Electronic Supplementary Information (ESI)

Straightforward Preparation of a Tough and Stretchable Ion Gel

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Experimental

Materials

[C$_2$mim][TFSI] was purchased from Kanto Chemical (Japan) and were

vacuum-dried at 120 °C for 24 hours before use. Methyl methacrylate (MMA) and

ethylene glycol dimethacrylate (EGDMA) were purchased from Tokyo Chemical

Industry (Japan) and Wako Pure Chemical Industries (Japan), respectively. They were

purified by passing them through aluminum oxide (90 active basic 0.063–0.200 mm,

Merck, Germany). 2,2-diethoxyacetophenone (DEAP) were purchased from Wako Pure

Chemical Industries (Japan) and used as received.

Synthesis of ion gels

Here, a representative synthetic procedure of the PMMA ion gel ([CL] = 0.01

mol%, [I] = 0.02 mol%) is described. MMA (1.50 g, 15.0 mmol), EGDMA (0.30 mg,

0.0015 mmol), DEAP (0.64 mg, 0.0031 mmol), and [C$_2$mim][TFSI] (3.50 g, 8.96

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

under UV (365 nm, 3 mW) irradiation for 22 hours at room temperature.

Monomer conversion was determined by ^{1}H-NMR. The molecular weight and

polydispersity index of the polymers obtained without cross-linker were determined by

GPC using a 10 mM lithium bromide (LiBr)/N,N-dimethylformamide (DMF) solution

as the eluent. The linear polymers were purified by precipitation using acetone as a

good solvent and methanol as a poor solvent. The columns (Showa Denko, Japan) were

calibrated using PMMA as molecular weight standards.

Transparency tests

The transmittance of the ion gel ([CL] = 0.01 mol%, [I] = 0.02 mol%) was tested by

ultraviolet-visible (UV-Vis) spectrophotometer UV-2600 (Shimadzu, Japan) from 800

to 400 nm. The sample was prepared in a septum-sealed quartz cell 10 mm in thickness.

Tensile tests

The tensile tests of the ion 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 using a 100 N load cell. The ion gels were stretched repeatedly within the strain of 0~300% for 80 cycles, with 600 s waiting times between each cycle.

Rheological measurements

Oscillatory shear measurements and stress relaxation tests were performed by an Anton Paar Physica MCR 102 (Anton Paar, Austria). Parallel plate geometry with a diameter of 12 mm and a gap spacing of approximately 1 mm were used for the measurement. Stress relaxation tests were performed with a 10% strain amplitude at 30 °C.

Electrochemical measurements

The ion gel ([CL]=0.01 mol%, [I]=0.02 mol%) was cut to a rectangular shape [60 mm (L) by 10 mm (W) by 1.5 mm (T)]. Copper electrodes (10 × 10 mm) were attached to both ends of the ion gel. The impedance tests were conducted using a VMP3

potentiostat/galvanostat (Bio-Logic Science Instruments, France) at a constant voltage

of 2.5 V, while the sample was manually subjected to 5 consecutive loading–unloading

cycles for each strain range (0–10, 0–25, 0–50%). The relative resistance changes

$(\Delta R/R_0)$ was calculated from following equation.

$$\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0}$$

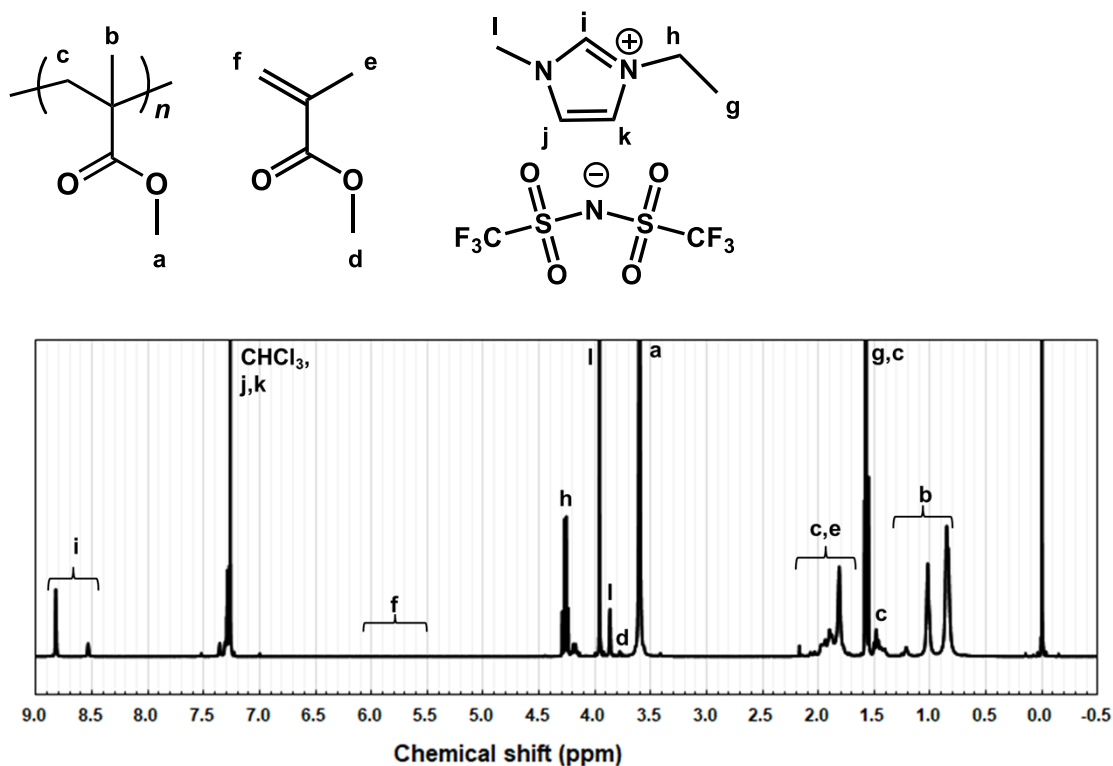where R and R_0 are the real-time and initial resistances, respectively.

Fig. S1 A ^{1}H NMR spectrum of a PMMA extracted from UHMW ion gel ([CL] = 0 mol%, [I] = 0.02 mol%) dissolved in CDCl$_3$. The conversion from MMA monomer to polymer was calculated the ratio of the integral values of the signals (a) and (f).
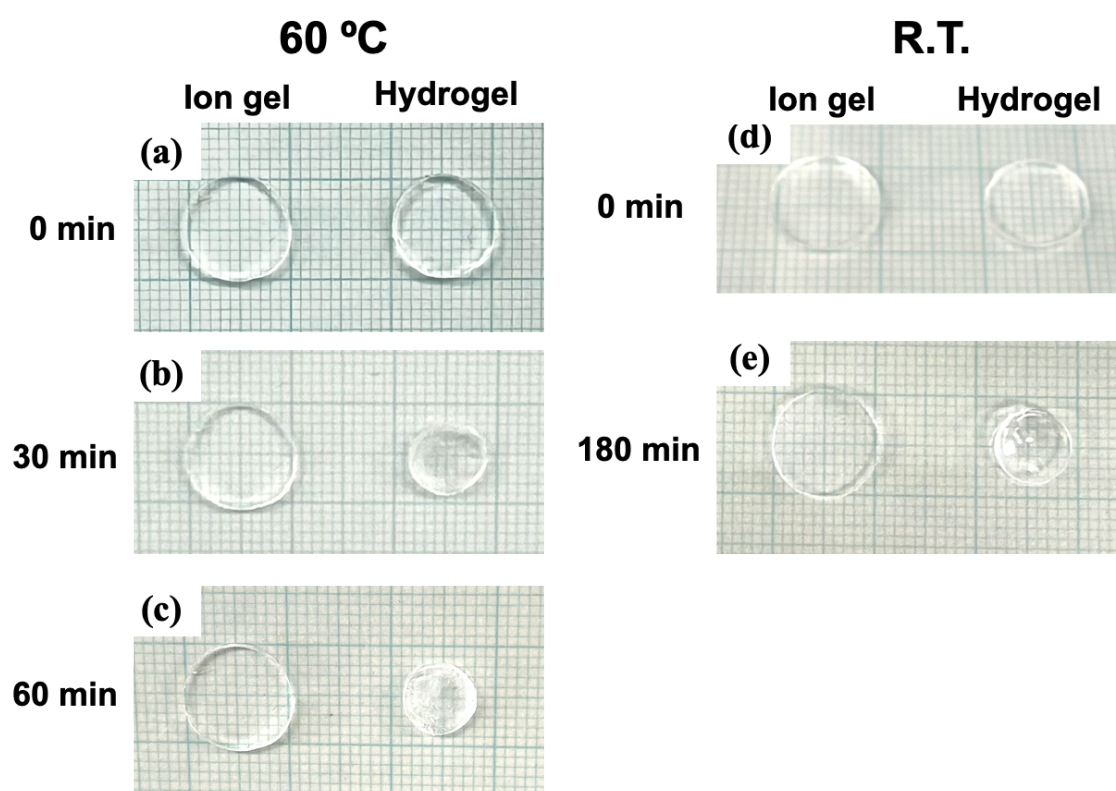

Fig. S2 Time course appearance changes of the ion gel ([CL] = 0.01 mol%, [I] = 0.02 mol%) and a hydrogel which is prepared by the same procedure with the corresponding ion gel heated after 60 ºC for (a) 0 min, (b) 30 min and (c) 60 min, and after placed at room temperature for (a) 0 min, and (b) 180 min. The hydro gel was prepared according to previously reported procedures[1] by mixing acrylamide (AAm), *N,N'*-

methylenebisacrylamide, *N,N,N',N'*-tetramethylethylenediamine, and ammonium

persulfate in deionized water as a monomer, a cross-linker, and a redox initiator,

respectively, with the same concentration of initiator and cross-linker ([CL] = 0.01

mol%, [I] = 0.02 mol% against AAm monomer in the feed) and the same molar

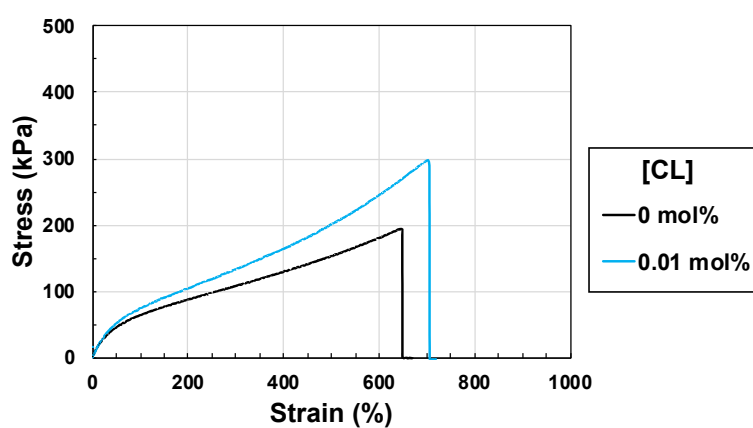concentration of monomer as the ion gel.

Fig. S3 Tensile stress–strain curves of ion gels with (0.01 mol%) and without (0 mol%)

cross-linker. The monomer concentration and initiator content are fixed to be 30 wt%

and 0.02 mol%, respectively.

Table S1 Gelation behavior in a variety condition of the cross-linker and the initiator.

Yes: A gel that can be handled is obtained. No: A viscous liquid or a gel that can not be

handled is obtained.

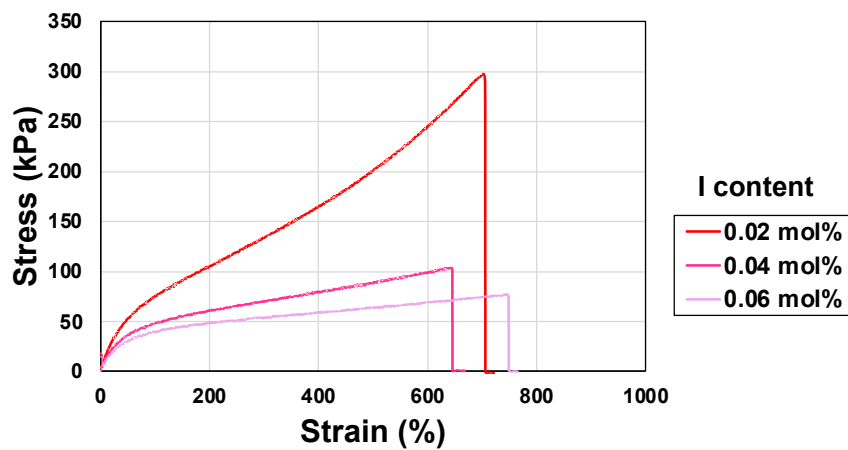|		Closs-linker content [mol%]		
		0	0.01	1
Initiator content [mol%]	0.02	Yes	Yes	Yes
	0.04	Yes	Yes	N.D.
	0.06	Yes	Yes	Yes
	0.2	No	No	N.D.
	2	No	No	Yes

Fig. S4 Tensile stress–strain curves of various ion gels ([CL] = 0.01 mol%) prepared
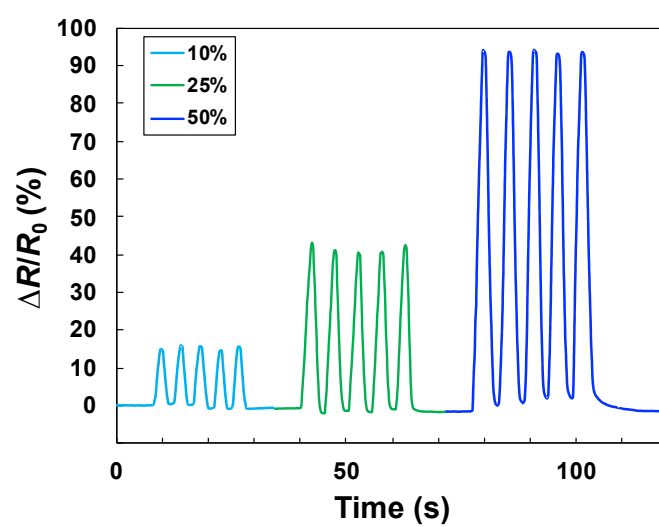
with different initiator contents.

Fig. S5 Real-time observation of the relative resistance while the ion gel was manually
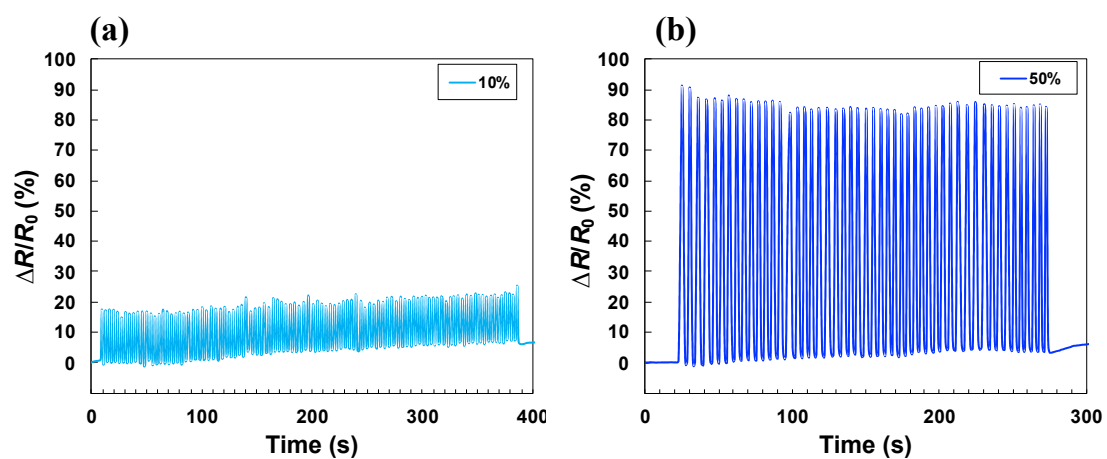
stretched to 10, 25 and 50% with each 5 cycles.

Fig. S6 Relative resistance response under successively stretched to (a) 10 and (b) 50%

with 100 cycles and 50 cycles, respectively.

Table S2 A comparison of the mechanical and optical properties between this work and representative previously reported ion gels.

	Sample [a]	IL content (wt%)	Number of preparation steps	Transparency test			Tensile test					Cyclic tensile test	
				Sample thickness (mm)	Wavelength (nm)	Trans-parency [b]	Strain rate (cm/min)	Young's modulus (kPa)	Elongation at break (%)	Fracture strength (kPa)	Toughness (MJ/m^3)	Strain (%)	Residual strain [c] (%)
This work	[CL]=0.01, [I]=0.02 mol%	70	1	10	400~800	Yes >97.5%	10	144	705	299	0.97	300	2.6
Ref.2	PU-IL$_2$	67	3	N.D.	N.D.	No	5	420	327	1560	N.D.	200	19
Ref.3	60%-Ionogel	40	1	N.D.	400~900	Yes >92%	N.D.	510	1590	510	4.78	200	0
Ref.4	PAMPS DN gel	66.4	4	N.D.	400~800	Yes >95%	N.D.	N.D.	158	380	N.D.	N.D.	N.D.
Ref.5	85-3-12	70	3	N.D.	N.D.	Yes	5	N.D.	2500	740	N.D.	300	55
Ref.6	88-PMMA-*r*-PBA	60	3	1	400~1100	Yes >98.5%	0.6	310	~850	~170	N.D.	100	< 3.2
Ref.7	HV12	70	7	N.D.	N.D.	Yes	0.6	340	720	~650	2.479	20	~0
Ref.8	40 mol%	~37	1	1	400~800	Yes ~96.6%	5	815	1400	~500	N.D.	100	~10
Ref.9	TPEI-2	77.7	1	N.D.	N.D.	No	2	~50	1030	135	N.D.	100	~0
Ref.10	PAMPS@PDMA A	67	2	N.D.	400~800	Yes	N.D.	N.D.	~3300	280	~5	N.D.	N.D.

Ref	Sample											
	ionogel				>90%							
Ref.11	Ionogel-4050	60	1	1.7	400~800	Yes >88%	10	58 ±9	1828 ±16	550±1	3.66 ±0.09	200	~0
Ref.12	PVDF-*co*-HFP-5545 / 43 wt% EMIOTf	43	1	0.01	400~800	Yes >77%	0.5	100	~1500	~4	N.D.	N.D.	N.D.
Ref.13	PACG$_4$-MBAA$_{0.05}$ ionogel	~70	3	N.D.	400~800	>50%	5	~70	~750	~130	~0.4	100	~15

Unless specified, the values were read from the figures in the papers.

[a] For details on the composition and abbreviation of each sample, see the respective reference papers. [b] Yes: transparent, No: turbid. When the transmittance measurements were not conducted, the transparency was judged from the photograph in the literature. [c] The residual strain after 1st cycle of loading-unloading.

References

1.   C. Norioka, Y. Inamoto, C. Hajime, A. Kawamura and T. Miyata, *NPG Asia Mater.*, 2021, **13**, 34.

2.   T. Li, Y. Wang, S. Li, X. Liu and J. Sun, *Adv. Mater.*, 2020, **32**, 2002706.

3.   T. Li, F. Liu, X. Yang, S. Hao, Y. Cheng, S. Li, H. Zhu and H. Song, *ACS Appl. Mater. Interfaces*, 2022, **14**, 29261-29272.

4.   Y. Ding, J. Zhang, L. Chang, X. Zhang, H. Liu and L. Jiang, *Adv. Mater.*, 2017, **29**, 1704253.

5.   Z. Tang, D. Liu, X. Lyu, Y. Liu, Y. Liu, W. Yang, Z. Shen and X. Fan, *J. Mater. Chem. C*, 2022, **10**, 10926-10934.

6.   Y. M. Kim and H. C. Moon, *Adv. Funct. Mater.*, 2020, **30**, 1907290.

7.   K. G. Cho, S. An, D. H. Cho, J. H. Kim, J. Nam, M. Kim and K. H. Lee, *Adv. Funct. Mater.*, 2021, **31**, 2102386.

8.   Z. Yu and P. Wu, *Adv. Mater.*, 2021, **33**, 2008479.

9.   Y. Wang, Y. Liu, R. Plamthottam, M. Tebyetekerwa, J. Xu, J. Zhu, C. Zhang and T. Liu, *Macromolecules*, 2021, **54**, 3832-3844.

10.   W. Li, L. Li, S. Zheng, Z. Liu, X. Zou, Z. Sun, J. Guo and F. Yan, *Adv. Mater.*, 2022, **34**, 2203049.

11.   L. Xu, Z. Huang, Z. Deng, Z. Du, T. L. Sun, Z. H. Guo and K. Yue, *Adv. Mater.*, 2021, **33**, 2105306.

12.   Y. Cao, T. G. Morrissey, E. Acome, S. I. Allec, B. M. Wong, C. Keplinger and C. Wang, *Adv. Mater.*, 2017, **29**, 1605099.

13.   S. Zheng, X. Chen, K. Shen, Y. Cheng, L. Ma and X. Ming, *ACS Appl. Mater. Interfaces*, 2024, **16**, 4035-4044.