Supplementary Information

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Materials and Method

Synthesis.

1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide, $[C_2mIm^+][TFSA^-]$ ionic liquid (solvent) was synthesized and characterized by a well established method, reported in the previous work.[1] The deuterated $[C_2mIm^+]$-$d_8$$[TFSA^-]$ used in the SANS experiments, where H atoms are substituted by D for ethyl group and imidazolium-ring of the cation and not for methyl group, was synthesized as follows. 1-methylimidazole was slowly added to an acetonitrile solution containing bromoethane-d_5 (slightly excess amount against the 1-methylimidazole) in a three-neck round-bottom flask at room temperature. After stirring for 12h, unreacted bromoethane-d_5 and acetonitrile were removed by evaporation to obtain a deuterated 1-ethyl-3-methylimidazolium bromide, $[C_2mim]$-d_5Br (white powder). To deuterate H within the imidazolium-ring, the $[C_2mim]$-d_5Br (0.312 mol) was added to D_2O solution with cesium hydroxide monohydrate (0.120 mol) and was stirred at 60 °C for 16 h. Li[TFSA] salt added into the D_2O solution to give a new phase of $[C_2mim]$-$d_8$$[TFSA^-]$, followed by washing with a large amount of D_2O. The Br content was checked by addition of $AgNO_3$. The $[C_2mim^+]$-$d_8$$[[TFSA^-]$ thus obtained was dried in a vacuum oven at room temperature (yield = 90.0 %). The water content was checked by a Karl

Fischer test to be less than 100 ppm. The chemical structure of [C_2mim^+]-d_8[$TFSA^-$] was confirmed by ^1H NMR. A peak assigned to H within the methyl group was observed and then to the ethyl group and imidazolium-ring position successfully disappeared [NMR result: δ=3.74 ppm (s, 3H); DMSO-d6]. It was found that the [C_2mim^+]-d_8[[$TFSA^-$] is 98.0 % and 97.5 % deuterated at the ethyl group and imidazolium-ring position, respectively. The chemical structure is shown in Figure S3.

Tetra-PEG ion gel containing [C_2mim^+][$TFSA^-$] ionic liquid as a solvent was prepared as follows. Constant amount of Tetraamine-terminated PEG (TAPEG) and Tetra-NHS-glutarate-terminated PEG (TNPEG) were dissolved in the [C_2mim^+][$TFSA^-$], respectively, and stirred at room-temperature. The TAPEG and TNPEG were synthesized from tetrahydoxyl-terminated PEG, which is described elsewhere in detail.[2] The two solutions were mixed at room-temperature and the resulting solution was poured into the mold. The solution was gelled within 1 min to obtain the freestanding and transparent Tetra-PEG ion gel.

Methods

Ionic conductivity: Ionic conductivity was measured by means of complex impedance measurements, using a computer-controlled impedance analyzer. The frequency range was covered from 5 Hz to 13 MHz at the amplitude of 10 mV. Tetra-PEG ion gel with 10 mm diameter and 2 mm thickness (area: 0.78 cm^2) was sandwiched between mirror-finished stainless steel electrodes sealed in a Teflon container. The measurements were carried out at 60 °C (highest temperature examined in this work), followed by a cooling to -20 °C. The samples were thermally equilibrated by waiting 1 h at each temperature, prior to the measurements.

Compression test: Compression tests were performed on cylinder-shaped specimens (15mm in diameter and 7.5mm in height) using a mechanical testing apparatus (INSTRON 3365; Instron Corporation, Canton, MA) at velocity of 1.05 mm/min.

Stretching test: Uniaxial stretching tests were carried out on rectangular-shaped specimens (30mm in length, 5mm in width, and 2mm in thickness) using a universal testing apparatus (EZ-test, Shimadzu, Kyoto, Japan) at velocity of 6 mm/min.

SANS: SANS measurements were carried out using a SANS spectrometer, SANS-U, installed on a JRR-3 reactor (JAEA, Tokai, Japan).[3-5] Sample-to-detector distance was 2 m to cover the momentum transfer q range (= $4\pi\sin\theta/\lambda$, where λ and 2θ denote the wavelength of neutron beam (= 7 Å) and the scattering angle, respectively) from 0.014 to 0.19 $Å^{-1}$. SANS profiles corrected for background using an empty cell were normalized with respect to the scattering of polyethylene as a secondary standard material. The SANS profiles thus obtained were further corrected for the incoherent scattering to obtain the scattering intensity, $I(q)$. The incoherent scattering intensity was estimated according to the procedure reported in our recent work.[6]

Table S1

The fitting parameters obtained from VTF equation for ionic conductivity for Tetra-PEG ion gels.

		TFSA system	
c mg/ml	σ_0 / S cm^{-1}	B / K	T_0 / K
100	0.34(2)	441(11)	181
50	0.44(3)	500(20)	171
0 [a]	0.551	534	167

		FSA system	
c mg/ml	σ_0 / S cm^{-1}	B / K	T_0 / K
50	0.45(3)	430(20)	168
0 [b]	0.23	310(20)	182

*Values in parentheses refer to a standard deviations. [a] ref. [7]. [b] ref. [8]

Figure S1

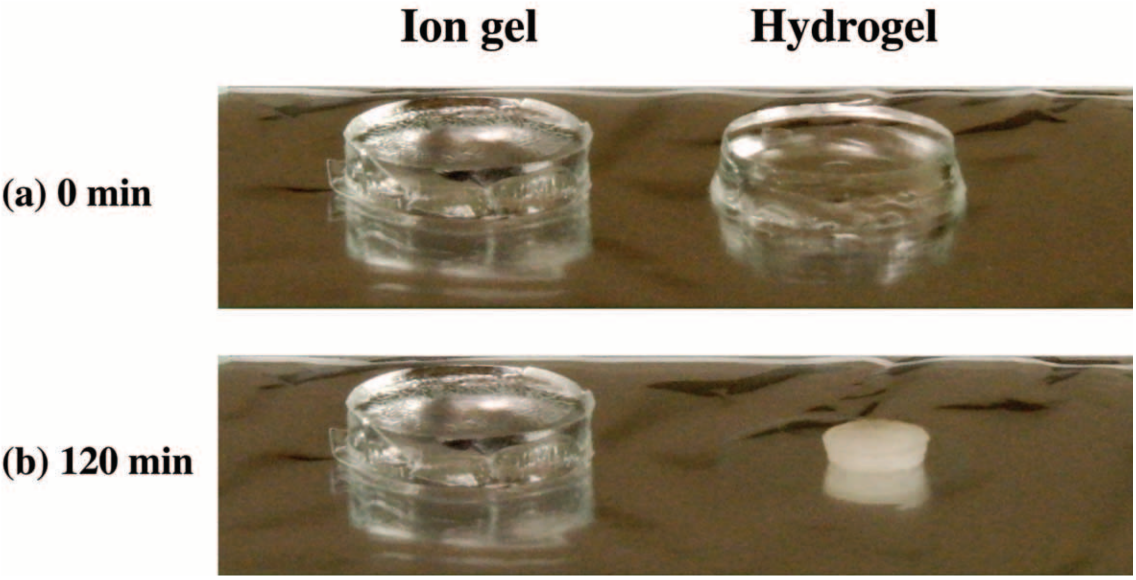

Figure S1. Aging variation of 50 mg/ml Tetra-PEG ion gel with [C_2mIm$^+$][TFSA$^-$] ionic liquid and the corresponding hydrogel on hot plate at 100˚C, after (a) 0 min and (b) 120 min.

Figure S2

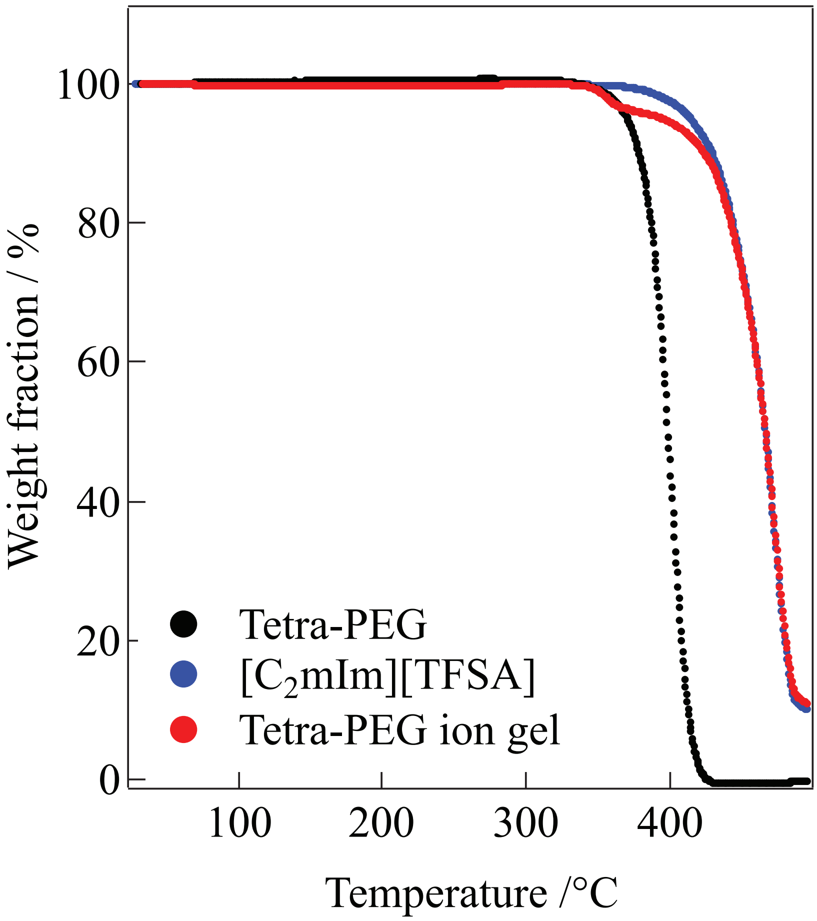

Figure S2. Result of thermogravimetric analysis for 50 mg/ml Tetra-PEG ion gel with [C_2mIm$^+$][TFSA$^-$] ionic liquid (red). The measurements were carried out under nitrogen atmosphere. The dotted lines with black and blue shows pure amine-terminated Tetra-PEG and [C_2mIm$^+$][TFSA$^-$], respectively. The rate of temperature increase was 10 ˚C/min. The first decrement in the red line at around 350 ˚C corresponds to the degradation of PEG component, and the second at around 400 ˚C to that of [C_2mIm$^+$][TFSA$^-$] one.

Figure S3

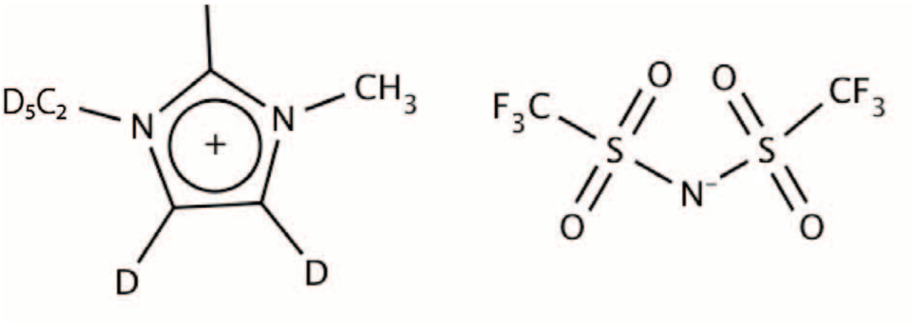

Figure S3. Chemical structure of d8-[C_2mim$^+$][TFSA$^-$] ionic liquid.

References

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