Preparation of tough, thermally stable, and water-resistant double-network ion gels consisting of silica nanoparticles/poly(ionic liquid)s through photopolymerisation of ionic monomer and subsequent solvent removal

Takaichi Watanabe, Ruri Takahashi, and Tsutomu Ono[*]

Department of Applied Chemistry, Graduate School of Natural Science, Okayama University, 3-1-1, Tsushima-naka, Kita-ku, Okayama, 700-8530, JAPAN

[*] Email: tono@okayama-u.ac.jp

Abstract

We report the preparation of tough, thermally stable, and water-resistant double-network (DN) ion gels, which consist of a partially-clustered silica nanoparticle network and poly(ionic liquid)s (PILs) network holding an ionic liquid. Silica nanoparticles/poly([Evim][Tf$_2$N]) DN ion gels are prepared by photo-induced radical polymerisation of [Evim][Tf$_2$N] in a mixture containing silica nanoparticles, [Bmim][Tf$_2$N], ionic liquid based cross-linker [(VIM)$_2$C$_4$][Tf$_2$N]$_2$, and ethyl acetate, followed by subsequent solvent evaporation. Tensile strength measurements show that the mechanical properties of the PILs DN ion gels were higher than those of the PILs single-network (SN) ion gel. Rheological study indicates that an enhancement in mechanical strength of the PILs DN ion gels can be achieved when silica nanoparticles form partial clusters in [Bmim][Tf$_2$N]. The cyclic stress-strain measurement of the PILs DN ion gels shows hysteresis loops, suggesting that the silica nanoparticle clusters rupture and dissipate the loading energy when the PILs DN ion gels undergo a large deformation. The fracture strength and Young's modulus of the PILs DN ion gels increase as the diameter of silica nanoparticles is decreased. Thermal gravimetric analysis measurement shows that the PILs DN ion gel has a high decomposition temperature of approximately 400 °C. Moreover, swelling test shows that the PILs DN ion gel possesses an excellent water-resistant property because of hydrophobic nature of the PILs backbone. We believe that such tough, thermally stable, and water-resistant PILs DN ion gels can be used as carbon dioxide separation membranes, and sensors and actuators for soft robotics.

Introduction

Ionic liquids (ILs) that are defined as organic salts with a melting temperature below 100 °C have received considerable interest as green solvents in the fields of organic synthesis,[1-5] electrolysis,[6-10] and separation technologies,[11-15] owing to their excellent physicochemical properties including negligible vapor pressure, low flammability, high ionic and thermal conductivity, and excellent thermal and chemical stability. In addition, in contrast to any other class of solvents, the physicochemical properties of ILs, such as melting temperature and solubility, can be easily tailored by changing the combination of their cations and anions,[16-20] and thus ILs are also known as "designer solvents".[21,22] This has broadened the functionalities of ILs as well as their applications.

For the last two decades, tremendous effort has been paid to develop IL-based soft materials including poly(ionic liquid)s (PILs), cross-linked PILs, ion gel, and PIL-based ion gel in order to apply ILs to functional materials such as solid-state polyelectrolytes,[23-28] super capacitors,[29,30] and separation membranes for carbon dioxide.[31-35] PILs are a subgroup of solid polyelectrolytes that are composed of a polymeric backbone and immobilized IL species in monomer repeating units. Because of the polymeric backbone of PILs, PILs can be treated as a pseudo solid state even at room temperature whilst keeping their IL properties, which has significantly improved handleability of ILs from the viewpoint of material science. When PIL molecules are three-dimensionally bonded with cross-linker,

cross-linked PILs are obtained. Cross-linked PILs are one kind of elastomers that exhibit higher

mechanical strength but lower ionic conductivity than PILs. Ion gels are one kind of polymeric gel

consisting of a three-dimensional polymer network and a large amount of IL.[28,36] Amongst ion gels,

ion gels consisting of cross-linked PILs networks and a large amount of IL are called as PILs ion gels.

Since PILs networks have a good compatibility with ILs, various kinds of IL can be incorporated in

their networks. In addition, PILs ion gels exhibit superior ionic conductivity and carbon dioxide

separation performance to PILs because a large amount of ILs incorporated in the PILs ion gels

facilitate ion transportation in the PILs network whilst keeping their elasticity originated from cross-

linked polymer matrix.[37,38] However, there is still a difficulty in the practical application of ion gels

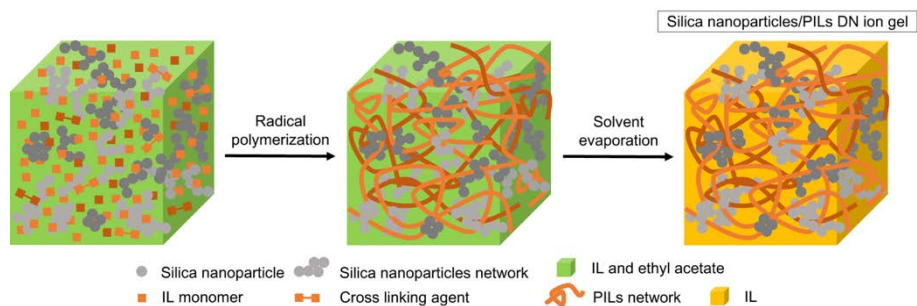owing to their low mechanical strength.

Recently, Kamio *et al.* have reported the preparation of high-strength inorganic/organic

composite ion gels[39] using a toughening mechanism of the well-known DN principles.[40] The

inorganic/organic composite ion gels were prepared with tetraethyl orthosilicate (TEOS) and *N,N*-

dimethylacrylamide (DMAAm) through a one-pot / one-step processing. They showed that silica-

particle-network-based clusters formed in the silica nanoparticles/poly(*N,N*-dimethylacrylamide

(PDMAAm) DN ion gels could serve as brittle microgel particles as an analogue to the microgel-

reinforced DN hydrogel and contribute to the toughening of the ion gel based on the energy dissipation

through the internal rupture of the silica-particle network in the clusters.[41] Yasui *et al.* have also

reported that high-strength silica nanoparticles/PDMAAm DN ion gels could be obtained even when using fumed silica nanoparticles as a starting material, instead of TEOS, which not only simplified the preparation process, but also prevented monomer and TEOS from evaporation during the preparation.[42] These studies have clearly demonstrated the potential of inorganic/organic DN network formation to improve the mechanical properties of ion gels. However, because of hydrophilic nature of cross-linked PDMAAm network in the DN ion gels, the DN ion gels tend to be swollen with water when the samples are exposed to high humidity or aqueous environment.

In this study, we report the preparation of tough, thermally-stable and water-resistant PILs-based DN ion gels, composed of a partially-clustered silica nanoparticle network and poly[Evim][Tf_2N] network holding [Bmim][Tf_2N], as an ionic liquid through photo-induced radical polymerisation of [Evim][Tf_2N] in a mixture containing fumed silica nanoparticles, [Bmim][Tf_2N] (IL), [$(VIM)_2C_4$] [Tf_2N]$_2$ (IL-based cross-linker), and ethyl acetate (solvent), and subsequent solvent evaporation (**Scheme 1**). The advantage of the use of PILs network for ion gels is that the physicochemical properties of PILs can be easily tuned by anion exchange reaction and combinatorial design of cation and anion species in PIL network will allow us to stably incorporate various kinds of ILs in PILs-based ion gel because of a good compatibility between PILs and IL. Specifically, in our study, we first chose [Bmim][Tf_2N] as an incorporated IL in the PILs ion gel because of high carbon dioxide absorption property.[43] Then, judging from the compatibility of [Bmim][Tf_2N] and polymer

network, we decided to use [Evim][Tf$_2$N] and [(VIM)$_2$C$_4$] [Tf$_2$N]$_2$ as the monomer and cross-linker, respectively to synthesize poly[Evim][Tf$_2$N] network. Because the poly[Evim][Tf$_2$N] is intrinsic hydrophobic PILs, we can expect that the silica nanoparticle/ poly[Evim][Tf$_2$N] DN ion gels will show not only high mechanical strength derived from DN structures, but also high thermal stability and high water resistant property, originated from poly[Evim][Tf$_2$N] network. To the best of our knowledge, this is the first report on the preparation of PILs-based DN ion gels. We first prepare silica nanoparticles/poly[Evim][Tf$_2$N] DN ion gel and poly[Evim][Tf$_2$N] single network (SN) ion gel and compare their mechanical properties. Then, we evaluate the effects of silica nanoparticle diameter, IL content, and cross-linker concentration on the mechanical strength of the DN ion gels and investigate when the DN structures are formed during their preparation. Next, to investigate the effect of the surface affinity of silica nanoparticles to ILs on the formation of the DN structure in the ion gels, we prepare PILs-based ion gels composed of silica nanoparticles having ILs surfaces and cross-linked PILs, and evaluate their mechanical properties. Finally, we evaluate the thermal stability and water-resistant property of the silica nanoparticles/poly[Evim][Tf$_2$N] DN ion gels by thermal gravimetric measurements and swelling tests of the samples immersed in water, respectively.

Scheme 1. Schematic illustration of silica nanoparticles/PILs DN ion gel prepared by photo-induced radical polymerisation and subsequent solvent evaporation.

Silica nanoparticles/PILs DN ion gel

Radical polymerization

Solvent evaporation

- ● Silica nanoparticle
- ■ IL monomer
- ●● Silica nanoparticles network
- ■—■ Cross linking agent
- ▮ IL and ethyl acetate
- PILs network
- ▮ IL

Experimental Section

Materials

As an ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([Bmim][Tf$_2$N]), which was purchased from FUJIFILM Wako Pure Chemical Corp. (Japan), was used after removing dissolved oxygen by bubbling dry nitrogen for more than 15 min. As an ionic monomer, 1-ethyl-3-vinylimidazolium bis(trifluoromethanesulfonyl)imide ([Evim][Tf$_2$N]) was purchased from FUJIFILM Wako Pure Chemical Corp. (Japan) and used as received. 1-vinylimidazole and 1,4-dibromobutane were purchased from FUJIFILM Wako Pure Chemical Corp. (Japan) and used without further purification. Ethanol, diethyl ether, and lithium bis(trifluoromethanesulfonyl)imide (LiTf$_2$N) were purchased from FUJIFILM Wako Pure Chemical Corp. (Japan) and used as received. Ciba® IRGACURE® 2959, which was purchased from Ciba Specialty Chemicals (Switzerland), was used as a photoinitiator to synthesize the poly([Evim][Tf$_2$N]) network in an ionic liquid. A series of fumed silica nanoparticles (AEROSIL® 300, 200, 50, and OX50), whose primary particle diameters were 7, 12, 30, and 40 nm, respectively, were kindly gifted from Nippon Aerosil Co., Ltd. (Japan) and used

7

without further purification to form an inorganic network in an ionic liquid. Ethyl acetate was obtained

from FUJIFILM Wako Pure Chemical Corp. (Japan) and used as a dispersant of fumed silica

nanoparticles without further purification. (3-Chloropropyl)trimethoxysilane and 1-methylimidazole

were purchased from Sigma-Aldrich Japan and used as received. Dimethyl sulfoxide-d_6 was purchased

from Kanto Chemical Co., Inc. (Japan) and used as received. Deionized water used in all experiments

was produced using an Elix UV purification system (Millipore, Japan). The chemical structures of

[Bmim][Tf$_2$N], [Evim][Tf$_2$N], Ciba® IRGACURE® 2959, [(VIM)$_2$C$_4$]Br$_2$, [(VIM)$_2$C$_4$][Tf$_2$N]$_2$, and the

ionic liquid silane coupling reagent with a Cl$^-$ anion, Cl$^-$ILSC, are shown in **Figure S1**.

Synthesis of 1,4-bis(3-vinylimidazolium-1-yl) butane bis(trifluoromethanesulfonyl)imide

[(VIM)$_2$C$_4$][Tf$_2$N]$_2$ as an ionic liquid cross-linking reagent

[(VIM)$_2$C$_4$][Tf$_2$N]$_2$ was synthesized by reaction of 1-vinylimidazole with 1,4-dibromobutane,

followed by an anion exchange reaction with LiTf$_2$N (**Scheme S1**).[44,45] First, 1-vinylimidazole (0.20

mol, 18.1 mL) and ethanol (15.0 mL) were added into a dried round-bottom flask under argon

atmosphere. Then, 1,4-dibromobutane (0.11 mol, 13.6 mL) was added dropwise into the flask and the

mixture was stirred at 70 °C under argon atmosphere for 24 h. After the reaction, the reaction mixture

was reprecipitated in ethyl acetate three times to remove unreacted reagents. [(VIM)$_2$C$_4$]Br$_2$ was

obtained after drying the purified product at 50 °C under reduced pressure overnight. The proton

8

nuclear magnetic resonance (^{1}H NMR) spectrum of [(VIM)$_2$C$_4$]Br$_2$ is shown in **Figure S2a**. The product yield was 74.3%. Next, anion exchange of [(VIM)$_2$C$_4$]Br$_2$ with LiTf$_2$N was performed as follows; 60 mL of aqueous solution dissolving [(VIM)$_2$C$_4$]Br$_2$ (7.5 mmol, 3.03g) was mixed with 60 mL of aqueous solution dissolving LiTf$_2$N (16.5 mmol, 4.74 g). The mixture was stirred at room temperature for 24 h under argon atmosphere to exchange the counter anion of Br$_2$ with [Tf$_2$N]$_2$ anions. To remove any residual salt, the obtained [(VIM)$_2$C$_4$] [Tf$_2$N]$_2$ was washed with pure water three times and then freeze dried for 24 h. ^{1}H NMR spectrum of [(VIM)$_2$C$_4$] [Tf$_2$N]$_2$ is shown in **Figure S2b**. The product yield was 66.0%.

Synthesis of ionic liquid silane coupling reagent with Cl$^-$ anion (Cl$^-$ILSC).

Cl$^-$ILSC was synthesized by reaction of (3-chloropropyl)trimethoxysilane with 1-methylimidazole (**Scheme S2**). First, (3-chloropropyl)trimethoxysilane (50 mmol, 9.23 mL) and 1-methylimidazole (55 mmol, 4.35 mL) were added into a dried round-bottom flask under argon atmosphere. The mixture was then reacted at 95 °C under stirring overnight. After the reaction, the same amount of diethyl ether (~14 mL) was added into the reaction mixture and stirred for 15 min. Subsequently, the reaction mixture was set aside for a few minutes. To eliminate any unreacted reagent, the supernatant was removed from the reaction mixture. This purification process was repeated three times. Then, the resultant Cl$^-$ILSC was concentrated using a rotary evaporator, followed by drying under high vacuum.

The product yield was 93.2%. ^{1}H NMR spectrum of Cl$^-$ILSC is shown in **Figure S3**.

Surface modification of silica nanoparticles using Cl$^-$ILSC and their anion exchange from Cl$^-$ to Tf$_2$N$^-$

Surface modifications of fumed silica nanoparticles were carried out using ionic liquid silane coupling reagents (**Scheme S3**).[46] First, silica nanoparticles (AEROSIL$^®$ 300, 2.0 g) were dispersed in 100 mL of pure water using sonication, which resulted in a homogeneous silica particle suspension. Then, the synthesized Cl$^-$ILSC (3.0 g) was added into the silica particle suspension and the reaction mixture was stirred and refluxed at 100 °C overnight. The product was washed with ethanol three times and collected using a centrifuge (himac CF15R, Hitachi, Japan) (15,000 rpm, 30 min). Silica nanoparticles with Cl$^-$ILSC (Cl$^-$ILSC-SiO$_2$ nanoparticles) were then obtained by evaporation in vacuo at 40 °C. To perform anion exchange of Cl$^-$ILSC-SiO$_2$ with Tf$_2$N, Cl$^-$ILSC-SiO$_2$ (2.0 g) was dispersed in 60 mL of pure water using sonication, which resulted in a homogeneous Cl$^-$ILSC-SiO$_2$ suspension. Separately, LiTf$_2$N (1.6 g) was dissolved in 60 mL of pure water. These two solutions were mixed at room temperature under stirring and an anion exchange reaction was proceeded for 1 day. The product was washed with pure water three times and collected using a centrifuge (himac CF15R, Hitachi, Japan) (15,000 rpm, 15 min). Silica nanoparticles with Tf$_2$N$^-$ILSC (Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles) were then obtained by evaporation in vacuo at 40 °C. The syntheses of Cl$^-$ILSC-SiO$_2$ nanoparticles

and Tf_2N^-ILSC-SiO_2 nanoparticles were confirmed by Fourier transform infrared spectroscopy (FT-IR) measurements (**Figure S4**) and thermal gravimetric analysis (**Figure S5**). Detailed results are summarized in **Table S1**.

Preparation of silica nanoparticles/PILs DN ion gels

Silica nanoparticles/PILs DN ion gels were prepared by photopolymerisation of an ionic monomer ([Evim][Tf_2N]) in the presence of ionic liquid ([Bmim][Tf_2N]), ethyl acetate, and fumed silica nanoparticles, followed by removal of ethyl acetate through vacuum drying at 40 °C. The following procedure is the typical experimental condition for the preparation of the silica nanoparticles/PILs DN ion gel. First, 0.2 g of fumed silica nanoparticles were added into a [Bmim][Tf_2N]/ethyl acetate mixture composed of 3.98 g of [Bmim][Tf_2N] and 2 mL (20 wt%) of ethyl acetate. Then, the mixture was vigorously stirred using a vortex mixer and sonicated for more than 20 min to disperse the silica nanoparticles in the ionic liquid solution. Subsequently, 3.25 g of [Evim][Tf_2N], 0.032 g of ionic liquid cross linker ([(VIM)$_2$C$_4$] [Tf_2N]$_2$) (0.50 mol% on [Evim][Tf_2N] basis), and 0.0018 g of photoinitiator (IRGACURE® 2959) (0.10 mol% on [Evim][Tf_2N] basis) were added to the suspension and stirred to completely dissolve them in the [Bmim][Tf_2N]/ethyl acetate mixture. To prepare silica nanoparticles/PILs DN ion gel films, the suspension was injected into a mold consisting of two glass plates with an FEP film and PTFE spacer with 1-mm thickness and was irradiated 365 nm UV light

for 9 h to facilitate the free radical polymerisation of [Evim][Tf$_2$N]. The resultant ion gel was dried in vacuo at 40 °C for more than 3 h to completely remove ethyl acetate. In this case, the compositions of the ionic liquid and the silica nanoparticles/PILs network in the ion gels were 53.3% and 46.7%, respectively.

Preparation of PILs SN ion gel

PILs SN ion gels were also prepared by photopolymerisation of ionic monomer ([Evim][Tf$_2$N]) in the presence of ionic liquid ([Bmim][Tf$_2$N]) and ethyl acetate, followed by removal of ethyl acetate through vacuum drying at 40 °C. The amount of ionic liquid ([Bmim][Tf$_2$N]) in the PILs SN ion gel was adjusted to 53.3% obtain a PILs network with the same content as that of the DN ion gels.

Preparation of silica nanoparticles with ionic liquid surface /PILs DN ion gels

Silica nanoparticles with ionic liquid surface/PILs DN ion gels were prepared by photopolymerisation of ionic monomer ([Evim][Tf$_2$N]) in the presence of ionic liquid ([Bmim][Tf$_2$N]), ethyl acetate, and Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles, followed by removal of ethyl acetate through vacuum drying at 40 °C. The compositions of the ionic liquid and the Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles/PILs network in the ion gels were 53.1% and 46.9%, respectively.

Mechanical property measurement of ion gels

The mechanical properties of the ion gels were evaluated using an automatic recording universal

testing instrument (EZ Test EZ-SX 500 N, Shimadzu Co., Japan) at room temperature. To perform the

stretching test, a dumbbell-shaped specimen having a length, width, and thickness of 35, 2, and 1.0

mm, respectively, was used. The detailed geometry of the dumbbell-shaped specimen was shown in

Figure S6. The fabricated sample was attached to the instrument at 15 mm between the jigs. A uniaxial

stretching test was conducted by stretching the sample at a constant strain rate of 50 mm/min. The

stress-strain curves were recorded automatically until the specimens were broken. The fracture stress,

fracture strain and fracture energy, and Young's modulus of the ion gels were obtained as the mean

value of measurements in triplicate for each sample. In the cyclic tensile test, the loading and

unloading operations were performed and stress-strain curves were recorded until the sample broke

whilst gradually increasing the stretching strain in steps of 0.3.

Rheological measurement of silica nanoparticles/ionic liquid dispersion

Dependence of viscosity on shear rate for the silica nanoparticles/ionic liquid dispersion as a sample

or only ionic liquid as a control was evaluated using a rheometer (MCR302; Anton Paar, Japan) with

a parallel-plate geometry (PP25; diameter = 50 mm, gap = 1.0 mm) at room temperature. Silica

nanoparticles dispersions were prepared by adding fumed silica nanoparticles to a mixture of

[Bmim][Tf$_2$N] and ethyl acetate under vigorous agitation using a vortex mixer and subsequent sonication, followed by completely removing ethyl acetate from the mixture through vacuum drying at 40 °C for more than 3 h. In the measurement, after pre-shear at 1000 s^{-1} for 60 s, the change in the viscosity of the solution was measured as a function of shear rate from 1000 to 0.01 s^{-1}.

FT-IR measurement of silica nanoparticles with ionic liquid surfaces

To confirm the syntheses of Cl$^-$ILSC-SiO$_2$ nanoparticles and Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles, FT-IR measurements of the samples were performed using a FT-IR spectrometer (IRPrestige-21, SHIMAZU, Japan).

Thermal gravimetric (TG) measurements of the samples

TG measurements of the samples were conducted using open Al pans on a thermogravimetry/differential thermal analyser (DTG-60, Shimazu, Japan) from room temperature to 600 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere. Each sample weight was fixed at 5 mg. Regarding silica nanoparticles with ionic liquid surface and original silica nanoparticles, the degree of ILSC substitution was calculated based on the difference in mass losses between modified silica nanoparticles and original silica nanoparticles. Regarding DN ion gels, the sample was heated from room temperature to 700 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere.

Transmission electron microscope (TEM) observation of silica nanoparticles/PILs DN ion gel

To confirm the morphology of clustered silica nanoparticles in the PILs DN ion gel, TEM observation of the sample was conducted using TEM mode of a scanning electron microscope (SEM, S-4700, Hitachi Ltd., Japan). A cubic sample of the ion gel with size at 1 mm was immersed in an enough amount of ethyl acetate for 12 h in order to exchange the IL in the sample for ethyl acetate. The sample was then immersed in a mixture of a precursor solution of UV-curable resin and ethyl acetate (1/1, w/w) for 6 h, followed by immersion in a precursor solution of UV-curable resin for 12 h to completely exchange the ethyl acetate for the precursor solution. The sample in the precursor solution was poured into a silicon mold and cured under a UV light ($\lambda = 365$ nm) for 1 h. The resin block embedding the gel was then thin-sectioned using an ultramicrotome (UC7, Leica Microsystems GmbH, Germany), and sections of 100 nm thickness were collected on a copper mesh TEM grid with a collodion membrane. The sample was observed by TEM with the acceleration voltage of the electron gun at 30 kV.

Evaluation of swelling behaviour of silica nanoparticles/PILs DN ion gel in water

Silica nanoparticles/PILs DN ion gel membranes with a length, width, and thickness of 8, 8, 1 mm were prepared (N = 3), and each sample weight was measured. Each sample was immersed in 20 mL

of pure water. At 1, 2, 3, 4, 5, and 6 h after onset of the experiment, the samples were picked up from

the water bath and the weights of samples were measured. After each measurement, the samples were

immersed again in the same water bath. After the experiment, the changes in the sample weights were

plotted as a function of immersion time. The initial sample weight was fixed at 100 wt% on the graph.

Results and Discussion

We prepared silica nanoparticles/PILs DN ion gels with different diameters of silica nanoparticles and

PILs SN ion gels, performed their uniaxial stretching tests, and compared their mechanical properties.

The PILs DN ion gels composed of silica nanoparticles and cross-linked poly([Evim][Tf$_2$N]) were

prepared by photo-induced radical polymerisation of [Evim][Tf$_2$N] in a mixture containing fumed

silica nanoparticles with different diameters, [Bmim][Tf$_2$N] (ionic liquid), [(VIM)$_2$C$_4$][Tf$_2$N]$_2$ (ionic

liquid cross linker), IRGACURE® 2959 (photoinitiator), and ethyl acetate (dispersion medium for

silica nanoparticles), and the subsequent removal of ethyl acetate through solvent evaporation. The

PILs SN ion gels were also prepared in almost the same manner without silica nanoparticles. In our

preliminary study, we found that when preparing the silica nanoparticles/PILs DN ion gels, ethyl

acetate was required to disperse the fumed silica nanoparticles in [Bmim][Tf$_2$N]. In the case of the

preparation of silica nanoparticles/PILs DN ion gels without the use of ethyl acetate, a reaction mixture

containing silica nanoparticles exhibited a high viscosity prior to polymerisation owing to hydrogen

bond formation between silica nanoparticles. This high viscosity of the silica

nanoparticles/[Bmim][Tf$_2$N] mixture led to inhomogeneous silica nanoparticle dispersion and low

reproducibility of the results of the ion gel preparation. Then, we investigated the effect of the amount

of ethyl acetate in the silica nanoparticles/[Bmim][Tf$_2$N] dispersion on the fluidity of the dispersion.

We found that when the amount of ethyl acetate was equal to and larger than 16 wt% in the system,

the silica nanoparticles dispersion maintained a sol state (**Figure S7**). Based on these results, in this

study, when preparing the silica nanoparticles/PILs DN ion gels, we decided to use ethyl acetate as a

dispersant for silica nanoparticles and fix the amount of ethyl acetate at 20 wt% in the system. After

the polymerisation, we could completely remove ethyl acetate from the ion gels by solvent evaporation.
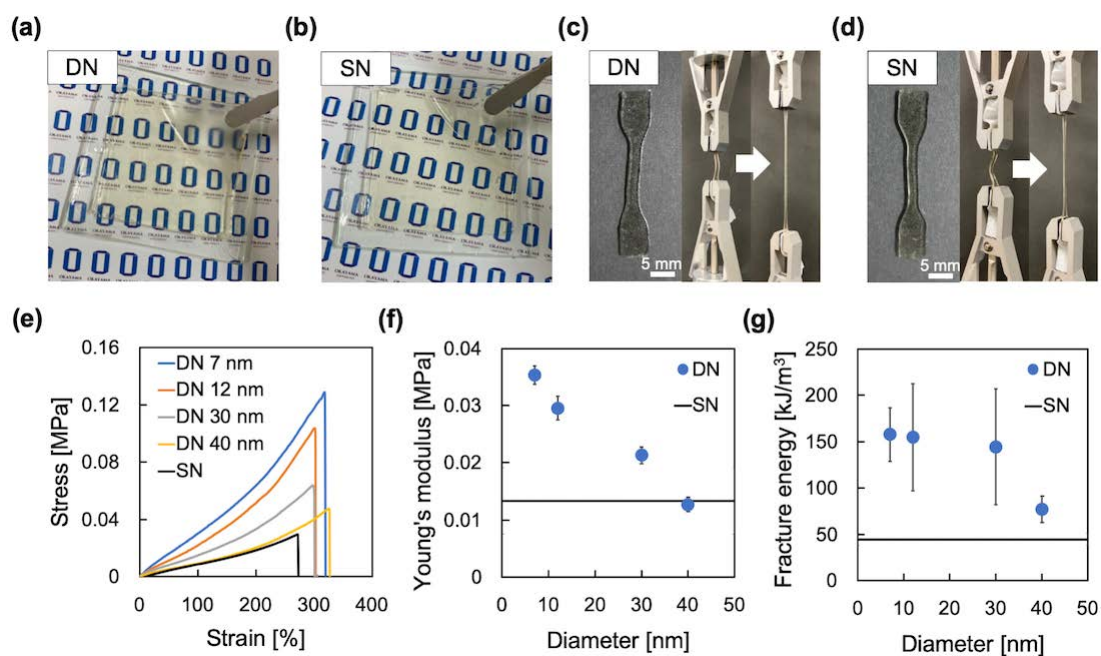
Figure 1. Representative photographs of **(a)** silica nanoparticles/PILs DN ion gel and **(b)** PILs SN ion

gel. Representative photographs of **(c)** the silica nanoparticles/PILs DN ion gel and **(d)** the PILs SN

ion gel upon tensile tests (left: dumbbell-like sample, middle: before stretching, right: after stretching).

(e) Tensile stress-strain curves of the silica nanoparticles/PILs DN ion gels with different diameters of silica nanoparticles and the PILs ion gels. Changes in **(f)** the Young's modulus and **(g)** the fracture energy of silica nanoparticles/PILs DN ion gels as a function of the diameters of silica nanoparticles. In all ion gels, the IL content was approximately 50 wt%.

Figure 1a and **b** shows representative photographs of the silica nanoparticles/PILs DN ion gel and PILs SN ion gel, respectively. We found that both the PILs DN ion gel and PILs SN ion gel showed the same appearance with high transparency and yellow colour. Then, we made dumbbell-like gel films of the ion gels and performed tensile tests, as shown in **Figure 1c** and **d**. **Figure 1e** shows the tensile stress-strain curves of the silica nanoparticles/PILs DN ion gels with different diameters of silica nanoparticles and the PILs SN ion gel. We found that regardless of the diameter of the silica nanoparticles incorporated in the PILs DN ion gels, the maximum fracture stress of the PILs DN ion gels was significantly larger than that of the PILs SN ion gel, whilst there was no significant difference in the fracture strain between them. This result indicated that the incorporation of silica nanoparticles in the PILs-based ion gel network contributed not to the increment of the fracture strain but to the enhancement of the fracture strength of the PILs ion gels. Moreover, we found that as the diameter of silica nanoparticles incorporated in silica nanoparticles/PILs DN ion gels was decreased, the Young's

modulus and fracture energy of the PILs DN ion gels increased, as shown in **Figure 1f** and **g**. We consider that this result was caused by the increment of the number density of the silica nanoparticle network in the PILs ion gel, in other words, by the increment of the total number of interparticle interactions, such as hydrogen bonding and van der Waals force, between silica nanoparticles in the PILs ion gels as the diameter of silica nanoparticles was decreased. To estimate the degree of interparticle interactions between silica nanoparticles in [Bmim][Tf$_2$N], we measured the shear rate dependence on the viscosity of [Bmim][Tf$_2$N] containing different diameters of silica nanoparticles using a rheometer. **Figure 2** shows the change in the viscosity of silica nanoparticles/[Bmim][Tf$_2$N] dispersions containing different diameters of silica nanoparticles as a function of shear rate. We found that the silica nanoparticles/[Bmim][Tf$_2$N] dispersion exhibited thixotropy; the viscosity of [Bmim][Tf$_2$N] containing silica nanoparticles decreased as the shear rate was increased and that the shear rate dependence of the viscosity became larger as the diameter of silica nanoparticles dispersed in [Bmim][Tf$_2$N] was decreased. These results indicated that as the diameter of silica nanoparticles decreased, the degree of interparticle interactions between silica nanoparticles was enhanced.

To evaluate the effect of IL content on the mechanical properties of PILs DN ion gels, we prepared PILs DN ion gels with different [Bmim][Tf$_2$N] contents (50, 60, and 70 wt%) and performed tensile tests (**Figure S8**). We found that as increasing the IL content in the PILs DN ion gels from 50 to 70 wt%, the maximum fracture stress, Young's modulus, and fracture energy

of the PILs DN ion gels significantly decreased whereas the fracture strain was slightly increased.

We also found that leakage of the IL from the PILs DN ion gels was not observed because of good

compatibility between PILs and [Bmim][Tf$_2$N]. The reduction in the mechanical strength of the

PILs DN ion gels as increasing the IL content in the PILs ion gels is due to the decrease in the

amount of PILs network in the ion gels. Next, to investigate the effect of cross-linker

concentration on the mechanical properties of PILs DN ion gels, we prepared PILs DN ion gels

and PILs SN ion gels, with different cross-linker concentrations (0, 0.25, 0.5, 0.75, and 1.0 mol%)

and performed uniaxial stretching tests (**Figure S9**). We found that the PILs DN ion gels showed

higher mechanical properties than the PILs SN ion gels, and that as increasing the cross-linker

concentration in the PILs ion gels from 0.5 to 1.0 mol%, the Young's modulus of both the PILs

ion gels increased whilst the fracture energy of both the PILs ion gels decreased. These results

indicated that as increasing the cross-linking density of the PILs ion gels, the flexibility of the

PILs networks decreased, leading to the decrease in the toughness of the ion gels. We also found

that PILs ion gels with cross-linker concentration less than or equal to 0.25 mol% were not self-

supporting due to low mechanical stability. Based on these results, as far as we tested, we

concluded that the best cross-linker concentration to keep the PILs ion gels tough should be 0.5
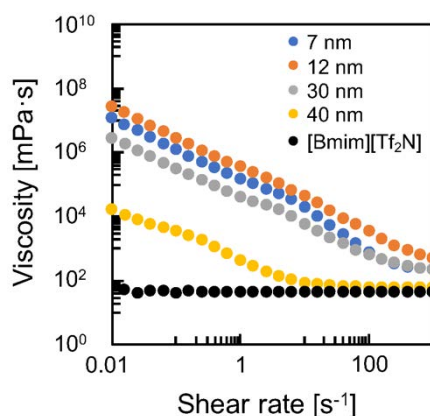
mol%.

Figure 2. Change in the viscosity of silica nanoparticles/[Bmim][Tf$_2$N] dispersions containing different diameters of silica nanoparticles as a function of shear rate.

We expected that the high mechanical property of silica nanoparticles/PILs DN ion gel was derived from the formation of inorganic/organic DN structures, as has previously been reported for other systems.[47] If the silica nanoparticles/PILs DN ion gel shows high mechanical properties based on the DN structures, the energy dissipation of the ion gel would occur by internal rupture of the first brittle silica nanoparticle cluster network upon deformation. To confirm whether the mechanical strength of the silica nanoparticles/PILs DN ion gel was enhanced based on an energy dissipation mechanism analogous to that of the well-known DN gel or not, we performed a cyclic tensile loading and unloading test using the PILs DN ion gels prepared with silica nanoparticles having a diameter of 7 nm. **Figure 3a** and **b** shows the cyclic stress-strain curves of the silica nanoparticles/PILs DN ion gel and the PILs SN ion gel, respectively. We confirmed that the PILs DN ion gel showed a hysteresis and softening behaviour like the DN gel, whilst the PILs SN ion gel did not. In addition, TEM

21

observation of the PILs DN ion gel revealed that there are two types of clustered silica nanoparticles: spherical aggregate and non-spherical partially developed silica nanoparticle cluster (**Figure 4**). These results strongly suggest that the toughening mechanism of the silica nanoparticles/PILs DN ion gel is based on the energy dissipation derived from the rupture of the clustered silica nanoparticles when a large strain is induced as shown in **Scheme S4**.
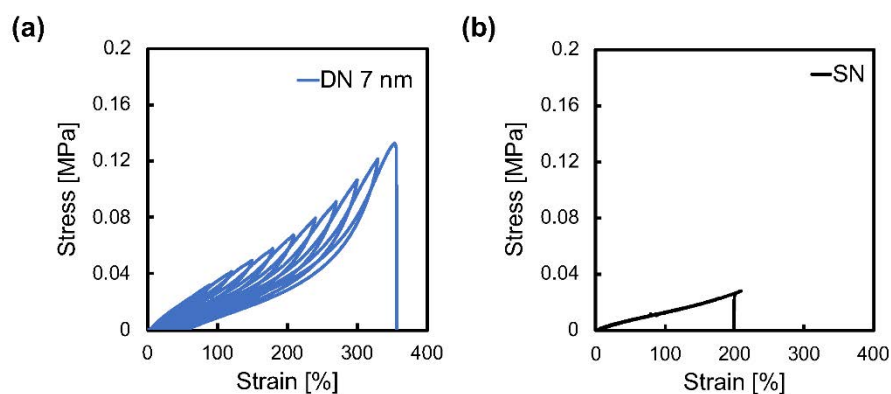

Figure 3. Cyclic tensile behaviour of **(a)** silica nanoparticles/PILs DN ion gel and **(b)** PILs SN ion gel. The PILs DN ion gel was prepared using silica nanoparticles having a diameter of 7 nm and the amount of [Bmim][Tf$_2$N] in the ion gels was fixed at approximately 50 wt%.
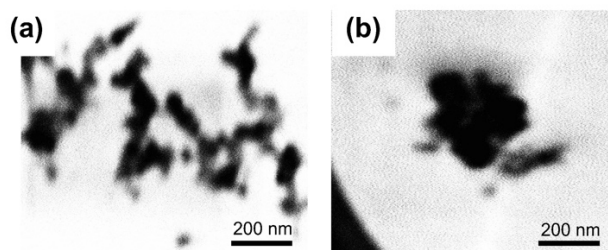
Figure 4. TEM images of the silica nanoparticle networks formed in silica nanoparticles/PILs DN ion

gels. **(a)** Partially developed silica nanoparticle cluster, **(b)** Spherical aggregate of silica nanoparticles.

Although we found that the silica nanoparticle network formation in PILs ion gel contributed

to the enhancement of the mechanical strength of the PILs-based ion gel, as shown in **Figure 1**, we

have not yet elucidated when the silica nanoparticle network is formed in the preparation process of

the PILs DN ion gels. Considering the preparation process, there are two options for where the first

silica nanoparticle network might be formed; one option is that formation of the silica nanoparticle

network is induced when ethyl acetate is removed from the ion gel. The other option is that the silica

nanoparticle network is formed when the silica nanoparticles are added into the mixture of IL and

ethyl acetate prior to polymerisation. If the latter case is true, the silica nanoparticles/PIL DN ion gels

before removing ethyl acetate will have the same level of mechanical strength as the silica

nanoparticles/PIL DN ion gels after removing ethyl acetate. Hence, we performed uniaxial stretching

tests and cyclic tensile loading and unloading tests using the PILs DN ion gels and PILs SN ion gels

before and after removal of ethyl acetate by drying. **Figure 5a** shows the tensile stress-strain curves

of the PILs DN ion gel and PILs SN ion gel before and after drying. We found that the maximum

fracture strength of the PILs DN ion gels before and after drying was considerably higher than that of

the PILs SN ion gels counterparts and that there was no significant difference in the mechanical

properties between the PILs DN ion gels before and after drying. Moreover, we found that the PILs

DN ion gel before drying exhibited a hysteresis and softening behaviour like that after drying, as

shown in **Figure 5b** and **c**. These results strongly suggest that the first silica nanoparticle network in

the PILs ion gel is formed when the silica nanoparticles are added into a mixture containing

[Bmim][Tf$_2$N] and ethyl acetate before the formation of the second soft PILs network and the removal
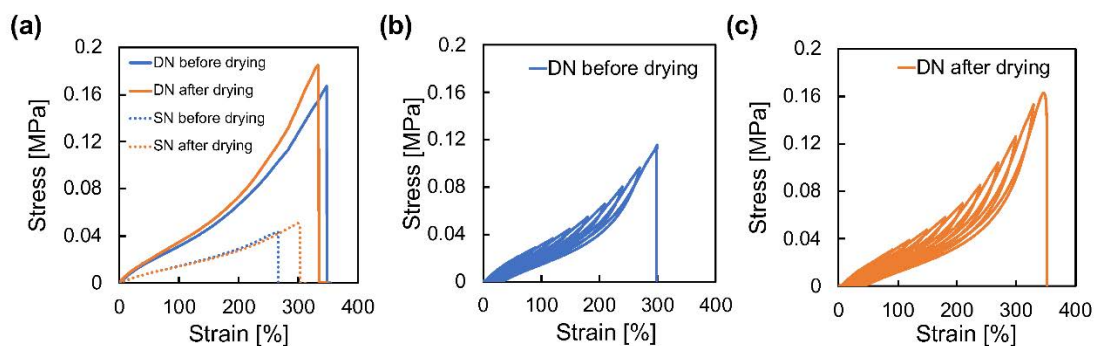
of ethyl acetate.

Figure 5. (a) Tensile stress-strain curves of silica nanoparticles/PILs DN ion gels and PILs SN ion gels

before and after drying. Cyclic tensile tests of silica nanoparticles/PILs DN ion gels **(b)** before drying and

(c) after drying. In all ion gels, the IL content was approximately 50 wt%.

As discussed above, we consider that the formation of a partially clustered silica

nanoparticle network in [Bmim][Tf$_2$N] through interparticle interactions, such as hydrogen bonding

and van der Waals force, is of importance to prepare a tough silica nanoparticles/PILs DN ion gel. If

this assumption is true, a silica nanoparticles/PILs DN ion gel will not be formed when silica

nanoparticles are dispersed in [Bmim][Tf$_2$N] without any interparticle interaction. To confirm this assumption, we synthesized silica nanoparticles having Tf$_2$N$^-$ surfaces, which were named Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles, using an ionic liquid silane coupling reagent (Cl$^-$ILSC) and subsequent anion exchange from Cl$^-$ to Tf$_2$N$^-$. We confirmed that the Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles showed no thixotropy in [Bmim][Tf$_2$N] because their Tf$_2$N$^-$ surfaces had a high affinity with [Bmim][Tf$_2$N] (**Figure 6**). Then, we prepared PILs-based ion gels composed of Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles and cross-linked PILs in the same manner as described above and performed uniaxial stretching tests and cyclic tensile loading and unloading tests using the Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles/PILs ion gel. **Figure 7a** shows the comparison of stress-strain curves among the silica nanoparticle/PILs DN ion gel, Tf$_2$N-ILSC-SiO$_2$ nanoparticles/PILs ion gel, and PILs SN ion gel. We found that when using Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles to prepare the PILs ion gel, the fracture strength of the Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles/PILs ion gel was the same level as that of the PILs SN ion gel. We also found that the cyclic stress-strain curve of the Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles/PILs ion gel hardly showed hysteresis and the shape was rather similar to that of the PILs SN ion gel (**Figure 7b–d**). These results indicated that the structure of the Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles/PILs ion gel differed from that of the silica nanoparticles/PILs DN ion gel, and that the Tf$_2$N$^-$ surface of the Tf$_2$N$^-$ILSC-SiO$_2$ nanoparticles incorporated in the PILs ion gel hindered the formation of a partially clustered silica particle network in the PILs ion gel owing to no hydrogen bonding formation in

[Bmim][Tf$_2$N]. Based on these results, we concluded that the hydroxide groups on the surface of

fumed silica nanoparticles are important to form a partially clustered silica nanoparticle network in

[Bmim][Tf$_2$N], and contribute to the toughening mechanism of the silica nanoparticles/PILs DN ion
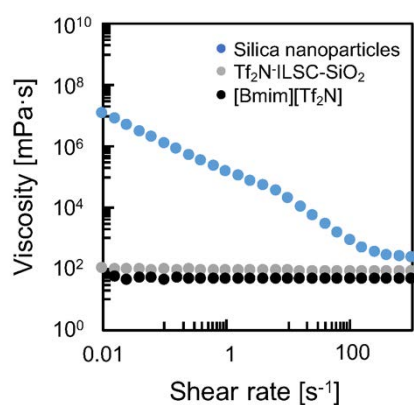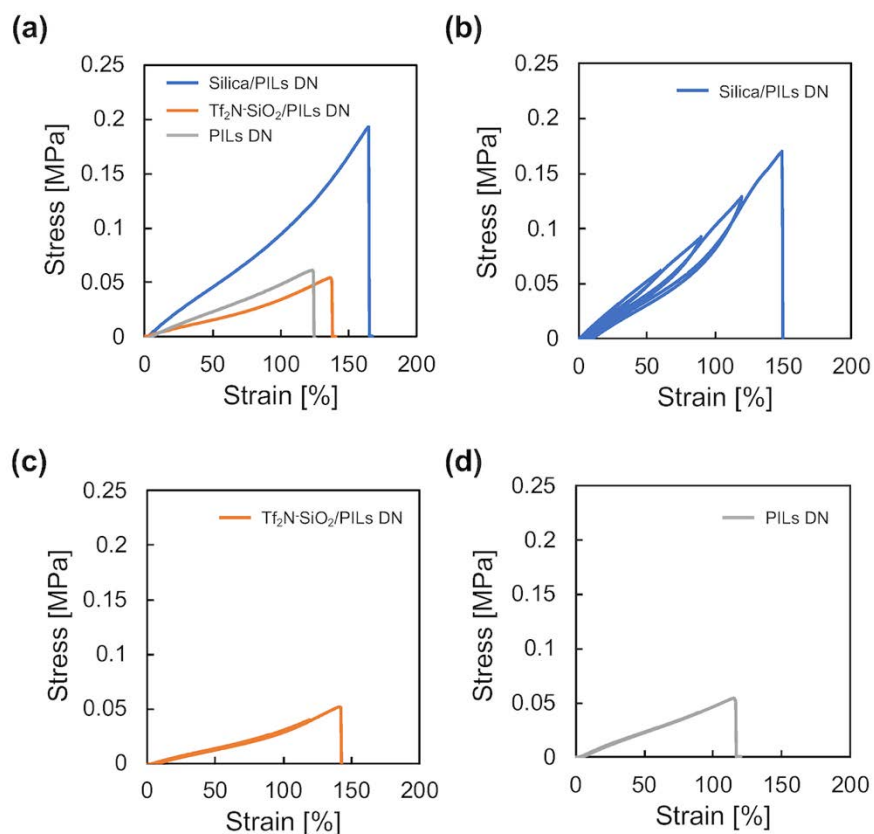
gel.

Figure 6. Change in viscosity of the silica nanoparticles/[Bmim][Tf$_2$N] dispersion, Tf$_2$N⁻ILSC-

SiO$_2$/[Bmim][Tf$_2$N] dispersion, and [Bmim][Tf$_2$N] as a function of shear rate.

Figure 7. (a) Tensile stress-strain curves of the silica nanoparticles/PILs DN ion gel, $Tf_2N^-ILSC-SiO_2$ nanoparticles/PILs ion gel, and PILs SN ion gel. Cyclic tensile tests of the **(b)** silica nanoparticles/PILs DN ion gel, **(c)** $Tf_2N^-ILSC-SiO_2$ nanoparticles/PILs ion gel, and **(d)** PILs SN ion gel. In all ion gels, the IL content was approximately 50 wt%.

It is expected that the PILs-based DN ion gel developed in this study shows a high thermal stability as well as a high water-resistant property because all components of the PILs ion gel including IL monomer, IL cross-linker, and incorporated IL, have negligible vapor pressure, non-flammability, and hydrophobicity. To evaluate the thermal stability of the PILs-based ion gel,

we performed thermal gravimetric measurements of the silica nanoparticles/PILs DN ion gel and PILs

SN ion gel. As shown in **Figure 8**, the decomposition temperatures of both the PILs DN ion gel and

PILs SN ion gel were approximately 400 °C, which were higher than those of other ion gels previously

reported.[28] We also evaluated the swelling behaviour of the PILs DN ion gel in water by measuring

the changes in volume and weight of the samples immersed in water as a function of time (**Figure 9**).

As shown in **Figure 9**, the volume and weight of PILs DN ion gel did not change at all for 6 h after

immersion of the sample in water. These results clearly showed that our PILs DN ion gels have a high

thermal stability and excellent water-resistant property. We believe that such PILs-based ion gels with

unique properties including toughness, high thermal stability and excellent water-resistant property

can be promising candidates for the applications of separation membranes and actuators for soft
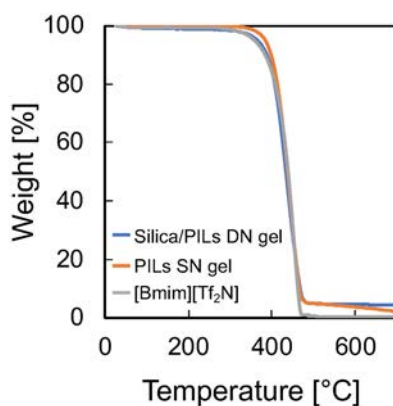
robotics.

Figure 8. Thermal gravimetric analysis curves of the silica nanoparticles/PILs DN ion gel, PILs SN

ion gel, and [Bmim][Tf$_2$N]. In all ion gels, the IL content was approximately 50 wt%.
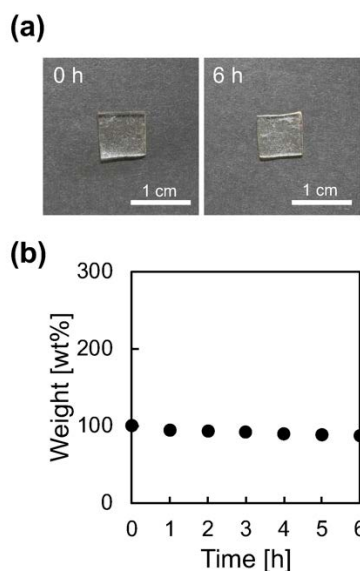
Figure 9. Swelling behaviour of PILs DN ion gels containing 50 wt% of [Bmim][Tf$_2$N] immersed in water as a function of immersion time. (a) Photos of PILs DN ion gel membrane at different immersion time in water, (b) Changes in the weight of samples as a function of immersion time in water.

Conclusions

We successfully prepared tough, thermally stable, and high water-resistant DN ion gels composed of a partially clustered silica nanoparticle network and PILs network holding [Bmim][Tf$_2$N] by photo-induced radical polymerisation and subsequent solvent evaporation. Tensile stress measurement showed that the silica nanoparticles/PILs DN ion gel had more than 4 times higher fracture stress (~125 kPa) than the PILs SN ion gel, and that as the size of silica nanoparticles incorporated in the PILs ion gel was decreased, the mechanical properties of the silica nanoparticles/PILs DN ion gel were increased. We found that the silica nanoparticles in the PILs ion gel could form a partially-clustered

network through interparticle interactions including hydrogen bonding and van der Waals force between the silica nanoparticles dispersed in [Bmim][Tf$_2$N], and that the silica particle network contributed to the enhancement in the mechanical properties of the PILs ion gel by an energy dissipation mechanism analogous to the DN principle; the silica nanoparticle network is ruptured when a large strain is induced. Thermal gravimetric analysis measurements showed that the silica nanoparticle/PILs DN ion gel had a high decomposition temperature of approximately 400 °C, which was derived from the second cross-linked PILs network. Moreover, swelling test clearly showed that the silica nanoparticle/PILs DN ion gel had an excellent water-resistant property because of hydrophobic nature of the cross-linked PILs network. We believe that such tough, thermally stable, and water-resistant PILs DN ion gels will be used as carbon dioxide separation membranes, and sensors and actuators for soft robotics.

Author Information

Corresponding author

E-mail: tono@okayama-u.ac.jp. Tel: +81-86-251-8083. Fax: +81-86-251-8083.

ORCID

Takaichi Watanabe: 0000-0002-5855-2583

Tsutomu Ono: 0000-0002-2880-7119

Author Contributions

T.W., R.T., and T.O. designed the experiments. R.T. performed the experiments and analysed the data. T.W., R.T., and T.O. interpreted the results and wrote the manuscript. T.W. and T.O designed the research.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and References

(1) J. A. Boon, J. A. Levisky, J. L. Pflug, J. S. Wilkes, *J. Org. Chem.,* 1986, **51**, 480-483.

(2) J. S. Wilkes, M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.,* 1992, 965-967.

(3) R. D. Rogers, K. R. Seddon, *Science,* 2003, **302**, 792-793.

(4) T. Welton, *Chem. Rev.,* 1999, **99**, 2071-2083.

(5) M. J. Earle, K. R. Seddon, C. J. Adams, G. Roberts, *Chem. Commun.,* 1998, 2097-2098.

(6) M. Galiński, A. Lewandowski, I. Stępniak, *Electrochim. Acta,* 2006, **51**, 5567-5580.

(7) P. Hapiot, C. Lagrost, *Chem. Rev.,* 2008, **108**, 2238-2264.

(8) J. Yoshida, K. Kataoka, R. Horcajada, A. Nagaki, *Chem. Rev.,* 2008, **108**, 2265-2299.

(9) A. Lewandowski, A. Świderska-Mocek, *J. Power Sources,* 2009, **194**, 601-609.

(10) T. Kuboki, T. Okuyama, T. Ohsaki, N. Takami, *J. Power Sources,* 2005, **146**, 766-769.

(11) J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser, R. D. Rogers, *Chem. Commun.,* 1998, 1765-1766.

(12) A. Berthod, M. J. Ruiz-Ángel, S. Carda-Brochc, *J. Chromatogr. A,* 2008, **1184**, 6-18.

(13) S. Dai, Y. H. Ju, C. E. Barnes, *J. Chem. Soc., Dalton Trans.,* 1999, 1201-1202.

(14) A. E. Visser, R. P. Swatloski, W. M. Reichert, S. T. Griffin, R. D. Rogers, *Ind. Eng. Chem. Res.,* 2000, **39**, 3596-3604.

(15) K. Shimojo, M. Goto, *Anal. Chem.,* 2004, **76(17)**, 5039-5044.

(16) M. Wagner, O. Stanga, W. Schröer, *Phys. Chem. Chem. Phys.,* 2003, **5**, 3943-3950.

(17) J. Yang, C. Peng, H. Liu, Y. Hu, *Ind. Eng. Chem. Res.,* 2006, **45**, 6811-6817.

(18) A. Arce, M. J. Earle, H. Rodríguez, K. R. Seddon, *J. Phys. Chem. B,* 2007, **111**, 4732-4736.

(19) P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.,* 1996, **35**, 1168-1178.

(20) R. P. Swatloski, A. E. Visser, W. M. Reichert, G. A. Broker, L. M. Farina, J. D. Holbrey, R. D. Rogers, *Green Chem.,* 2002, **4**, 81-87.

(21) G. A. Baker, S. N. Baker, S. Pandey, F. V. Bright, *Analyst,* 2005, **130**, 800-808.

(22) S. P. M. Ventura, A. M. M. Gonçalves, T. Sintra, J. L. Pereira, F. Gonçalves, J. A. P. Coutinho, *Ecotoxicology,* 2013, **22(1)**, 1-12.

(23) L. Porcarelli, A. S. Shaplov, M. Salsamendi, J. R. Nair, Y. S. Vygodskii, D. Mecerreyes, C. Gerbaldi, *ACS Appl. Mater. Interfaces,* 2016, **8**, 10350-10359.

(24) W. Ogihara, J. Sun, M. Forsyth, D. R. MacFarlane, M. Yoshizawa, H. Ohno, *Electrochim. Acta,* 2004, **49**, 1797-1801.

(25) Y. Kohno, S. Saita, Y. Men, J. Yuan, H. Ohno, *Polym. Chem.,* 2015, **6**, 2163-2178.

(26) B. Qiu, B. Lin, F. Yan, *Polym. Int.,* 2013, **62**, 335-337.

(27) A. Vioux, L. Viau, S. Volland, J. L. Bideau, *C. R. Chimie,* 2010, **13**, 242-255.

(28) M. A. B. H. Susan, T. Kaneko, A. Noda, M. Watanabe, *J. Am. Chem. Soc.,* 2005, **127**, 4976-4983.

(29) T. Y. Kim, H. W. Lee, M. Stoller, D. R. Dreyer, C. W. Bielawski, R. S. Ruoff, K. S. Suh, *ACS Nano,* 2011, **5(1)**, 436-442.

(30) L. Miao, H. Duan, M. Liu, W. Lu, D. Zhu, T. Chen, L. Li, L. Gan, *Chem. Eng. J.,* 2017, **317(1)**, 651-659.

(31) J. Tang, W. Sun, H. Tang, M. Radosz, Y. Shen, *Macromolecules,* 2005, **38**, 2037-2039.

(32) J. Tang, H. Tang, W. Sun, M. Radosz, Y. Shen, *J. Polym. Sci. Pol. Chem.,* 2005, **3**, 5477-5489.

(33) J. E. Bara, S. Lessmann, C. J. Gabriel, E. S. Hatakeyama, R. D. Noble, D. L. Gin, *Ind. Eng. Chem. Res.,* 2007, **46**, 5397-5404.

(34) J. E. Bara, C. J. Gabriel, E. S. Hatakeyama, T. K. Carlisle, S. Lessmann, R. D. Noble, D. L. Gin, *J. Membrane. Sci.,* 2008, **321**, 3-7.

(35) Y. Gu, T. P. Lodge, *Macromolecules,* 2011, **44**, 1732-1736.

(36) A. Noda, M. Watanabe, Electrochimica Acta, 2000, **45**, 1265-1270.

(37) M. G. Cowan, A. M. Lopez, M. Masuda, Y. Kohno, W. M. McDanel, R. D. Noble, D. L. Gin, *Macromol. Rapid Commun.,* 2016, **37**, 1150-1154.

(38) J. E. Bara, E. S. Hatakeyama, D. L. Gin, R. D. Noble, *Polym. Adv. Technol.,* 2008, **19**, 1415-1420.

(39) E. Kamio, T. Yasui, Y. Iida, J. P. Gong, H. Matsuyama, *Adv. Mater.,* 2017, **29**, 1704118.

(40) J. P. Gong, Y. Katsuyama, T. Kurokawa, Y. Osada, *Adv. Mater.,* 2003, **15**, 1155-1158.

(41) J. Hu, K. Hiwatashi, T. Kurokawa, S. M. Liang, Z. L. Wu, J. P. Gong, *Macromolecules,* 2011, **44**, 7775-7781.

(42) T. Yasui, E. Kamio, H. Matsuyama, *Langmuir,* 2018, **34**, 10622-10633.

(43) S. N. V. K. Aki, B. R. Mellein, E. M. Saurer, J. F. Brennecke, *J. Phys. Chem. B*, 2004, **108**, 20355-20365.

(44) H. Zhang, M. Li, B. Yang, *J. Phys. Chem. C,* 2018, **122**, 2467-2474.

(45) H. Nakajima, H. Ohno, *Polymer,* 2005, **46**, 11499-11504.

(46) S. S. Moganty, S. Srivastava, Y. Lu, J. L. Schaefer, S. A. Rizvi, L. A. Archer, *Chem. Mater.,* 2012, **24**, 1386-1392.

(47) J. P. Gong, *Soft Matter,* 2010, **6**, 2583-2590.

A table of contents entry
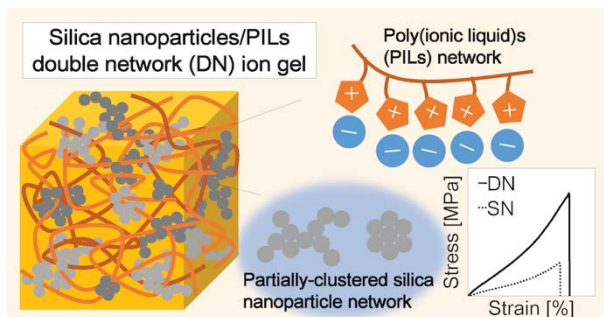
A tough, thermally stable, and water-resistant silica nanoparticles / poly(ionic liquid)s double-network

ion gel was developed.