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Kamio, Eiji
Kinoshita, Masayuki
Yasui, Tomoki
Lodge, Timothy P.
Matsuyama, Hideto

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Preparation of inorganic/organic double-network ion gels using a cross-linkable polymer in an open system

Eiji Kamio,[*,1] *Masayuki Kinoshita,*[1] *Tomoki Yasui,*[1] *Timothy P. Lodge,*[2] *and Hideto Matsuyama*[*,1]

1: Department of Chemical Science and Engineering, Research Center for Membrane and Film Technology, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe, Hyogo 657-8501, Japan.

2: Department of Chemistry and Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455-0431, United States

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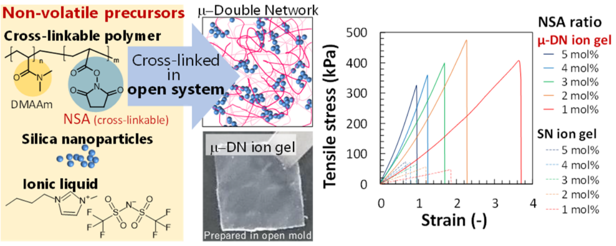

ABSTRACT

Tough micro-double-network (μ-DN) ion gels, composed of interpenetrating inorganic and organic networks swollen with 80 wt% of an ionic liquid, were fabricated in an open system using nonvolatile materials: silica nanoparticles for the inorganic network, a cross-linkable polymer for the organic network, and an ionic liquid. The cross-linkable copolymer, poly(*N,N*-dimethylacrylamide-*co*-*N*-succinimidyl acrylate) synthesized by reversible addition-fragmentation chain transfer polymerization, was cross-linked in situ with a diamine to form the organic network. On the application of load, the inorganic network was partly destroyed resulting in substantial energy dissipation, but the organic network acted as hidden length to suppress the macroscopic destruction of the μ-DN ion gel. The modulus, fracture strength, and strain-to-break of the μ-DN ion gels were tuned by varying the cross-linking degree of the organic network, which could be controlled by changing either the succinimidyl acrylate content of the cross-linkable polymer or the cross-linkable polymer concentration in the precursor solution.

INTRODUCTION

Ion gels, containing a large amount of an ionic liquid (IL) and having the characteristic properties of ILs such as nonvolatility, nonflammability, high thermal and chemical stabilities, and sustained fluidity in a wide temperature range, have attracted great interest for applications in a wide range of fields.[1-4] In particular, because ion gels can contain task-specific ILs having tuned properties such as high ionic conductivity and high and selective CO_2 absorption, they are expected to find use in electrochemistry and CO_2 separation membranes.[1-3] For these applications, the ion gel should be shaped into a thin film. In addition, to exploit the unique properties of the IL incorporated in the ion gel, the proportion of IL in the gel should be as high as possible. However, conventional ion gels without a well-designed network tend to be very weak and brittle, and it is difficult to prepare thin ion gel films that can be used for practical applications. Moreover, generally, there is a trade-off relationship between the mechanical strength and IL content of the ion gel; i.e., the mechanical strength decreases as the IL content increases. Therefore, for the development of high-performance ion-gel films, this trade-off must be overcome, and thin ion-gel films having a high IL content must be developed.

In recent years, several methods to tackle the trade-off problem have been suggested, including the development of ion gels having high mechanical strength. For example, Fujii *et al.* developed ion gels with up to 96.8 wt% IL and a small amount of a tetra-arm poly(ethylene glycol) network (termed tetra-PEG ion gels).[5, 6] The tetra-PEG ion gel with 96.8 wt% IL had a Young's modulus of 2.8 kPa, a fracture strain of 3.7, and a fracture stress of 15 kPa. Because of the high IL content, the ion gel membrane showed high ionic conductivity and CO_2 permeability. Other high-mechanical-strength ion gels composed of a large amount of IL and specially designed triblock copolymers have been developed,[3, 7, 8] and some of these have been used as ion-gel electrolytes and CO_2 separation membranes.[9-12] In addition, an ion gel membrane composed of an IL and sulfonated polyimide showed a modulus of more than 10 MPa and good CO_2 separation performance.[13] Furthermore, micellar ion gels composed of IL and diblock copolymers having an IL-phobic block and a hydrogen-bonding block have been developed, and these materials show excellent mechanical and electrochemical properties.[14] We have also fabricated tough ion gels[15-20] based on the double-network principle[21, 22] and used the double-network ion gels (termed DN ion gels) as a material for CO_2 separation membranes.[15-17]

The earliest DN ion gels were prepared via multi-step processes, but it was challenging to form thin membranes because of the complicated multi-step preparation process. Since the first development of DN ion gels, some other DN ion gels have been reported.[18-20, 23-27] Although many still require multi-step network formation,[23-25] some tough DN ion gels including inorganic/organic DN ion gels have been prepared via "one-pot" single-step network formation.[18-20, 26, 27] Our inorganic/organic DN ion gels have an interpenetrating inorganic/organic network formed via the sol-gel reaction of tetraethoxysilane (TEOS) and free radical polymerization of *N*,*N*-dimethylacrylamide (DMAAm). Owing to the inorganic/organic double-network, the DN ion gels have excellent mechanical strength (e.g., compressive fracture stress > 25 MPa), and therefore enable increasing the IL content up to 90 wt%. However, the formation of very thin films from the inorganic/organic DN ion gel is still challenging. To prepare thin polymer films, roll-to-roll, casting, spin-coating, and dip-coating methods are used. In general, these processes are performed in an open system. Thus, to utilize these thin-film formation processes, the DN ion gel must also be prepared in an open system. However, the inorganic and organic double-networks are formed in the IL using volatile raw chemicals, such as TEOS (precursor of the inorganic network), DMAAm (monomer of the organic network), and formic acid (solvolytic agent for sol-gel reaction). These volatile chemicals are rapidly evaporated from the precursor solution of the DN ion gel if the precursor solution is spread into a thin liquid film. Fortunately, ILs are nonvolatile; thus, using nonvolatile raw materials for the formation of the inorganic and organic networks could solve this problem. Therefore, the development of methods to prepare DN ion gels using nonvolatile raw materials for the network formation is the key challenge facing thin DN ion gel film fabrication.

We recently proposed the formation of a partially developed inorganic network using silica nanoparticles as the nonvolatile building block of the inorganic network.[19] In an IL, silica nanoparticles can aggregate to form network-like structures.[28, 29] We found that the aggregated silica nanoparticles acted as an inorganic network to dissipate the load on the ion gel. We named this ion gel having a partially developed silica nanoparticle network as a "micro-DN ion gel" (μ-DN ion gel). The μ-DN ion gel had a mechanical strength that was comparable with those of DN ion gels prepared using TEOS and DMAAm. Thus, the evaporation loss of the raw material of the inorganic network was overcome. However, a nonvolatile raw material for the organic network formation is still required.

There are two routes to organic network formation using nonvolatile raw materials. One is the use of cross-linkable polymers,[26] and the other is the use of an IL monomer.[27] In this study, we opted to use a cross-linkable polymer as the building block of the organic network because cross-linkable polymers allow rapid network formation. In general, polymerization reactions to form high-molecular-weight polymers are slow. In contrast, cross-linking polymerization involves only the cross-linking reaction, for which the reaction rate can be controlled by selecting a fast cross-linking reaction. Considering the large-scale production of ion gel-based thin films by roll-to-roll, dip-coating, and casting processes, fast production of the ion gel is desirable. Thus, we focused on an amide cross-linking via the reaction between *N*-hydroxysuccinimide (NHS) ester and primary amine. This amide cross-linking reaction is often used in peptide synthesis because the reaction is usually quantitative and proceeds without any side reactions at room temperature.[30] In addition, this reaction has been used to form tetra-PEG networks for ion gels.[5, 31, 32] Thus, this reaction is known to proceed in an IL. In particular, in aprotic ILs, this reaction occurs quickly because the active ester can easily react with amines in a low proton concentration medium.[6, 33] Therefore, we synthesized the cross-linkable polymer composed of PDMAAm and poly(*N*-succinimidyl acrylate) having NHS ester as the cross-linking group and used it as the nonvolatile building block of the organic network. Owing to the nonvolatility of the silica nanoparticles and the cross-linkable polymer, the inorganic/organic μ-DN ion gel could be prepared in an open system. We also examined the mechanical strength of the μ-DN ion gels prepared using the cross-linkable polymer, and we propose criteria to control the mechanical strength of the μ-DN ion gels prepared in an open system.

EXPERIMENTAL SECTION

Reagents

As the cross-linkable polymer, we synthesized poly(*N*,*N*-dimethylacrylamide-*co*-*N*-succinimidyl acrylate) (poly(DMAAm-*co*-NSA)). To focus on the effect of the cross-linking degree on the mechanical strength of the prepared μ-DN ion gels, as well as those without silica nanoparticles (denoted SN ion gel), cross-linkable polymers having almost the same molecular weight but different NSA ratios were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. As the monomers yielding the main and cross-linkable parts of the cross-linkable polymer, *N*,*N*-dimethylacrylamide (DMAAm) and *N*-succinimidyl acrylate (NSA), respectively, were used. These were purchased from Tokyo Chemical Industry Co., Ltd., Japan. DMAAm was used after removing the polymerization inhibitor by passing it through an activated alumina column. As the radical initiator and solvent for RAFT polymerization, 2,2′-azobis(2,4-dimethylvaleronitrile) (ADVN) and super dehydrated 1,4-dioxane were used, respectively. They were purchased from FUJIFILM Wako Pure Chemical Co., Japan and used as received. As the chain transfer agent (CTA), 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid purchased from Sigma–Aldrich Co., (St. Louis, MO) was used. Tetrahydrofuran (THF) and *n*-hexane were used as the good and poor solvents to purify the synthesized poly(DMAAm-*co*-NSA) by precipitation, respectively. Dimethyl sulfoxide-d_6 (d_6-DMSO; purchased from FUJIFILM Wako Pure Chemical Co., Japan) was used as the solvent for ^{1}H-NMR measurements. To determine the NSA ratio introduced in the poly(DMAAm-co-NSA), *tert*-butylamine, NHS, and *N*-tertiary butylacrylamide purchased from Tokyo Chemical Industry Co., Ltd. were used as received. Maleic acid was purchased from FUJIFILM Wako Pure Chemical Co. and used to determine the purity of poly(DMAAm-*co*-NSA). High-performance liquid chromatography (HPLC)-grade THF was purchased from FUJIFILM Wako Pure Chemical Co. and triethylamine (TEA) was purchased from Tokyo Chemical Industry Co., Ltd. and were used as solvents for the samples as well as the mobile phase, and amine additive for size-exclusion chromatography (SEC) analysis, respectively.

As the IL of the μ-DN and SN ion gels, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_4mim][Tf_2N], purchased from Sigma–Aldrich Co.) was used without further purification. The organic networks of the ion gels were formed by cross-linking the synthesized poly(DMAAm-*co*-NSA) using diethylene glycol bis(3-aminopropyl)ether (DGBE), which was purchased from Tokyo Chemical Industry Co., Ltd. As the building block of the inorganic network of the μ-DN ion gel, silica nanoparticles (fumed silica having a primary particle diameter of 12 nm; Aerosil 200 provided by Nippon Aerosil Co. Ltd., Japan) were used as received. Ethanol was purchased from FUJIFILM Wako Pure Chemical Co. and used as the dispersion stabilizer for the silica nanoparticles in [C_4mim][Tf_2N] as well as the diluent of the precursor solution of the μ-DN and SN ion gels.

Synthesis of poly(DMAAm-*co*-NSA)

The cross-linkable polymer, poly(DMAAm-*co*-NSA), was synthesized by the following procedure (Scheme S1). RAFT polymerization was conducted in a three-necked flask. Before the experiment, the flask was sealed with silicone rubber stoppers and purged with N_2 gas. In the N_2-purged three-necked flask, a solution of ADVN (0.004 mmol) dissolved in 20.0 g of 1,4-dioxane and mixture of DMAAm (0.1 mol), NSA (1.01, 2.04, 3.09, 4.17, or 5.26 mmol), and CTA (0.040 mmol) were added using a syringe. We controlled the NSA ratio in the copolymer from 1 to 5 mol% by changing the amount of NSA used. After purging the solution by N_2 bubbling for 30 min, the flask was placed in an oil bath maintained at 333 K to start the polymerization reaction. During the reaction, the solution was vigorously agitated by a magnetic stirrer. The reaction was conducted for 24 h. After 24 h, the solution was cooled at room temperature (about 298 K), collected in a 200-cm^3 eggplant-shaped flask using THF, and the 1,4-dioxane and THF were removed by evaporation at 333 K for 2 h. The obtained white precipitate was dissolved in 40 g of THF and reprecipitated in hexane. The reprecipitation process was conducted twice, and the obtained white precipitate was dried for 24 h at 373 K under vacuum. The purity of the samples was determined by ^{1}H-NMR measurement using maleic acid as the internal standard. The ^{1}H-NMR spectra were measured using an ECZ-400S NMR spectrometer (JEOL). The determined purities of the copolymers are shown in Table 1.

Table 1. Characterization of poly(DMAAm-co-NSA)

	Molar ratio of NSA (mol%)		Purity	Molecular weight (kg/mol)		
	Target	Determined	(wt%)	M_n	M_w	M_w/M_n
Sample 1	1	0.95	95.0	123	196	1.6
Sample 2	2	2.06	93.5	130	205	1.6
Sample 3	3	3.15	93.5	139	218	1.6
Sample 4	4	4.08	94.3	140	220	1.6
Sample 5	5	4.99	95.5	151	227	1.5

Characterization of the synthesized poly(DMAAm-*co*-NSA)

Molecular weight measurement

The molecular weight (number-average (M_n) and weight-average (M_w)) and dispersity (M_w/M_n) of the synthesized poly(DMAAm-*co*-NSA) were determined using SEC system with a light scattering detector (GPCmax, TDA305, triple detection model with refractive index detector, right angle light scattering and low angle light scattering detectors and viscometer, Malvern Panalytical Ltd.) equipped with a column for the organic solvent system (Shodex LF-804, i.d. 8.0 mm, 300 mm, Showa Denko K.K., Japan). The measurements were performed at 313 K. In the SEC measurements, 0.02 g of the synthesized poly(DMAAm-*co*-NSA) sample was dissolved in 5 cm^3 of THF. THF containing 5 wt% TEA was used as the SEC mobile phase at a flow rate of 1.0 cm^3/min.

For the calculation of molecular weight, the refractive index increment (dn/dc) of each sample and apparatus constant were determined. The refractive index of the copolymer solution was measured at 313 K using an Abbé refractometer (Abbemat550, Anton Paar). The apparatus constant was determined using a polystyrene standard with M_w = 105.4 kg/mol and $M_w/M_{n.}$ = 1.02. The determined M_n, M_w, and M_w/M_n values of the copolymers are listed in Table 1.

Determination of the molar ratio of NSA introduced in the poly(DMAAm-*co*-NSA)

Because of the similar chemical shifts of the hydrogen atoms in the side chains of DMAAm (2.88 ppm) and NSA (2.84 ppm), it was difficult to determine the molar ratio of the DMAAm and NSA units in the synthesized poly(DMAAm-*co*-NSA) from the ^{1}H-NMR results directly. Therefore, in this study, we determined the NSA ratio in poly(DMAAm-*co*-NSA) from the peak area of the hydrogen atoms in the dimethylamine group of DMAAm in the copolymer and that in the NHS released from the copolymer via the reaction between the NSA group in the copolymer and the primary amine. We confirmed in advance that the chemical shifts of the hydrogen atoms of the released NHS, unreacted tertiary butylamine, DMAAm in the copolymer, and the tertiary butylacrylamide formed in the copolymer via the reaction between the NSA unit and tertiary butylamine do not overlap significantly. An example of the ^{1}H-NMR spectrum of the poly(DMAAm-*co*-NSA) solution after the reaction with tertiary butylamine is shown in Figure S1 in the Supporting Information.

To measure the ^{1}H-NMR spectra, the following experiments were conducted. A small amount of the synthesized poly(DMAAm-*co*-NSA) (0.02 g) and an excess amount of tertiary butylamine (0.08 g) were dissolved in 0.7 g of d_6-DMSO, and the reaction between the NSA unit and tertiary butylamine was carried out for 12 h at room temperature (around 298 K). The solution was placed in a thermostatic oven maintained at 333 K for 2 h to remove the unreacted tertiary butylamine. Then, the ^{1}H-NMR spectrum of the solution was measured, and the NSA molar ratio in the synthesized copolymer was determined from the ratio of the integrated peak area of the protons in the DMAAm unit and those in the released NHS. The determined NSA ratios in the copolymers are listed in Table 1.

Preparation of the μ-DN and SN ion gels

In this study, μ-DN and SN ion gels containing ca. 80 wt% of [C_4mim][Tf_2N] were prepared. The weights of the chemicals used to prepare the ion gels are listed in Table 2. The weight ratio of ethanol/IL is expressed as *r*, and was varied between 2, 2.5, 3, 3.5, and 4 (g/g). The molar ratio of NSA in the copolymer to DGBE (mol-NSA/mol-DGBE) was adjusted as 2.0 for all conditions. As shown in Table 2, we prepared the μ-DN and SN ion gels using poly(DMAAm-*co*-NSA) with different NSA ratios and precursor solutions with different *r*, and we investigated the effects of the NSA ratio and *r* on the mechanical strength of the ion gels.

The ion gels were prepared using the following procedure. The precursor solution was prepared by mixing the following three solutions: (A) a solution of poly(DMAAm-*co*-NSA) dissolved in ethanol, (B) a solution of cross-linker (DGBE) dissolved in ethanol, and (C) an IL/ethanol suspension of silica nanoparticles. To prepare the SN ion gel, an IL/ethanol mixture without silica nanoparticles was used as solution C. Before use, suspension C was vigorously agitated by vortex mixing for 1 min to disperse any silica nanoparticle aggregates in the IL/ethanol mixture. Subsequently, the silica nanoparticles were well dispersed by ultra-sonication for 20 min. Then, solution B was added to suspension C, mixed by vortex mixing for 1 min, and then degassed for 1 min by ultra-sonication. Finally, the obtained mixture was added dropwise to solution A with agitation for 1 min.

Table 2. Synthetic parameters of the μ-DN and SN ion gels.

(a) μ-DN ion gels	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
IL, [C_4mim][Tf_2N] (g)	6.4	6.4	6.4	6.4	6.4
Inorganic network, Aerosil200 (g)	0.4	0.4	0.4	0.4	0.4
Organic network (g)	1.20	1.20	1.20	1.20	1.20
Poly(DMAAm-*co*-NSA) (g)	1.188	1.174	1.16	1.149	1.139
Mass fraction of NSA (wt%)	1.6	3.5	5.3	6.8	8.2
Cross-linker; DGBE (g)	0.013	0.027	0.040	0.051	0.061
Ethanol	6.4*r*	6.4*r*	6.4*r*	6.4*r*	6.4*r*

r: ethanol/IL weight ratio (g/g). In the case of open preparation, *r* was fixed at 2 g/g.

(b) SN ion gels	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
IL, [C_4mim][Tf_2N] (g)	6.4	6.4	6.4	6.4	6.4
Organic network (g)	1.60	1.60	1.60	1.60	1.60
Poly(DMAAm-*co*-NSA) (g)	1.583	1.565	1.547	1.533	1.519
Mass fraction of NSA (wt%)	1.6	3.5	5.3	6.8	8.2
Cross-linker; DGBE (g)	0.017	0.035	0.053	0.068	0.081
Ethanol	6.4*r*	6.4*r*	6.4*r*	6.4*r*	6.4*r*

r: ethanol/IL weight ratio (g/g). In the case of open preparation, *r* was fixed at 2 g/g.

The obtained precursor solution (about 12 g) was poured in a glass plate mold with a fluorinated ethylene propylene (FEP) copolymer film and a polytetrafluoroethylene (PTFE) spacer of 5 mm thickness. The depth of the precursor solution in the plate was about 2.5 mm. We prepared the ion gels using both closed and open molds. When we prepared the ion gels in closed molds, the mold was covered with an acrylic plate with a FEP film after the precursor solution had been poured into the mold; the mold was then sealed with clips. When the ion gels were prepared in open molds, no cover was used. In both cases, the molds were placed in a thermostatted oven maintained at 333 K for 24 h to complete the cross-linking reaction between NSA groups of the poly(DMAAm-*co*-NSA) and diamine (DGBE). The schematic diagram of the cross-linking reaction is shown in Scheme S2. In this work, we conducted the cross-linking reaction at 333 K because the mechanical strength of the u-DN ion gel was higher than that prepared at 298 K (Figure S2). In the case of closed system preparation, the acrylic plate was removed after the cross-linking process. The mold was then placed on a hot plate maintained at 333 K for 24 h to remove the ethanol in the gel. The compositions of the IL in the obtained ion gels were determined as 82.4 ± 1.4 wt% from the weights of the IL and the inorganic/organic skeleton, which were obtained via IL extraction using sufficient ethanol, followed by drying at elevated temperature.

Measurement of the extent of NHS ester group reaction with DGBE

The degree of the NHS ester group in the copolymer reacted with the cross-linker was determined from the amount of NHS generated from the cross-linking reaction. The prepared ion gel was immersed in d_6–DMSO to extract the NHS generated via the cross-linking reaction and the IL, and ^{1}H-NMR measurements were carried out to determine the NHS/IL molar ratio. Because the amount of NHS formed via the cross-linking reaction is equimolar to the reacted NHS ester group, the determined NHS/IL ratio approximates the molar ratio between the reacted NHS ester groups and IL in the gel sample, i.e., $n_{\mathrm{NHS\ ester,reacted}}/n_{\mathrm{IL}} = R_1$. On the other hand, the total amount of NHS ester group in the poly(DMAAm-*co*-NSA), $n_{\mathrm{NHS\ ester,0}}$, can be calculated from the used weight of poly(DMAAm-*co*-NSA), the weight fraction of NSA in the poly(DMAAm-*co*-NSA), and the molecular weight of NSA. The molar amount of IL used to prepare the ion gels, $n_{\mathrm{IL,0}}$, was calculated from the used amount and the molecular weight of the IL. Thus, the molar ratio between NSA in the poly(DMAAm-*co*-NSA) and IL, $n_{\mathrm{NSA,0}}/n_{\mathrm{IL,0}} = R_2$, can be calculated. Here, we considered that the IL used to prepare the ion gel was completely incorporated in the ion gel, $n_{\mathrm{IL}} = n_{\mathrm{IL,0}}$. Therefore, the ratio of R_1/R_2 equals $n_{\mathrm{NHS\ ester,reacted}}/n_{\mathrm{NSA,0}}$, which is the fraction of the reacted NHS ester group in the copolymer via the cross-linking.

Mechanical properties

The mechanical properties of the ion gels were evaluated using an automatic recording universal testing instrument (EZ-LX, Shimadzu Co., Japan) at room temperature (about 298 K). Dumbbell-shaped specimens having lengths and widths of 17.0 and 2.0 mm, respectively, were used for the stretching tests. The thicknesses of the samples were measured using a micrometer (IP65, Mitsutoyo Co., Japan). Because the gel samples were soft, they were sandwiched between glass plates; then, the total thickness of the sample and the glass plates was measured, and the sample thickness was determined as the difference between the total thickness and the thickness of the glass plates. The thickness measurements were carried out at least 10 times at different spots on each sample, and the average was used as the gel thickness. Because the ion gels contain no volatile components, the mechanical properties could be measured in air without compositional changes during the measurements. A uniaxial stretching test was conducted at a constant strain rate of 100 mm/min. The fracture stress, fracture strain, and Young's modulus were measured in triplicate for each sample. In the cyclic stretching tests, the stretching and return operations were performed until the sample broke, while incrementally increasing the stretching strain in steps of 0.5.

Transmission electron microscopy observation

The inorganic network in the μ-DN ion gels was observed by field-emission transmission electron microscopy (FE-TEM, JEM-2100F, JEOL Ltd., Japan) as described previously.[34] A cubic sample of the ion gel (1 mm × 1 mm × 1 mm) was immersed in a sufficient volume of ethanol for 12 h to exchange the IL in the sample for ethanol. The sample was then immersed in a solution of epoxy resin (Plain Resin Kit, Nisshin EM Co., Ltd., Tokyo, Japan)/ethanol mixture (weight ratio of 1:1 g/g) for 6 h and then immersed in the solution of epoxy resin for 12 h to exchange the ethanol in the sample with the epoxy resin solution completely. The epoxy resin solution impregnated sample was embedded in a silicon mold; subsequently, the epoxy resin solution was poured into the mold and cured at 343 K for 5 d. The resin block embedding the gel sample was subsequently thin-sectioned using an ultramicrotome (UC7, Leica Microsystems GmbH, Wetzlar, Germany), and sections of thickness 100 nm were collected on a copper mesh TEM grid with a microgrid mesh and observed by FE-TEM. The acceleration voltage of the electron gun used for observation was 200 kV.

RESULTS AND DISCUSSION

μ-DN ion gel prepared using poly(DMAAm-*co*-NSA) with different NSA ratios

The μ-DN ion gels prepared using poly(DMAAm-*co*-NSA) with 5 mol% of NSA in closed and open molds are shown in Figures 1(a) and 1(b), respectively. In both closed and open molds, self-standing ion gels were formed using the cross-linkable polymer as the building block of the organic network. In addition, ion gels were also successfully prepared with and without silica nanoparticles using the cross-linkable polymers with different NSA ratios. The successful preparation of the SN ion gels without silica nanoparticles demonstrated that a three-dimensional polymer network was formed by the intermolecular cross-linking between the cross-linkable polymers and diamine cross-linkers. In addition, we confirmed the inorganic network formation in the μ-DN ion gels by FE-TEM observation. As shown in Figures 1(c) and 1(d), partially developed silica nanoparticle networks were formed in the μ-DN ion gels prepared in both open and closed molds. It was found that the structures of the inorganic networks formed in the μ-DN ion gels prepared in open molds were almost the same as those prepared in closed molds. This means that the inorganic network structure was fixed in the precursor solution of the μ-DN ion gel, and that the structure was not significantly changed by the evaporation of ethanol during organic network formation in the open mold. Based on these results, organic and inorganic network formation in the μ-DN ion gels using the cross-linkable polymer and silica nanoparticles as the nonvolatile building blocks was successful. If the polymer network and the silica nanoparticle network are successfully interpenetrated, the prepared μ-DN ion gels should have much higher mechanical strength than the SN ion gels and should show characteristic hysteresis in the cyclic tensile stress–strain curves. Thus, we next evaluated the mechanical properties of the prepared μ-DN and SN ion gels.

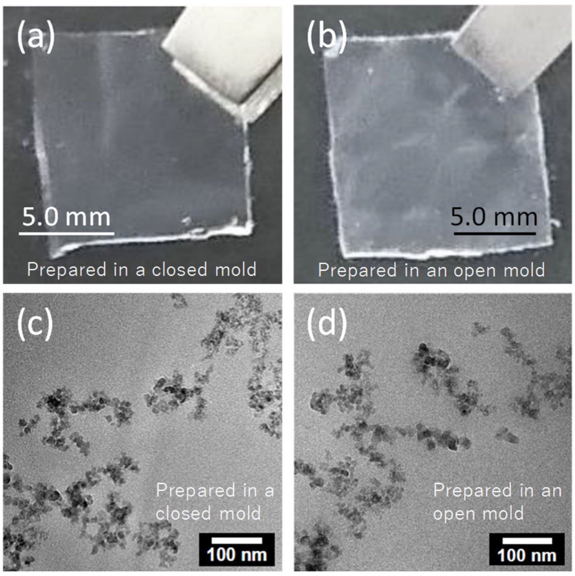

Figure 1. μ-DN ion gels prepared using poly(DMAAm-*co*-NSA) with 5 mol% of NSA in closed (a) and open molds (b), and the inorganic network structures formed in these μ-DN ion gels prepared in closed (c) and open molds (d). The μ-DN ion gels were prepared using the precursor solutions with $r = 2$ g/g.

The results of uniaxial tensile stress loading tests are shown in Figure 2. From the stress–strain curves, the mechanical properties of the μ-DN and SN ion gels, including fracture stress, fracture strain, Young's modulus, and fracture energy, were determined, and these are summarized in Figure 3. Comparing the mechanical strengths, the μ-DN ion gels clearly have higher mechanical strengths than the SN ion gels. In addition, the fracture stress of the μ-DN ion gels prepared in both closed and open molds were about 350–400 kPa, which is comparable to those of μ-DN ion gels prepared using DMAAm as the raw material of the organic network formation (about 400 kPa),[19] and is higher than those of DN ion gels (about 250 kPa).[20] To confirm the toughening mechanism, cyclic tensile stress–strain curves were measured for the μ-DN ion gels. Typical results are shown in Figure 4, and others can be found in Figures S3 and S4.

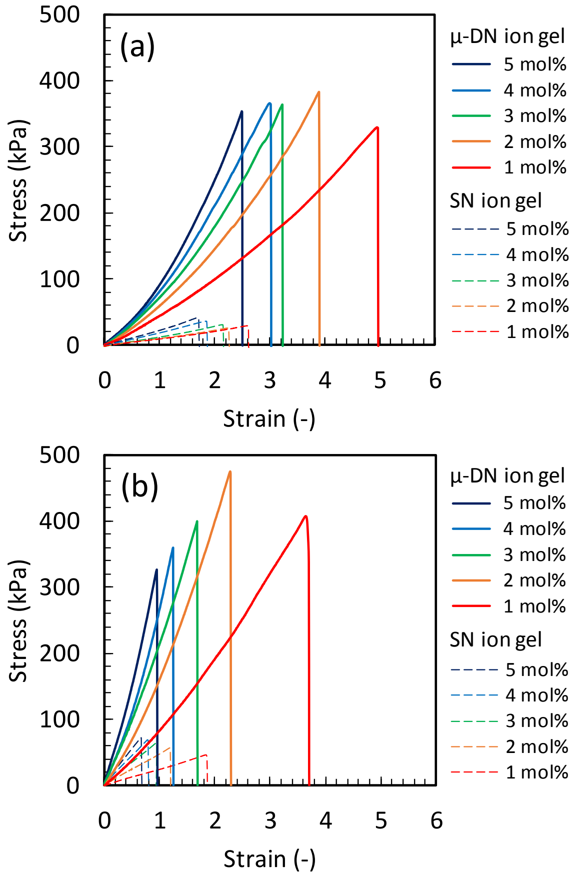

Figure 2. Uniaxial stress–strain curves of the μ-DN and SN ion gels prepared using the cross-linkable polymer with different NSA ratios. The ion gels were prepared in closed (a) and open molds (b) using the precursor solutions with *r* = 2 g/g.

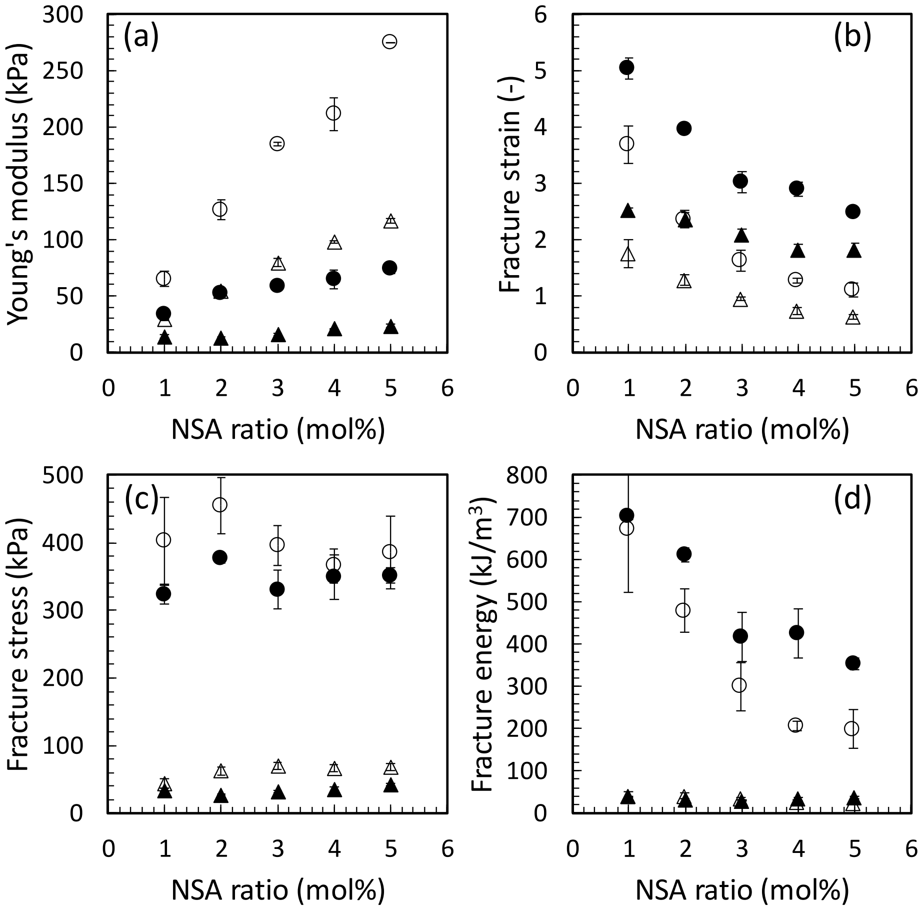

Figure 3. Mechanical properties of the μ-DN and SN ion gels prepared using the cross-linkable polymer with different NSA ratios. Black circles and triangles indicate the results for the μ-DN and SN ion gels prepared in closed molds, respectively. White circles and triangles represent the results for the μ-DN and SN ion gels prepared in open molds without an acrylic cover, respectively. The μ-DN and SN ion gels were prepared using the precursor solutions with *r* = 2 g/g.

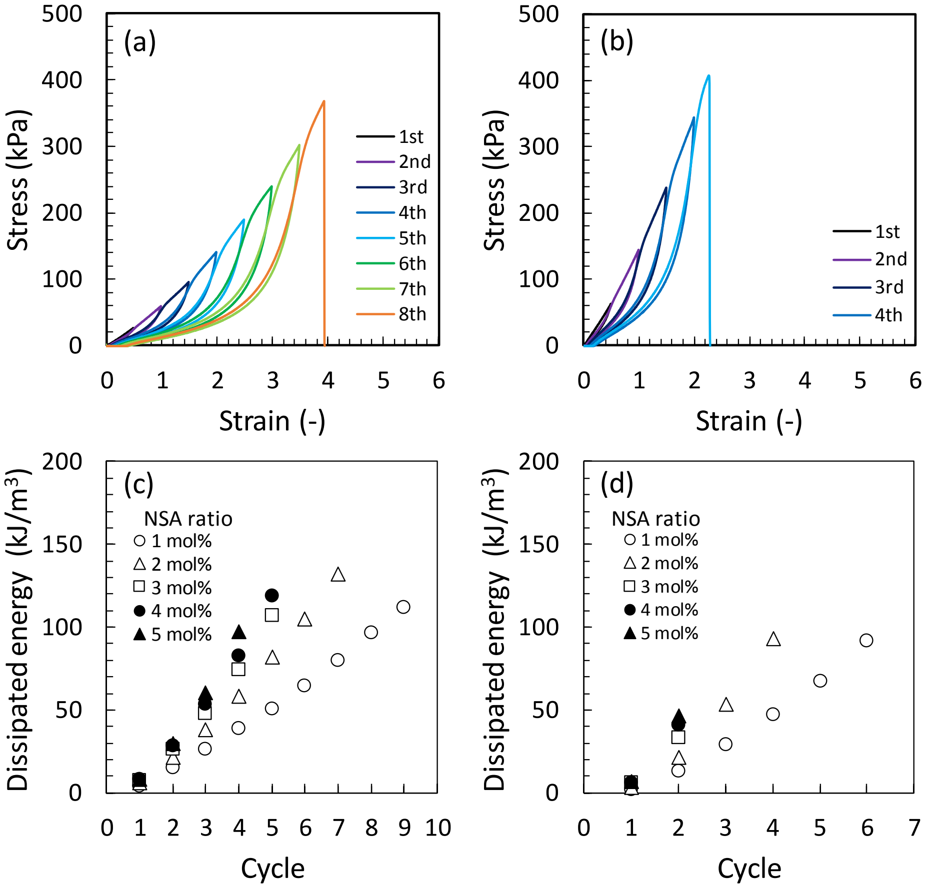

Figure 4. Energy dissipation of the μ-DN ion gels. (a, b) Cyclic tensile loading–unloading curves of the μ-DN ion gels prepared using cross-linkable polymers with 2 mol% of NSA ratio. (c, d) Dissipated energy of the μ-DN ion gels prepared using cross-linkable polymers with various NSA ratios at certain cycles in the cyclic tensile loading test. The μ-DN ion gels were prepared under the diluent condition of $r = 2$g/g in (a, c) a closed mold and (b, d) an open mold.

As expected, a clear hysteresis in the cyclic tensile stress–strain curves was observed for all the μ-DN ion gels, as shown in Figures 4, S3, and S4. The hysteresis in the cyclic tensile stress–strain curves indicates the softening behavior of the gel after stress loading. This softening behavior is characteristic of μ-DN ion gels. In addition, the large hysteresis is strong evidence that energy dissipation is the basis of the toughening mechanism of the μ-DN ion gels. This large hysteresis was also observed in cyclic stress–strain curves of the DN and μ-DN ion gels prepared using DMAAm for organic network formation.[18-20] Therefore, the large hysteresis observed in Figures 4, S3, and S4 indicate that the toughening mechanism of the μ-DN ion gels prepared using the cross-linkable polymer was the energy dissipation mechanism arising from the internal fracture of the inorganic network.[35] In other words, in the μ-DN ion gels, the silica nanoparticle network clusters acted as sacrificial bonds, whereas the cross-linkable polymer-based organic networks acted as a hidden length; when combined, these features toughen the prepared μ-DN ion gels.

Because of the double-network structure, the Young's modulus and fracture strain of the μ-DN ion gels were higher than those of the SN ion gels, as shown in Figure 3(a). The Young's modulus of the μ-DN ion gels reflects the additive contributions of the organic and inorganic networks. Therefore, compared to that of the SN ion gel, the Young's modulus of the μ-DN ion gel increased because of the contribution of the inorganic network. This means that the low strain elasticity originating from the inorganic network was much greater than that originating from the organic network. Regarding the fracture strains, because the partially destroyed inorganic network clusters formed in the μ-DN ion gels by the applied force still interpenetrated the polymer network, they act as multi-functional cross-linking points for the polymer network.[22] Therefore, the fracture strains of the μ-DN ion gels were larger than those of the SN ion gels. This characteristic enhancement of the Young's modulus and the fracture strain of the μ-DN ion gel also suggests that the polymer network formed by poly(DMAAm-*co*-NSA) acted as a hidden length and ruptured the inorganic network during the application of force to the μ-DN ion gels.

We then investigated the effects of the cross-linking degree on the mechanical properties of the μ-DN ion gels prepared using poly(DMAAm-*co*-NSA) with different NSA ratios. As clearly shown in Figures 3(a), (b), and (d), the Young's modulus, fracture strain, and fracture energy of the μ-DN ion gels were strongly dependent on the NSA ratio in the cross-linkable polymer. To confirm the cross-linking degree of the prepared μ-DN and SN ion gels, the extent of reaction of the NHS ester group in the polymer networks and the swelling ratio of the network of the μ-DN and SN ion gels in pure water were determined. Figures S5(a) and (b) shows the relationship between the degree of the reacted NHS ester group, $n_{\mathrm{NHS\ ester,reacted}}/n_{\mathrm{NSA},0}$, and the NSA ratio of the cross-linkable polymer used to prepare the ion gels. As shown in this figure, the fraction of the NHS ester group that reacted was approximately 0.8, and was not dependent on the NSA ratio in the cross-linkable polymer or the preparation conditions, such as the use of an open or closed system. On the other hand, the swelling ratio of the gel network in pure water was dependent on the NSA ratio and the preparation conditions (Figure 5). The swelling ratios of the ion gels prepared in open molds were lower than those prepared in closed molds, and decreased with increase in the NSA ratio of the cross-linkable polymer. That is, some parts of the cross-linkable polymer were cross-linked with another cross-linkable polymer to form intermolecular cross-linking, but intramolecular cross-links were also formed.[36] The decrease of the swelling ratio with increase in the NSA content indicated that the intermolecular cross-linking degree of the ion gel prepared using the polymer having a large NSA ratio was higher. At the same time, the degree of intermolecular cross-linking of the ion gels prepared in the open molds were higher than those of the ion gels prepared in closed molds, presumably because of the evaporation of ethanol during the cross-linking reaction. When the ion gels were prepared in open molds, a considerable amount of ethanol was lost from the precursor solution because the ion gels were prepared at 333 K. The evaporation of ethanol led to an increase in the concentration of the cross-linkable polymer in the precursor solution. As a result, the distance between the cross-linkable polymers was reduced, and intermolecular cross-linking was facilitated. Crucially, the intermolecular cross-linking degree of the organic network is dependent on the NSA ratio of the cross-linkable polymer and the preparation conditions. Therefore, the mechanical properties of the ion gels are dependent on the intermolecular cross-linking degree of the organic network.

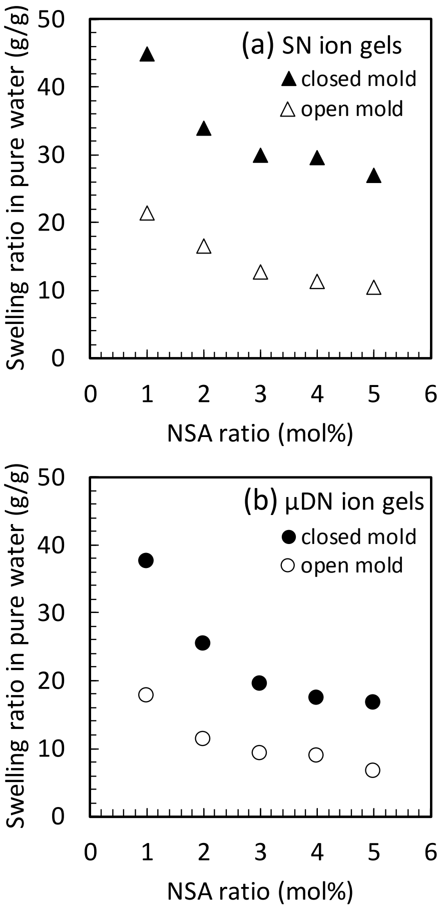

Figure 5 Swelling ratio of the networks in the μ-DN and SN ion gels in pure water. The μ-DN and SN ion gels were prepared using cross-linkable polymers with different NSA ratios. Black circles and triangles represent the results for the μ-DN and SN ion gels, respectively, prepared in closed molds. White circles and triangles represent the results for the μ-DN and SN ion gels, respectively, prepared in open molds. All ion gels were prepared using the precursor solutions with *r* = 2 g/g.

In general, the mechanical properties of a gel are dependent on the degree of intermolecular cross-linking (hereafter, the *intermolecular cross-linking degree* is simply written as the *cross-linking degree*). As shown in Figure 3(a), the Young's moduli of the μ-DN and SN ion gels increased with the increase in the NSA ratio of the cross-linkable polymer. For the SN ion gel, the increase is understandable because of the higher cross-linking density of the organic network formed using the cross-linkable polymer with a higher NSA ratio. In addition, as expected from the results of the swelling tests, the Young's moduli of the SN ion gels prepared in open molds were higher than those prepared in closed molds. Regarding the Young's modulus of the μ-DN ion gel, the trend was the same as that for the SN ion gels. Notably, the degree of increase in the Young's modulus with the increase in the NSA ratio was greater than that of the SN ion gel. This difference in the degree of the increase in the Young's moduli of the μ-DN and SN ion gels can be explained as resulting from the contribution of the inorganic network in the μ-DN ion gels.

The Young's modulus of a μ-DN ion gel is the sum of the moduli of the organic and inorganic networks. In general, flexible polymer chains can freely slide in the interstices of the silica nanoparticle aggregate (inorganic network). However, cross-linking points are more likely to be obstructed by the inorganic network. Therefore, until the cross-links are caught by the inorganic network, the load is sustained by polymer network. On the other hand, when the cross-linking point is caught on the inorganic network, both the organic and inorganic networks sustain the load. In the case of a more loosely cross-linked polymer, the cross-linking point is only restricted by the inorganic network at a higher elongation. For a highly cross-linked polymer, the cross-linking point is caught on the inorganic network even at low strains. That is, when the cross-linking degree of the organic network is high, the contribution of the inorganic network to sustaining the applied stress is increased. As a result, the increase in the cross-linking degree of the organic network enhances not only the Young's modulus originating from the organic network but also that from the inorganic network. As the result, the degrees of increase in the Young's moduli of the μ-DN ion gels with increase in the NSA ratio were higher than in the SN ion gels.

The cross-linking degree also affects the fracture strain of the SN and μ-DN ion gels. As shown in Figure 3(b), the fracture strain of the SN and μ-DN ion gels monotonically decreased with the increase in the NSA ratio in the cross-linkable polymer. In addition, the fracture strains of the SN and μ-DN ion gels prepared in closed molds were higher than those of the SN and μ-DN ion gels prepared in open molds. These results indicated that the μ-DN ion gels having loosely cross-linked polymer networks could elongate to a greater extent.

The fracture energy of the μ-DN ion gel also affected by the cross-linking degree of the polymer. As shown in Figure 3(d), the fracture energy of the μ-DN ion gels increased with decrease in the cross-linking degree of the polymer network. Similarly, the tearing energy of the μ-DN ion gel also depended on the degree of cross-linking of the polymer network, and the μ-DN ion gel with a polymer network with low cross-linking degree had high tearing energy (Table S1). The tensile fracture energy (703 kJ/m^3) and the tearing energy (124 J/m^2) of the μ-DN ion gel prepared using the cross-linkable polymer with 1 mol% NSA were about 1.5 times higher than those of the classical DN ion gel prepared from TEOS and DMAAm (437 kJ/m^3 and 82.1 J/m^2, respectively[20]). The excellent toughness of the μ-DN ion gel with loosely cross-linked polymer network is due to the contribution of both of the inorganic and organic networks. When the μ-DN ion gel was stretched, the inorganic network clusters entangled with the organic networks were ruptured. In the μ-DN system, the inorganic network clusters act as sacrificial bonds, and the loaded energy is dissipated when the inorganic network clusters are ruptured. The amount of dissipation increased with the increase in the number of ruptured inorganic network clusters. Because the highly cross-linked polymer network has many cross-linking points, which are caught on and rupture the inorganic network, the number of the inorganic network clusters ruptured could depend on the cross-linking degree of the polymer network. The energies dissipated in each cycle of elongation were shown in Figures 4(c) and (d). As shown in these figures, at the same stretching cycle, the dissipated energy increased with the increase in the NSA ratio of the cross-linkable polymer. This is because of the higher cross-linking degree of the polymer network with the higher NSA ratio. As the supporting evidence, it is demonstrated in Figures 4(c), 4(d) and 5 that the enhancement of the dissipated energy shows the same trend as the decrease of swelling ratio with the increase of the NSA ratio. When the NSA ratio was small, the dissipated energy and the swelling ratio were strongly varied with the increase in the NSA ratio. On the other hand, when the NSA ratio was large, the variations became small. From these results, it can be said that the μ-DN ion gel with the highly cross-linked polymer network dissipated larger energy when the strain of the μ-DN ion gel was the same. However, as mentioned before, the fracture strain of the μ-DN ion gel increases with the decrease in the cross-linking degree of the polymer network. The number of ruptured inorganic network cluster increases with the increase in tensile strain. Therefore, in the μ-DN ion gel with loosely cross-linked polymer network, many inorganic network clusters are broken in the highly stretched state. As shown in Figure 3(d), the enhancement of the fracture energy of the μ-DN ion gels with the decrease in the NSA ratio in the cross-linkable polymer indicates that the fracture energy is dominated by the increased fracture strain due to the loosely cross-linked polymer network.

On the other hand, the fracture energy of the SN ion gels was not dependent on the cross-linking degree of the cross-linkable polymer (Figure 3(d)). This is because SN ion gels does not contain silica nanoparticle clusters. Thus, the loaded energy was not dissipated when the SN ion gels were stretched. Therefore, the fracture energy of the SN ion gel was not dependent on the cross-linking degree of the cross-linkable polymer.

In contrast to the fracture energy, the fracture stresses of the SN and μ-DN ion gels were dependent and independent, respectively, on the cross-linking degree of the cross-linkable polymer (Figures 2 and 3). The trends in the fracture stress of the SN ion gels with respect to cross-linking degree are shown clearly in Figure 2. The fracture stress of the SN ion gels increased with increase in the NSA ratio in the cross-linkable polymer. In addition, by comparing the fracture stresses of the SN ion gels prepared in open and closed molds using the cross-linkable polymer with the same NSA ratio, we confirmed that the fracture stress values of the SN ion gels prepared in open molds were higher than those prepared in closed molds. When the cross-linking degree of the polymer network increased, the average strand length decreased. As a result, the inhomogeneity of the strand length, and the number of polymer chains supporting the loaded stress, increased. Thus, the fracture stress of the SN ion gels increased with increase in the NSA ratio of the cross-linkable polymer, and the fracture stress of the SN ion gels prepared in open molds became higher than those prepared in closed molds. On the other hand, the fracture stress of the μ-DN ion gel showed no clear dependence on the cross-linking degree of the cross-linkable polymer. In the μ-DN system, the fracture stress is the sum of the stress loaded on the organic and inorganic networks at the breaking point. It can be assumed that the stress sustained by the organic network would be the same as that of the SN ion gels. As shown in Figures 2 and 3(c), the stress sustained by the inorganic/organic double-network in the μ-DN ion gels was much larger than that sustained by the organic network in the SN ion gels. Thus, the stress sustained by the inorganic network is much larger. Considering the extended network that sustains the applied load, all the inorganic network composed of silica nanoparticle aggregates could be regarded to be in the extended state, whereas the organic network with a distribution of molecular weights between cross-linking points was in a partially extended state. In other words, the whole inorganic network and some of the polymer chains in the μ-DN ion gels sustained the load. Although the stress is sum of the load sustained by the inorganic network and a part of organic network, it would be mainly originated by the inorganic network because the small amount of extended polymer chain cannot sustain large load. Therefore, the inorganic network can sustain a higher load than the organic network. At the breaking point at which macroscopic destruction of the μ-DN ion gels occurred, the applied load on the μ-DN ion gel was mainly sustained by the inorganic network, and the contribution of the organic network in sustaining the applied load was negligible. When the inorganic networks in the μ-DN ion gels were formed using same amounts of silica nanoparticles, the structures of the inorganic networks in all the μ-DN ion gels were very similar (Figures 1(c) and 1(d)). This means that the load sustained by the inorganic networks in all the μ-DN ion gels should be comparable. Therefore, the fracture stress of the μ-DN ion gel was mainly determined by the inorganic network, as shown by the similar fracture stress values (within experimental error) and independence on the cross-linking degree of the polymer.

μ-DN ion gels prepared using a precursor solution with different ethanol/IL ratios

On the basis of these results, we concluded that the different mechanical properties of the μ-DN ion gels prepared in closed and open molds arose because of the different cross-linking degree of the polymers. Accordingly, the cross-linking degree of the μ-DN ion gels prepared in open molds would be increased with increase in cross-linkable polymer concentration in the precursor solution because of the evaporation of ethanol during the cross-linking reaction. To confirm this, we prepared μ-DN ion gels in closed molds using precursor solutions with different ethanol/IL ratios.

The properties of the prepared ion gels are summarized in Figure 6(a), which shows the uniaxial tensile stress–strain curves of the μ-DN and SN ion gels. In the range of diluent ratios of the precursor solutions investigated, the μ-DN ion gels had much higher mechanical strengths than the SN ion gels. The improved mechanical properties are due to the energy dissipation made possible by the rupture of the silica nanoparticle clusters in the μ-DN ion gels (Figure 6(b)). The energy dissipation of the prepared μ-DN ion gels is shown in Figures 6(c) and S5. As demonstrated in these figures, all μ-DN ion gels prepared using the precursor solutions with r = 2–4 g/g showed clear mechanical hysteresis. In addition, the extent of NSA reaction for all μ-DN and SN ion gels were approximately 0.8 (Figure S5(c)), similar to those of the μ-DN and SN ion gels prepared in closed and open molds using the cross-linkable polymer with different NSA ratios (Figure S5(a) and (b)). To investigate the effect of the dilution of the precursor solutions on the intermolecular cross-linking degree in the μ-DN and SN ion gels, the swelling ratios of the networks were measured in pure water, and the results are shown in Figure 6(d). As expected, the swelling ratio of the gel network skeleton increased with increase in r. In addition, as shown in Figure S6(f), the dissipated energy of the μ-DN ion gels at the same strain increased with decrease in r. Furthermore, the trend of the variations of the dissipated energy and the swelling ratio along with the change of r was similar. That is, when r was changed, not only the dissipated energy but also the swelling ratio gradually and monotonically changed. These results indicated that the cross-linking degree increased with the increase in the concentration of the cross-linkable polymer in the precursor solution with lower r.

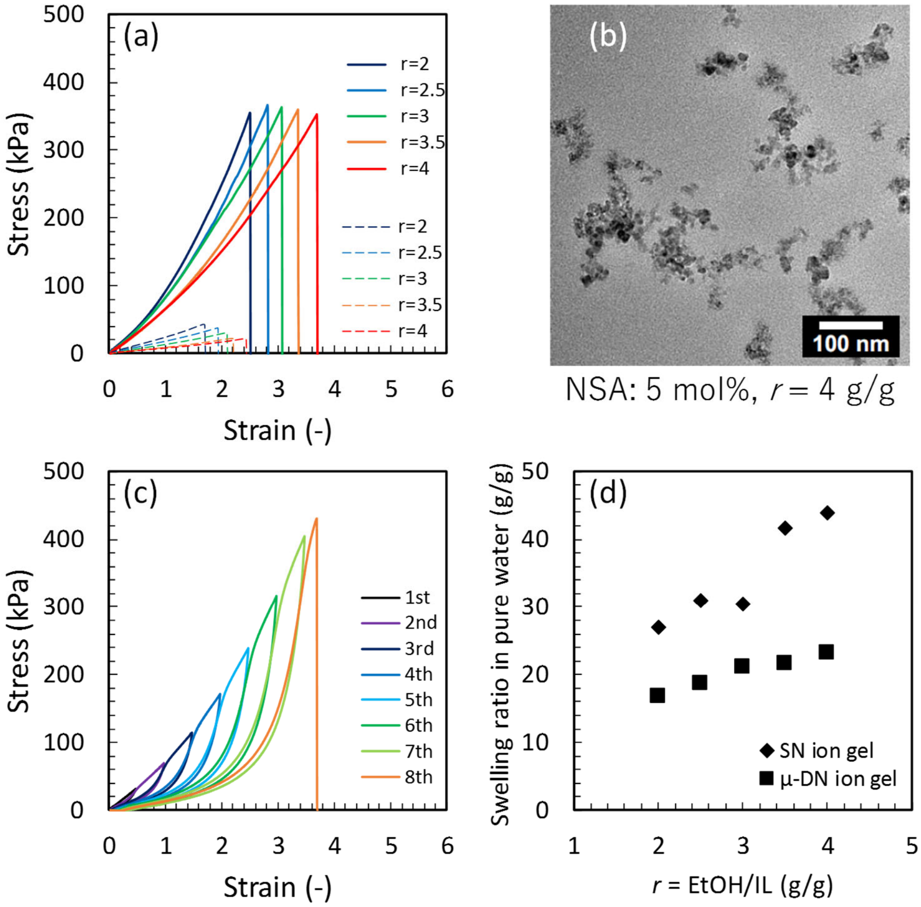

Figure 6. Properties of the ion gels prepared in closed molds using precursor solutions with different ethanol/IL weight ratios, *r*. The cross-linkable polymer contained 5 mol% of NSA. (a) Uniaxial tensile stress–strain curves of the μ-DN and SN ion gels. (b) TEM image and (c) cyclic tensile stress loading–unloading curves of the μ-DN ion gel prepared using the precursor solution with *r* = 4 g/g. (d) Swelling ratios of the μ-DN and SN ion gels prepared using the precursor solutions with different *r*.

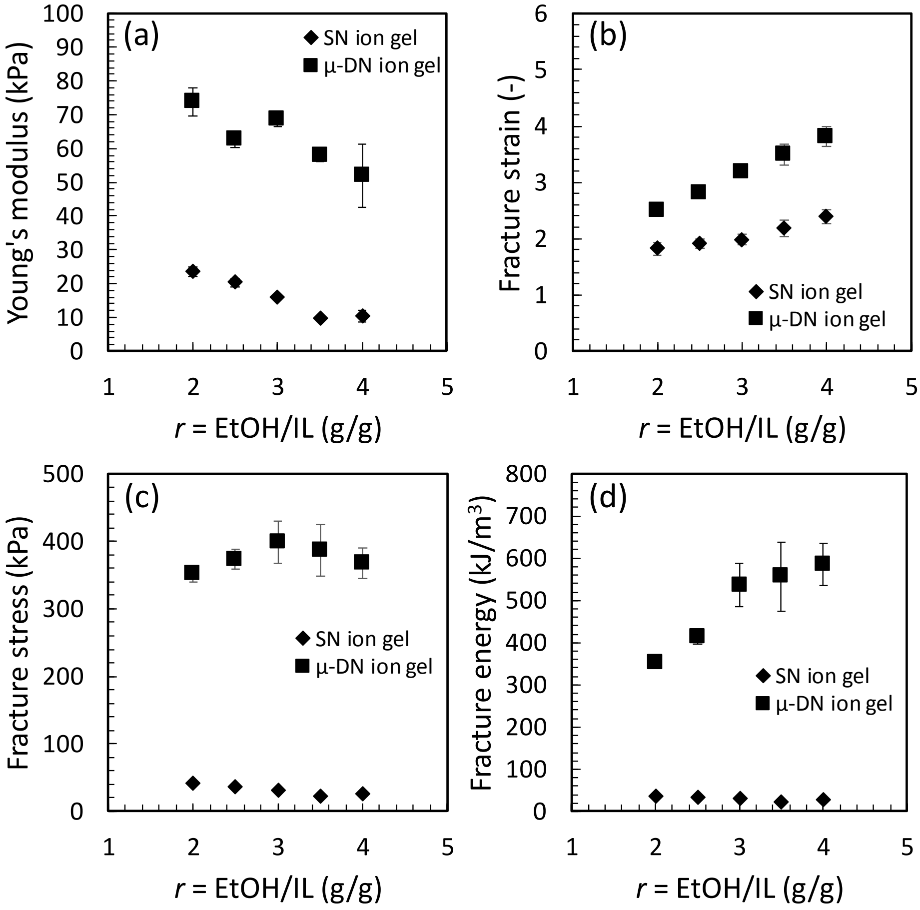

Figure 7. Mechanical properties of the μ-DN and SN ion gels prepared in closed molds using precursor solutions with different ethanol/IL ratios, *r*. The NSA ratio of the cross-linkable polymer was 5 mol%.

The mechanical properties of the ion gels also varied with cross-linking degree, as expected (Figure 7). As shown in Figure 7(a), the Young's modulus of the SN and μ-DN ion gels increased with decrease in *r*. At the same time, the fracture strain and fracture energy decreased with the decrease in *r* (Figure 7(b) and (d)). Furthermore, the fracture stress of the SN ion gels also increased with the decrease in *r* (Figures 6(a) and 7(c)). These results are expected because of the associated increase in cross-linking degree. On the other hand, the fracture stress of the μ-DN ion gels showed no dependence on *r*. This is also reasonable because the fracture stress of the μ-DN ion gels is dominated by the inorganic network, and the effect of the cross-linking degree of the organic network was negligible, as noted before.

The cross-linking degree of the polymer and the mechanical strength of the μ-DN ion gel can be increased by reducing the concentration of the cross-linkable polymer in the precursor solution. In addition, the dilution of the precursor solution could provide further advantages for thin film formation. One is a reduction of viscosity of the precursor solution, enabling spreading in very thin liquid films, and another is the significant shrinkage of the formed ion gel by the evaporation of the diluent, which could further reduce the film thickness (Figure S7). For example, we estimate that about 10 μm thickness of the liquid film and less than 1 μm thickness of the DN ion gel layer could be formed using the precursor solution with $r = 5$ g/g by spin-coating at 7000 rpm. Therefore, using a precursor solution diluted by ethanol as much as possible while still allowing gelation would be preferable to make tough and thin DN ion gels. Based on the findings reported here, the development of thin μ-DN ion gel films will be studied next.

SUMMARY

To develop a thin μ-DN ion gel film preparation technology, μ-DN ion gels were prepared using nonvolatile materials: an IL, silica nanoparticles, and cross-linkable polymer. A series of cross-linkable poly(DMAAm-*co*-NSA) polymers having almost same molecular weight but different NSA ratios was synthesized by RAFT polymerization. Using the cross-linkable polymer, μ-DN ion gel films were successfully prepared in open molds. Tensile stress–strain measurements confirmed that the inorganic network formed in the μ-DN ion gel acted as a sacrificial bond network, which dissipated the loaded energy, whereas the organic network acted as a hidden length, which suppressed the macro-destruction of the μ-DN ion gel. The prepared μ-DN ion gels had excellent mechanical strengths, similar to those of previously reported inorganic/organic DN ion gels and μ-DN ion gels prepared in closed molds using DMAAm as the raw material of the organic network. Thus, tough μ-DN ion gel films can be prepared in an open system by using a cross-linkable polymer as the nonvolatile organic network precursor.

In addition, detailed investigation of the mechanical properties of the cross-linkable polymer-based μ-DN ion gels were conducted to propose criteria to control the mechanical strength of μ-DN ion gels prepared in open systems. The mechanical properties, such as the Young's modulus, fracture stress, and fracture strain, of the μ-DN ion gels depended on the NSA ratio of the cross-linkable polymer, i.e., the cross-linking degree of the organic network. The cross-linking degree was also controlled by changing the concentration of the cross-linkable polymer. The cross-linkable polymer concentration can be controlled by changing the amount of ethanol added to the precursor solution, and this also varied because of the evaporation of ethanol during cross-linking in the open environment. Thus, the mechanical properties of the μ-DN ion gel film prepared in an open system can be controlled by controlling the NSA ratio in the cross-linkable polymer and the rates of diluent evaporation and the cross-linking reaction.

ASSOCIATED CONTENT

Supporting Information.

The following files are available free of charge. Synthesis scheme for poly(DMAAm-*co*-NSA), ^{1}H-NMR spectrum of poly(DMAAm-*co*-NSA) solution after reaction with tertiary butylamine, cyclic tensile stress loading-unloading curves of the μ-DN ion gels, extent of NHS ester group reaction with DGBE (PDF).

AUTHOR INFORMATION

Corresponding Author

Eiji Kamio − Department of Chemical Science and Engineering, Research Center for Membrane and Film Technology, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe, Hyogo 657-8501, Japan. (https://orcid.org/0000-0002-1331-0871; E-mail: e-kamio@people.kobe-u.ac.jp).

Hideto Matsuyama − Department of Chemical Science and Engineering, Research Center for Membrane and Film Technology, Kobe University, 1-1 Rokkodai-cho, Nada-ku, Kobe, Hyogo 657-8501, Japan. (https://orcid.org/0000-0003-2468-4905; E-mail: matuyama@kobe-u.ac.jp)

Notes

The authors declare no competing financial interest.

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