

Inorganic/Organic Double-Network Gels Containing Ionic Liquids

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Highly robust ion gels, termed double-network (DN) ion gels, composed of inorganic/organic interpenetrating networks and a large amount of ionic liquids (ILs), are fabricated. The DN ion gels with an 80 wt% IL content show extraordinarily high mechanical strength: more than 28 MPa of compressive fracture stress. In the DN ion gel preparation, a brittle inorganic network of physically bonded silica nanoparticles and a ductile organic network of polydimethylacrylamide (PDMAAm) are formed in the IL. Because of the different reaction mechanisms of the inorganic/organic networks, the DN ion gels can be formed by an easy and free-shapeable one-pot synthesis. They can be prepared in a controllable manner by manipulating the formation order of the inorganic and organic networks via not only multistep but also single-step processes. When silica particles form a network prior to the PDMAAm network formation, DN ion gels can be prepared. The brittle silica particle network in the DN ion gel, serving as sacrificial bonds, easily ruptures under loading to dissipate energy, while the ductile PDMAAm network maintains the shape of the material by the rubber elasticity. Given the reversible physical bonding between the silica particles, the DN ion gels exhibit a significant degree of self-recovery by annealing.

Ion gels are promising soft materials that contain a large amount of ionic liquids (ILs) in a polymer network. The unique properties of ILs such as their nonvolatility, nonflammability, and thermal, chemical, and electrochemical stabilities are retained in the quasi-solid soft material. Various types of ion gels can be prepared via several methods such as the simple blending of polymers with ILs, in situ free-radical polymerization of various vinyl monomers in ILs, sol-gel processing,

and the use of low-molecular-weight gelators and oligomeric electrolyte gelators.^[1] Ion gels have recently attracted considerable interest for their application in electrochemical devices, actuators, and gas-separation membranes.^[2–7] In practical applications, the high mechanical strength of ion gels is an indispensable property of this soft material. Development of tough ion gels with a large amount of ILs is a critical challenge for overcoming the limitations in practical applications.

In the past decade, great progresses have been achieved on developing high-strength and tough hydrogels based on different strategies,^[8–22] which in principle could be adopted to toughen “ion gels.”^[19,21,23–25] Among several tough hydrogels, the double-network (DN) hydrogels, consisting of brittle first network and ductile second network, show extraordinary high strength and toughness comparable to biological cartilages and industry rubbers.^[10,14] Extensive studies

on the mechanism of DN hydrogels have shown that the enhanced toughness of DN gels is due to the internal fracture of the brittle first network, which effectively dissipates energy and increases the resistance against the crack propagation.^[26–28] The ductile second network gives rise to the rupture of the first network over a large zone through their mutual entanglement. The studies on DN hydrogels suggest that introduction of any effective sacrificial bonds that rupture upon deformation will toughen the materials.^[15,17,22,29–33] Based on this concept, various structures of sacrificial bonds are used for toughening of hydrogels.^[31,32] One successful structure is using brittle microgel networks as sacrificial bonds to replace the brittle bulk network of the conventional DN hydrogels.^[30,34] This strategy could also be applicable to toughen ion gels. In this study, we adopted the DN strategy to create robust ion gels containing a large amount of ILs, in which inorganic component was used to form brittle physical network and organic component was used to form chemically crosslinked ductile network. The strategic approach for the development of the inorganic/organic DN ion gels involves the precise control of the microstructure of the brittle physical network of the inorganic component. To the best of our knowledge, this is the first report on the synthesis of robust DN ion gels composed of IL solvent and inorganic/organic networks.

We selected inorganic silica particles that form physical networks as the inorganic component and polydimethylacrylamide (PDMAAm) that has no strong adsorption to silica particles as

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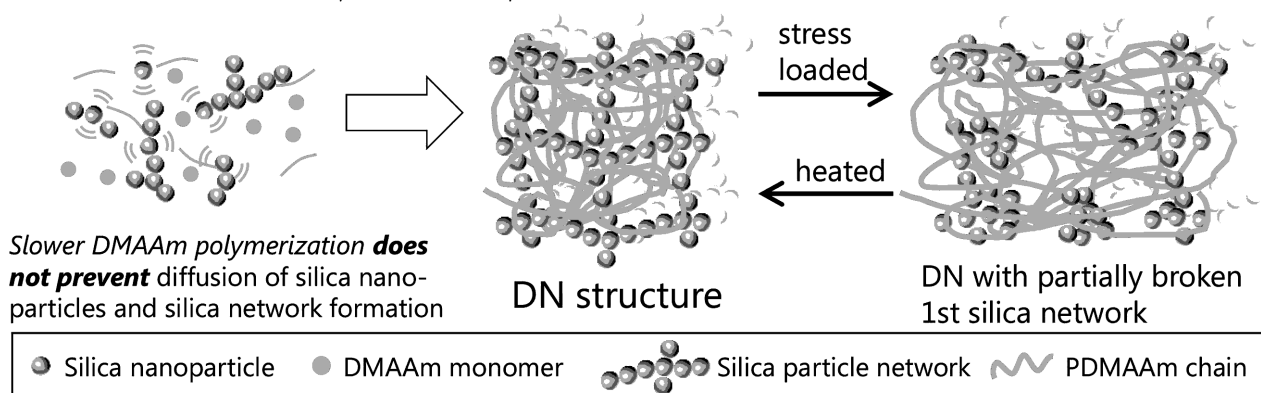
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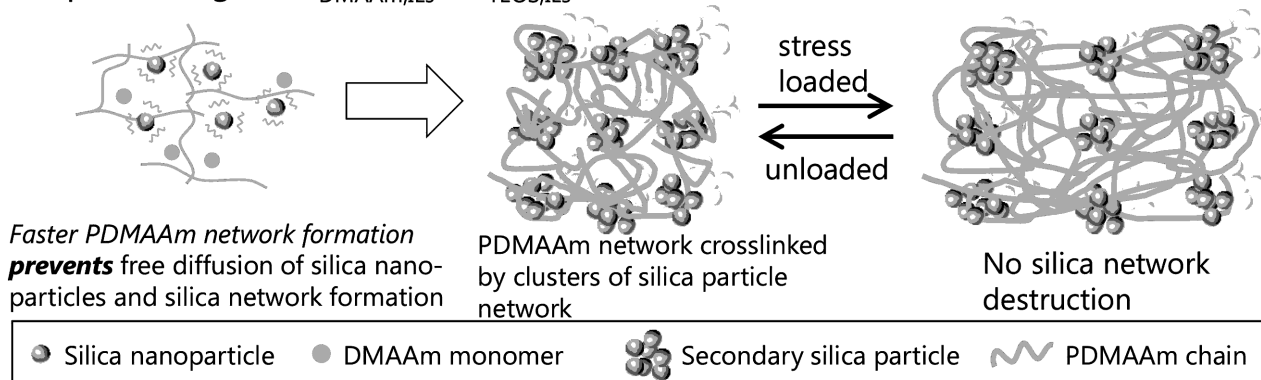
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(a) DN ion gels ; $r_{\text{TEOS,ILs}} > r_{\text{DMAAm,ILs}}$



(b) μ -DN ion gels ; $r_{\text{DMAAm,ILs}} > r_{\text{TEOS,ILs}}$



Scheme 1. Schematic illustrations of the concept of selective formation of inorganic/organic composite in an IL. a) When the silica particles are allowed to synthesize prior to the PDMAAm network, spatially continuous silica particle network is formed to obtain DN ion gels. b) When the PDMAAm network is synthesized prior to the silica particles, spatially dispersed clusters of silica particle network are formed to obtain μ -DN ion gels.

the organic component. The silica particles were formed via condensation polymerization of tetraethoxysilane (TEOS), and the chemically crosslinked PDMAAm network was formed via free-radical polymerization of dimethylacrylamide (DMAAm). Given their completely different reaction mechanisms, we can conduct the formations of the silica particle network and PDMAAm network independently in the same IL pot. Furthermore, we can easily manipulate the microstructure of the silica particle network by the reaction kinetics or formation order of the inorganic/organic components. As shown in **Scheme 1a**, when the formation of the silica particle network is faster than PDMAAm network propagation, the silica particles form continuous network structure, and the subsequent PDMAAm network propagation throughout the silica particle network enables formation of an inorganic/organic DN in an IL. The silica particles provide a rigid and fragile 3D inorganic framework originating from interparticle physical bonding among the silica particles in an IL,^[35,36] which is expected to effectively serve as the sacrificial first network for the toughening DN ion gel. On the other hand, when the PDMAAm network propagates prior to silica nanoparticles formation (Scheme 1b), the silica nanoparticles form spatially dispersed network clusters because the PDMAAm network induces a large diffusion

resistance to the silica nanoparticles. The network clusters of silica particles in such composite gels, as like the DN hydrogels consist of dispersed brittle microgels imbedded in the continuous ductile network, are also expected to make contribution to toughen the composite ion gels. In this work, we referred to the latter case as μ -DN ion gels.

We achieved the inorganic/organic composite network formation of different microstructure by two methods: one-pot/two-step and one-pot/one-step processes. The one-pot/two-step process involves a step-by-step sequential network formation in one pot, whereas the one-pot/one-step process involves in situ network formation in the same pot at the same time.

Figure 1 and Figures S1 and S2 (Supporting Information) show typical examples of the fabricated ion gels with an 80 wt% IL content synthesized with different methods. Through one-pot synthesis, the ion gels were easily and freely designed in different shapes, such as in the form of films, tubes, and fish-like shapes (Figure 1a–c; Figures S1 and S2c,d in the Supporting Information). The gelation could be performed in the same manner in hydrophilic 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF₄]) as well as hydrophobic 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Bmim][Tf₂N]) (the contents of ILs in the gels are listed in Table S1, Supporting

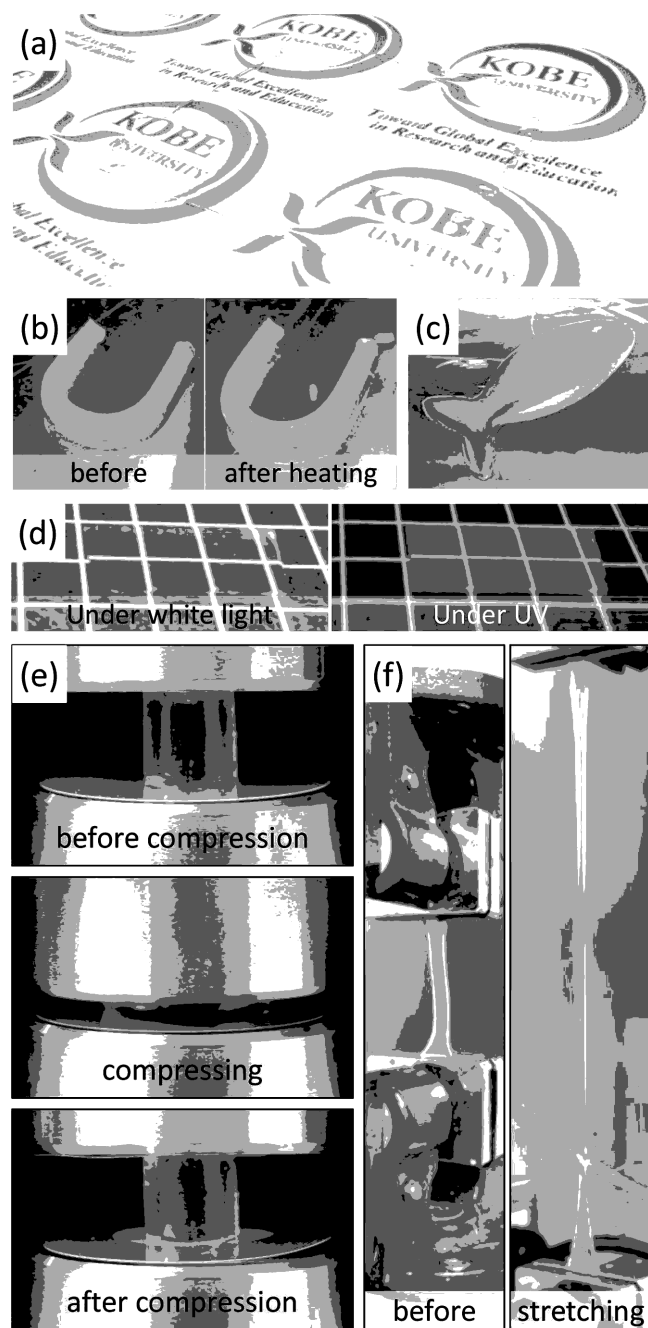


Figure 1. Photographs of the inorganic/organic DN ion gels demonstrating their free-shapeable property: a) a film, b) tubes, and c) a fish-shaped sample; unique properties based on the nature of ILs: b) thermal stability and d) photofluorescence by UV absorption; and exceptional mechanical strength exhibited on e) compression and f) stretching. The DN ion gels containing [Bmim][Tf₂N] (samples (a), (d), and (f)) and [Bmim][BF₄] (samples (b), (c), and (e)) were prepared using VA-086 at 353 K and AIBN at 333 K, respectively. The IL content in the gels was approximately 80 wt%. All samples were prepared via a one-pot/one-step process. DN ion gel samples prepared via one-pot/two-step process and μ -DN ion gels prepared via one-pot/one-step and one-pot/two-step processes are shown in Figures S1 and S2 (Supporting Information), respectively.

Information). The ion gels showed good thermal stability at elevated temperatures (Figure 1b and Figure S3, Supporting Information) and fluorescence under UV light (Figure 1d), which

are properties characteristic of ILs. The most important feature of the composite ion gels is their excellent mechanical strength. As shown in Figure 1e,f and Figures S4 and S5 (Supporting Information), both the inorganic/organic composite ion gels with DN and μ -DN structures withstood high-level deformation under compression and elongation, much higher than that of the SN ion gels.

To investigate the structure–property relationship, we first study the structures and mechanical properties of ion gels formed by the one-pot/two-step process that permits us to completely control the individual inorganic and organic network formation in the desired order, as expected from Scheme 1. The microstructures of the composite ion gels synthesized in [Bmim][Tf₂N] by different orders were studied by scanning probe microscopy observation. A network-like microstructure of silica particles was observed for the composite ion gels in which the silica nanoparticles were synthesized prior to the DMAAm polymerization, confirming the DN structure (Figure S6, Supporting Information). On the other hand, a dispersed silica particle structure was observed for the composite ion gels in which the DMAAm polymerization was performed prior to the silica nanoparticles formation, suggesting the μ -DN structure (Figure S6, Supporting Information). The network formation of silica nanoparticles in ILs was previously reported due to strong attractive interactions based on van der Waals force and interparticle hydrogen bonding,^[37] which was confirmed by shear thinning behavior of the silica SN ion gel (Figure S7, Supporting Information). The physical network formation of silica particles in the DN ion gel was further confirmed by the temperature dependence of the storage modulus of the DN ion gels, which decreased with increase in the temperature (Figure S8a, Supporting Information), owing to the weakening of the physical bonding between silica particles at the elevated temperature. On the other hand, as shown in Figure S8b (Supporting Information), the μ -DN ion gels show weak frequency dependence and no temperature dependence. Given the PDMAAm network has weak frequency dependence and negligible temperature dependence, as shown by Figure S8c (Supporting Information), these results show that in μ -DN ion gels, the silica particles are not in continuous phase, and the PDMAAm network dominates the modulus of the μ -DN ion gels. The frequency- and temperature-independent behaviors of the μ -DN ion gels also confirm that the silica particles have no physical adsorption to the PDMAAm chains. As a summary, DN ion gels were formed when the silica particle network was formed prior to the organic network, and the μ -DN gels were formed when the organic network was synthesized prior to the synthesis of silica particles.

Figure 2 shows the mechanical properties of the two types of ion gels with the different inorganic/organic networks synthesized in [Bmim][Tf₂N] by different orders. As shown in Figure 2a, the two sets of composite ion gels, regardless of their synthesis order of the inorganic and organic components, sustained a compressive stress of more than 28 MPa, which are substantially higher than their individual single-network (SN) ion gels (Figure 2b). As shown in Figure 2c, the two sets of composite ion gels exhibited tensile fracture stress and strain higher than those of the PDMAAm SN ion gel in [Bmim][Tf₂N]. It should be noted that the tensile properties of silica SN ion gels could not be measured because of their severe fragility.

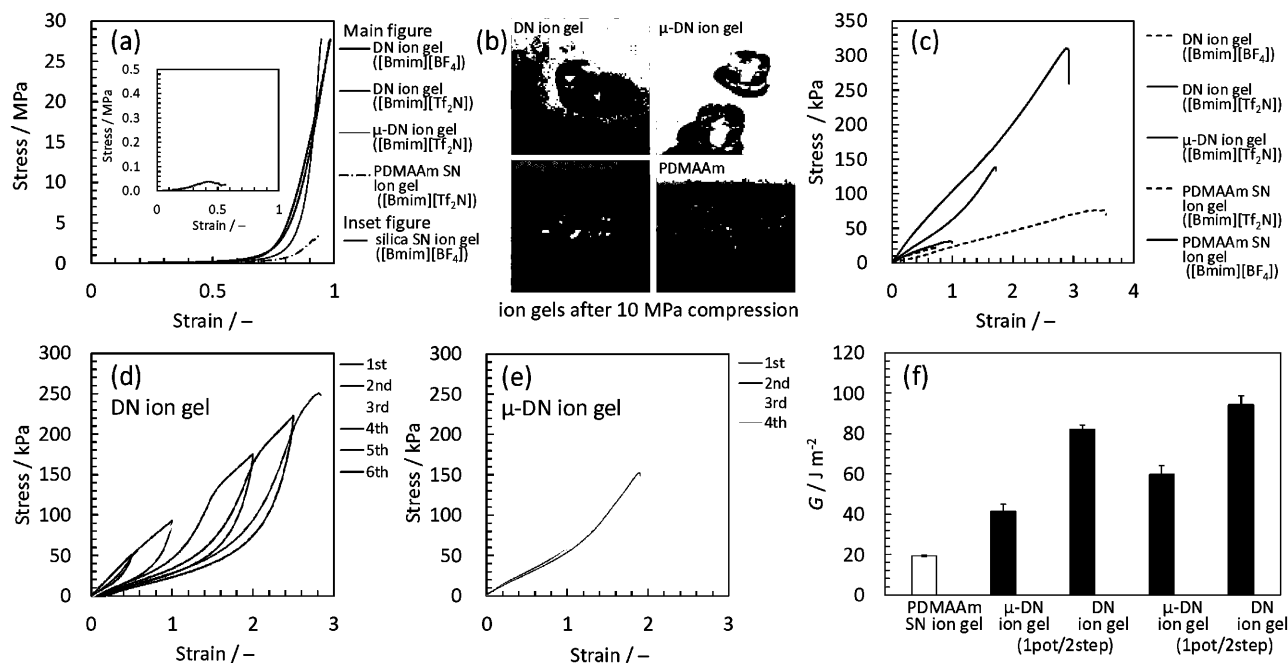


Figure 2. Mechanical properties of the silica/PDAAm composite ion gels with DN and μ -DN structures prepared via a one-pot/two-step process. a) Compressive stress–strain curves for the SN, DN, and μ -DN ion gels. b) Photographs demonstrating the brittleness of the silica SN and PDMAAm SN ion gels containing [Bmim][Tf₂N] and the robustness of the composite ion gels containing [Bmim][Tf₂N]. c) Tensile stress–strain curves of SN, DN, and μ -DN ion gels. Cyclic tensile behaviors of d) the DN and e) μ -DN ion gels containing approximately 80 wt% [Bmim][Tf₂N]. f) Tearing energy of ion gels.

Furthermore, the modulus and the tensile strength of the DN ion gel are higher than those of the μ -DN gels. DN ion gels prepared in the [Bmim][BF₄] also exhibited enhancement in fracture stress and strain than those of the PDMAAm SN ion gel, but the modulus of the DN in [Bmim][BF₄] was lower than that of DN ion gels in [Bmim][Tf₂N]. This result could be explained by [Bmim][BF₄]-based steric hindrance or solvation force.^[37] [Bmim][BF₄] could adsorb on the surface of silica particles and provided an effective repulsive barrier to weaken the interaction between the silica nanoparticles.^[37–39]

The enhanced mechanical strength of the composite ion gels is an expected result owing to the inorganic/organic DN structures.^[28] To confirm the occurrence of internal fracture of the brittle silica particle network by deformation, which is the feature of the DN mechanism, we performed the cyclic tests of the two sets of ion gels. The DN ion gels exhibited pronounced strain softening and mechanical hysteresis (Mullins effect),^[26] which increased with the increase of strain (Figure 2d). In addition, after being loaded to a strain 1.5, the unloaded DN ion gels showed approximately 10% residual strain. These results indicate the occurrence of the internal rupture of the brittle silica particle network in the DN ion gels.^[17] On the other hand, the μ -DN ion gels showed almost elastic behavior (Figure 2e), without residual strain. These results suggest that the μ -DN ion gels have dispersed silica cluster structure that hardly ruptured during the sample deformation,^[18] which is consistent with the observations that the μ -DN ion gels were not as strong as the DN ion gels.

In the DN ion gels, the brittle silica particle-based first network provided a “sacrificial bond” that easily ruptured, dissipated the loaded energy, and resulted in exceptional toughness.

The soft PDMAAm-based second network provided the “hidden length,” which connected the ruptured silica particle-based first networks to provide remarkable fracture strain and shared the applied force to give additional toughness.^[14,18] Consequently, the DN ion gels demonstrated high mechanical strength. The tensile fracture energy of the DN ion gel was 437 kJ m⁻³, which was calculated from the stress–strain curve in Figure 2c, was 23.4 times larger than that of the PDMAAm SN ion gel (18.7 kJ m⁻³). By the 5th elongation (strain 2.5), the energy dissipated by destruction of the silica particle network in the DN ion gel, which was calculated from the stress–strain curve in Figure 2d, was 141 kJ m⁻³, which was almost half of the applied energy (279 kJ m⁻³). Owing to the destruction of the silica particle network during deformation and dissipation of the loaded elastic energy at fracture, the fracture energy of the DN ion gel measured by tearing test (82.1 J m⁻²) was about four times that of the PDMAAm SN ion gel (20.0 J m⁻²), as shown in Figure 2f and Figure S9c (Supporting Information). Although the μ -DN ion gels showed no Mullins effect, their tensile fracture energy calculated from the tensile stress–strain curve in Figure 2e (102.1 kJ m⁻³) and the tearing energy measured from the tearing test shown in Figure 2f (41.5 J m⁻²) were also higher than those of PDMAAm SN ion gels (18.7 kJ m⁻³ and 19.3 J m⁻², respectively). Given the fact that the μ -DN ion gels were stronger than the PDMAAm SN ion gels, the dispersed silica particle cluster interpenetrated by PDMAAm chains might still play some role to disperse the load and dissipate energy, although they showed elastic behavior.^[8,28]

The above investigation on the ion gels prepared via a one-pot/two-step process clearly demonstrated that the formation order of the silica particle network and PDMAAm network determines

the inorganic/organic network structure and the mechanical property of the ion gels. Although the abovementioned kinds of composite ion gels were prepared via a two-step heating/UV process, they could be also selectively prepared via a two-step heating/heating process in principle. In fact, a DN ion gel with a pronounced softening behavior was prepared via primary heating for TEOS polycondensation at a low temperature followed by secondary heating at an elevated temperature for DMAAm polymerization using a thermal radical initiator with a high 10-hour half-life temperature (Figure S10, Supporting Information). The successful DN formation via the two-step heating/heating process suggests that the selective preparation of the composite ion gels could also be achieved via a one-pot/one-step process by selecting the gelation temperature to control the reaction order of TEOS polycondensation and radical polymerization of DMAAm. A simple one-pot/one-step process has significant advantages in the mass production of robust ion gels such as easy operation, a simple manufacturing setup, and fast production.

The selective preparation of the composite ion gels via a one-pot/one-step process was carried out at various temperatures with different radical initiators to change the propagation rates of the silica particle network and the PDMAAm network. Although the propagation rates of both inorganic/organic networks could be increased monotonically by increasing the temperatures, the order of the inorganic and organic network formation could be switched at a certain gelation temperature because of the different temperature dependence behaviors of the inorganic and organic network formation. In other words, the order of TEOS and DMAAm polymerization can be controlled by selecting an appropriate combination of the radical initiator and gelation temperature. To confirm the one-pot/one-step concept for the selective formation of the two kinds of composite ion gels, we prepared silica/PDMAAm ion gels using different radical initiators at various temperatures. For the radical initiators, we used azo initiators with different 10-hour half-time temperatures: 2,2'-azobis(isobutyronitrile) (AIBN, with a 10-hour half-life temperature $T_{1/2}$ of 338 K), 2,2'-azobis[2-(2-imidazolin-2-yl)propane] dihydrochloride (VA-044, with a $T_{1/2}$ of 317 K), and 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, with a $T_{1/2}$ of 303 K) were used for [Bmim][BF₄]; AIBN, 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086, with a $T_{1/2}$ of 359 K) and 2,2'-azobis[N-(2-propenyl)-2-methylpropionamide] (VF-096, with a $T_{1/2}$ of 369 K) were used for [Bmim][Tf₂N]. At the same gelation temperature, the network formation rate of PDMAAm using the initiator with a higher $T_{1/2}$ would be lower than that using one with a lower $T_{1/2}$. A PDMAAm network formation slower than the silica particle network formation leads to a DN ion gel. Therefore, it is expected that DN ion gels could be prepared at a higher temperature using an initiator with a higher $T_{1/2}$.

The ion gels prepared via a one-pot/one-step process are shown in Figure 1 and Figure S1a,b (Supporting Information). All the inorganic/organic composite ion gels prepared via a one-pot/one-step process showed good thermal stability (Figure S3e,f, Supporting Information) and high mechanical strength (Figures S4e,f and S5e,f, Supporting Information). The ion gels could sustain more than 28 MPa of compressive fracture stress (Figure S11a, Supporting Information) and exhibited higher tensile fracture stress and fracture energy than the SN ion gels did (Figures S6d and S11b, Supporting Information).

The compressive and tensile fracture stresses were almost same as those of the ion gels prepared via the one-pot/two-step process. In addition, as expected, by controlling the rates of the network propagation using various radical initiators at certain temperatures, two kinds of ion gels could be selectively prepared via the one-pot/one-step process. The DN ion gels were prepared using VA-086 at 349 K and AIBN at a temperature lower than 317 K for [Bmim][Tf₂N] (Figure 3a; Figure S12a–d, Supporting Information), respectively) and VA-044 at 313 K and AIBN at 323 and 333 K for [Bmim][BF₄] (Figure S13b–d, Supporting Information). They exhibited clear hysteresis and pronounced softening behavior in the cyclic stress–strain curves, which indicated the DN structure for the ion gels obtained. The DN ion gels demonstrated permanent deformation after unloading the stress (Figure S11c, Supporting Information). They showed clear temperature dependence of the storage modulus (Figure S14a, Supporting Information), which constituted additional evidence supporting the formation of an inorganic/organic DN in the ion gel. In contrast, μ -DN ion gels were prepared using AIBN at a temperature higher than 318 K for [Bmim][Tf₂N] and V-70 at 303 K for [Bmim][BF₄]. They showed negligible softening behavior (Figure 3b; Figures S12e,f and S13a, Supporting Information) and no residual strain. Furthermore, the storage modulus of the μ -DN ion gels did not exhibit a clear temperature dependence (Figure S14b, Supporting Information). This observation was the same as what was noted for the μ -DN ion gels prepared via a one-pot/two-step process.

The abovementioned results confirmed that the concepts proposed in Scheme 1 could be adopted for a one-pot/one-step process, as well. According to the concept, selective ion gel preparation could be performed by controlling the formation rates of the inorganic and organic networks by simply controlling the gelation temperature. As shown in Figure S12a–f (Supporting Information), the cyclic stress–strain curves for the ion gels prepared using AIBN at various temperatures clearly demonstrated that the softening behavior disappeared at 318 K. The ion gels prepared at temperatures lower than 316 K showed a high Young's modulus (≈ 120 kPa), whereas those prepared at temperatures higher than 318 K showed a low value (≈ 60 kPa). A comparison of the Young's moduli of the ion gels prepared via the one-pot/one-step and one-pot/two-step processes is shown in Figure S12i (Supporting Information). The Young's moduli of the DN ion gels prepared via the one-pot/one-step process at temperatures under 316 K were almost the same as those prepared via the one-pot/two-step method. This result indicated that a silica particle network was formed even in the DN ion gel prepared via the one-pot/one-step at low temperatures. The Young's modulus of the ion gel prepared at 317 K (74.2 kPa) was between those of the DN ion gels and μ -DN ion gels, which suggested that a partially propagated silica particle network was formed in the ion gel. These results implied that the structure of the inorganic/organic composite network changed at around 318 K. In other words, the formation order of the silica particle network and PDMAAm network could be switched at around 318 K.

In order to confirm the above hypothesis, we measured the time required for the completion of each network formation

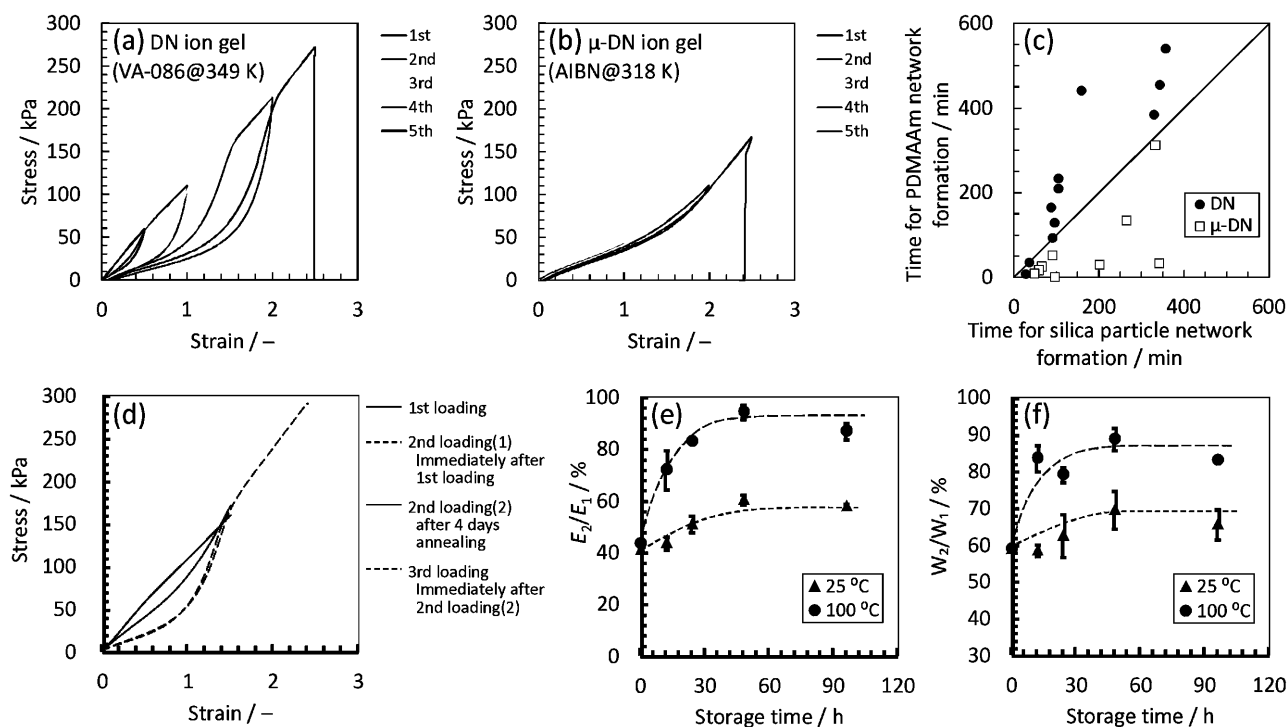


Figure 3. Cyclic tensile stress–strain curves of DN (a) and μ -DN (b) ion gels containing [Bmim][Tf₂N] prepared via a one-pot/one-step process. c) Relationship between the network formation times of PDMAAm and silica particle. The filled circles and unfilled squares represent, respectively, the composite ion gels with DN and μ -DN structures, determined from the S–S curves of the cyclic tensile test. Detailed data are provided in Table S2 in the Supporting Information. Healing properties of the DN ion gel sample shown in (a). d) Stress–strain curves of the original sample (first loading; black solid curve), that of the sample immediately after first loading (second loading (1); black broken curve), that of the sample after storage of the 1st loaded sample for 4 d at 373 K (second loading (2); red solid curve), and that of the sample immediately after second loading (2) (third loading; red broken curve). Recovery of elastic modulus (e) and work of extension (f) of the DN ion gel stored for different durations at different temperatures. In all ion gels, the IL content was approximately 80 wt%.

from rheology measurements during network formation at various temperatures. Figure S15 (Supporting Information) shows the typical results of the time dependence of the storage modulus during gel network formation. For PDMAAm network, it can be confirmed that the network was formed when the storage modulus became higher than the loss modulus. Therefore, the times required for the PDMAAm network formation were determined from the results shown in Figures S16–S19 (Supporting Information) and plotted against the gelation temperature in Figure S20 (Supporting Information). In Figure S20 (Supporting Information), the times required for silica particle network formation, determined from the time at a value of 0.15 for normalized G' in Figure S16 (Supporting Information), were also plotted (the reason why the time at normalized $G' = 0.15$ was considered is explained in the Supporting Information). Because the reciprocals of the network formation time could be considered as the apparent network formation rates, they were plotted against the temperature according to the Arrhenius relationship (Figure S21, Supporting Information).^[40,41] The solid and broken lines in Figure S20 (Supporting Information) represent the calculated values for each network formation using the apparent Arrhenius parameters determined from Figure S21 in the Supporting Information. Thus, we can predict and evaluate the times required for silica particle network formation and PDMAAm network formation at a certain temperature. In Table S2 (Supporting Information), the

times predicted for each network formation have been listed. They have also been plotted in Figure 3c using experimental data determined from cyclic tensile stress–strain measurements. Based on the order proposed for the specific inorganic/organic composite network formation (Scheme 1), as shown in Table S2 (Supporting Information) and Figure 3c, the types of the ion gels were clearly divided into composite ion gels with and without the global DN structure. Even in the one-pot/one-step process, we can selectively prepare two kinds of robust ion gels with different mechanical properties simply by changing the gelation temperature to control the network formation order.

It is worth mentioning that the developed DN ion gel has another excellent property: the self-healing of the inorganic/organic DN formed in the IL. It is well recognized that softening of conventional DN hydrogels after permanent deformation of the first network is a serious drawback in some practical applications.^[31] In principle, it is unavoidable because the exceptional toughness of DN gels is realized by the energy dissipation owing to the destruction of the covalent bond in the first network. Therefore, several efforts have been made to realize DN gels with a recoverable first network.^[17,22,31] One of the straightforward strategies in achieving this is the utilization of physical crosslinking for the formation of the first network.^[22,31] The designed DN ion gels in this work had a physically crosslinkable silica particle-based first network. Owing to the benefits of the physical first network crosslinking, our DN ion

gels exhibited network healing property (Figure 3d–f and Figure S22 (Supporting Information) for the DN ions prepared via one-pot/one-step and one-pot/two-step processes, respectively). The extents of recovery of the Young's modulus (E_2/E_1) and the toughness (W_2/W_1) were defined by the ratios of their values for the second and first loadings. As shown in Figure 3d, the DN ion gel showed obvious softening behavior after stretching. The softening was recovered to some extent by storing the DN ion gel at room temperature for 48 h after stretching (Figure 3e,f). Furthermore, once the sample was annealed in an oven at 373 K, the Young's modulus and the toughness were recovered to a greater extent; i.e., the E_2/E_1 and W_2/W_1 were approximately 90% and 85%, respectively, after annealing for 48 h. These results suggest that the internal damage in the DN ion gel healed considerably by annealing. Furthermore, the annealed sample again showed a hysteresis and softening behavior after re-loading the tensile stress (Figure 3d), which strongly suggests that the first silica particle network of the DN ion gel was reformed by the annealing.

The network reforming properties of the DN ion gels would result from the specific nature of both the silica and PDMAAm networks. The mechanism could be explained as follows. When a large stress was applied to the DN ion gel, the silica particle network broke into small clusters. When the stress was unloaded, the shape of the DN ion gel was recovered to some extent owing to the elasticity of PDMAAm, but it was not fully recovered because the formed silica particle network clusters could not be packed in the original density. The small spaces among the clusters resulted in the macrodeformation of the gel. Under ambient temperature conditions, the silica clusters would maintain their deformed shape and restrict the refolding of the PDMAAm network. Moreover, the intercluster connection via the physical bonding between the silica clusters would be formed at only very few positions and could hardly contribute to the energy dissipation in the second stress loading. As a result, the elastic moduli of the DN ion gels stored at room temperature for 96 h recovered to some extent (Figure 3e) and the pronounced softening remained. However, when the DN ion gel was kept in an elevated temperature environment after the first stress loading, the hydrogen bonding and van der Waals attraction between the silica nanoparticles weakened. In this situation, the silica nanoparticles would become free from the physical bonding and would no longer restrict the refolding of the PDMAAm network. As a result, the packing of the first network slowly recovered. When the DN ion gel was cooled again after annealing, the hydrogen bonding and van der Waals interaction would be recovered between neighboring silica nanoparticles. Owing to the recovered physical interactions, the silica particle network was reformed and the Young's modulus as well as the toughness was recovered.

In summary, we have fabricated a new class of robust ion gels containing a large amount of ILs. We present four novel and attractive findings from the formation of the specific inorganic/organic network in ILs. (1) Two kinds of robust ion gels can be prepared by forming an inorganic/organic composite network in an IL. (2) An inorganic/organic DN could be synthesized in a controllable manner via not only a two-step method but also a one-step process in one pot. (3) A brittle inorganic silica particle network is useful as the first network in the DN ion gels and

dissipates loaded energy to give a higher fracture energy than that of ion gels without a global inorganic/organic DN structure. (4) The physically bonded silica particle network imparts self-healing property to the DN ion gels. Both hydrophobic and hydrophilic ILs can be retained in the silica/PDMAAm composite network. The one-pot preparation methods developed are simple and allow forming free-shapeable robust ion gels. The fabricated DN ion gels, constituting a specific kind of inorganic/organic composite ion gels, exhibited excellent mechanical strength, good thermal stability, and self-healing property. The distinctive properties and simple preparation of the robust ion gels make them applicable in various devices such as electrochemical devices, actuators, and gas separation membranes. We believe that these robust ion gels have high potential for use in these applications, and new areas of application might open up for this class of materials.

Experimental Section

Experimental details are provided in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

double network, inorganic/organic composites, ionic liquids, robust gels, selective network formation

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