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Inorganic/organic double-network ion gels with partially developed silica-particle network

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Tough inorganic/organic composite network gels consisting of a partially developed silica-particle network and a large amount of an ionic liquid, named micro-double-network (μ-DN) ion gel, are fabricated via two methods. One is a one-pot/one-step process conducted using a simultaneous network formation via sol–gel reaction of tetraethyl orthosilicate and free radical polymerization of *N*,*N*-dimethylacrylamide in an ionic liquid. When the network formation rates of the inorganic and organic networks are almost the same, the μ-DN structure is formed. The second method is simpler and involved the use of silica nanoparticles as the starting material. By controlling the dispersion state of the silica nanoparticles in an ionic liquid, the μ-DN structure is formed. In the both μ-DN ion gels, silica nanoparticles partially aggregate and form network-like clusters. When a large deformation is induced in the μ-DN ion gels, the silica particle clusters rupture and dissipate the loaded energy. The fracture stress and Young's modulus of the μ-DN ion gel increase as the size of the silica nanoparticles decreases. The increment in the mechanical strength would have been caused by the increase in the total van der Waals attraction forces and the total number of hydrogen bonding in the silica particle networks.

INTRODUCTION

A gel containing a large amount of an ionic liquid, termed ion gel, is a material that combines the unique properties of ionic liquids and the quasi-solid properties of gels. Ion gels can be prepared by forming a three-dimensional network structure in an ionic liquid. Various methods such as the use of a polymer blend with an ionic liquid, in situ polymerization of a vinyl monomer in an ionic liquid, sol–gel processing, and addition of a low-molecular-weight and oligomeric gelator in an ionic liquid have been proposed as methods for preparing ion gels.[1] Such ion gels are expected to be applied in electrochemical devices, actuators, gas separation membranes, etc. owing to the specific properties of ionic liquids such as non-volatility, non-flammability, and high thermal, chemical, and electrochemical stabilities.[2-10] However, the majority of ion gels are limited in practical applicability owing to their low mechanical strength.[7] For instance, in the case of ion gels formed by the radical polymerization of vinyl monomers, as three-dimensional polymer networks formed by radical polymerization contain various heterogeneities,[11-12] the ion gels are easily ruptured by a stress concentration in short cross-linking distances of polymer chains.[7] Therefore, in order to ensure sufficient mechanical strength for practical applications, conventional ion gels require a large network content. Increasing the network content in a gel not only reduces its ionic liquid content but also increases the amount of network that acts as the diffusion resistance, thus causing a significant decrease in ion and solute diffusivities. As a result, the performance of the ion gels, such as ionic conductivity and gas permeability, is limited. The trade-off relationship between mechanical strength and intra-gel diffusivity is the most serious drawback of ion gels. In recent years, in order to overcome this drawback, ion gels having a high mechanical strength have been developed.[8, 13-17] However, some of them were prepared using specific chemicals such as triblock copolymer with ionic liquid moiety and tetra-armed polyethylene glycols,[13-14] and the others were prepared via complicated multistep preparation processes.[8, 15-17]

In our previous work, we developed high-strength ion gels with specific inorganic/organic composite networks[18] using the toughening mechanism of well-known double-network (DN) hydrogels.[19-29] The inorganic/organic composite ion gels could be prepared with tetraethyl orthosilicate (TEOS) and *N*,*N*-dimethylacrylamide (DMAAm) via simple one-pot/one-step processing. In addition, by controlling the formation order of the inorganic silica particle network and organic poly(*N*,*N*-dimethylacrylamide) (PDMAAm) network, we can selectively prepare two types of high-strength ion gels with different network structures; one is a DN ion gel with an interpenetrating composite network composed of a highly developed silica particle network and PDMAAm network, and the other is a μ-DN ion gel having a composite network comprising inorganic silica nanoparticles and a PDMAAm network. Although the mechanical properties of the DN and μ-DN ion gels are completely different, both of them exhibit an extremely high compressive fracture stress of more than 25 MPa at 80 wt% of ionic liquid content. Therefore, it can be said that the toughening of an ion gel has been successfully achieved by forming specific inorganic/organic DN and μ-DN structures in an ionic liquid.

However, there still remains some challenges in preparing DN ion gels that can be used in practical applications: (1) the network formation is time consuming and (2) the volatile monomer and silica particle precursor are evaporated during the network formation in open environment. These challenges limit the continuous production of thin DN ion gel films on a large scale and its practical applications.

In this study, we report a breakthrough for the inorganic network formation, which simultaneously overcomes the aforementioned challenges faced in inorganic network formation. This breakthrough involves the invention of a partially developed inorganic network by silica nanoparticles and has the advantages of the toughening mechanism of DN ion gels and the network structure of μ-DN ion gels. In our previous investigations, we clarified that the DN and μ-DN structures can be selectively formed in an ionic liquid via one-pot/one-step processing by controlling the preparation temperature in order to control the formation order of the inorganic and organic networks, i.e., DN ion gels can be prepared if the preparation temperature is lower than the critical temperature (T_c), and μ-DN ion gels can be prepared at a temperature higher than T_c. In this work, we focused on μ-DN ion gels with partially developed inorganic silica-particle-based networks, termed inorganic silica-particle-network-based clusters, which were interpenetrated with PDMAAm networks. This concept was based on the microgel-reinforced DN hydrogel (MR gel).[30-33] Because the silica-particle-network-based clusters formed in the μ-DN ion gels could act as a brittle microgel particles in an MR gel, they would facilitate the toughening of the ion gel based on the energy dissipation principal through the internal fracture of the silica particle network in the clusters. Based on the invention of the partially developed inorganic network cluster formation via the one-pot/one-step process, we further developed a simple method of preparing high-mechanical-strength μ-DN ion gels. In this preparation, silica nanoparticles were used as the starting material instead of TEOS. Because silica nanoparticles are solid, they are not evaporated from the precursor solution during network formation. In addition, the use of silica nanoparticles shortens the time required for the inorganic network formation, which was the most time-consuming step in the preparation process of high-strength inorganic/organic composite ion gels. These achievements substantially promote the industrial-based large-scale production of high-strength thin ion gel films, which could be used as high-performance conductive films and gas separation membranes.

EXPERIMENTAL SECTION

Materials

As an ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_4mim][Tf_2N]), which was purchased from Sigma-Aldrich Co. (St Louis, MO, USA), was used after eliminating the dissolved water by bubbling dry nitrogen for more than 15 min. *N*,*N*-dimethylacrylamide (DMAAm) as a monomer of polydimethylacrylamide (PDMAAm), 2-oxoglutaric acid (OA) and 2,2'-azobis(isobutyronitrile) (AIBN) as photo- and thermal-radical initiators, respectively, and *N*,*N*'-methylenebis(acrylamide) (MBAA) as a cross-linker of PDMAAm were used to form the organic PDMAAm network in an ionic liquid. DMAAm and OA were purchased from Tokyo Chemical Industry Co. (Tokyo, Japan) and used as received. MBAA and AIBN from Wako Pure Chemicals Industry Ltd. (Osaka, Japan) were used after purification by recrystallization in ethanol. In order to form the silica nanoparticle-based inorganic network, TEOS from Sigma-Aldrich Co. (St Louis, MO, USA) and a series of silica nanoparticles (Aerosil 300, 200, 130, 90G, 50, and OX50, of which primary particle diameters were 7, 12, 16, 20, 30, 40 nm, respectively), which were kindly provided by Nippon Aerosil Co. Ltd., were used as received. Formic acid and ethanol purchased from Wako Pure Chemicals Industry Ltd. (Osaka, Japan) were used as the solvolytic agent for the sol–gel reaction of TEOS and as a dispersant of the fumed silica nanoparticles, respectively; they were used without further purification. The chemical structures of TEOS, DMAAm, MBAA and [C_4mim]Tf_2N] are shown in Figure S1.

Preparation of μ-DN ion gel and PDMAAm single network ion gel via one-pot/one-step process

Inorganic/organic μ-DN ion gels were prepared via one-pot/one-step process by inducing a thermally initiated sol–gel reaction of TEOS and the free radical polymerization of DMAAm in an ionic liquid simultaneously. A precursor solution comprising 8.90 g of [C_4mim][Tf_2N], 0.54 g of TEOS, 1.55 g of DMAAm (molar ratio of TEOS/DMAAm = 1/6 mol/mol), 9.6 mg of MBAA (0.4 mol% on DMAAm basis), and 25.6 mg of AIBN (1.0 mol% on DMAAm basis) were prepared by mixing them until the solution became completely transparent. In the precursor solution, 0.94 g of formic acid was added and stirred until it was completely dissolved. The solution was injected in a mold consisting of two glass plates with a fluorinated ethylene propylene copolymer (FEP) film and a polytetrafluoroethylene (PTFE) spacer (1.0 mm thickness) and remained at a certain temperature in an incubator (with an accuracy of ±0.4 K) for 72 h. The temperature was controlled in the range of 316.5 K and 322.5 K in order to control the rates of the sol–gel reaction of TEOS and the free radical polymerization of DMAAm. The obtained ion gel was maintained at 373 K for 12 h under vacuum in order to remove the formic acid, unreacted monomer, and generated ethanol through the sol–gel reaction of TEOS. The compositions of the ionic liquid and the inorganic/organic network in the obtained ion gels were determined as 81.0±1.2 wt% and 19.0±1.2 wt%, respectively, from the weights of the ionic liquid and the inorganic/organic skeleton which were obtained via ionic liquid extraction using enough amount of ethanol followed by drying at elevated temperature.

A PDMAAm single network (SN) ion gel was also prepared in the same manner without using the chemicals for the sol–gel reaction of TEOS. The content of [C_4mim][Tf_2N] in an SN ion gel was adjusted to 85 wt% in order to obtain the same composition of PDMAAm in the both SN ion gel and μ-DN ion gel (ca. 15 wt%).

Preparation of μ-DN ion gel using silica nanoparticles as the starting material

A μ-DN ion gel was prepared using fumed silica nanoparticles as the starting material instead of TEOS. At first, 0.54 g of fumed silica nanoparticles was added to 9.68 g of [C_4mim][Tf_2N]/ethanol mixture (ethanol/[C_4mim][Tf_2N] = 0.1 g/g). The suspension was vigorously agitated using a vortex mixer and sonicated for 20 min in order to disperse the silica nanoparticles in the ionic liquid solution. Subsequently, 1.63 g of DMAAm, 10.2 mg of MBAA (0.4 mol% on DMAAm basis), and 2.4 mg of OA (0.1 mol% on DMAAm basis) were added to the suspension and stirred to completely dissolve them in the [C_4mim][Tf_2N]/ethanol mixture. The suspension was injected into a mold consisting of two glass plates with an FEP film and PTFE spacer (1.0 mm thickness) and was irradiated with 365 nm UV light for 9 h in order to induce the free radical polymerization of DMAAm. The obtained ion gel was maintained at 373 K for 12 h under vacuum in order to remove the unreacted monomer and ethanol. The compositions of the ionic liquid and the inorganic/organic network in the ion gels were 79.3±1.0 wt% and 20.7±1.0 wt%, respectively, which were determined in the same manner described above.

In addition, a PDMAAm SN ion gel was also prepared using the [C_4mim][Tf_2N]/ethanol mixture without silica nanoparticles. This SN ion gel was used to confirm the structure of silica nanoparticles in the ionic liquid/ethanol mixture and the mechanical properties of the SN ion gels before the ethanol removal. The [C_4mim][Tf_2N] content in the PDMAAm SN ion gel was adjusted to 85 wt% to obtain a PDMAAm network of the same content as that of the SN and μ-DN ion gels.

Mechanical property measurement

The mechanical properties of ion gels were evaluated using an automatic recording universal testing instrument (EZ-LX, Shimadzu Co., Japan) at room temperature. A dumbbell-shaped specimen having a length, width, and thickness of 75.0, 4.0, and 1.0 mm was used for the stretching test. Because the inorganic/organic composite ion gels except for that contained ionic liquid/ethanol mixture had no volatile component, the mechanical properties was able to be measured in open environment without considering any composition change during the measurement. In the case of the mechanical property measurement of the ion gel with ionic liquid/ethanol mixture, the sample was coated with silicon oil (KF96SP, Shin-Etsu Chemical Co., Ltd.) to minimize evaporation of ethanol from the gel during testing. For all measurement, the sample was attached to the instrument at a distance of 35 mm between the jigs. A uniaxial stretching test was conducted by stretching the sample at a constant strain rate of 100 mm/min. The fracture stress, fracture strain, and Young's modulus were measured at least three times for each sample. In the cyclic stretching test, the stretching and return operations were performed until the sample broke while incrementally increasing the stretching strain in steps of 0.5. Furthermore, an ion gel film of 75 mm length with 20 mm initial notch, 15 mm width, and 1.0 mm thickness was used for the tearing test to measure the tearing energy of the ion gels. The ion gel sample was teared by pulling the sample at a constant velocity of 50 mm/min. The tearing energy was calculated by dividing the average force applied during the tearing test by the thickness of the sample.

Transmission electron microscope observation

The silica-particle-based inorganic network in the ion gels was observed using a field-emission transmission electron microscope (FE-TEM) (JEM-2100F, JEOL Ltd., Japan). A cubic sample of the ion gel with of size 1 mm was immersed in a sufficient volume of ethanol for 12 h to exchange the ionic liquid in the sample for ethanol. The sample was immersed in a precursor solution of UV-curable resin/ethanol mixture (weight ratio of 1 g/1 g) for 6 h and then immersed in a precursor solution of UV-curable resin for 12 h in order to completely exchange the ethanol in the sample with the precursor solution. The sample in the precursor solution was poured into a silicon mold and cured under a UV light. The resin block embedding the gel sample 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 carbon support film and observed by FE-TEM and STEM-EDX modes. The acceleration voltage of the electron gun used for observation was 200 kV.

RESULTS AND DISCUSSION

μ-DN ion gel prepared with TEOS

Figures 1 and 2 show the results of the uniaxial stretching test of the inorganic/organic composite ion gels prepared at various temperatures and the temperature dependence of the mechanical properties such as fracture stress, fracture strain, Young's modulus and tearing energy, respectively. As shown in these figures, it was found that the fracture strain, fracture stress, and Young's modulus of the inorganic/organic composite ion gels were much larger than those of the PDMAAm SN ion gel. This indicated that the inorganic component of the inorganic/organic composite ion gels contributed to the increase in the strength of the ion gels. In addition, as shown in Figure 1, it was found that the mechanical properties of the inorganic/organic composite ion gels were affected by the preparation temperature of the gel, i.e., the shape of the stress–strain curve varied with an increase in the preparation temperature, which means that the network structure of the inorganic/organic composite gel prepared in the range of 318.0 K to 322.5 K varied continuously. In particular, as more clearly shown in Figures 2(a), (c), and (d), the fracture stress, Young's modulus, and tearing energy of the inorganic/organic composite ion gel were drastically decreased as the preparation temperature increased from 318 K to 321 K. On comparing the Young's moduli of the inorganic/organic composite ion gels and PDMAAm SN ion gel, as shown in Figure 2(c), the Young's modulus of the inorganic/organic composite ion gels prepared at more than 321 K was found to exhibit the same value as that of the PDMAAm SN ion gel. This result indicated that the inorganic component in the inorganic/organic composite ion gel prepared at a high temperature hardly contributed to the rigidity of the ion gels. Therefore, it was inferred that the inorganic silica particle network could not be highly developed in the inorganic/organic composite ion gels prepared at a high temperature. On the other hand, as shown in Figure 2 (b), the fracture strain of the μ-DN ion gels did not depend on the preparation temperature. Because the fracture strain of the μ-DN ion gels should be strongly affected by the PDMAAm network structure, such as the chain length and cross-linking degree of the PDMAAm network, no dependence on the fracture strain indicated that the structure of the PDMAAm network in the μ-DN ion gels was hardly changed in the preparation temperature range investigated in this study. From these results, it can be considered that the dependence of the mechanical strength of the μ-DN ion gel on the preparation temperature was mainly due to the difference in the configuration of the inorganic network.

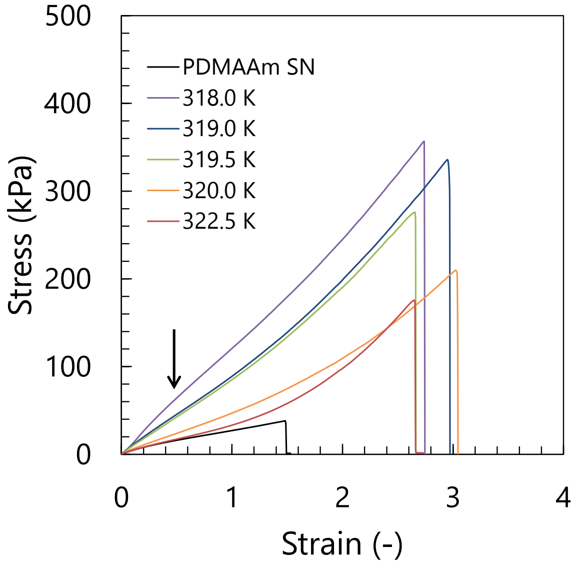

Figure 1. Stress–strain curves of inorganic/organic composite ion gels containing ca. 80 wt% of $[C_4mim][Tf_2N]$ prepared via one-pot/one-step process at various preparation temperatures.

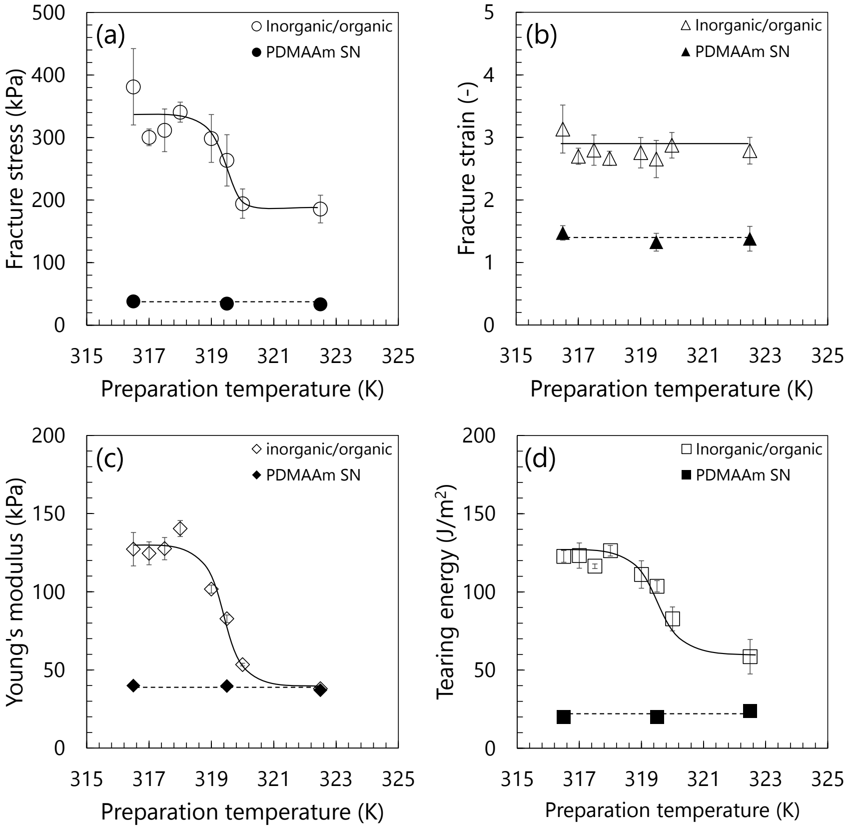

Figure 2. Mechanical properties of inorganic/organic composite ion gels containing ca. 80 wt% of [C_4mim][Tf_2N] prepared via one-pot/one-step process at various preparation temperatures. (a) Fracture stress, (b) fracture strain, (c) Young's modulus, and (d) tearing energy.

On comparing the stress–strain curves of the inorganic/organic composite ion gels prepared at various temperatures (Figure 1), it was found that the stress–strain curve of the inorganic/organic composite ion gel prepared at 318.0 K exhibited a different shape from those of the ion gels prepared at temperatures above 319.0 K, i.e., an S-shaped stress–strain curve with a small yielding point at approximately a 0.5 strain (pointed by an arrow in Figure 1) was found for the ion gel prepared at 318.0 K. This S-shaped stress–strain curve is similar to that of inorganic/organic DN ion gels.[18] However, no yielding point was found in the stress–strain curves of the inorganic/organic composite ion gels prepared at more than 319.0 K, i.e., a J-shaped stress–strain curve was observed. The stress–strain curve of the inorganic/organic composite ion gel changed from S-shaped to J-shaped with the increase in the preparation temperature. Here we consider the relationship between the J-shaped stress–strain curves and the structure of the gel network of the inorganic/organic composite ion gels prepared at high temperature. When the inorganic/organic composite ion gels were prepared at high temperatures, the silica nanoparticles could not form a complete network structure because the silica nanoparticles were formed after the development of the PDMAAm network in the ionic liquid. Therefore, it could be suggested that partially developed silica particle clusters were formed when the inorganic/organic composite ion gels were prepared at a high temperature. The network structure in which the first network components are uniformly dispersed in the gel is very similar to that of the MR-gel presented by Hu *et al*.[30-33]

The MR gel is a special type of DN hydrogel composed of first-network-based gel particles and second network. The MR gel forms an interpenetrating network structure between the first and second networks within the first network gel particle and develops a high strength based on the energy dissipation due to the partial destruction of the first network inside the gel particle. The first network gel particles are homogeneously dispersed in the MR gel. As the second network mainly contributes to sustaining the stress increment of the MR gel at a low elongation state, the MR gel shows a lower Young's modulus than the DN gel.[30] Moreover, in the high-strain region, the contribution of the first network gel particles in sustaining the stress increase becomes large, such that the stress rapidly increases as the strain increases. As the MR gel has a homogeneously dispersed interpenetrating network structure in the first network gel particles, its stress–strain curve has a J-shape.

As shown in Figure 1, the inorganic/organic composite ion gels prepared in the temperature range of 319.0 K to 322.5 K also exhibited J-shaped stress–strain curves. This result suggested that the network of the inorganic/organic composite ion gels prepared at an elevated temperature had a structure similar to that of an MR gel. In other words, it was considered that the inorganic/organic composite ion gel prepared at high temperatures had an interpenetrating network structure in which inorganic network clusters were homogeneously dispersed throughout the ion gel. The possible network structure and the chemical structures of the inorganic and organic networks are shown in Figure S1(b).

In order to confirm the above speculation, the inorganic network structure of the inorganic/organic composite ion gel prepared at each temperature was observed using a TEM (Figure 3). The dark-colored particles shown in Figure 3 are silica nanoparticles (see Figure S2). As shown in Figure 3, the inorganic network structures of the inorganic/organic composite ion gels prepared at each temperature clearly differed from each other. In the ion gel prepared at a low temperature, the silica particle network structure comprising silica nanoparticles that were continuously connected in a wide range was formed (Figure 3(a)). Such an inorganic network structure is a characteristic structure of inorganic/organic DN ion gels.[18] Moreover, as the preparation temperature increased, the inorganic network obtained a cluster-like structure with a size of approximately several hundred nanometers (Figures 3(b) and (c)). The inorganic/organic composite ion gels with such inorganic network clusters were referred to as μ-DN ion gels. The μ-DN ion gels prepared at 319.5 K and 320.0 K had a lower transparency than the DN ion gel prepared at 316.5 K (Figure S3) because uniformly dispersed inorganic network clusters in the μ-DN ion gel scattered visible light. Therefore, it was strongly suggested that the preparation of μ-DN ion gels between 319.0 K and 322.5 K could increase their mechanical strength owing to the energy dissipation due to the rupture of uniformly dispersed inorganic network clusters in the μ-DN ion gels. The mechanism for increasing the mechanical strength would be similar to that of the MR gel.

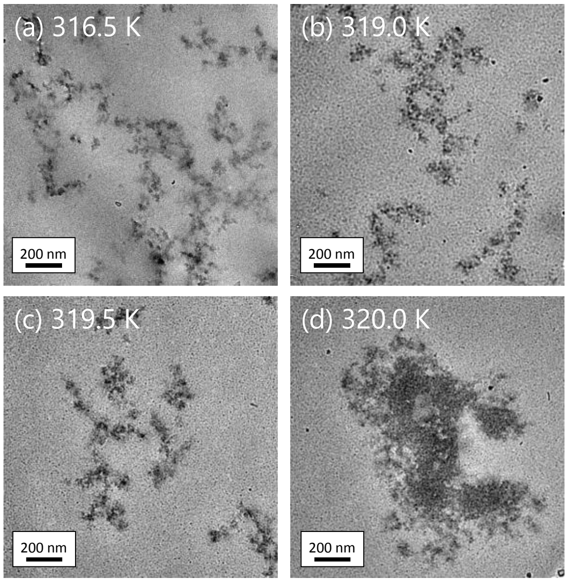

Figure 3. TEM images of the silica particle networks in inorganic/organic composite ion gels prepared via one-pot/one-step process at (a) 316.5 K, (b) 319.0 K, (c) 319.5 K, and (d) 320.0 K.

If the mechanical strength of the μ-DN ion gel prepared in the temperature range of 319.0 K to 322.5 K was increased based on an energy dissipation mechanism similar to that of the MR gel, the μ-DN ion gel should show an energy dissipation based on the fracture of the first network cluster dispersed in the ion gel and softening behavior after the force application to the ion gel. Such an energy dissipation and softening behavior can be confirmed from the cyclic tensile stress–strain curves. Therefore, a cyclic tensile stress loading–unloading test was performed using the μ-DN ion gels prepared at each temperature. The resulting cyclic stress–strain curves are shown in Figure 4.

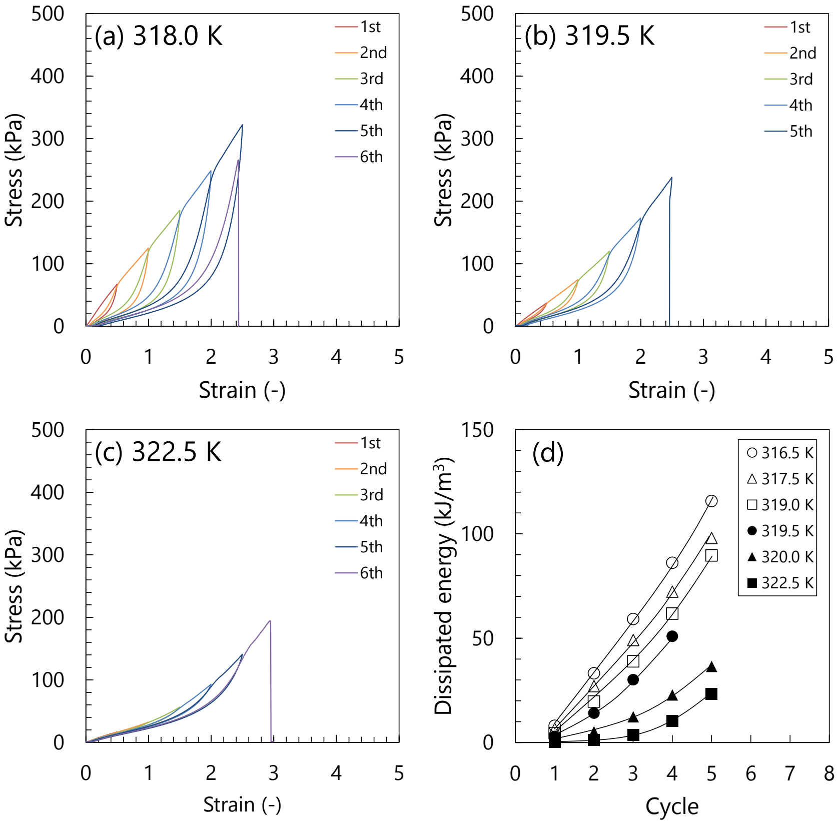

Figure 4. Energy dissipation of the inorganic/organic composite ion gels prepared via one-pot/one-step process at various temperatures. (a)–(c) cyclic loading–unloading curves of the ion gels prepared at 318.0 K, 319.5 K, and 322.5 K, respectively. (d) Relationship between dissipated energy and cycle for cyclic loading test.

As shown in Figures 4(a)–(c), it was confirmed that all μ-DN ion gels prepared at a temperature between 318.0 K and 322.5 K exhibited hysteresis and softening behavior. Furthermore, the energy dissipated in each cycle of elongation is shown in Figure 4(d). As shown in Figure 4(d), although the dissipated energy of the ion gel prepared at 316.5 K increased linearly with the stretching cycle, the initial slope decreased as the preparation temperature of the ion gel increased. The initial slope in Figure 4(d) represented the amount of energy dissipated in the small elongation. Inorganic/organic composite ion gels prepared at a low temperature (DN ion gels) indicated a large energy dissipation even when it was slightly elongated. The large energy dissipation was a result of the highly developed inorganic silica particle network in the ion gels (Figure 3(a)). In contrast, the inorganic/organic composite ion gels prepared at an elevated temperature of approximately 320 K (μ-DN ion gels) dissipated little energy at a low elongation. This result was observed because the inorganic network clusters dispersed in μ-DN ion gels hardly contributed to the energy dissipation in the small elongation state. In other words, because the inorganic network clusters were dispersed in the μ-DN ion gels, the soft second network contributed mainly to sustaining the stress increment in low-elongation state and the inorganic network cluster contributed to sustaining the loaded stress in the high-elongation state. This toughening mechanism is similar to that observed in the MR gel.[30-33] From the results, it was demonstrated that the μ-DN ion gels having a high mechanical strength, which was based on the energy dissipation mechanism accompanying the destruction of inorganic network clusters, can be prepared through a fine control of the preparation temperature. The toughening mechanism of the μ-DN ion gel is shown in Figure 5. In the μ-DN ion gel, the silica particle network clusters are uniformly dispersed (Figure 5(a)). When a low strain was induced in the μ-DN ion gel, destruction of the silica particle network cluster and energy dissipation hardly occurred although the soft PDMAAm network was extended (Figure 5(b)). In contrast, when a large strain was induced in the μ-DN ion gel, destruction of the silica particle network cluster along with further elongation of PDMAAm occurred, and the applied energy was dissipated (Figure 5(c)). As a result, the μ-DN ion gels exhibited a larger fracture stress and fracture energy than those of PDMAAm SN ion gel.

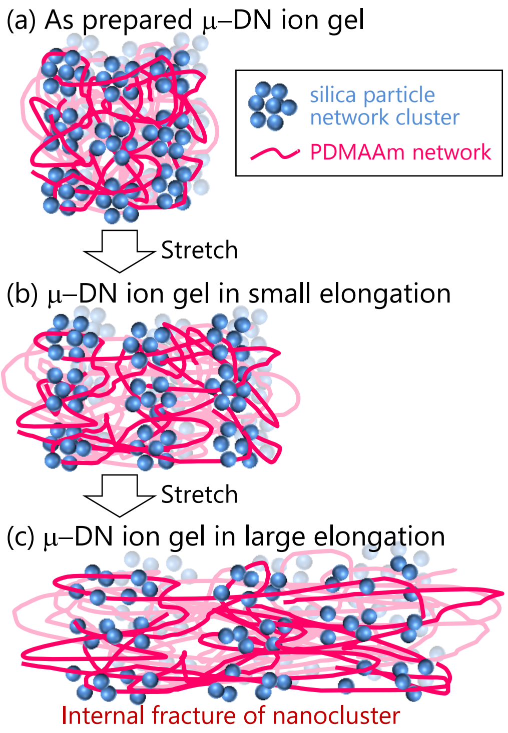

Figure 5 Schematic of the toughening mechanism of inorganic/organic μ-DN ion gel during elongation. (a) As prepared μ-DN ion gel, (b) μ-DN ion gel with a small elongation, and (c) μ-DN ion gel with a large elongation.

Silica-nanoparticle-based μ-DN ion gel

A μ-DN ion gel with the silica-particle-based cluster as the energy dissipating source can be prepared by using silica nanoparticles as the starting material. The silica-particle-based cluster can be formed in an ionic liquid by controlling the dispersion stability of the silica nanoparticles. The use of the silica nanoparticles as the starting material provides several benefits such as the simple and fast preparation of the μ-DN ion gels and easy control of the configuration of the inorganic network. In particular, with respect to the configuration of the inorganic network, it is expected that the number of inorganic networks per unit volume of the ion gel, which would directly affect the mechanical strength of the μ-DN ion gel, would be increased on decreasing the size of the silica nanoparticles.

The dispersion and aggregation states of the silica nanoparticles in the ionic liquid were controlled through the addition of ethanol as a dispersion stabilizer. In order to determine the conditions under which the silica nanoparticles are partially aggregated to form silica particle network clusters, a gelation test was performed by adding silica nanoparticles in [C_4mim][Tf_2N] with various concentrations of ethanol. The result of the gelation test is shown in Figure 6. When 5 wt% or less ethanol was added, the ionic liquid with 5 wt% of Aerosil 200 was completely gelled, which indicated that highly developed silica particle network would have been formed in the ionic liquid/ethanol mixture. In contrast, when 10 wt% of ethanol was added, the ionic liquid containing silica nanoparticles became viscous while maintaining its fluidity. When 15 wt% of ethanol was added, the ionic liquid maintained its sol state. The state change of the silica nanoparticle suspension would be happened by the adsorption of ethanol on the silica nanoparticles. Regarding adsorption of alcohol molecules on silica surface, it was reported that alcohol molecules could adsorb on silica surface in organic solvents by hydrogen bonding.[34-35] In addition, it was reported that water molecules could adsorb on silica surface in an ionic liquid by hydrogen bonding.[36] In the same manner, it was considered that ethanol could adsorb on the surface of silica nanoparticles via hydrogen bonds in an ionic liquid. As the result of ethanol adsorption, the formation of hydrogen bonds between the silica nanoparticles could be inhibited. With the increase in ethanol concentration, the adsorption amount of ethanol would be increased and the interaction between the silica nanoparticles would be weakened. Therefore, when more than 10 wt% ethanol was added, the silica particles no longer keep highly developed network structure; i.e. silica particle network clusters were formed, and the gelation state of the silica nanoparticle suspension was changed to sol. Because of the formation of the silica particle network clusters, the composite ion gels were prepared using an ionic liquid/ethanol mixture with 10 wt% of ethanol as the dispersion stabilizer of the silica nanoparticles.

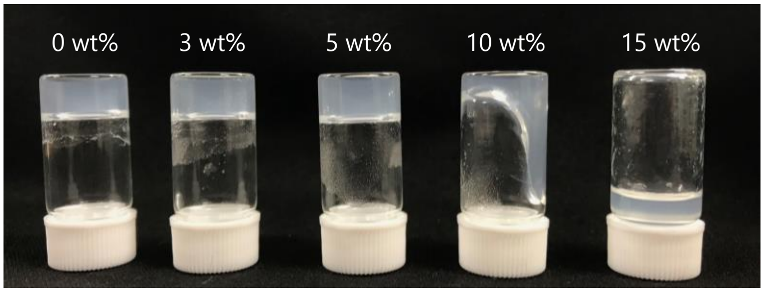

Figure 6. Photographs of silica nanoparticle/[C_4mim][Tf_2N]/ethanol mixture with various ethanol compositions. The samples were prepared by adding 5 wt% of silica nanoparticles having a 12-nm diameter (Aerosil 200) to [C_4mim][Tf_2N]/ethanol mixture. The ethanol concentration was varied between 0 wt% (left) and 15 wt% (right) on [C_4mim][Tf_2N] basis.

To confirm the silica particle network structure of an inorganic/organic composite ion gel containing 80 wt% of an ionic liquid prepared using silica nanoparticles of various particle sizes, the state of the silica nanoparticles in the prepared ion gel was observed using a TEM. The TEM photographs of the formed silica particle networks in the ion gels are shown in Figure 7. It was observed that all the silica nanoparticles formed silica particle network clusters in the inorganic/organic composite ion gels. Therefore, as expected, even when silica nanoparticles were used as the starting material, the μ-DN structure was formed by controlling the aggregation state of the silica nanoparticles in the ionic liquid.

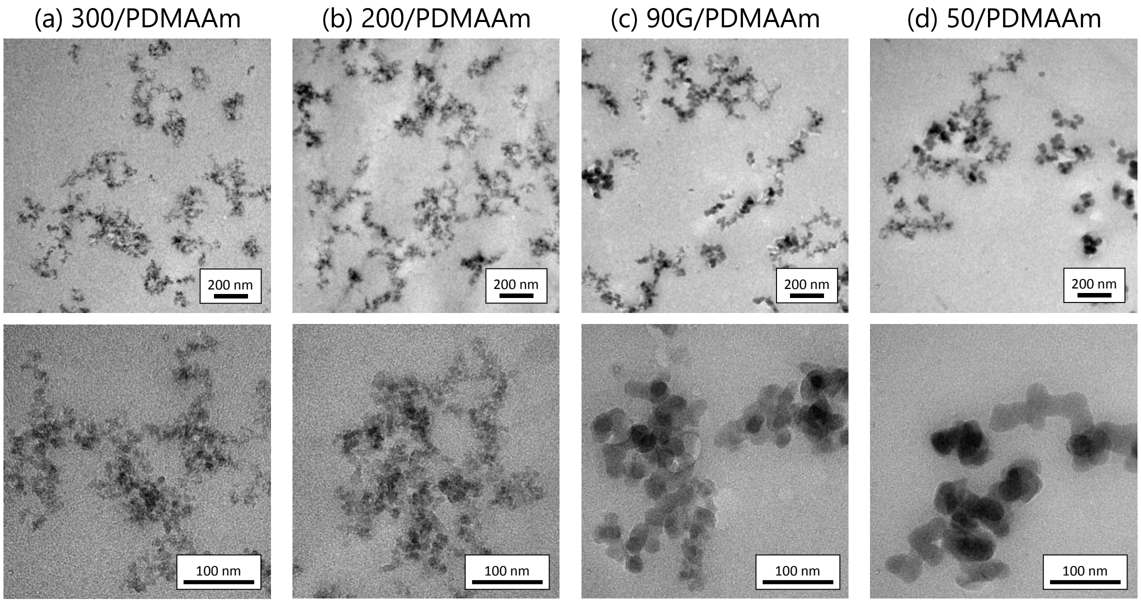

Figure 7. TEM images of the silica particle networks in the inorganic/organic composite ion gels prepared using silica nanoparticles with various primary diameters, d (nm). (a) Aerosil 300 (d = 7 nm), (b) Aerosil 200 (d = 12 nm), (c) Aerosil 90G (d = 20 nm), and (d) Aerosil 50 (d = 30 nm).

In order to investigate the mechanical strength of the silica-particle-based inorganic/organic composite ion gels, uniaxial stretching tests of the inorganic/organic composite ion gels prepared using silica nanoparticles with various particle sizes were conducted. In addition, in order to confirm the toughening mechanism of the composite ion gels, a cyclic tensile loading–unloading test was conducted for each ion gel. The results are shown in Figures 8 and 9, respectively. The result for the PDMAAm SN ion gel, which was prepared using an ionic liquid/ethanol mixture with 10 wt% of ethanol, is also shown in Figure 8. As shown in Figure 8, it was confirmed that the fracture stress, fracture strain, and Young's modulus of the inorganic/organic composite ion gels prepared using silica nanoparticles were larger than those of the PDMAAm SN ion gel. Thus, it was strongly suggested that the silica particle network clusters in the inorganic/organic composite ion gels prepared using silica nanoparticles as a starting material also contributed to an increase in the mechanical strength of the ion gels. Furthermore, as shown in the small strain region (in the strain range between 0 and 1), the stress–strain curves of the composite ion gels had a J shape. This result is the same as that observed for the μ-DN ion gels prepared via one-pot/one-step process using TEOS as the starting material (Figure 1). As the composite ion gels prepared from TEOS and silica nanoparticles had a similar network structure, their mechanical behaviors were also the same. The same mechanical property was also observed in the results for the cyclic stress–strain curve. As shown in Figures 9(a)–(e), the cyclic stress–strain curves of the inorganic/organic composite ion gels prepared using silica nanoparticles also showed clear hysteresis and softening behavior. The silica particle clusters, which were formed by partial agglomeration of silica nanoparticles in ionic liquids, could dissipate the loaded energy when they are ruptured by the force applied to the ion gel. In addition, as shown in Figure S4, the silica particle network of the silica nanoparticle-based inorganic/organic composite ion gels showed a self-healing property, which had also been confirmed for the inorganic network of inorganic/organic DN ion gels prepared with TEOS as the starting material.[18] In order to clearly elucidate the toughening mechanism of the silica nanoparticle-based inorganic/organic composite ion gels, we identified the relationship between the dissipated energy and stretching cycle during the cyclic tensile test, which are shown in Figure 9(f). It can be observed that the silica nanoparticle-based inorganic/organic composite ion gels dissipated little energy at a low elongation and large energy at a high elongation. This trend is same as that of the μ-DN ion gels prepared via the condensation polymerization of TEOS (Figure 4(d)). Thus, it can be considered that the energy dissipation in the low-elongation range became small because the silica-particle-network-based clusters formed by partial agglomeration of the added silica nanoparticles were hardly broken in the small deformation. These characteristic mechanical properties strongly indicated that the toughening mechanism of the silica nanoparticle-based inorganic/organic composite ion gel would be according to the DN principal.[22] Therefore, it can be concluded that the inorganic/organic ion gels prepared using silica nanoparticles as the inorganic network source are μ-DN ion gels.

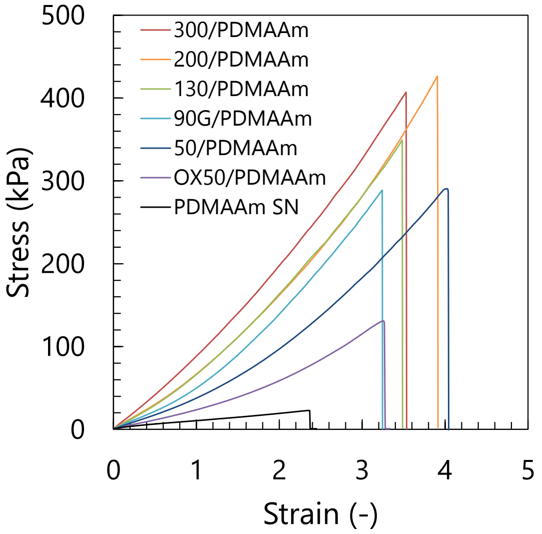

Figure 8. Stress–strain curves of inorganic/organic composite ion gels prepared using silica nanoparticles with various primary diameters.

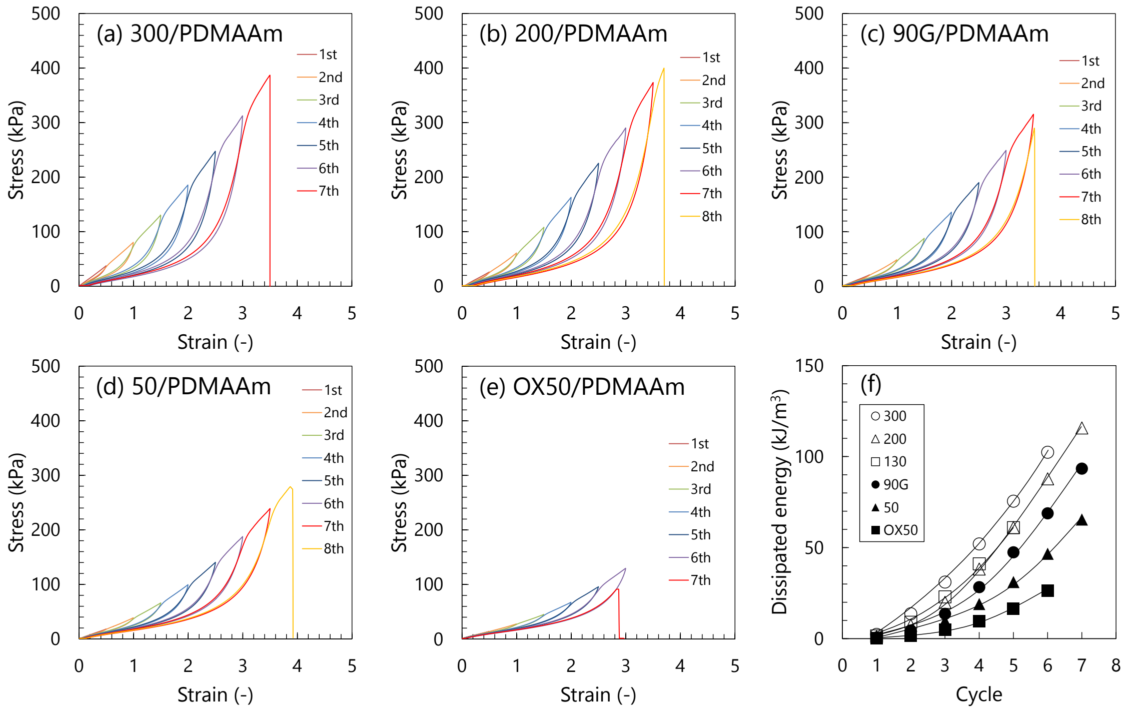

Figure 9. Energy dissipation of the inorganic/organic composite ion gels prepared using silica nanoparticles with various diameters. (a)–(e) Cyclic loading–unloading curves of inorganic/organic composite ion gels prepared using (a) Aerosil 300 (*d* = 7 nm), (b) Aerosil 200 (*d* = 12 nm), (c) Aerosil 90G (*d* = 20 nm), (d) Aerosil 50 (*d* = 30 nm), and (e) Aerosil OX50 (*d* = 40 nm). (f) Relationship between the dissipated energy and cycle for cyclic loading test.

We then compared the mechanical properties of the inorganic/organic composite ion gels prepared using silica nanoparticles of a different size. As shown in Figure 7, it was observed that a silica particle network composed of a large number of silica nanoparticles was formed in the ion gel prepared using smaller silica nanoparticles. Considering the number density of the silica particle network cluster and the inter-particle attraction forces, it is expected that the inorganic/organic composite ion gels prepared using very small silica nanoparticles could dissipate a large amount of energy and exhibit a high mechanical strength. In Figure 10, the relationship between the mechanical properties of the silica nanoparticle-based composite ion gels and the nominal primary particle diameter of the used silica nanoparticles is summarized. As clearly shown in Figure 10(a), (c) and (d), the fracture energy, Young's modulus, and tearing energy increased as the size of the used silica nanoparticles decreased. It should be noted that, as shown in Figure 10(a), the fracture stress of the ion gels prepared using the silica nanoparticle with ca. 10 nm diameter were more than 400 kPa, which was much higher than that of inorganic/organic DN ion gels (ca. 250 kPa).[18] In addition, the tearing energy of the composite ion gel prepared using silica nanoparticles of a diameter smaller than 10 nm (ca. 140 J/m^2; see Figure 10(d)) was higher than those of the DN ion gels (ca. 125 J/m^2) and the μ-DN ion gels (60–120 J/m^2). With respect to the dissipated energy, as shown in Figures 9(a)–(e), the hysteresis of the stress–strain curves (i.e., the dissipated energy) also increased as the size of the silica nanoparticles decreased. Furthermore, the Young's modulus of the silica nanoparticle-based composite ion gel was increased with the decrease of the size of the silica nanoparticles (Figure 10(c)). Thus, it can be considered that the inorganic network, especially that composed of smaller-sized silica nanoparticles, could strongly contribute to an increase in the mechanical strength of the composite ion gels owing to the inclement of the number density of the inorganic network; i.e. the smaller the particle diameter of the silica nanoparticles, the higher the number density of the silica particle network clusters in the ion gel. Because interactions based on hydrogen bonding and van der Waals force occurred between the silica nanoparticles in the ionic liquid,[37-41] the total number of hydrogen bonding and total of van der Waals attractive force in the silica particle network would be increased with decreasing the silica nanoparticle size. Therefore, the mechanical strength of the silica nanoparticle-based μ-DN ion gel increased with the decrease of the size of the silica nanoparticles. On the other hand, as indicated in Figure

10(b), the fracture strain of the silica nanoparticle-based composite ion gels was independent of the size of the silica nanoparticles and almost the same as those of the inorganic/organic DN ion gels[18] and μ-DN ion gels (Figure 2(b)). This result indicated that the PDMAAm propagated in the μ-DN ion gels prepared using TEOS and silica nanoparticles as the inorganic network source as well as that in the DN ion gels would form similar network structure.

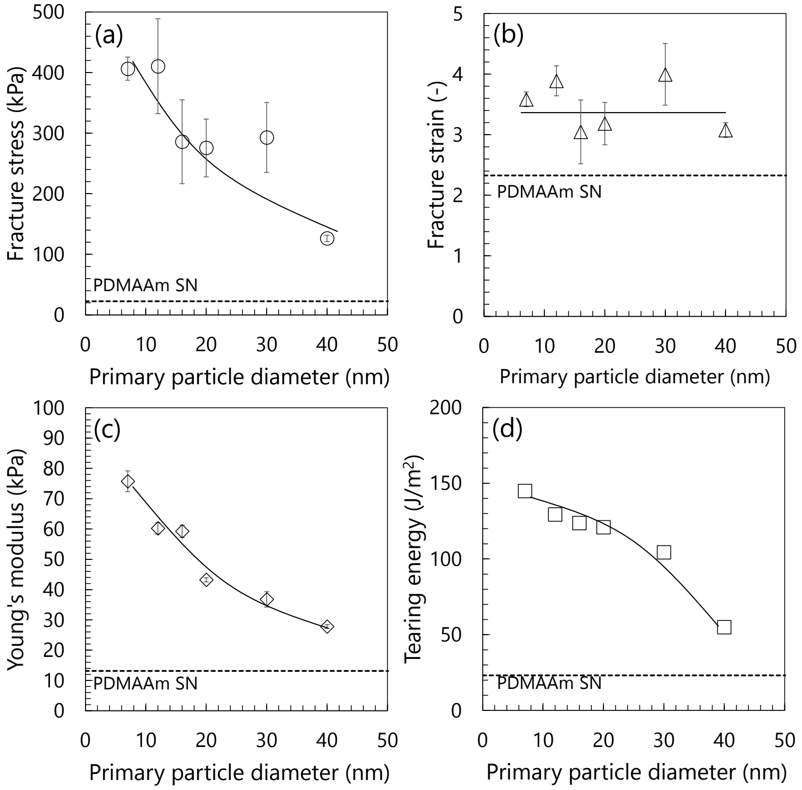

Figure 10. Effect of the primary diameter of silica nanoparticles on (a) fracture stress, (b) fracture strain, (c) Young's modulus, and (d) tearing energy of the inorganic/organic composite ion gels containing ca. 80 wt% of [C_4mim][Tf_2N] prepared using silica nanoparticles of various particle diameters. Dotted lines indicate the data of the PDMAAm SN ion gel.

Network formation mechanism of silica-nanoparticle-based μ-DN ion gels

Finally, the formation mechanism of the silica particle network of silica nanoparticle-based μ-DN ion gel was investigated. It can be considered that there are two possible network formation mechanisms. The first possibility is that the PDMAAm network was formed after the formation of the silica particle network cluster in an ionic liquid/ethanol mixture. The schematic of this mechanism is shown in Figure S4. In this case, owing to the dispersion stabilization of the silica nanoparticles due to the adsorption of ethanol onto their interface, the clusters of silica nanoparticles are dispersed in the ionic liquid. The results of the gelation tests shown in Figure 6 supported the consideration of the formation of a silica particle network in the ionic liquid/ethanol mixture, i.e., the ionic liquid/ethanol mixture with 10 wt% of ethanol became viscous after the addition of the silica nanoparticles, which would be due to the partially developed silica-particle network formation. Thus, it is considered that the aforementioned network formation mechanism seems reasonable. However, there is another possible network formation mechanism in which well-dispersed silica nanoparticles, which were stabilized by the adsorption of ethanol on their surface, formed clusters of silica nanoparticles during the evaporation of the ethanol after the PDMAAm network formation. In order to clarify the network formation mechanism, we observed the network structure of the ion gel before the evaporation of ethanol and measured the mechanical properties of the ion gel before and after the ethanol removal. The results are shown in Figure 11. As shown in Figure 11(a), it was clearly observed that a partially developed silica-particle network was formed in the ionic liquid/ethanol mixture. The network structure is similar to that shown in Figure 7(a). In addition, as shown in Figure 11(b), the ion gel before the removal of the ethanol exhibited a much larger Young's modulus, fracture stress, and fracture strain than those of the PDMAAm SN ion gel. Furthermore, the cyclic stress–strain curve of the ion gel before the ethanol removal (Figure 11(c)) as well as that after the ethanol removal (Figure 11(d)) showed clear hysteresis and softening behavior. These mechanical properties of the silica nanoparticle-based μ-DN ion gel before the ethanol evaporation supported the silica particle network formation in the ionic liquid/ethanol mixture.

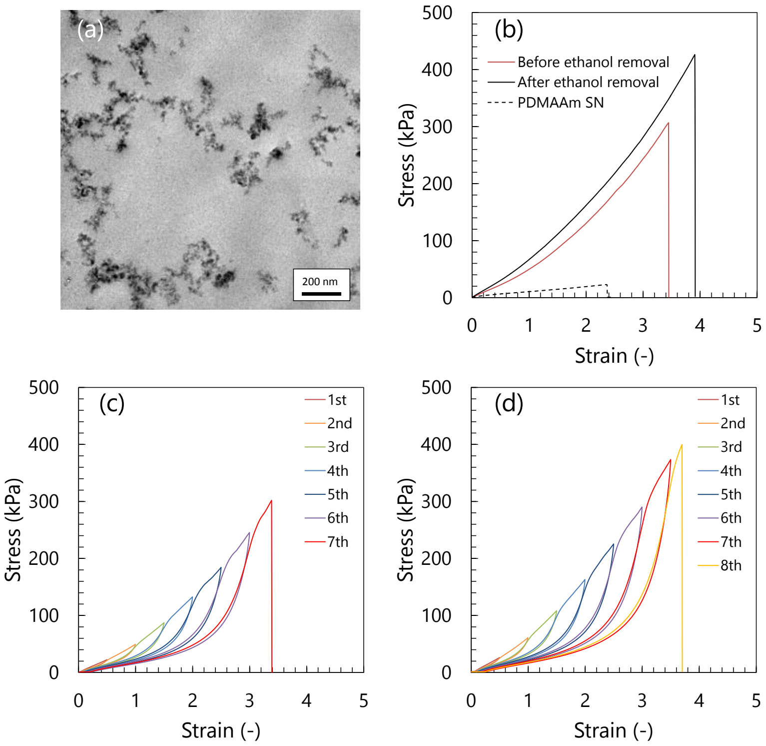

Figure 11. Network structure and mechanical behavior of inorganic/organic composite ion gels prepared using Aerosil 200 (*d* = 12 nm) and [C$_4$mim][Tf$_2$N]/ethanol mixture with 5 wt% of ethanol. (a) TEM image of the silica particle network, (b) stress–strain curves of the ion gels before and after ethanol removal, and (c) and (d) cyclic loading–unloading curves of the ion gels before and after ethanol removal, respectively.

Therefore, it can be concluded that the silica particle network was formed in the ionic liquid/ethanol mixture before the PDMAAm network formation. It is expected that the mechanical strength of the silica-particle-based μ-DN ion gels could be further increased through the fine control of the structure of the silica particle network cluster in an ionic liquid/ethanol mixture using a suitable dispersion stabilizer.

CONCLUSIONS

In this study, we developed highly tough inorganic/organic μ-DN ion gels with a characteristic inorganic network composed of silica particle clusters, named silica-particle-network-based clusters. The μ-DN ion gels consisted of partially developed fragile silica-particle-network-based clusters and a highly propagated flexible PDMAAm network were prepared using two methods: (1) one-pot/one-step network-formation process at a temperature at which the formation rates of the silica particle network and PDMAAm network were almost equal and (2) forming a PDMAAm network in a precursor solution in which the silica nanoparticles were dispersed as a source of the inorganic network. From the characteristic mechanical properties of the μ-DN ion gels, it was found that the silica-particle-network-based clusters contributed to energy dissipation, which provided the μ-DN ion gels with high toughness according to the toughening mechanism of DN gels, i.e., the excellent mechanical strength of the μ-DN ion gel was attributed to the silica-particle-network-based clusters and PDMAAm network, which acted as a sacrificial bond and hidden length, respectively.

The μ-DN ion gels prepared with silica nanoparticles of a small particle size of ca. 10 nm as the starting material for the inorganic network formation had the highest fracture stress and fracture energy among the inorganic/organic composite ion gels reported thus far. The dependence of the mechanical strength of the μ-DN ion gels on the particle size of the silica nanoparticles would be due to the interaction among the silica nanoparticles constituting the silica-particle-network-based clusters. As the particle size of the silica nanoparticles decreased, the amount of dissipated energy increased. Therefore, very small silica nanoparticles could provide μ-DN ion gels with a high mechanical strength.

The μ-DN ion gels prepared using silica nanoparticles as the starting material could have the advantage of easy and rapid inorganic network formation in an open environment. The advantages of toughness and preparation process of the μ-DN ion gel are indispensable in the continuous and large-scale production of a very thin ion gel film having sufficient mechanical strength for practical use. In order to prepare a very thin ion gel film, it is necessary to realize the formation of an organic network using non-volatile materials. This objective shall be pursued in our future research.

ASSOCIATED CONTENT

Supporting Information.

The supporting information is available free of charge.

Figures showing the EDX elemental mapping results of inorganic/organic composite networks prepared via one-pot/one-step process at 319.5 K, photographs of inorganic/organic composite networks prepared via one-pot/one-step process at various temperatures, self-healing behaviors of silica nanoparticle network in inorganic/organic composite ion gels prepared using silica nanoparticles, and schematic of the formation mechanism of inorganic/organic μ-DN structure formed using silica nanoparticles (PDF).

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Notes

The authors declare no competing financial interest.

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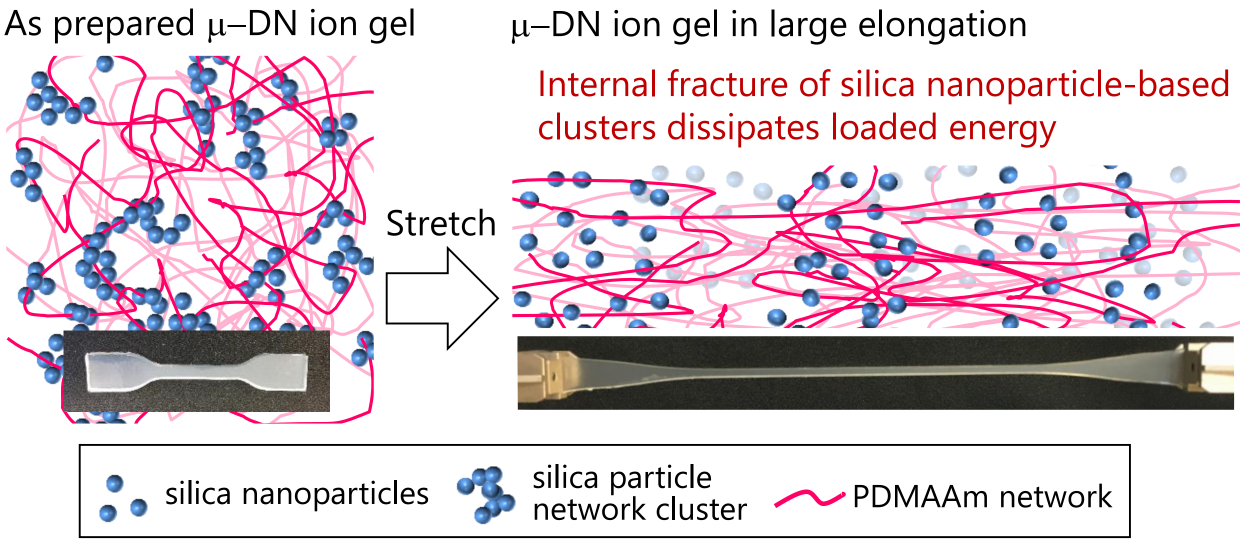
TOC graphic


As prepared μ–DN ion gel
μ–DN ion gel in large elongation
Internal fracture of silica nanoparticle-based clusters dissipates loaded energy
Stretch
silica nanoparticles
silica particle network cluster
PDMAAm network

Supporting information

Inorganic/organic double-network ion gels with partially developed silica-particle network

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Table of contents

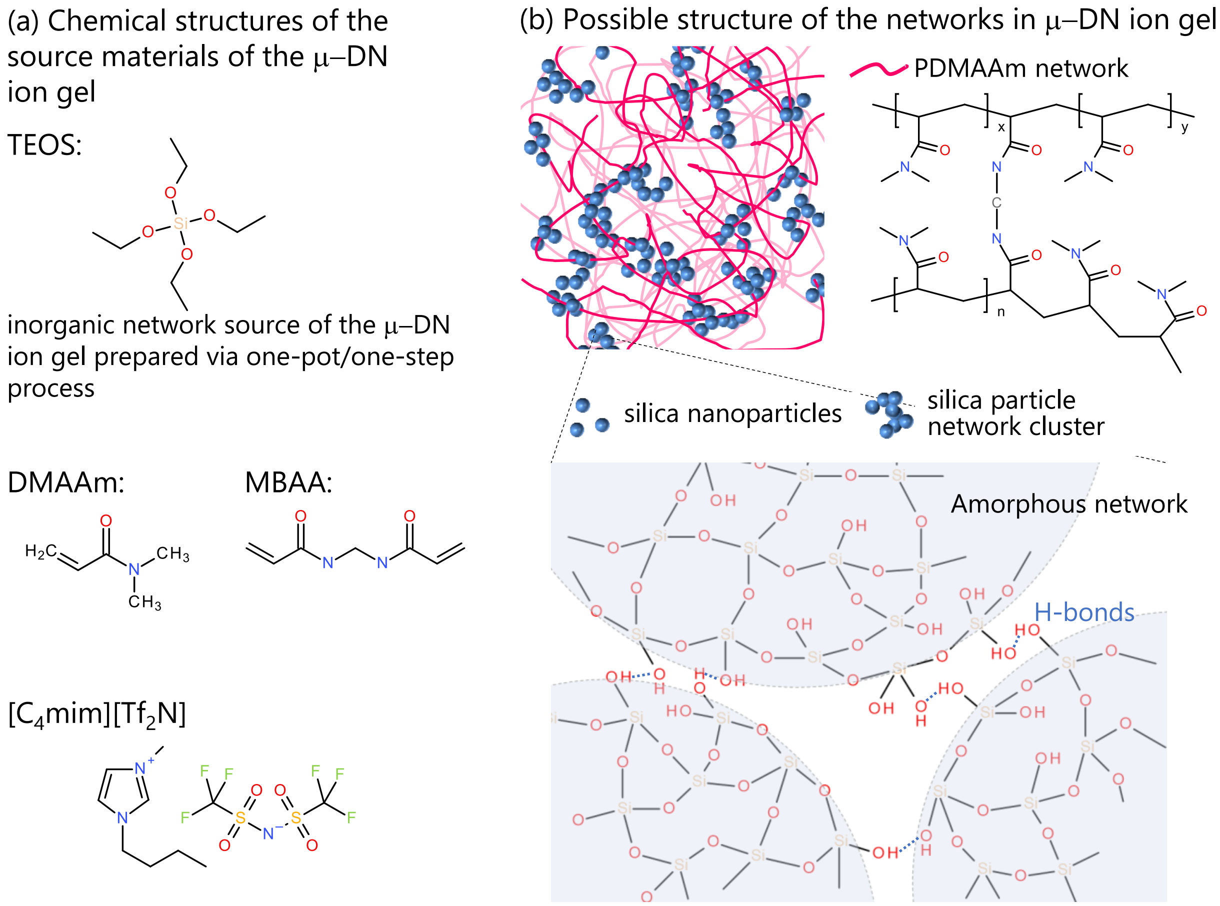
Figure S1: (a) Chemical structures of the source materials of the μ-DN ion gels, and (b) Possible structure of the networks in μ-DN ion gel.

Figure S2: EDX elemental mapping results of inorganic/organic composite networks prepared via one-pot/one-step process at 319.5 K

Self-healing test of the μ-DN ion gel. Figure S3: Photographs of inorganic/organic composite networks prepared via one-pot/one-step process at various temperatures

Figure S4: Self-healing behaviors of silica nanoparticle network in inorganic/organic composite ion gels prepared using silica nanoparticles

Figure S5: Schematic of formation mechanism of inorganic/organic μ-DN structure formed using silica nanoparticles



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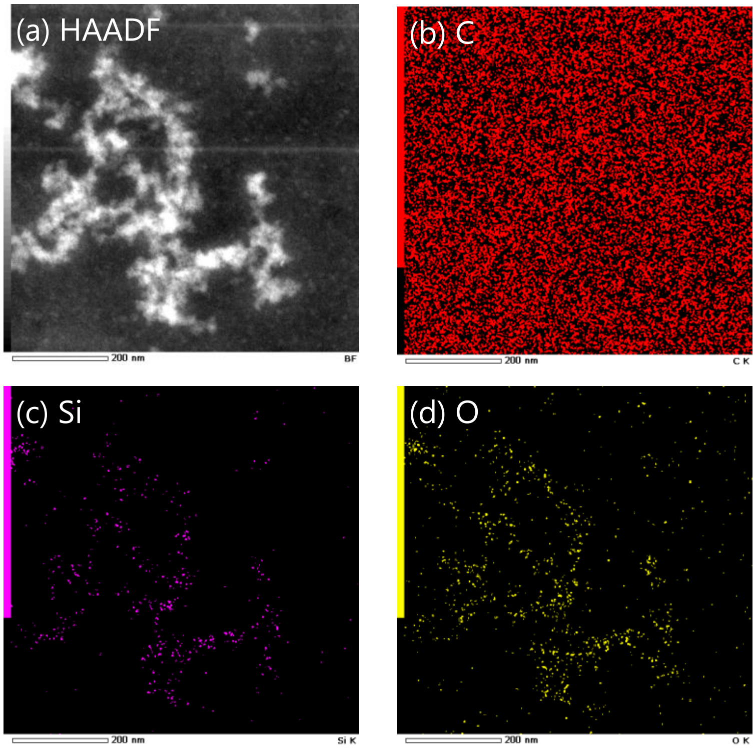

Figure S2. EDX elemental mapping results of inorganic/organic composite networks prepared via one-pot/one-step process at 319.5 K. (a) HAADF-STEM image, (b) carbon distribution, (c) silicon distribution, and (d) oxygen distribution.

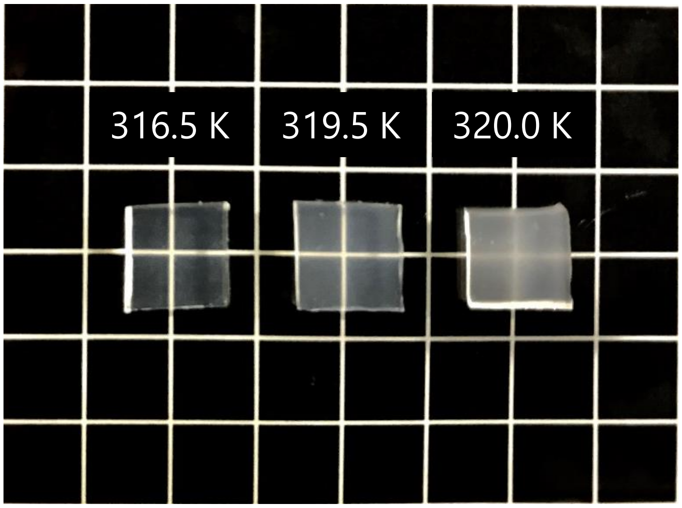

Figure S3. Photographs of inorganic/organic composite networks prepared via one-pot/one-step process at 316.5 K, 319.5 K, and 320.0 K.

Self-healing test

In our previous research, it was found that although inorganic/organic DN ion gels showed permanent deformation and softening behavior after a stress loading, the ruptured inorganic silica particle network could be considerably recovered by annealing the stress-loaded sample, i.e., the inorganic/organic DN ion gel had a self-healing property (Kamio *et al.*, *Adv. Mater.*, 2017, **29**(47), 1704118). As the μ-DN ion gels also have a silica-particle-based inorganic network, it could be expected that the mechanical property of the stress-loaded μ-DN ion gels could be recovered by performing annealing. The self-healing property of the ion gels was evaluated by measuring the mechanical properties of the sample before and after annealing. The dissipated energies and Young's moduli of as prepared sample and the stress-loaded sample followed by annealing treatment were determined from the following stress–strain curve measurement. The dumbbell-shaped specimen having a length, width, and thickness of 75.0, 4.0, and 1.0 mm was elongated at a stretching velocity of 100 mm/min until a strain of 2 was realized, and then immediately returned to its initial position at the same velocity. The stress-loaded sample was detached from the apparatus and annealed at 373 K. After annealing, the stress–strain curve was obtained in the same manner. From the stress–strain curves, the dissipated energy U and Young's modulus E were determined. The dissipated energy U was calculated using the following equation.

$$U = \int_0^2 \sigma \, \mathrm{d}\epsilon \Big|_{\mathrm{loading}} - \int_0^2 \sigma \, \mathrm{d}\epsilon \Big|_{\mathrm{unloading}} \qquad (1)$$

The degree of healing was evaluated using the dissipated energies and the Young's moduli of the samples before and after annealing. The extents of recovery of the Young's modulus and the dissipated energy were defined as E_1/E_0 and U_1/U_0, respectively, where the subscripts “0” and “1” indicate the original and stress-loaded samples after annealing, respectively.

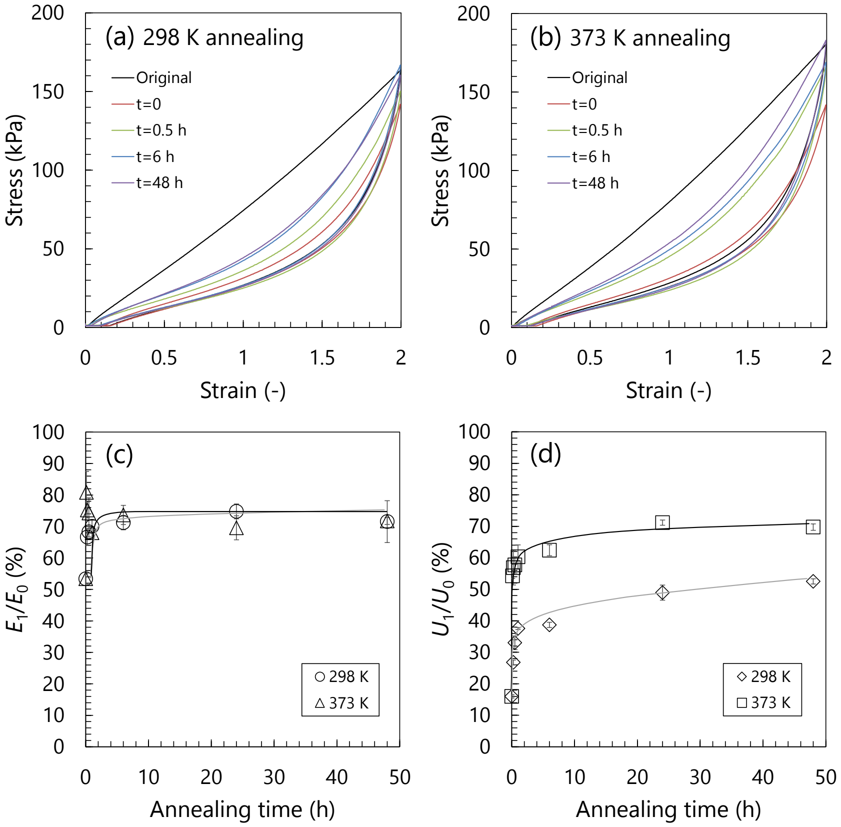

Figure S4. Self-healing behaviors of the silica nanoparticle network in inorganic/organic composite ion gels prepared using Aerosil 200 (*d* = 12 nm). Cyclic loading curves of the ion gels before and after annealing for various times at 298 K (a) and 378 K (b), and effect of annealing time on recovery ratio of Young's modulus (c) and dissipated energy (d).

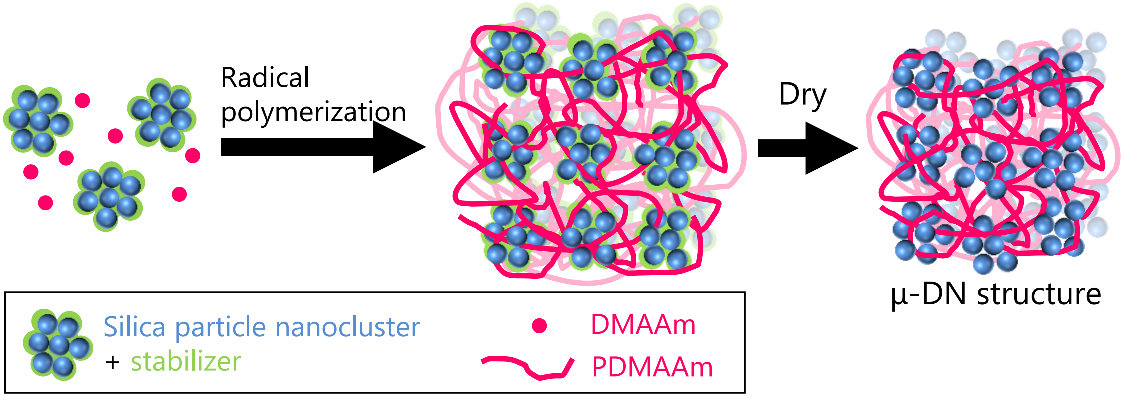

Figure S5. Schematic of formation mechanism of inorganic/organic μ-DN structure formed with silica nanoparticles as the starting material.