel microparticles containing carbon black pigment as a colorant. The light modulator demonstrated transmittance change with temperature fluctuations. The light modulator was transparent at 10 °C and turned dark at 60 °C. We believe a light modulator utilizing the semi-IPN gel consisting of PAAm gel and linear PAAc has strong potential as a smart glass.

References and Notes

(1) Tanaka, T. *Phys. Rev. Lett.* **1978**, *45*, 820.
(2) Tanaka, T.; Fillmore, D.; Sun, S. T.; Nishio I.; Swislow, G.; Shah, A. *Phys. Rev. Lett.* **1980**, *45*, 1636.
(3) Hirokawa Y.; Tanaka, T. *J. Chem. Phys*. **1984**, *81*, 6379.
(4) Hirotsu, S.; Hirokawa, Y.; Tanaka, T. *J. Chem. Phys*. **1987**, *87*, 1392.
(5) Hirotsu, S. *J. Chem. Phys*. **1988**, *88*, 427.
(6) Okuzaki, H.; Osada, Y. *Macromolecules* **1994**, *27*, 502.
(7) Annaka, M.; Tanaka, T. *Nature* **1992**, *355*, 430.
(8) Tanaka, T.; Nishio, I.; Sun, S. T.; Ueno, S. *Science* **1982**, *218*, 467.
(9) Irie, M.; Kunwatchakun, D. *Macromolecules* **1986**, *19*, 2476.
(10) Suzuki, A.; Tanaka, T. *Nature* **1990**, *346*, 345.
(11) Liu, Z.; Calvert, P. *Adv. Mater*. **2000**, *12*, 288−291.
(12) Osada, Y.; Kishi, R.; Hasebe, M. *J. Polym. Sci., Part C: Polymer Lett.* **1987**, *25*, 481.
(13) Osada, Y.; Okuzaki, H.; Hori, H. *Nature* **1992**, *355*, 242.
(14) Hirai, T.; Nemoto, H.; Hirai, M.; Hayashi, S. *J. Appl. Polym. Sci.* **1994**, *53*, 79.
(15) Shinohara, S.; Tajima, N.; Yanagisawa, K. *J. Intell. Mater. Syst. Struct.* **1996**, *7*, 254.
(16) Bae, Y. H.; Okano, T.; Hsu, R.; Kim, S. W. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 481.
(17) Okano, T.; Bae, Y. H.; Jacobs, H.; Kim, S. W. *J. Controlled Release* **1990**, *11*, 255.
(18) Katano, H.; Maruyama, A.; Sanui, K.; Ogata, N.; Okano, T.; Sakurai, Y. *J. Controlled Release* **1991**, *16*, 215.
(19) Kataoka, K.; Miyazaki, H.; Bunya, M.; Okano, T.; Sakurai, Y. *J. Am. Chem. Soc*. **1998**, *120*, 12694.
(20) Akashi, R.; Tsutsui, H.; Komura, A. *Adv. Mater.* **2002**, *14*, 1808.
(21) Bozler, E. *Z. Vgl. Physiol*. **1929**, *8*, 371.
(22) Cloney, R. A.; Florey, E. *Z. Zellforsch.* **1968**, *89*, 250.
(23) Ilmain, F.; Tanaka, T.; Kokufuta, E. *Nature* **1991**, *349*, 400.
(24) (a) Tanaka, T.; Hocker, L. O.; Benedek, G. B. *J. Chem. Phys*. **1973**, *59*, 5151. (b) Tanaka, T.; Fillmore, D. J. *J. Chem. Phys.* **1979**, *70*, 1214.
(25) Freitas, R. F. S.; Cussler, E. L. *Chem. Eng. Sci.* **1987**, *42*, 97.
(26) (a) Ishidao, T.; Akagi, M.; Sugimoto, H.; Iwai, Y.; Arai, Y. *Macromolecules* **1993**, 26, 7361. (b) Ishidao, T.; Akagi, M.; Sugimoto, H.; Onoue, Y.; Iwai, Y.; Arai, Y. *Fluid Phase Equilib.* **1995**, *104*, 119. (c) Ishidao, T.; Song, I. S.; Ohtani, N.; Sato, K.; Iwai, Y.; Arai, Y. *Fluid Phase Equilib.* **1997**, *136*, 163.
(27) Tsutsui, H.; Mikami, M.; Akashi, R. *Adv. Mater.* **2004**, *16*, 1925.

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