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Robust Imogolite Hydrogels with Tunable Physical Properties

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Mechanically tough hydrogels with tunable physical properties (*i.e.,* mechanical strength and stimuli responsiveness) were obtained by *in situ* copolymerization of various vinyl monomers such as acrylic acid (AA), 2-hydroxyethyl acrylate (HEA), acrylamide (AAm), and *N*-isopropylacrylamide (NIPA) in an aqueous media containing imogolite (IG), an aluminosilicate nanotube clay. *In situ* copolymerization of AA and NIPA in the presence of IG gave robust hydrogels that showed thermo-responsive volume change owing to coil/globule transitions of the NIPA fragments. Furthermore, the mode of interaction between IG and the organic polymer was critical for determining the mechanical properties of the resultant hydrogel. Thus, IG gels with tunable physical properties were produced by designing the molecular structure of polymers, *i.e.,* by modulating the strength of interaction between IG nanotubes and organic polymer units.

Introduction

Hydrogels have the potential to play an important role as functional soft materials because of their mechanical flexibility and quick stimuli-responsive properties derived by, for instance, thermo-responsive volume transitions.[1] However, industrial and biomedical applications of hydrogels are usually limited by their poor mechanical strength owing to inhomogeneous network structures that may bring about local stress condensation.[1-4] Last few decades have witnessed the development of novel hydrogels by high precision molecular design; such hydrogels exhibit improved mechanical strength and have well-defined structures.[5-7] Previously, our group has successfully developed robust hydrogels that showed strain-induced structural ordering by hybridization with imogolite (henceforth denoted as IG), a rigid inorganic nanotube.[8-10]

IG is a single-walled, high aspect ratio aluminosilicate tubular inorganic polymer with the composition $(HO)_3Al_2O_3SiOH$.[11-16] IG's external and internal diameters are approximately 2 and 1 nm, respectively, while its length can range from several tens nanometers to several micrometers. Since IG is a perfectly rigid polyelectrolyte,[17,18] it has been used as a constituent of inorganic-organic nanocomposites.[19-22] The outer and inner surfaces of IG are covered with $Al(OH)_2$ (proton-capturing) and $Si(OH)$ (proton-releasing) groups, respectively. Thus, the charge density of IG surfaces varies with the pH and ionic strength of aqueous media. Consequently, the dispersibility of IG in water changes drastically with pH; they disperse as thin bundles or even as monofilaments in acidic and relatively low ionic strength aqueous media (pH ≈ 4), resulting in opaque to transparent solutions. However, they assemble into thick bundles or networks in aqueous solutions with higher pH and/or ionic strength and yield apparently turbid

dispersions.[23] It has also been reported that amine or amide molecules with size smaller than the internal diameter of IG nanotubes can be trapped in the hollows due to the interaction between $-NH_2$ or $-CONH_2$ groups and $Si(OH)$ groups.[18,24-26]

In the present work, we synthesized IGs that gave slightly opaque aqueous dispersions with a nanotube concentration of 6.4 w/v% by sonication in pure water. The average length of IGs was shortened to about 130 nm.[10] These IG nanotube dispersions turned to robust hydrogels (henceforth denoted as IG gels) after *in situ* radical polymerization of a co-existing vinyl monomer, acryl amide (AAm) even without using any crosslinking reagent.[8-10] The resulting IG gels exhibited distinct, reversible isotropic-anisotropic structural transition in response to small tensile strain, depending on the type and feed ratio of the component species. The strain-induced anisotropic ordering of nanotubes in the IG-PAAm (*in situ* polymerized) nullified upon relaxation. Nevertheless, the order is restored by the second *in situ* polymerization owing to the formation of interpenetrating polymer networks that formed new materials with stable anisotropic mechanical and/or optical properties.[10]

To develop IG gels with tunable mechanical/stimuli-responsive properties, we investigated polymer units containing different functional groups as candidates for hybridization with IG nanotubes (Table 1). The physical and optical properties of the obtained IG gels were estimated by tensile strain testing and birefringence changes. The structural change with the temperature was also studied for IG gels containing thermo-responsive units.

Experimental

Chemicals

Deionized water was used, which was further purified by a Milli-Q® Advantage A10® system (Millipore™, Eschborn, Germany) is utilized for all the experiments. AAm (Junsei Chemical Co., Ltd., Japan)

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Table 1 Candidate Polymers to be Hybridized with IG, Their Expected Interaction with IG and Plausible Nature of the Expected IG gels.

Polymer	Expected interaction with IG	Expected nature of IG gel
PAAm[8-10] [Poly(acryl amide)]	>C=O ⋯ HO-Si- and -CONH$_3^+$ ⋯ $^-$O-Si-	Elasticity
PHEA [Poly(hydroxyethyl acrylate)]	-OH ⋯ HO-Al-[19]	Rigidity
PAA [Poly(acrylic acid)]	>C=O ⋯ HO-Al- and -COOH ⋯HO-Al-[20,21, 27]	Rigidity
PNIPA [Poly(N-isopropyl acrylamide)]	No interaction due to bulkiness	Thermo-responsive volume change

recrystallized from chloroform and ethanol was utilized. AA and HEA were distilled under reduced pressure. All other chemicals were reagent grade and were used as received.

Imogolite synthesis[10]

Aqueous solutions of $AlCl_3 \cdot 6H_2O$ (9.96 g in 369 mL of purified deionized water) and Na_4SiO_4 (6.90 g in 362 mL of purified deionized water) were mixed to prepare a solution containing 12.5 and 2.5 mol/L of Al and Si, respectively. The pH of the mixture was adjusted to 6.0 by rapidly adding ~26 mL of 1.0 mol/L NaOH *aq*. The resulting solution was stirred for 1 h. The resultant white precipitates were collected by centrifugation and were redispersed in 400 mL of water under stirring. After adding another 2400 mL of water, the solution pH was adjusted to 4.5 by adding 7-8 mL of 1.0 mol/L HCl. The solution was then carefully and continuously heated for 4 days at 100 °C under gentle stirring. The solution was then cooled to room temperature and a fine powder of sodium chloride (16.4 g) was added to it under vigorous stirring. The resulting gel was collected by centrifugation (5000 rpm, 30 min) and was subsequently washed portionwise with 500 mL water using a 100 nm Millipore filter under suction. The wet products were added to 1800 mL of tetrahydrofuran (THF; stabilizer-free grade) under stirring, and the fluffy precipitates were collected by filtration and dried in vacuum. The product yield was 42%.

Preparation of IG-polymer gels (IG gels) by *in situ* polymerization

A literature procedure[10] was modified for the present synthesis. A calculated amount of IG in pure water was sonicated (FU-21H, SD-Ultra Ltd., Korea) for 4 h at 100 W power and r.t. By this procedure, slightly opaque dispersions of up to 5.5 w/v% could be prepared, and the average length of IG in the dispersion reduced to about 130 nm, as estimated from the results of transmission electron microscopy.[10] The amide group-containing vinyl monomers employed are AAm, NIPA, and *N*-methylacrylamide (MAAm). These amide monomers are expected to interact with IG's inner Si(OH) groups,[18] as shown in Scheme 1. HEA and AA are the vinyl monomers containing the hydroxyl and carboxyl groups, respectively. These functional groups are expected to interact with IG's outer Al(OH)$_2$ groups[19-21] (Scheme 1). The vinyl monomers except for NIPA, and an initiator, 4,4'-azobis-4-cyanovaleric acid (ACVA; 0.1 mol% *vs.* monomer), were added to an IG (5.0 w/v% as final conc. after mixed) aqueous dispersion or pure water under N$_2$ atmosphere. The mixture was then placed in a polymerization cell compartment consisting of a pair of glass plates with 1.0 mm silicon film spacers. After conducting radical polymerization at 60 °C for 24 h, the resulting IG gels were equilibrated by immersing them in running pure water for a week. The reference gel was obtained by the polymerization of a mixture of a vinyl monomer, ACVA (0.1 mol% *vs.* monomer), and a crosslinker [tetra(ethyleneglycol) diacrylate (TEGDA); 0.1 mol% *vs.* vinyl monomer].

The *in situ* polymerized NIPA-*co*-AA IG gels were prepared as follows: NIPA and AA were added to an ice-cooled aqueous dispersion of IG (5.0 w/v%) under N$_2$ atmosphere. The mixtures were then placed in polymerization cells, as described earlier. After conducting redox polymerization at 15 °C for 72 h by adding ammonium peroxodisulfate (APS; 0.1 mol% *vs.* vinyl monomer) and *N,N,N',N'*-tetramethylethylenediamine (TMD; 0.1 mol% *vs.* vinyl monomer), the resulting IG gels were equilibrated as described earlier. The reference gel was obtained by the polymerization of a mixture of NIPA and AA, crosslinker, (TEGDA; 0.1 mol% *vs.* vinyl monomer), APS (0.1 mol% *vs.* monomer), and TMD (0.1 mol% *vs.* monomer).

The equilibrated aqueous phases were evaporated to confirm that there were negligible amounts of unreacted monomers or polymer strands unassociated with the gel networks.

Preparation of IG-preformed polymer mixture

The preformed polymers were synthesized by the polymerization of corresponding monomer without IG under the same conditions as those used for IG gel preparation. The obtained polymer was dissolved in pure water and membrane-filtered (0.5 μm). Prescribed amount of polymer solution (see Table 2 for concentrations) was added dropwise into the aqueous IG solution while stirring appropriately at room temperature. The mixture was aged for 2 days without agitation.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)
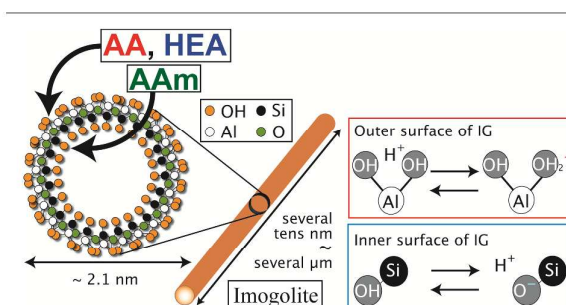
Scheme 1 Predicted Interaction of Various Vinyl Monomers and IG Surface.

A literature procedure[21] was modified for the present analysis. For the Z-contrast imaging and elemental analysis, HADDF-STEM and energy dispersive X-ray spectroscopy (EDS) were carried out using a JEM-2200FS with an energy filter (In-column Omega filter, JEOL Co. Ltd., Japan), and a JED-2300, which was equipped with a 30 mm^2 lithium-drifted silicon detector (JEOL Co Ltd., Japan). The accelerating voltage was 200 kV, and all images were acquired by a high-resolution charge-coupled device (CCD) detector using a 2 k × 2 k pixel device (UltraScan 1000, Gatan Co., Ltd., USA). The sol-state aqueous mixture of 3.2 w/v% of IG, 0.008 mol/L of bis[2-carboxy ethyl germanium(IV)] sesquioxide (for probing of carboxylic acids by Ge atoms), and 0.072 mol/L of maleic acid (for prevention of aggregating IGs by their cross-bridging[21]) was dropped on carbon-coated grids (Oken Shouji Co., Tokyo), of which surface was turned to hydrophilic by glow discharge in a reduced pressure. After 3 min, the sample on the grids was blotted by a filter paper, and then the grid was dried. A cold finger and a cold trap cooled with liquid nitrogen were used to prevent sample contamination by the electron beams.

Water content determination

The water content of the gels cut into approximately 5.0 × 5.0 ×1.5 mm blocks was determined using a heater-type moisture analyzer (MS-70, A&D Co. Ltd., Japan).

Tensile measurement of gels

For tensile testing, the gels were cut into dumbbell-shaped test pieces standardized by JIS-K6251-7 (length 35 mm, width 6 mm, thickness approximately 2 mm, gauge length 12 mm, inner width 2 mm) with a cutting machine (Dumb Bell Co., Ltd). The sample length between two chucks was 15–20 mm. The tensile stress-strain measurements were performed on a tensile-compressive tester (Tensilon RTC-1310A, Orientec Co.) at a constant stretch rate of 100 mm/min. Since the tensile measurements finished within short period (< 3 min), the degree of swelling was almost constant until the testing.

Birefringence estimation of gels

The center points of the dumbbell-shaped samples described above were observed at room temperature by a polarized optical microscope (POM; BX51, Olympus, Japan) under crossed nicols. The images were obtained using a CCD camera (Olympus, Japan). The birefringence, Δn, was measured from the retardation values using a Berek compensator (U-CBE, Olympus, Japan). The birefringence of gels during elongation was measured by POM by fixing the two ends of the sample on a vernier caliper and elongating it under a certain strain.

Estimation of thermal sensitivity of IG gels

The thermo-responsive volume transition of PNIPA-containing IG gels was estimated by measuring the volume change from their initial size (10 mm × 10 mm × 1 mm) in pure water. The size of gels at various temperatures was measured from the pictures obtained by a digital microscope (DILITE30, AnMo Electronics, US).

Results and discussion

Phase state of the mixture of IG and polymers

Based on the classification shown in Table 1, we examined the phase states of the mixtures of 5.0 w/v% IG and polymers containing various functional groups (4.0 mol/L), as shown in Table 2. The postmixing concentrations of IG and polymer were 5.0 w/v% and 1.0–4.0 mol/L, respectively.

As mentioned earlier, PAAm units and IG nanotubes are known to interact with each other through -NH$_2$ or >C=O and Si(OH) groups, respectively.[10] However, the combination of *preformed* PAAm and IG did not result in gel formation because PAAm does not interact with the IG's outer walls and the penetration of macromolecular strands into the hollow structure of IG nanotubes is difficult and rare. Based on these observations, the following two conclusions can be derived[10]:

1) Gels exhibit considerable mechanical strength as monomeric AAm molecules can penetrate the hollows and then polymerize, and

2) A few PAAm strands can be anchored to the mouth of an IG nanotube to create pseudo-crosslinking.

Such pseudo-crosslinking could cause the IG-PAAm gel to display elastic properties when large deformation is induced in the gels.[10]

No gel was formed when *N*-alkylated acrylamide units such as MAAm or NIPA were used, either by mixing with preformed polymers or by *in situ* polymerization. This is because the bulkiness of the substituents prevented monomer penetration into the hollows and curtailed the pseudo-crosslinking abilities of the polymers. The above mentioned reasons also nullify the possibility of gelation by chain-transfer anchoring of the propagating polymer strands to the IG surfaces during the polymerization.

Poly(vinyl alcohol) (PVA) had been observed to hybridize with IG; casting the PVA/IG solution resulted in mechanically tough films.[19,22] Since no gel was found in the mixed, rather dilute, solution, it is unclear how strong the interaction between the IGs' outer Al(OH)$_2$ groups and the hydroxyl groups of PVA are. In the present study, HEA was used instead, because it allows us to test both the *in situ* polymerization and the preformed polymer mixing

Table 2 Phase State of the Mixture of IG (5.0 w/v%) and Polymers.

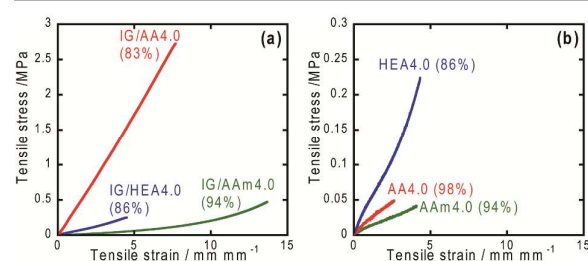| Polymer	Mixing method	Conc. (mol/L)	Phase of mixture
PAAm	Preformed polymer	4.0	No gels[8-10]
	In situ polymerized	4.0	Gelation[8-10]
		2.0	Gelation[8-10]
PMAAm	Preformed polymer	1.0	No gels
	In situ polymerized	4.0	No gels
PNIPA	Preformed polymer	1.0	No gels
	In situ polymerized	2.0	No gels
PHEA	Preformed polymer	1.0	No gels
	In situ polymerized	4.0	Gelation
PAA	Preformed polymer	1.0	Precipitation
	In situ polymerized	2.0	Gelation
		4.0	Gelation
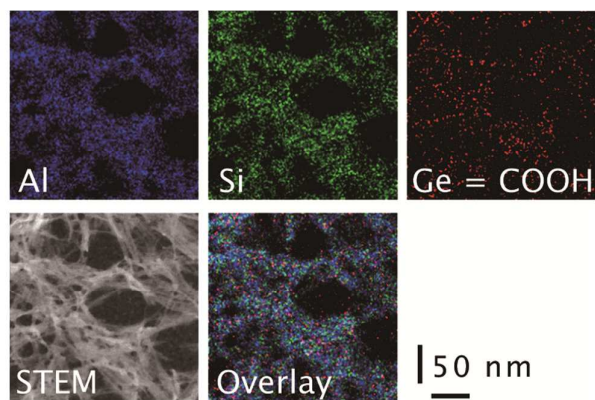
Fig. 1 HAADF-STEM image and elemental mapping by EDS of mixture of IG, bis[2-carboxyethyl germanium(IV)] sesquioxide, and maleic acid. The Ge atoms (*i.e.,* carboxylic acids) localized on the IG nanotubes that indicate the presence of interaction between carboxylic acids and IG nanotubes.

Fig. 3 Typical tensile stress-strain curves of IG/AAm/AA gels. Inserted percentage is the degree of swelling.
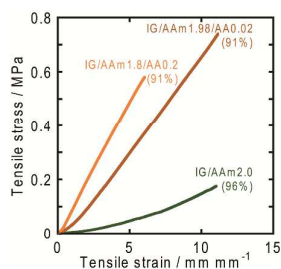
method. Gradual addition of the preformed PHEA solution resulted in a homogeneous mixture of [IG] (5.0 wt/v%) and [PHEA] (1 mol/L). Use of a more concentrated PHEA solution resulted in the formation of local hard gel-like precipitate indicating the presence of sufficient interactions between IG and PHEA. Further investigation by using the *in situ* polymerization technique revealed that the concentration of HEA units could be increased to 4.0 mol/L to obtain macroscopically homogeneous gels.

Poly(carboxylic acid)s are known to interact with the IGs' outer $Al(OH)_2$ groups by hydrogen bonding and related polar interactions.[20,21] As shown in the HAADF-STEM images of the dried mixture of germanium bonded carboxylic acids and IG (Fig. 1), the carboxylic acids attach to IG surface. However, such interactions are too strong, resulting in instantaneous phase separation and formation of hard solid particles upon mixing IG and preformed poly(acrylic acid) (PAA) in the concentrated state. Meanwhile, mixing IG (5.0 wt/v%) with monomeric AA (4.0 mol/L) resulted in a clear, homogeneous solution; the subsequent *in situ* polymerization produced clear, macroscopically homogeneous gels.

Thus, *in situ* polymerization is better than mere mixing of IG and preformed polymers. Additionally, one can note that the properties
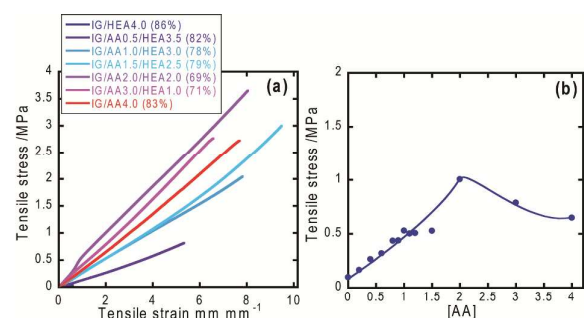
of the resulting gels vary on changing the interacting repeating units. The gels show various types of interactions such as interactions with the IG inner walls or outer walls, and the strength of these interactions also varies from weak, moderate to strong interactions. Various possibilities exist to tune the properties of IG gels by varying the combination of monomers and the feeding ratio of monomers that are to be *in situ* polymerized. Hereafter, we abbreviate the corresponding gels as "IG/AAm*X*, IG/HEA*X*, IG/AA*X*, IG/AAm*X*/AA*Y*," where *X* and *Y* denote the concentrations of monomer feed in mol/L. We will first discuss the mechanical properties of IG gels with a single component polymer, IG/AAm*X*, IG/HEA*X*, and IG/AA*X*.

Mechanical properties of IG gels prepared by *in situ* polymerization

The stress-strain curves estimated from the tensile testing results on the IG/AAm4.0, IG/HEA4.0, or IG/AA4.0 gels are illustrated in Fig. 2. The IG gels are tough and their breakdown stress/strain and Young's modulus greatly depends on the type of vinyl monomers. The breakdown strain of the IG/AAm gel was larger than that of the other two gels, *i.e.,* the IG/AAm gel was more elastic than the others owing to fewer pseudo-crosslinking IG-to-IG tying points than those formed by the outer sidewall anchoring in IG/HEA or IG/AA. This difference in tying is also reflected in the spatial density or degree of swelling; 93%–94%, 86%, and 83% of water content for the IG/AAm4.0, IG/HEA4.0, and IG/AA4.0 gels, respectively.

The IG/AA4.0 gel exhibited extremely high breakdown stress compared to that shown by the IG/AAm4.0 gel. Strong anchoring is possible when every aluminol group on the outer wall of IG interacts with an AA molecule; a theoretical limit of 0.83 mol/L out of existing 4.0 mol/L would enable such anchoring. *In situ* polymerization produced "polymerized sheaths," from which PAA strands grew outward by consuming the remaining 3.17 mol/L portion. Crosslinking among the sheaths occurred by radical recombination of the propagating PAA strands.

Polymer sheaths also formed in the IG/HEA gel. However, the breakdown stress and strain of IG/HEA4.0 are much lower than those of IG/AA4.0. Because the mechanical strength of AA4.0 is lower than that of HEA4.0 in the absence of IG nanotubes, the physical properties of IG gels are strongly dependent on the molecular structure of organic polymers. Both the IG/AA and IG/HEA systems exhibit strong variations in mechanical strength owing to multiple interaction points between IG and organic

Fig. 2 Typical tensile stress-strain curves of *in situ* polymerized (a) IG gels and (b) their reference gels. AA*X*, AAm*X*, and HEA*X*, respectively, indicate the gels consisting of AA or AAm or HEA with X mol/L and 0.1 mol% of TEGDA *vs.* vinyl monomer. Inserted percentage is the degree of swelling.

Fig. 4 (a) Typical stress-strain curves of IG/AA*X*/HEA*Y* gels and (b) stress of IG/AA*X*/HEA*Y* gels at strain = 2.0 for various [AA], where *X* + *Y* = 4.0. Inserted percentage is the degree of swelling.

Fig. 5 (a) Typical stress-strain curves of AA*X*/HEA*Y* gels (X + Y = 4.0) and (b) stress of AA*X*/HEA*Y* gels at strain = 2.0 for various [AA], where *X* + *Y* = 4.0. Inserted percentage is the degree of swelling.

polymer in IG/AA and IG/HEA gels compared to those in the IG/AAm gel. As shown in Table 1, the C=O and COOH groups of PAA interact with Al-OH[21,27] on IG in the IG/AA gel; in contrast, only OH of PHEA interact with Al-OH on IG. It seems that the number of interacting groups between IG and the organic polymer determines the mechanical properties of IG/organic polymer gels.

Thus, the physical properties of IG gels drastically change with the interaction manner between IG and the organic polymer (*i.e.*, tying or sheathing). Basically, tying of the polymer to IG nanotubes (IG/AAm system) produces stretchable IG gels; in contrast, sheathing of the polymer on IG nanotubes (IG/AA and IG/HEA system) makes IG gels stiff, depending on the strength of interaction between IG and the organic polymer.

These results indicate that gel properties can be controlled by changing the anchoring units, crosslinking styles, and network chains. The IG/AAm/AA gels are of particular interest, as the AAm strand is capable of pseudo-crosslinking through the hollows of IG nanotubes and AA strand provides strong anchoring onto the IG outer walls. Unfortunately, feeding AAm and AA mixture in 4.0 mol/L to the 5.0 wt/v% IG dispersion led to local inhomogeneity; the total monomer concentration thus reduced to 2.0 mol/L. Since the penetration of AAm molecules into the IG hollows requires an equilibration period, AA was added 1 h after adding AAm to the IG solution. Fig. 3 illustrates the tensile stress-strain curves of an IG/AAm2.0 gel and two IG/AAm/AA gels.

As mentioned earlier in the discussions about Fig. 2, the AAm strands also yielded an elastic gel in IG/AAm2.0. It was surprising that the incorporation of a very small amount of AA into the IG/AA system brought about high breakdown stress. By changing the composition from IG/AAm2.0 to IG/AAm1.98/AA0.02, the breakdown stress increased by about fivefold to become 0.75 MPa, while the breakdown strain remained unchanged. The IG/AAm/AA system exhibited low breakdown strain at [AA] > 0.02, as shown in Fig. 3. The breakdown stress reduced on changing the composition from IG/AAm1.98/AA0.02 to IG/AAm1.8/AA0.2. Further increase in [AA] increased the IG gel breakdown stress, *i.e.*, the breakdown stress and strain of IG/AA2.0 were 2.0 MPa and 3.0, respectively.

Hereafter, other combinations such as IG/AA/HEA, IG/AAm/NIPA, and IG/AA/NIPA were examined. The combination of both outer
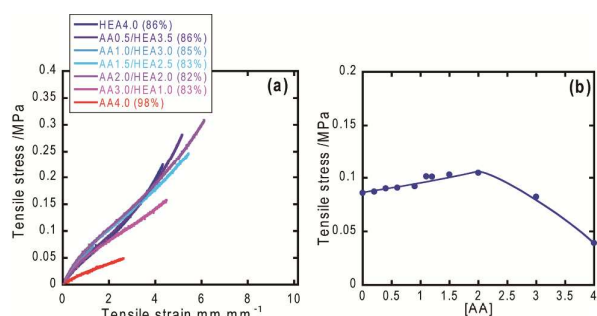
wall-anchoring types, AA and HEA, may allow the production of IG gels with tunable mechanical properties. Furthermore, including PNIPA chains to the IG gel by their copolymerization with PAA causes thermo-responsive volume transition of the IG gel because of the thermo-responsive coil/globule transition of the PNIPA chains. Based on these presumptions, we conducted *in situ* radical copolymerization of AA and HEA or NIPA monomers in the presence of IGs to obtain IG gels with tunable mechanical properties and thermo-responsiveness.

Mechanical and optical properties of IG/AA/HEA binary gels

Hereafter, the gel names such as "IG/AA3/HEA1" and "AA0.2/NIPA1.8" represent IG5 w/v%/AA3 mol/L/HEA1 mol/L and AA0.2 mol/L/NIPA1.8 mol/L/0.1 mol% of TEGDA *vs.* vinyl monomer, respectively.

Tensile stress-strain measurements were carried out at various AA/HEA ratios to understand the relationship between the mechanical properties and monomer component of IG/AA*X*/HEA*Y* gels.

As shown in Fig. 4b and 5b, IG/AA*X*/HEA*Y* and AA*X*/HEA*Y* gels with [AA] = [HEA] = 2.0 mol/L exhibit the maximum tensile stress at strain = 2.0. At [AA] = 0–2.0, the tensile stress of the IG/AA*X*/HEA*Y* gel at strain = 2.0 (henceforth denoted as $\delta_{2.0}$) increased with increasing [AA]. In this concentration region, "the interaction between IG nanotubes and PAA chains" and "the inter polymer complexes (IPC) between PAA chains (COOH) and PHEA chains (OH)[28]" are simultaneously formed. The drastic increase in $\delta_{2.0}$ until [AA] ≈ 1.0 is attributed to the interactions between 1.99×10^{-3} moles of Al(OH)$_2$ present on the IG surface in IG/AA*X*/HEA*Y* gels and 0.83 mol/L of AA. Subsequently, the IPC interactions increase with increase in [AA].

Under pH condition of IG/AA/HEA mixture (pH ≈ 2.7), the maximum amount of IPC (henceforth denoted as M.IPC) should occur at [HEA]/[AA] ≈ 2.0.[28] Since approx. 1.0 mol/L of AA interacts with IG in the IG/AA/HEA gel, M.IPC occurs at [HEA]/[AA] = 1.0 in the IG/AA/HEA gel (*i.e.,* approx.1.0 mol/L of PAA interact with PHEA in the IG/AA/HEA gel), as shown in Fig. 4b. In AA*X*/HEA*Y* gels, the M.IPC also occurs at [HEA]/[AA] = 1.0 (Fig. 5b), as the absence of IG leads to low pH conditions of the reaction mixture that decreases

the [HEA]/[AA] value to realize M.IPC.[28] At [AA] > 2.0, $\delta_{2.0}$ decreased with IPC.

IG/AAX/HEAY and AAX/HEAY gels exhibited birefringence only under tensile strain owing to the strain-induced uniaxial ordering of IG nanotubes and polymer chains *via* shear inducing, as shown in the IG/AAm gel.[9,10] Here, to reveal the relationship between the optical properties and the ratio of AA and HEA of IG/AAX/HEAY gels, the gels' birefringence changes (Δn) as a function of the applied strain were estimated.

As shown in Fig. 6, the Δn values linearly increase with the tensile strain for both IG/AAX/HEAY and AAX/HEAY gels owing to the positive birefringence effect of PAA and PHEA chains, whereas, the PAAm chains show negative birefringence effect.[9,10] It is clear that the birefringence effect is similar for both PAA and PHEA, as shown in Fig. 6b.

As shown in Fig. 7, on increasing [AA], Δn at strain = 0.5 (henceforth denoted as $\Delta n_{0.5}$) of IG/AAX/HEAY gels also increased; in contrast, there is no change in $\Delta n_{0.5}$ for AAX/HEAY gels with [AA]. From these results, the following deductions can be made:
1. The $\Delta n_{0.5}$ value increases with interaction between IG and PAA. (*i.e.*, pulling of PAA chains by IG nanotubes) and PAA and PHEA (*i.e.*, IPC formation) at [AA] = 0–2.0.
2. Since IG-PAA interactions and the IPC saturation are expected at [AA] = 2.0, $\Delta n_{0.5}$ remains almost constant in the range [AA] = 2.0–4.0.

Thus, the mechanical/optical properties of IG gels are specifically determined by the interactions between IG and the polymer chain, which, in turn, depend on the number/species of functional groups in polymer.

Synthesis of thermo-responsive IG gels with PNIPA chains
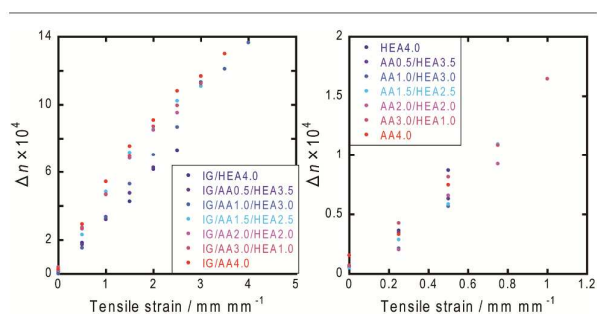
Fig. 6 The Δn values of (a) IG/AAX/HEAY gels and (b) AAX/HEAY gels ($X + Y = 4.0$) at a certain strain.
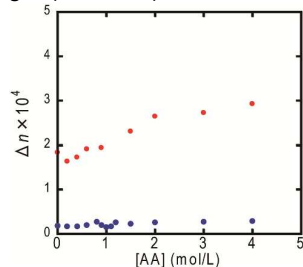

Fig. 7 Strain-induced Δn change of IG/AAX/HEAY gels (red) and AAX/HEAY gels (blue) ($X + Y = 4.0$) at strain = 0.5 for various [AA].

Hereafter, the components of IG gels are switched from AA/HEA to AAm/NIPA or AA/NIPA in order to attain thermo-responsive volume transition of IG gels for potential applications such as soft-actuators. The combination of IG, AAm, and NIPA produced amorphous gel-like blobs at 4.0 mol/L total monomer concentration. The blobs are too soft to be treated as self-standing materials; consequently, it is not possible to test their mechanical strength. However, the blobs showed the thermo-responsive reversible shrinking/bulging behavior because of the coil/globule transition of PNIPA chains.

The mixture of AA aqueous solution and NIPA (liquid state) exhibited phase separation when the total monomer concentration ([AA] + [NIPA]) is higher than 2.0 mol/L and when the mixing ratio of [AA]/[NIPA] is higher than 0.11, even at 2.0 mol/L of total monomer concentration. Therefore, IG/AAX/NIPAY gels were prepared at 2 mol/L of total monomer concentration and less than 0.11 [AA]/[NIPA] ratio.

As shown in Fig. 8, the breakdown stress of IG/AAX/NIPAY gels increases with increase in [AA]; in contrast, the gels showed high elasticity (*i.e.*, higher breakdown strain and lower Young's modulus) at low [AA]. The results indicate that the number of interaction points between IGs and AA-*co*-NIPA polymer, *i.e.*, the amount of AA units, controls the mechanical strength of IG/AAX/NIPAY gels. In contrast, the AA0.2/NIPA1.8 gel is very weak. Furthermore, AA0.1/NIPA1.9 and AA0.02/NIPA1.98 gels are too brittle to measure the tensile stress-strain behavior.
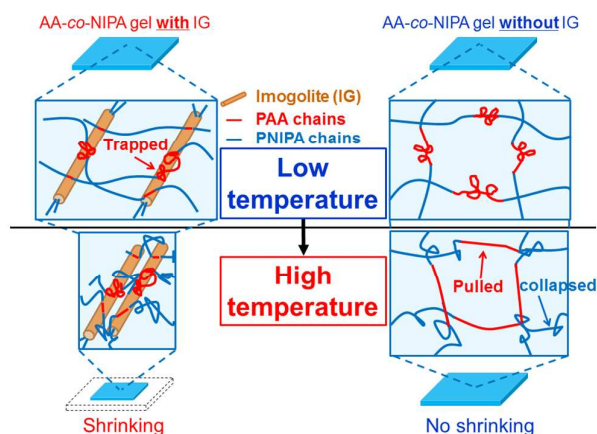
The IG/AAX/NIPAY gels exhibited thermo-responsive reversible
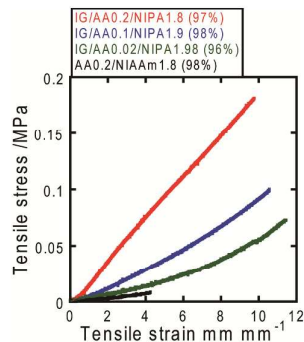
Fig. 8 Typical stress-strain curves of IG/AAX/NIPAY gels ($X + Y = 2.0$) and AA0.2/NIPA1.8 gels. Inserted percentage is the degree of swelling
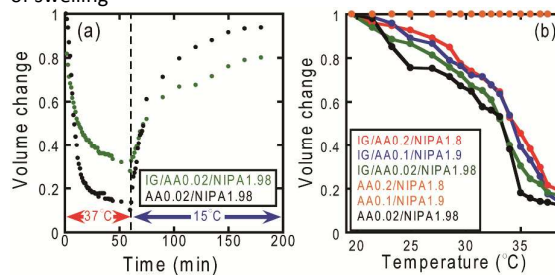
Fig. 9 (a) Typical shrinking/bulging behavior of IG/AA0.02/NIPA1.98 gel and AA0.02/NIPA1.98 gel. (b) Temperature-dependent volume change of the IG/AA/NIPA and AA/NIPA gels.

Fig. 10 Potential interaction mechanism of thermo-responsive volume transition of the AA-*co*-NIPA gels with IG (left) or without (right) IG nanotubes.

shrinking/bulging behavior because of the coil/globule transition of PNIPA chains (Fig. 9a). Addition of IG diminished the total shrinking/swelling volume of gels compared to the initial gel because the presence of rigid IG nanotubes in the gel network inhibits the volume change.

The volume transition of IG/AA*X*/NIPA*Y* gels was confirmed in the region of AA/NIPA = 0.01–0.11; in contrast, AA-*co*-NIPA gels without IG showed the volume transition only at AA/NIPA = 0.01 (Fig. 9b).

As shown in Fig. 10, the coil/globule transition of PNIPA chains induces the volume transition of gels only when PAA chains are trapped by stiff IG nanotubes or when PAA units are very few ([AA]/[NIPA] = 0.01). If PAA chains in the copolymer network can move freely at [AA]/[NIPA] > 0.01, the shrinking/bulging of the PAA-*co*-PNIPA network never occurs because of the coil/globule transition of PNIPA chains caused by the pulling of PAA chains.

Conclusions

Strong IG hydrogels with tunable physical properties such as mechanical strength and polarized nature were obtained by *in situ* copolymerization of vinyl monomers with various functional groups. Furthermore, *in situ* copolymerization of AA and NIPA in the presence of IG nanotubes produced strong hydrogels that exhibit thermo-responsive volume transition because of the coil/globule transition of PNIPA chains. Thus, the mechanical properties and stimuli (strain/thermo)-responsiveness of IG gels are determined by the molecular structure of organic polymers owing to their interaction with IG nanotubes. The promising results will encourage the use of robust IG gels as multistimuli-responsive material, mechano-optical sensors, and artificial biological tissues.

Acknowledgements

Notes and references

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