Highly stretchable and self-healable polymer gels from physical entanglements of ultrahigh–molecular weight polymers

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Highly stretchable and self-healable polymer gels formed solely by physical entanglements of ultrahigh–molecular weight (UHMW) polymers were fabricated through a facile one-step process. Radical polymerization of vinyl monomers in ionic liquids under very low initiator concentration conditions produced UHMW polymers of more than 10^6 g/mol with nearly 100% yield, resulting in the formation of physically entangled transparent polymer gels. The UHMW gels showed excellent properties, such as high stretchability, high ionic conductivity, and recyclability. Furthermore, the UHMW gel exhibited room temperature self-healing ability without any external stimuli. The tensile experiments and molecular dynamics simulations indicate that the nonequilibrium state of the fractured surfaces and microscopic interactions between the polymer chains and solvents play a vital role in the self-healing ability. This study provides a physical approach for fabricating stretchable and self-healing polymer gels based on UHMW polymers.

INTRODUCTION

Polymer gels have a three-dimensional (3D) network structure that swells upon absorbing solvents. Because of their high solvent absorbance properties, polymer gels have been applied in various fields, such as biomedical engineering and electronics (1–7). In conventional polymer gels, copolymerization of monomers and multifunctional cross-linkers permanently cross-link the polymer chains to form a 3D network. However, conventional polymer gels are generally brittle and have low mechanical strength because of stress localization under mechanical loading caused by the immobilized inhomogeneous cross-linking points (8). To address this problem, extensive research on introducing reversible bonds, such as noncovalent bonds and dynamic covalent bonds, into the polymer gel network has been conducted. The introduction of reversible bonds can enhance the mechanical properties of the polymer gels through an energy dissipation function associated with the cleavage of the cross-linking points and a self-healing function imparted by the reformation of the reversible cross-linking points (9–16).

The topological effect is another promising approach for the molecular design of polymer networks to yield mechanically tough polymer gels. Recently, polymer gel structures that judiciously use topological constraints have been proposed. For example, slide-ring gels developed by Ito and co-workers realized movable cross-linking points by chemically connecting the ring molecules of polyrotaxane chains (17–19). Under deformation, the cross-linking points can slide along the axis polymer, thereby suppressing the stress localization. More recently, the seminal work by Miyata and colleagues demonstrated that tough hydrogels formed by abundant physical entanglement could be prepared by optimizing the monomer concentration and the chemical cross-linker concentration (20). Suo and co-workers also reported tough hydrogels in which polymer entanglement outnumbered the chemical cross-linking points (21).

In this study, we developed stretchable and self-healable polymer gels that are formed solely by the physical entanglement of ultrahigh–molecular weight (UHMW) polymers, that is, UHMW gels. We found that the radical polymerization of vinyl monomers using ionic liquids (ILs) as a solvent yielded a monomer conversion of almost 100% even at extremely low initiator concentrations. As the polymerization proceeded, transparent polymer gels were formed in situ solely by the physical entanglements of the UHMW polymers (>10^6 g/mol); this was considered as a class of gel polymerization (Fig. 1) (22, 23). Owing to the entanglement of the UHMW polymer chains, the UHMW gels exhibit superior mechanical properties, such as high extensibility, compressibility, and self-standing stability. In addition, as there is no chemical cross-linker, the UHMW gel can be easily recycled by the hot pressing process. The UHMW gel also showed excellent self-healing properties at room temperature due to the reformation of the polymer entanglements across the damaged interfaces. Although there is a report on self-healing hydrogels that used entanglement of dangling chains, the mechanical properties were sacrificed as the gelation needed to be controlled near the sol-gel transition point to express the self-healing ability (24, 25). Furthermore, tensile experiments and molecular dynamics (MD) simulations indicated that the polymer-solvent interactions play a crucial role in the self-healing ability of the UHMW gels. The present strategy enables the fabrication of polymer gels with excellent mechanical properties by a simple one-step method without using specially synthesized functional groups and is expected to have a wide range of applications, such as electrolytes for flexible and wearable devices.
RESULTS

Synthesis of UHMW gels by in situ radical polymerization

ILs have been extensively studied as media for various chemical reactions. Although it is known that free-radical polymerization in ILs leads to a higher molecular weight compared to that in common organic solvents (26–29), research focus has been limited to living radical polymerization (30). Here, we demonstrate that by extremely reducing the amount of the radical initiator, UHMW polymers can be obtained via in situ free-radical polymerization of vinyl monomers in ILs without compromising monomer conversion. Although the definition of “UHMW” varies in the literature, in this study, polymers with number-average molecular weights ($M_n$) exceeding $10^6$ g/mol are defined as UHMW polymers according to much of the literature (23, 31, 32). Figure 2A shows the relationship between the initiator [2,2'-azobis(isobutyronitrile) (AIBN)] amount ($c_{\text{AIBN}}$) and $M_n$ for the free-radical polymerization of methyl methacrylate (MMA) in a conventional IL, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([C$_2$mIm][TFSI]), and an organic solvent, toluene. Gel permeation chromatography (GPC) curves, nuclear magnetic resonance (NMR) spectra, and a summary of the polymerization are described in the Supplementary Materials (figs. S1 and S2 and table S1). For the MMA-toluene system, the monomer conversion notably decreased with decreasing $c_{\text{AIBN}}$, and $M_n$ did not reach the UHMW range (>10$^6$ g/mol). On the other hand, in the case of the MMA-IL system, a high monomer conversion (>99%) was maintained even at a very low $c_{\text{AIBN}}$ (<1 mM), and UHMW PMMA (>10$^6$ g/mol) was obtained. The polymerization products with the low $c_{\text{AIBN}}$ formed transparent gels because of the physical entanglement of the UHMW PMMA chains (Fig. 2B). In general, high-molecular weight polymers in radical polymerization can be ascribed to the (i) stabilization of the propagation radicals to lower activation energy and (ii) slow termination rate derived from high viscosity, the so-called Trommsdorff effect (33, 34). To validate these assumptions, free-radical polymerization of MMA was carried out in a series of ILs with different viscosities and corresponding toluene systems with controlled viscosities as the reaction media; the viscosities of toluene were controlled by dissolving different concentrations of commercial PMMA ($M_w$ = 1.5 x 10$^4$ g/mol). As shown in Fig. 2C, the $M_n$ for the IL system slightly increased with an increase in the viscosity of the ILs (i.e., [C$_2$mIm][NFSI] > [C$_2$mIm][BETI] > [C$_2$mIm][TFSI]) [NFSI, bis(nonafluorobutanesulfonyl)imide; BETI, bis(pentafluoroethanesulfonyl)imide]; however, the difference is not substantial. In addition, there is almost no correlation between the viscosity and $M_n$ for the viscosity-controlled toluene systems. Furthermore, their $M_n$ values are much lower than those of the MMA-IL systems. These results imply that the high $M_n$ and high monomer conversion for the IL systems are derived not from the high viscosity of the ILs but from the stabilization of the propagation radicals in the IL systems. The relationship between the monomer concentration and the resultant $M_n$ in [C$_2$mIm][TFSI] is shown in Fig. 2D. The maximum $M_n$ value was obtained at a concentration of approximately 30 weight % (wt %) of monomer content, which exceeded the value obtained by bulk polymerization; this is indicative of the acceleration effect of the ILs that generates the higher-molecular weight polymers. As another fabrication strategy, by taking advantage of the nonvolatility of ILs, it was investigated to prepare the UHMW PMMA/[C$_2$mIm][TFSI] gel by using a commercially available UHMW PMMA through the cosolvent method (15). However, in the case of UHMW PMMA, it is difficult to prepare homogeneous UHMW PMMA/[C$_2$mIm][TFSI] gels because during
the evaporation of the cosolvent, inhomogeneous precipitation of the polymer and the IL occurred. Therefore, the one-step fabrication strategy presented here is the superior methodology to prepare the homogeneous UHMW gels without using volatile organic solvents.

**Physicochemical characterization of UHMW gels**

Notably, owing to the extremely high monomer conversion, the UHMW gel formed by the in situ polymerization can be used without further purification. Temperature sweep measurements of the storage ($G'$) and loss moduli ($G''$) for the PMMA/[C2mIm][TFSI] systems with various molecular weights of PMMA at a polymer concentration of 30 wt % are shown in Fig. 3A. The UHMW gel based on UHMW PMMA (1740 kDa) maintained a gel state (i.e., $G' > G''$) over a wide temperature range despite the absence of a chemical cross-linker. This could be attributed to the large number of transient physical cross-links due to the high entanglement density of the UHMW polymer chains. On the other hand, the crossover of $G'$ and $G''$ was observed for the 175-kDa PMMA/[C2mIm][TFSI] system at approximately 70°C, indicating the existence of a gel-to-sol transition at high temperatures. The 41-kDa PMMA/[C2mIm][TFSI] system exhibited liquid-like behavior ($G' < G''$) for all temperature ranges. Figure S3 shows the temperature dependence of tan δ. Compared to the 41- and 175-kDa PMMA/[C2mIm][TFSI] systems, the 1740-kDa UHMW PMMA/[C2mIm][TFSI] gel showed a tan δ value much lower than 1. Thus, for the 1740-kDa UHMW PMMA/[C2mIm][TFSI] gel, the solid-like integrity is maintained for all temperature range, and energy dissipation is notably lower than that in the 41- and 175-kDa PMMA/[C2mIm][TFSI] systems. The frequency sweep data also show that the crossover was not observed over the frequency range of 0.1 to 100 rad s$^{-1}$ at a high temperature of 120°C (fig. S4). Time-temperature superposition (TTS) master curves of $G'$, $G''$, and tan δ were constructed at a reference temperature of 10°C (fig. S5). Consistent with the temperature sweep measurements, the UHMW gel showed a substantially wider rubbery plateau compared to the PMMA/[C2mIm][TFSI] systems with moderate molecular weights (35), and the crossover of $G'$ and $G''$ was not observed over the entire frequency range. The 175-kDa PMMA/[C2mIm][TFSI] system exhibits a narrower rubbery plateau and terminal flow behavior ($G' \propto \omega^2$ and $G'' \propto \omega$) in the low-frequency region, indicating that it behaves as a liquid over a long time scale. The 41-kDa PMMA/[C2mIm][TFSI] system shows $G' < G''$; thus, tan(δ) > 1 over the entire frequency range. Consistent with the rheological properties, the UHMW PMMA/[C2mIm][TFSI] gel exhibited superior long-term shape stability (Fig. 3B), and the integrity of...
its shape was maintained even after 1 week; in contrast, the 175-kDa PMMA/[C$_2$Im][TFSI] systems showed large flow deformation. The UHMW gel also exhibited good shape stability at a high temperature of 120°C.

The microscopic polymer dynamics in the gel were evaluated using software-based dynamic light scattering (DLS) measurements that record both the temporal variation of the scattered light intensity and its time correlation function (36). Figure 3C shows the temporal variation of the scattered light intensity for the 41-kDa PMMA/[C$_2$Im][TFSI] solution and the UHMW PMMA/[C$_2$Im][TFSI] gel (1740 kDa). It was observed that the absolute scattered light intensity from the UHMW gel was approximately one order of magnitude smaller than that of the 41-kDa PMMA/[C$_2$Im][TFSI] solution. This suggests the formation of a homogeneous network in the UHMW gel by dynamic optimization of the network structure through transient physical cross-links. In addition, a fluctuation of the scattered light intensity over a long time scale was observed for the 41-kDa PMMA/[C$_2$Im][TFSI] solution, whereas the UHMW gel showed minimal scattering fluctuations. This indicates that the diffusion of the polymer aggregates was restricted by the high entanglement density of the UHMW polymers. The time correlation functions of the scattered light intensity also suggest that there is no long–time scale (~1-s) relaxation for the UHMW PMMA/[C$_2$Im][TFSI] gel, whereas the 41-kDa PMMA/[C$_2$Im][TFSI] solution showed a long–time scale relaxation mode (fig. S6). In the case of the 41-kDa PMMA/[C$_2$Im][TFSI] solution, the number of cross-links made from entanglements is not enough to construct a robust 3D network. As a result, a part of PMMA aggregates can move freely in the network, which is detected as short–time scale relaxation in the time correlation function of the scattered light intensity. In contrast, the UHMW PMMA/[C$_2$Im][TFSI] gel is robust enough to trap all of the PMMA polymers in the network. In this case, the detected fluctuation of the scattered light intensity originates from only the restricted fluctuations of polymers between cross-linking points, which is detected as short–time scale relaxation, similar to the conventional polymer gels (37). Therefore, the lack of long–time scale relaxation for the DLS result implies the formation of a robust 3D network that is consistent with the temporal variation of the scattered light intensity shown in Fig. 3C.

**Mechanical properties and self-healing behavior of UHMW gels**

Despite the absence of chemical cross-linking, the UHMW gel exhibited excellent stretchability and toughness because the high density of the entangled chains behaved as transient physical cross-links. Figure 4A shows the tensile stress–strain curves of the UHMW gels and a conventional gel of comparable Young’s modulus that contained a chemical cross-linker. The UHMW gel exhibited a high fracture stress and strain of 0.12 MPa and 570%, respectively. Comparison of stress–strain curves for PMMA/[C$_2$Im][TFSI] systems with different molecular weights of PMMA is shown in fig. S7. Moreover, fig. S8 shows cyclic tensile stress–strain curves for the UHMW PMMA/[C$_2$Im][TFSI] gel and PMMA/[C$_2$Im][TFSI] systems with lower–molecular weight PMMA. Hysteresis observed in the UHMW PMMA/[C$_2$Im][TFSI] gel could be attributed to energy dissipation resulting from the relaxation of physical entanglement between UHMW polymers. The residual strain gradually increases with cyclic testing, indicating the disentanglement of the polymer chains. However, the hysteresis and residual strain of the UHMW gel are notably low compared to that of the lower–molecular weight PMMA/[C$_2$Im][TFSI] systems, suggesting that the disentanglement of polymer chains during the cyclic tensile testing is greatly suppressed for the UHMW PMMA/[C$_2$Im][TFSI] gel. The UHMW gel also showed excellent compressive strength with a fracture stress of more than 100 MPa (fig. S9 and movies S1 and S2). Owing to the negligible volatility of the ILs (fig. S10) and the absence of covalent bonding in the gel network, recycling of the UHMW gel was also possible by the facile hot pressing process (fig. S11). The stress–strain curve of the UHMW gel remained unchanged before and after reprocessing, indicating that neither the degradation of the polymer nor the evaporation of the solvent occurred during the recycling process (Fig. 4A). Figure S12 shows the effect of the repeated recycling process on the tensile properties of the UHMW gel; nearly identical stress–strain curves and toughness were maintained up to 10 recycling cycles. Furthermore, as the UHMW polymers can be polymerized in situ in various types of ILs, the physical properties of the UHMW gels can be largely modulated by selecting a suitable combination of monomer and IL chemical structures (Fig. 4B and fig. S13). In general, to control the mechanical properties of polymer gels, the molecular design...
of polymer networks has been extensively investigated (8, 39–41). In contrast, in this system, the mechanical properties can be easily and effectively modulated by the molecular design of the solvent. The UHMW PMMA/[C$_2$mIm][TFSI] gel exhibited outstanding self-healing capabilities. Upon cutting the gel sheet into two pieces and then immediately bringing them into contact, spontaneous self-healing behavior was observed under ambient conditions without applying any external stimuli (Fig. 4C). The self-healing efficiency was evaluated by tensile testing the UHMW gel with different healing times. With increasing healing time, the tensile strength gradually recovered, and the stress–strain curve and toughness of the healed gel after 6 hours were almost the same as those of the pristine sample (Fig. 4D and fig. S14). This indicates that the entanglements of the PMMA chains reformed across the cut surface during the healing process. The speed of healing is faster for lower–molecular weight PMMA/[C$_2$mIm][TFSI] systems; however, the mechanical properties were greatly deteriorated (fig. S15). Furthermore, by exploiting the mechanical robustness of the UHMW gel at high temperature (Fig. 3, A and B), the self-healing rate can be accelerated by conducting the healing process at elevated temperatures (fig. S16). In addition to its superior mechanical properties, the UHMW gel exhibited good electrochemical properties, such as an ionic conductivity of 0.23 mS cm$^{-1}$ at 25°C, which can be attributed to the high IL content (fig. S17). The Nyquist plots showing the impedance spectra of the stretched and unstretched UHMW gels before and after self-healing suggest that the electrochemical properties were also recovered after the self-healing process, rendering the UHMW gel as a promising stretchable electrolyte for flexible/wearable devices (Fig. 4E).

DISCUSSION
As demonstrated above, the UHMW PMMA/[C$_2$mIm][TFSI] gel exhibited self-healing ability at room temperature within 6 hours, although the gel was formed by the physical entanglement of the UHMW polymers with a long relaxation time; the crossover point of $G'$ and $G''$ was much larger than 10$^5$ s (~28 hours) (fig. S5a). Notably, when the cut samples were brought into contact after some
waiting time, the healing efficiency decreased with longer waiting times (Fig. 5A), although complete healing was also achieved for the sample with a waiting time of 72 hours by extending the healing time to 24 hours (fig. S18). These results indicate that the waiting time has an influence to decelerate the speed of the self-healing process. This phenomenon was also observed for self-healing supramolecular polymers (42, 43) and the crack healing of glassy polymers (44, 45). In the case of the self-healing supramolecular polymers, the ratio of nonassociated free stickers at the cut surfaces decreased with longer delays, leading to a deteriorated self-healing efficiency. This suggests that, immediately after cutting, a large number of the UHMW PMMA chains at the cut surfaces are in a nonequilibrium disentangled state, which more rapidly reform entanglements than two equilibrated surfaces (Fig. 5B).

Furthermore, it was revealed that the chemical structure of the polymer chain greatly affects the self-healing efficiency of the UHMW gel. The tensile properties before and after the self-healing process were compared for UHMW PMMA/[C$_{2mIm}$][TFSI] and poly(ethyl methacrylate) (PEMA)/[C$_{2mIm}$][TFSI] gels (Fig. 5C). PEMA is also compatible with [C$_{2mIm}$][TFSI], and the glass transition temperature ($T_g$) of the UHMW PEMA/[C$_{2mIm}$][TFSI] gel ($T_g = -74^\circ$C) was lower than that of the UHMW PMMA/[C$_{2mIm}$][TFSI] gel ($T_g = -71^\circ$C) (fig. S19), suggesting that the PEMA polymer chains were more mobile in the IL at the same temperature because of the large free volume. Nevertheless, the UHMW gel with PEMA showed a poor self-healing efficiency of approximately 50% than that with PMMA (Fig. 5C). This implies that the self-healing behavior of the UHMW gels is affected not only by the $T_g$ but also by the microscopic interactions between the solvent molecules and polymer chains.

Thus, the solvation structures of PMMA and PEMA (20-mer) in [C$_{2mIm}$][TFSI] were analyzed by MD simulations, and the difference in the self-healing behavior is discussed from the perspective of the solvation structures and polymer conformation. The MD simulations were carried out in the isobaric-isothermal (NTP) ensemble, and the radial distribution function [$G_{\text{total}}(r)$] was calculated from the trajectory obtained from the MD calculations (fig. S20). $G_{\text{total}}(r)$ is separated into intramolecular [$G_{\text{intra}}(r)$] and intermolecular [$G_{\text{inter}}(r)$] contributions, and $G_{\text{inter}}(r)$ can be further divided into partial functions of (i) polymer-cation [$G_{\text{poly–cation}}(r)$], (ii) polymer-anion [$G_{\text{poly–anion}}(r)$], and (iii) cation-anion [$G_{\text{cation–anion}}(r)$] interactions. The extracted $G_{\text{poly–cation}}(r)$ and $G_{\text{poly–anion}}(r)$ of the PMMA/[C$_{2mIm}$][TFSI] and PEMA/[C$_{2mIm}$][TFSI] systems are shown in fig. S21. Atom-atom contribution for $G_{\text{poly–cation}}(r)$ and $G_{\text{poly–anion}}(r)$ indicates that the C$_{2mIm}$ cations were in the first solvation zone and the TFSI anions were in the second solvation zone of PMMA and PEMA (fig. S22). The atom-atom pair correlation function between the oxygen atom of the methacrylate polymers and the proton atoms of the imidazolium cations shows that the height of the nearest peak of ~2.5 Å for C$_{2mIm}$-PMMA is larger than that for C$_{2mIm}$-PEMA (Fig. 5, D and E). This implies that PMMA is better solvated by the C$_{2mIm}$ cations than PEMA. Consistent with this
result, the intramolecular radial distribution function $G_{\text{intra}}(r)$ for PEMA has a narrower peak than that for PMMA, suggesting that PHEMA adopts a more extended conformation in [C$_2$mIm][TFSI] (fig. S23). Consequently, the calculated radius of gyration ($R_g$) for PMMA is larger than that for PEMA (Fig. 5F). Furthermore, intermolecular contribution of the radial distribution function $G_{\text{Poly-Poly}}(r)$ revealed that different polymer chains are located in more proximity for the PMMA/[C$_2$mIm][TFSI] system than for the PEMA/[C$_2$mIm][TFSI] system (fig. S24). These results indicate that the interfacial entanglement is more likely to occur for the UHMW PMMA/[C$_2$mIm][TFSI] gel than the UHMW PEMA/[C$_2$mIm][TFSI] gel. Therefore, microscopic polymer-solvent interactions seem to play a crucial role in the self-healing capability of the UHMW gels. However, note that in these MD calculations, the polymerization degree is 20, which is much lower than that of UHMW polymers. Although it is expected that the microscopic solvation structure of polymers and ILs is not largely dependent on the polymerization degree, the large-scale MD calculations at polymerization degree over the entanglement molecular weight are currently underway.

In summary, stretchable and self-healing polymer gels based on a facile one-step in situ polymerization of UHMW polymers in ILs is presented. The UHMW gel is formed solely by physical entanglements of the UHMW polymers. This is in contrast to self-healing materials using reversible bonds, such as hydrogen bonding, host-guest interactions, and dynamic covalent bonding, which have been actively investigated in recent years. With the appropriate combination of the polymer and solvent structures, the UHMW gel exhibits rapid self-healing behavior at room temperature. Furthermore, the tensile experiments and MD simulations suggest that the microscopic interactions between the polymer and IL play an important role in the expression of the self-healing phenomena. The universal concept of stretchable and self-healing polymer gels based on the physical entanglements of UHMW polymers is expected to expand into various polymeric systems. Because of the universal and simple concept of the present UHMW gels, synergetic effects for mechanical properties might also be expected by combining the strategy of the UHMW gels with the other toughening strategies such as block copolymer self-assembly, nanocomposites, and supramolecular interactions.

**MATERIALS AND METHODS**

**Materials**

[C$_2$mIm][TFSI] was purchased from Kanto Chemical (Japan). ILs composed of other anions were synthesized according to a method described in a previous report with slight modifications (46). All of the ILs were vacuum-dried at 120°C for 24 hours before use. MMA and EMA were purchased from Kanto Chemical (Japan) and purified by passing them through basic alumina. AIBN and toluene were purchased from Wako Pure Chemical Industries (Japan) and used without further purification.

**In situ polymerization and characterization of methacrylate polymers in the ILs**

Here, a representative synthesis of the UHMW PMMA/[C$_2$mIm][TFSI] gel is described. MMA (0.300 g, 3.00 mmol), [C$_2$mIm][TFSI] (0.700 g, 1.79 mmol), and AIBN (0.1 mg, 0.61 × 10$^{-3}$ mmol) were charged in a glass vial and sealed with a rubber septum, through which argon was bubbled for 15 min at room temperature. Polymerization was conducted at 80°C for 24 hours. Monomer conversion was determined by $^1$H-NMR. The molecular weight and polydispersity index of the polymer were determined by GPC using a 10 mM lithium bromide (LiBr)/N,N-dimethylformamide (DMF) solution as the eluent. The GPC system was equipped with a PU-2080 Plus HPLC pump, a DG-2080-53 3-Line degasser, an RI-4030 refractive index detector, a UV-2075 Plus UV/VIS detector, an LC-NetII/ADc interface box, and a CO-4060 column oven (all equipment is manufactured by JASCO, Japan). Two columns (SB-806M HQ, Showa Denko, Japan), which were kept in a column heater at 40°C, were used for separation and calibrated using PMMA standards. For the characterization $^1$H-NMR and GPC, the as-prepared UHMW gel pieces were dissolved in CDCl$_3$ (ca. 1 wt %) and 10 mM LiBr/DMF (0.1 wt %) under stirring at room temperature overnight.

**Transparency tests**

The transparency tests were performed on an ultraviolet-visible (UV-Vis) spectrophotometer UV-2600 (Shimadzu, Japan). The sample was prepared in a septum-sealed quartz cell 10 mm in thickness. The wavelength for testing was set from 800 to 400 nm.

**Rheology**

Rheological measurements were performed using an Anton Paar MCR 102 rheometer (Anton Paar, Austria). A parallel plate geometry with a Ø12-mm plate and a gap spacing of 0.5 mm were used for all the measurements. Temperature sweep measurements were conducted from 10°C to 120°C (heating rate: 1°C min$^{-1}$) at a frequency of 1 rad s$^{-1}$ and a strain amplitude of 1%. The TSST master curves were constructed from the results of the frequency sweep measurements over a frequency range of 0.1 to 100 rad s$^{-1}$ with a strain amplitude of 1% at different temperatures.

**Tensile and compressive tests**

The tensile and compressive tests of the gels were performed using a Shimadzu AGS-X tester (Shimadzu, Japan). For the tensile test, gels cut into a dumbbell shape (size of the rectangular portion: 2.0 mm by 12.0 mm by 1.0 mm) were stretched at a speed of 10 cm min$^{-1}$ using a 100 N load cell. To investigate the self-healing behavior, the gel was cut at the center into two equal pieces. Then, the two cut surfaces were gently attached and allowed to stand for various healing times at room temperature, after which tensile tests were performed. For the compressive test, gels molded into a cylindrical shape (Ø10 mm × 10 mm in height) were compressed at a speed of 100% min$^{-1}$ using a 10 kN load cell.

**Electrochemical measurements**

The ionic conductivity of the gel was evaluated by impedance measurements using a VMP3 potentiostat/galanostat (Bio-Logic Science Instruments, France) over a frequency range of 0.1 Hz to 1 MHz with an AC of 10-mV amplitude. The gel was held between two stainless steel disk electrodes using a polytetrafluoroethylene spacer [1.0 mm (T) × 8.5 mm inside diameter (ID)]. The measurements were conducted over a temperature range of 20°C to 120°C at intervals of 10°C. The sample was allowed to equilibrate for at least 1 hour at each temperature before each measurement.

The impedance tests for the stretched and unstretched gels were conducted using a rectangular gel sheet [60 mm (L) by 10 mm (W) by 2.5 mm (T)]. Copper electrodes (10 × 10 mm) were attached to both ends of the sample. The impedance measurements were...
then performed with (300%) and without stretching strain. For the self-healing test, the gel sheet was cut at the center, and the two cut surfaces were brought into contact. After 6 hours at room temperature, impedance measurements were performed on the healed gel sheet.

**Thermal analysis**

Differential scanning calorimetry (DSC) was performed using an X-DSC7000 instrument (Hitachi High-Tech, Japan). The samples were semi-sealed in aluminum pans. The samples were heated to 200°C, followed by cooling to −150°C, and then reheated to 200°C at a cooling and heating rate of 10°C min⁻¹. The $T_g$ (the midpoint temperature of the heat capacity change) and melting point [the on-set temperature of the endothermic peak $(T_m)$] were determined from the DSC thermograms during the programmed reheating steps. Thermogravimetric measurements of the samples were conducted in open Al pans using a thermogravimetry/differential thermal analyzer (TG-DTA 6200, Seiko Instruments, Japan) from room temperature to 550°C at a heating rate of 10°C min⁻¹.

**DLS measurement**

A schematic of the developed software-based DLS apparatus is presented in fig. S6A. The output of a single-frequency continuous-wave diode-pumped laser (Cobolt Samba, 0532-04-01-0100-700, 100 mW, Sweden) at a wavelength of 532.1 ± 0.3 nm was focused on a quartz cell filled with the sample. The temperature of the sample was maintained at 23°C during the measurements using a temperature-controlled cuvette holder (qX3, Quantum Northwest, USA). Scattered light was collected at a scattering angle of 90° and guided onto a photon-counting module (C13001-01, Hamamatsu Photonics, Japan) through an optical fiber. The aperture size just before the collection lens was set at 0.8 mm. The electronic signal pulses from the photon-counting module were transferred to a time-to-digital converter (C13001-01, Hamamatsu Photonics, Japan) controlled cuvette holder (qX3, Quantum Northwest, USA). Scattered light was maintained at 23°C during the measurements using a temperature-controlled cuvette holder (qX3, Quantum Northwest, USA). Scattered light was collected at a scattering angle of 90° and guided onto a photon-counting module (C13001-01, Hamamatsu Photonics, Japan) through an optical fiber. The aperture size just before the collection lens was set at 0.8 mm. The electronic signal pulses from the photon-counting module were transferred to a time-to-digital converter (C13001-01, Hamamatsu Photonics, Japan).

**MD simulation**

An all-atom MD simulation was conducted using the GROMACS 2020.1 program under the isobaric-isothermal (NTP) ensemble (298 K and 1 atm) in a cubic cell. The procedural details were similar to those reported in our previous studies (47, 48). The compositions (i.e., number of ILs and polymers) in the simulation box are listed in Table S2. A 20-mer equivalent of approximately 2 kDa was used as the polymer moiety owing to computing performance issues. The total simulation time was set to 25.0 ns. The data collected at 0.1-ns intervals from the last 500 ps were analyzed to determine the radial distribution function $G(r)$. The resulting density values from the current MD simulations are in good agreement with the corresponding density values estimated from the respective densities of the IL and polymer, which are listed in Table S2. C-LAP and OPLS-AA force fields including intermolecular Lennard-Jones, Coulombic interactions, and intramolecular interactions (i.e., bond stretching, angle bending, and torsion of dihedral angles) were used for C₂mM, TFSI, and the polymers (49–51). The radius of gyration $(R_g)$ of the polymer was calculated using intramolecular $G_{\text{intra}}(R)$ according to the following equation

$$R_g^2 = \frac{\int_0^r r^2 4\pi r^2 G(r) \, dr}{\int_0^r 4\pi r^2 G(r) \, dr}$$

**SUPPLEMENTARY MATERIALS**

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**REFERENCES AND NOTES**

1. A. S. Hoffman, Hydrogels for biomedical applications. Adv. Drug Deliv. Rev. 64, 18–23 (2012).
2. N. Peppas, Hydrogels in pharmaceutical formulations. Eur. J. Pharm. Biopharm. 50, 27–46 (2000).
3. D. Seliktar, Designing cell-compatible hydrogels for biomedical applications. Science 336, 1124–1128 (2012).
4. C. Yang, Z. Suo, Hydrogel iontronics. Nat. Rev. Mater. 3, 125–142 (2018).
5. J. Y. Song, Y. Y. Wang, C. C. Wan, Review of gel-type polymer electrolytes for lithium-ion batteries. J. Power Sources 77, 183–197 (1999).
6. C. Keplerling, J.-Y. Sun, C. C. Foo, P. Rothermund, G. M. Whitesides, Z. Suo, Stretchable, transparent, ionic conductors. Science 341, 984–987 (2013).
7. Y. Kitazawa, K. Ueno, M. Watanabe, Advanced materials based on polymers and ionic liquids. Chem. Rev. 138, 391–409 (2018).
8. C. Creton, 50th anniversary perspective: Networks and gels: Soft but dynamic and tough. Macromolecules 50, 8297–8316 (2017).
9. T. L. Sun, T. Kurokawa, S. Kuroda, A. Bini, A. T. Akasaki, K. Sato, M. A. Haque, T. Nakajima, J. P. Gong, Physical hydrogels composed of polyampholytes demonstrate high toughness and viscoelasticity. Nat. Mater. 12, 932–937 (2013).
10. J.-Y. Sun, X. Zhao, W. R. K. Illeperuma, O. Chaudhuri, K. H. Oh, D. J. Mooney, J. J. Vlassak, Z. Suo, Highly stretchable and tough hydrogels. Nature 489, 133–136 (2012).
11. X. Hu, M. Vatanaklah-Varnoosfaderani, J. Zhou, Q. Li, S. S. Sheikh, Weak hydrogen bonding enables hard, strong, tough, and elastic hydrogels. Adv. Mater. 27, 6899–6905 (2015).
12. K. Imato, M. Nishihara, T. Kanehara, Y. Amamoto, A. Takahara, H. Otsuka, Self-healing of chemical gels cross-linked by diarylbenzofuranone-based trigger-free dynamic covalent bonds at room temperature. Angew. Chem. Int. Ed. 51, 1138–1142 (2012).
13. E. Kamio, T. Yasui, Y. Iida, J. P. Gong, H. Matsuya, Inorganic/organic double-network gels containing ionic liquids. Adv. Mater. 29, 1704118 (2017).
14. S. Y. Zheng, H. Ding, J. Qian, J. Yin, Z. L. Wu, Y. Song, Q. Zheng, Metal-coordination complexes mediated physical hydrogels with high toughness, stick–slip tearing behavior, and good processability. Macromolecules 49, 9637–9646 (2016).
15. R. Tamate, K. Hashimoto, T. Horii, M. Hirasa, Y. Li, M. Shibayama, M. Watanabe, Self-healing micellar ion gels based on multiple hydrogen bonding. Adv. Mater. 30, 1802792 (2018).
16. S. Wang, M. W. Urban, Self-healing polymers. Nat. Rev. Mater. 5, 562–583 (2020).
17. Y. Okumura, K. Ito, The polyrotaxane gel: A topological gel by figure-of-eight cross-links. Adv. Mater. 13, 485–487 (2001).
18. K. Ito, Novel entropic elasticity of polymeric materials: Why is slide-ring gel so soft? Polym. J. 44, 38–41 (2012).
19. C. Liu, N. Morimoto, L. Jiang, S. Kawahara, T. Noritomi, H. Yokoyama, K. Mayumi, K. Ito, Tough hydrogels with rapid self-reinforcement. Science 372, 1078A–1081B (2021).
20. C. Nishida, Y. Inamoto, C. Hajime, A. Kawamura, T. Miyata, A universal method to easily design tough and stretchable hydrogels. NPG Asia Mater. 13, 34 (2021).
21. J. Kim, G. Zhang, M. Shi, Z. Suo, Fracture, fatigue, and friction of polymers in which entanglements greatly outnumber cross-links. Science 374, 212–216 (2021).
22. E. Read, A. Guinaudeau, D. J. Wilson, A. Cadix, F. Violette, M. Destarac, Low temperature RAFT/MADIX gel polymerisation: Access to controlled ultra-high molar mass polyacrylamides. Polym. Chem. 5, 2202–2207 (2014).
23. Z. An, 100th anniversary of macromolecular science viewpoint: Achieving ultrahigh molecular weights with reversible deactivation radical polymerization. ACS Macro Lett. 9, 350–357 (2020).
24. M. Yamaguchi, S. Ono, K. Okamoto, Interdiffusion of dangling chains in weak gel and its application to self-repairing material. Mater. Sci. Eng. B 162, 189–194 (2009).
25. M. Yamaguchi, R. Maeda, R. Kobayashi, T. Wada, S. Ono, S. Nobukawa, Autonomic healing and welding by interdiffusion of dangling chains in a weak gel. Polym. Int. 61, 9–16 (2012).
26. K. Hong, H. Zhang, J. W. Mays, A. E. Visser, C. S. Brael, J. D. Holbrey, W. M. Reichert, R. D. Rogers, Conventional free radical polymerization in room temperature ionic liquids: A green approach to commodity polymers with practical advantages. Chem. Commun. 13, 1368–1369 (2002).

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27. S. Harrisson, S. R. Mackenzie, D. M. Haddleton, Unprecedented solvent-induced acceleration of free-radical propagation of methyl methacrylate in ionic liquids. Chem. Commun. 2, 2850–2851 (2002).

28. V. Srethmel, A. Laschewsky, H. Wetzel, E. Görmitz, Free radical polymerization of n-butyl methacrylate in ionic liquids. Macromolecules 39, 923–930 (2006).

29. P. Kubisa, Application of ionic liquids as solvents for polymerization processes. Prog. Polym. Sci. 29, 3–12 (2004).

30. P. Kubisa, Kinetics of radical polymerization in ionic liquids. Eur. Polym. J. 133, 109778 (2020).

31. R. N. Carman, T. E. Becker, M. B. Sims, B. S. Sumerlin, Ultra-high molecular weights via aqueous reversible-deactivation radical polymerization. Chem. 2, 93–101 (2017).

32. Z. Liu, Y. Lv, Z. An, Enzymatic cascade catalysis for the synthesis of multiblock and ultrahigh-molecular-weight polymers with oxygen tolerance. Angew. Chem. Int. Ed. 56, 13852–13856 (2017).

33. T. J. Tulig, M. Tirrell, On the onset of the Trommsdorff effect. Macromolecules 15, 459–463 (1982).

34. Y. Suzuki, D. S. Cousins, Y. Shinagawa, R. T. Bell, A. Matsumoto, A. P. Stebner, Phase separation during bulk polymerization of methyl methacrylate. Polym. J. 51, 423–431 (2019).

35. M. M. Mok, X. Liu, Z. Bai, Y. Lei, T. P. Lodge, Effect of concentration on the glass transition and viscoelastic properties of poly(methyl methacrylate)/ionic liquid solutions. Macromolecules 44, 1016–1025 (2011).

36. T. Hiroi, S. Samitsu, K. Ishioka, Post-processing noise reduction via all-photon recording in dynamic light scattering. Sci. Technol. Adv. Mater. Methods 1, 134–142 (2021).

37. M. Shibayama, Spatial inhomogeneity and dynamic fluctuations of polymer gels. Macromol. Chem. Phys. 199, 1–30 (1998).

38. S. Ishii, H. Kokubo, K. Hashimoto, I. Imazumi, M. Watanabe, Tetra-PEG network containing ionic liquid synthesized via Michael addition reaction and its application to polymer actuator. Macromolecules 50, 2906–2915 (2017).

39. T. Sakai, T. Matsunaga, Y. Yamamoto, C. Ito, Y. Lei, T. P. Lodge, Effect of concentration on the glass transition and viscoelastic properties of poly(methyl methacrylate)/ionic liquid solutions. Macromolecules 44, 1016–1025 (2011).

40. J. P. Gong, Why are double network hydrogels so tough? Soft Matter 6, 2583–2590 (2010).

41. X. Zhao, X. Chen, H. Yuk, S. Lin, X. Liu, G. Parada, Soft materials by design: Unconventional polymer networks give extreme properties. Chem. Rev. 121, 4309–4372 (2021).

42. P. Cordier, F. Tournilhac, C. Soulié-Ziakovic, L. Leibler, Self-healing and thermoreversible rubber from supramolecular assembly. Nature 451, 977–980 (2008).

43. E. B. Stukalin, L.-H. Cai, N. A. Kumar, L. Leibler, M. Rubinstein, Self-healing of entangled polymer networks with reversible bonds. Macromolecules 46, 7525–7541 (2013).

44. R. P. Wool, K. M. O’Connor, A theory crack healing in polymers. J. Appl. Phys. 52, 5953–5963 (1981).

45. S. Prager, M. Tirrell, The healing process at polymer-polymer interfaces. J. Chem. Phys. 75, 5194–5198 (1981).

46. A. Noda, K. Hayamizu, M. Watanabe, Pulsed-gradient spin–echo 1H and 19F NMR diffusion coefficient, viscosity, and ionic conductivity of non-chloroaluminate room-temperature ionic liquids. J. Phys. Chem. B 105, 4603–4610 (2001).

47. K. Fuji, T. Ueki, K. Hashimoto, Y. Kobayashi, Y. Kitazawa, K. Hirotsu, M. Matsuqami, K. Ohara, M. Watanabe, M. Shibayama, Microscopic structure of solvated polybenzyl methacrylate) in an imidazolium-based ionic liquid: High-energy x-ray total scattering and all-atom MD simulation study. Macromolecules 50, 4780–4786 (2017).

48. Y. Kamiyama, M. Shibata, R. Kanaki, K. Fuji, Lithium-ion coordination-induced conformational change of PEG chains in ionic-liquid-based electrolytes. Phys. Chem. Chem. Phys. 22, 5561–5567 (2020).

49. W. L. Jorgensen, D. S. Maxwell, J. Tirado-Rives, Development and testing of the OPLS all-atom force field on conformational energetics and properties of organic liquids. J. Am. Chem. Soc. 118, 11225–11236 (1996).

50. W. D. Cornell, P. Cieplak, C. L. Bayly, I. R. Gould, K. M. Merz, D. M. Ferguson, D. C. Spellmeyer, T. Fox, J. W. Caldwell, P. A. Kollman, A second generation force field for the simulation of proteins, nucleic acids, and organic molecules. J. Am. Chem. Soc. 117, 5179–5197 (1995).

51. J. N. Canongia Lopes, A. A. H. Pádua, Molecular force field for ionic liquids II: Imidazolium, pyridinium, and phosphonium cations; chloride, bromide, and dicyanamide anions. J. Phys. Chem. B 110, 19586–19592 (2006).