Homogeneous Polymer Network Ion Gels Based on Metal Ion-Complexation-Induced Cross-Linking in Ionic Liquids

Saori Takano,[a] *Itsuki Takubo,*[a] *Takeshi Ueki,*[b,c] *and Kenta Fujii*[a]*

[a] Graduate School of Sciences and Technology for Innovation, Yamaguchi University, 1-16-2 Tokiwadai, Ube, Yamaguchi 755-8611, Japan

[b] Research Center for Functional Materials, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.

[c] Graduate School of Life Science, Hokkaido University, Kita 10, Nishi 8, Kita-ku, Sapporo, Hokkaido, 060-0810, Japan.

KEYWORDS: Ion gel, Homogeneous polymer network, TetraPEG, Ionic liquid, Metal ion complexation

ABSTRACT

We report a facile one-step synthesis of homogeneous polymer network ion gels. The end-functionalization of tetra-branched poly(ethylene glycol) (TetraPEG) with catecholamine (Cat–NH_2) and the complexation between metal ions and Cat groups proceeded simultaneously in ionic liquid to yield free-standing TetraPEG ion gels cross-linked by the metal–Cat complexes. The mechanical strength of the ion gels strongly depended on the coordination bond strengths of the metal–Cat complexes, displaying the following trend: $Ni^{2+} > Mg^{2+} > Li^{+}$. We measured their ionic conductivities and found that the ion gels exhibited high ionic conductivity regardless of the employed metal ions.

Polymer networks filled with ionic liquids (ILs), i.e., ion gels (or ionogels), are promising soft electrolyte materials for flexible, safe electrochemical devices owing to the inherent unique properties of ILs (such as nonvolatility, nonflammability, high ionic conductivity, and electrochemical stability).[1-3] However, imparting ion gels with high mechanical strength and stretchability is critical to their applications in devices, and these features strongly depend on the polymer network structure. Thus, several conceptual polymer networks, e.g., double-network,[4-5] slide-ring network,[6-7] and homogeneous polymer network[8-9] structures, have been proposed and combined with ILs to enhance the mechanical strength of the ion gels. We have reported the syntheses of homogeneous polymer network-based ion gel and organogel electrolytes using tetra-branched poly(ethylene glycol) (TetraPEG); these gels were utilized as solid electrolyte materials for lithium-ion batteries (LIBs) and electric double-layer capacitors (EDLCs).[10-13] The TetraPEG networks were readily formed by one-step synthesis in IL solutions by mixing two polymer solutions. In detail, two terminals TetraPEG terminals (e.g., maleimide (MA)- and thiol-terminated TetraPEGs) can be chemically cross-linked in ILs to form covalent linking points and yield nearly ideal polymer network gels with few structural defects.

To enhance the mechanical properties of these gels and develop a designable smart gel system, dynamic cross-linking points with reversible interactions or dynamic bonds (e.g., hydrogen bonding interactions,[14-15] electrostatic interactions, and coordination bond formation between metal ions and chelate ligands) have recently attracted attention. Further, metal coordination bonds, particularly the reversible bonds in the chelate complex comprising Fe^{3+} and catechol (Cat) groups, have been examined for application as a dynamic linking point in hydrogel systems to impart them with specific mechanical and self-healable properties.[16-18] The complexation of

Fe^{3+} with Cat strongly depends on the pH values of the aqueous solutions, i.e., the deprotonation of the hydroxyl (OH) groups within Cat induces stepwise complexation reactions to yield mono-, bis-, tris-Cat–Fe^{3+} complexes, directly reflecting the viscoelastic and mechanical properties of the hydrogels.[18-19] Lu et al. prepared TetraPEG–Cat hydrogels by synthesizing a TetraPEG prepolymer that was end-functionalized with Cat using dopamine.[20] The resultant hydrogels exhibited good mechanical and self-healing properties, particularly at an optimum pH, 9; moreover, the bis- and tris-Cat–Fe^{3+} complexes acted as dynamic cross-linking points in the TetraPEG network at this pH. However, the application of such a metal–ligand coordination bond-based concept to IL (ion gel) systems is still limited and only applicable to hydrogel systems. Herein, we report the one-step synthesis of TetraPEG–Cat-based ion gels, via simultaneous (1) end-functionalization of TetraPEGs with Cat groups and (2) gelation induced by metal–ligand complexation in the IL electrolyte solutions containing metal ions (Li^{+}, Mg^{2+}, and Ni^{2+}), as illustrated in Figure 1.

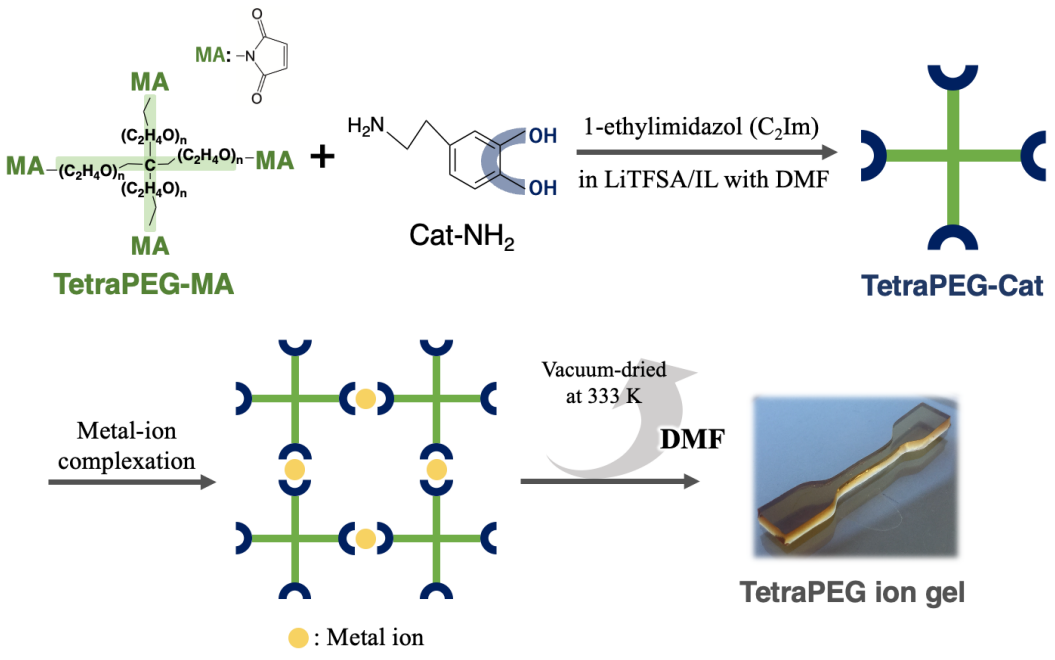


Figure 1. Schematic of the one-step synthesis of the TetraPEG ion gels cross-linked by metal-ion complexation.

In detail, the gelation proceeded via two reactions: (1) the Micheal addition reaction between MA-terminated TetraPEG (TetraPEG–MA: molecular weight (M_w) = 20,000 g mol^{-1}) and catecholamine (or dopamine, Cat–NH_2) and (2) the formation of a chelate complex between the metal ion and Cat group. TetraPEG–MA (polymer content: 10 wt%) and Cat–NH_2 hydrochloride (Cat–NH_2·HCl) were dissolved in 1-ethyl-3-methylimidazolium bis(trifluorosulfonyl)amide ([C_2mIm][TFSA]) containing M(TFSA)$_n$ salt, (M = Li, Mg, and Ni; n = 1 for Li and 2 for Mg and Ni). As Cat–NH_2·HCl was insoluble in M(TFSA)$_n$/[C_2mIm][TFSA] solutions, we added *N*,*N*-dimethylformamide (DMF), a good solvent for Cat–NH_2, to the solutions to obtain solutions with completely dissolved Cat. The molar ratios of the MA terminal to Cat (MA:Cat) and IL to DMF (IL:DMF) were fixed at 1:1 and 1:11 (corresponding to a weight ratio of IL:DMF = 1:2.1), respectively. The resulting IL solution was stirred for 10 min at room temperature to initiate the Michael addition reaction between the MA terminals and amine groups within Cat–NH_2 to yield Cat-modified TetraPEG prepolymers. The reaction was promoted by adding 1-ethylimidazole (C_2Im) as a base catalyst to the IL solution, as established in our previous study;[12, 21] additionally, the molar ratio was adjusted to Cat:C_2Im = 1:20. The terminal conversion efficiency of TetraPEG–Cat was confirmed by ultraviolet–visible (UV–vis) spectroscopy, as would be discussed in detail. After 24 h, the gelation of the IL solution was achieved by the metal ion complexation of the M^{n+} ions with the Cat groups (M^{n+}–Cat), which yielded a self-standing ion gel, i.e., the M^{n+}–Cat complex acted as a cross-linking point for the formation of the homogeneous TetraPEG network. The resulting gel was vacuum dried at 333 K for 48 h to completely remove the residual DMF, as quantitatively confirmed by infrared (IR) spectroscopy (Figure S1). The results of IR spectroscopy revealed that the peak at 1660 cm^{-1} (attributed to the vibration of DMF) disappeared completely in the resulting TetraPEG ion gels, confirming the

complete removal of the residual DMF. Thus, we obtained a TetraPEG-network-based ion gel with a polymer content of 10 wt% and metal ion concentration (c_M) of 0.016 or 0.01 M. The experimental details (UV–vis spectroscopy, mechanical stretching test, rheological measurement, and ionic conductivity (σ_{ion})) are described in the Supporting Information.

First, we confirmed the terminal conversion of TetraPEG–Cat, i.e., reaction efficiency of the Michael addition of the MA terminals (TetraPEG–MA) with the NH_2 groups (Cat–NH_2) in the IL solutions by time-dependence UV–vis spectroscopy. Figure 2a shows the typical UV–vis spectra

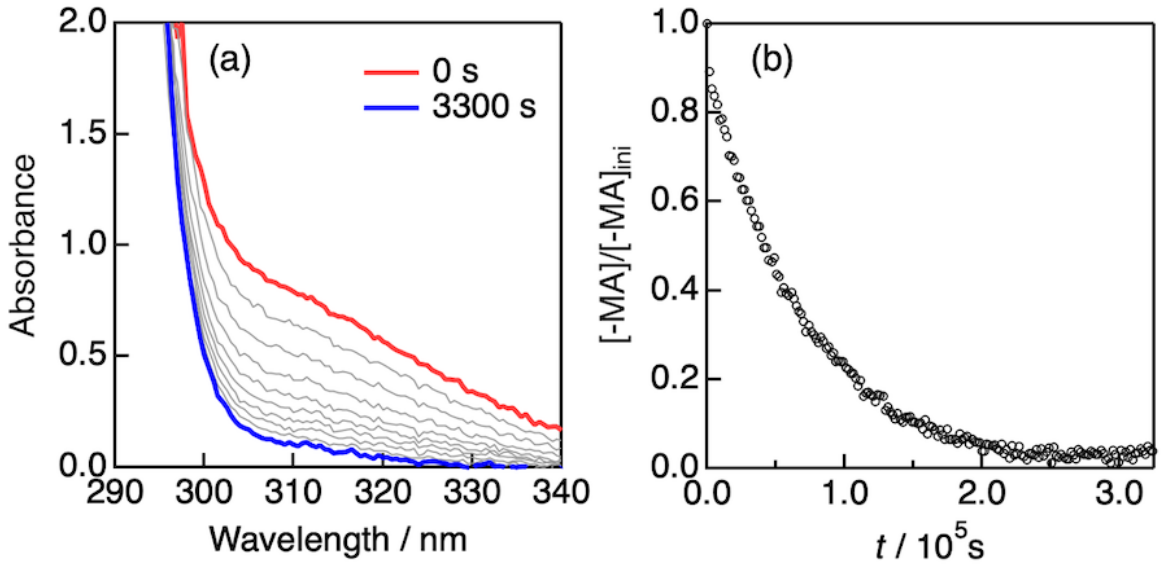


Figure 2. (a) Time-dependent UV–vis spectra of the Michael addition reaction of TetraPEG–MA and Cat–NH_2 in DMF-containing IL solutions with Li salt. (b) Plot of the unreacted –MA concentration, [–MA]/[–MA]$_{ini}$, against *t*.

of the product of the Michael addition reaction in DMF-containing IL solution with Li salt (Li salt concentration: $c_{Li} = 2.5 \times 10^{-3}$ M). The intensity of the peak around 310 nm, which was attributed to the unreacted –MA terminal,[12, 21-22] decreased gradually with the increasing reaction time, *t*, indicating that the Michael addition reaction between -MA and -NH_2 successfully proceed to form MA-NH bonds, i.e., terminal modification of TetraPEG–Cat. The residual concentration of the unreacted –MA at each *t* was calculated using the absorbance, *A*, at 310 nm

based on the Lambert–Beer law: [–MA] = $A_{310}/\varepsilon_{310}l$, where ε_{310} and l are the molar absorbance coefficiency and cell thickness (1 cm), respectively. The [–MA] values were normalized with the initial concentration, $[–MA]_{ini}$ (5.0×10^{-3} M), as shown in Figure 2b. The reaction efficiency, $([–MA]_{ini} - [–MA])/[–MA]_{ini} \times 100$, exceeded 95% after the reaction (~24 h), indicating the conversion of TetraPEG–MA to TetraPEG–Cat.

Figure 3a shows the stretching stress (σ_{stress})-elongation curves for the 10 wt% TetraPEG ion gels containing Ni^{2+}, Mg^{2+}, and Li^{+} (c_M = 0.016 M, corresponding to the molar ratio of metal ion-to-ligand, M^{n+}:Cat = 1:2). The TetraPEG ion gels exhibited excellent stretchability, enduring

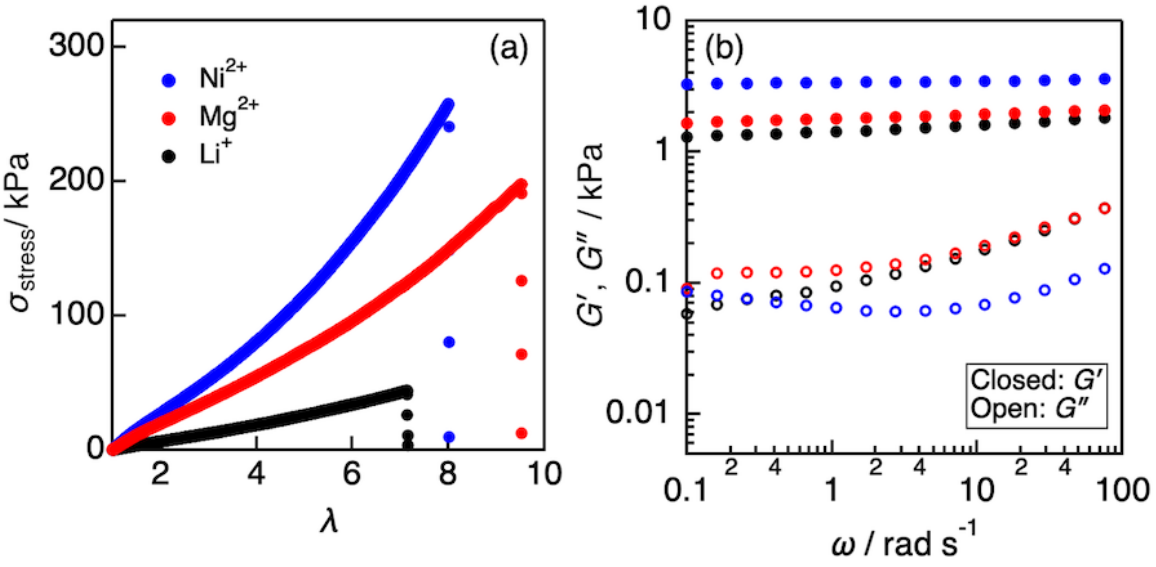


Figure 3. (a) Stress-elongation curves of the 10 wt% TetraPEG ion gels containing Ni^{2+} (blue), Mg^{2+} (red), and Li^{+} (black) at c_M = 0.016 M (stretch rate: 30 mm s^{-1}), and their (b) storage (G', circle) and loss (G'', triangle) elastic moduli as a function of frequency ω (0.1−100 rad s^{-1}) at constant strain of 2%.

over sevenfold elongation regardless of the examined metal ion species. This stretchability value is much higher than those of reported chemically cross-linked TetraPEG ion gels.[21-22] The shape of stress-strain curve exhibited clear elastic response without any σ_{stress} decrement during elongation. This indicates that the cross-links via metal ions are stable, and any flow deformation

does not occur within this time scale of stretch rate. Further, σ_{stress} increased linearly with λ, reaching maximum breaking stress values of 260, 200, and 40 kPa for the Ni, Mg, and Li systems, respectively. We estimated Young's modulus (E) using the initial slope of the observed σ_{stress}. The result revealed the strong dependence of E on the utilized metal ion species: 26.4 kPa (Ni system), 18.4 kPa (Mg system), and 6.3 kPa (Li system). The resulting E values were lower than that in the chemically cross-linked TetraPEG/[C_2mIm]TFSA] ion gel at the same polymer concentration (10 wt%), E = 54.2 kPa, which reflected the difference in the bond strength of the cross-links. Figure 3b shows the G' and G'' moduli as a function of ω obtained for the 10 wt% TetraPEG ion gels containing Ni, Mg, and Li ions. In all the systems, the G' value was almost constant and greater than the G'' value in the entire ω region examined, indicating the metal complex cross-links are stable and show typical rubbery plateau within this time scale. Further, the G' value increased in the following order: Ni^{2+} > Mg^{2+} > Li^{+}, which is consistent with the aforementioned behavior of the E value. Figure 4 shows the σ_{stress}–λ curve of the 10 wt%

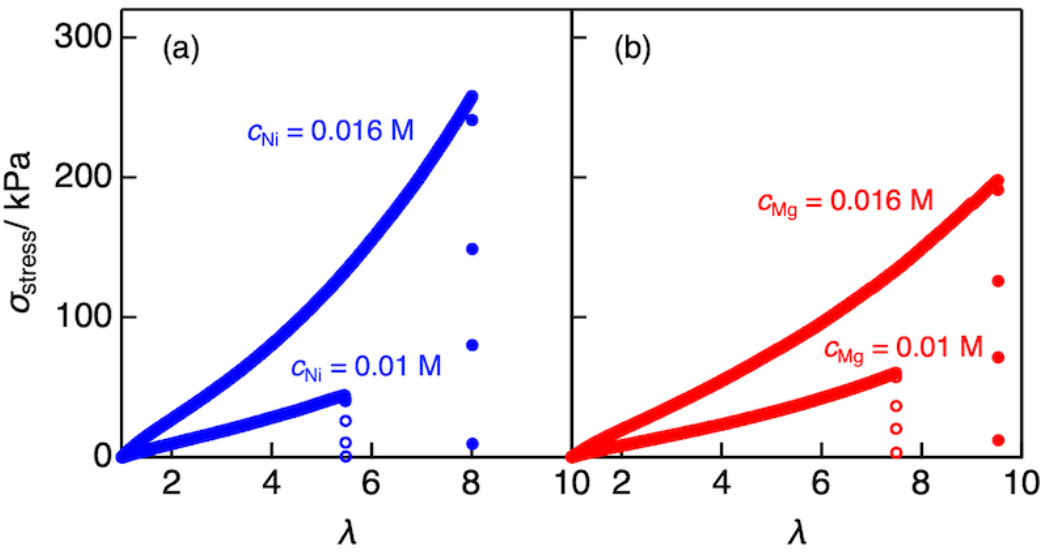


Figure 4. Stress-elongation curves of the 10 wt% TetraPEG ion gels containing (a) Ni^{2+} and (b) Mg^{2+} with varying c_M.

TetraPEG ion gels with varying c_M values (0.016 M and 0.01 M, corresponding to the molar ratio M^{n+}:Cat = 1:2 and 1:3, respectively). The results indicated the significant enhancement of the mechanical strength by increasing c_M in the Ni and Mg systems. It is generally known that the mechanical properties of polymer networks are directly related to the density of the cross-linking point. Regarding the TetraPEG–Cat-based network, the M^{n+}–Cat complex acted as the cross-linking point to form the homogeneous polymer network. Put differently, increasing the c_M value increased the linking point to enhance the mechanical properties of higher-c_M systems. Based on these results, we proposed the following relationship between the mechanical properties and metal ion complexation of TetraPEG–Cat network gels: the Li ions are coordinated with the Cat groups within the TetraPEG–Cat prepolymers via an electrostatic interaction to form Li^+–Cat complexes. The bond strength or stability of the Mg^{2+}–Cat complex is higher than that of the Li^+–Cat complex owing to the stronger electrostatic interaction between Cat and divalent Mg^{2+}. Conversely, Ni^{2+} (a first-transition metal ion) forms more stable complexes with the Cat groups via stronger coordination bonds using its *d*-orbitals. This difference in the M–Cat complexes contributed to the enhanced mechanical strength of the TetraPEG–Cat ion gels. Put differently, the mechanical properties could be readily controlled by metal ion complexation depending on the metal ion–ligand combination.

To gain more insight into the M^{n+}–Cat complexes formed in our TetraPEG network, we investigated the formation of the Ni^{2+}–Cat complex using the UV–vis spectra of a model solution system comprising $Ni(TFSA)_2$ salt in a DMF solution (Figure S2). Here, we controlled Cat deprotonation to generate the linking point via M^{n+}–Cat complexation, as follows. In this gelation system, as described above, we employed C_2Im (a Brønsted base) to catalyze the Michael addition reaction for the terminal modification of TetraPEG. Notably, C_2Im can

simultaneously induce the release of H^+ from the OH moieties within Cat, facilitating the complexation of M^{n+} with Cat. Figure S2 shows that the characteristic peaks of the Ni^{2+} solution without C_2Im appeared at 420 and 680–800 nm and were attributed to the octahedral solvation complex of Ni^{2+} with a solvent molecule,[23] i.e., no complexation occurred between Ni^{2+} and Cat. The spectrum changed drastically when C_2Im was added to the solution, indicating the formation of $[Ni(Cat)_x]$ complexes using deprotonated Cat as a chelate ligand to Ni^{2+}. The characteristic peaks indicating stepwise complexation (x = 1, 2, and 3) appeared with the increasing C_2Im concentrations, resulting in $[Ni(Cat)_3]$ and/or $[Ni(Cat)_2]$ formation at the highest concentration examined (Cat:C_2Im = 1:5).[19-20] During gelation, we added the C_2Im base to the polymer solution at a Cat:C_2Im of 1:20, as described in the synthesis section, indicating that the Ni ions in the TetraPEG–Cat-based ion gel existed as a Ni–Cat complex, which subsequently acted as the cross-linking points in the TetraPEG network. Indeed, the UV–vis spectrum of the 10 wt% TetraPEG ion gel containing $Ni(TFSA)_2$ salt exhibited the characteristic peaks corresponding to the formation of the Ni–Cat complex (Figure S3).

Finally, we measured ionic conductivity σ_{ion} of the TetraPEG–Cat network-based ion gels as a first step toward facilitating their applications as electrolyte materials for electrochemical devices. Figure 5 shows the temperature dependences of σ_{ion} of the 10 wt% TetraPEG ion gels containing Ni^{2+}, Mg^{2+}, and Li^+ at a c_M value of 0.016 M. A similar σ_{ion} profile was observed regardless of the utilized metal ion species. This is due to a large amount of the solvent, IL (i.e., C_2mIm^+ and $TFSA^-$) in the gels, which dominated the ion conduction of the TetraPEG ion gels. The observed σ_{ion} data fitted well with the calculation lines based on the Vogel–Tammann–Fulcher equation: $\sigma_{ion} = \sigma_0 \exp[-B/(T - T_0)]$, where σ_0, B, and T_0, are adjustable fitting parameters. The results are presented in Table S1. The B value, corresponding to the activation

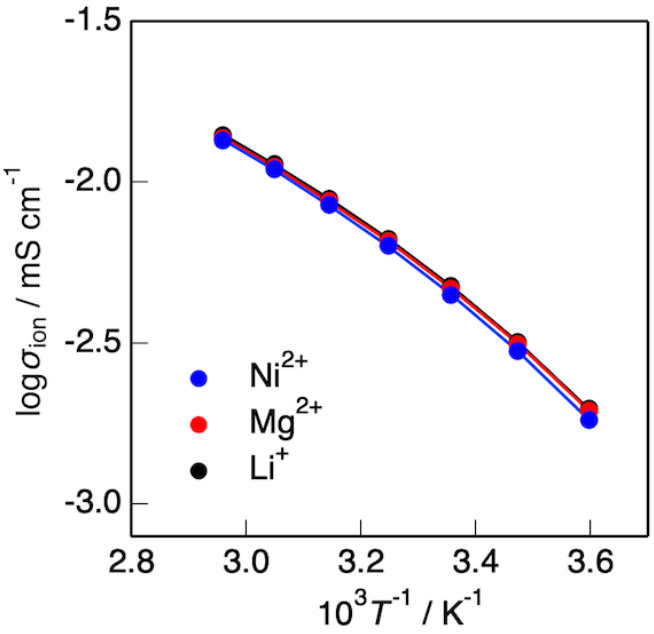


Figure 5. Ionic conductivities of the 10 wt% TetraPEG ion gels containing Ni^{2+} (blue), Mg^{2+} (red), and Li^{+} (black) ions at c_M = 0.016 M.

energy for ion conduction, was almost the same for the three systems examined, indicating that the mechanical strength of the gels could be easily controlled by a combination of metal ions and ligands (i.e., stability in the M–ligand complexes), with no change in the ion-conducting properties. Furthermore, the resulting parameters are almost similar with those for the corresponding chemically cross-linking TetraPEG gel (σ_0: 0.34 S cm^{-1}, B: 440 K, and T_0: 181 K) reported previously. This result suggests that the cross-linking manner (i.e., chemical bond or coordination bond using metal ions) in the polymer network does not affect the ion-conducting behavior that is dominated by the interactions between PEG-chains and solvent ions and the carrier ion concentration in the bulk. Finally, we confirmed that the σ_{ion} values of the current TetraPEG gel systems were slightly lower than that of the corresponding polymer solution system (10 wt% linear PEG in an IL solution containing 0.016 M LiTFSA salt, Figure S4). The origin of such difference in the gel and polymer solution systems is still unknown. We need

further investigation on the ion-transport properties in the TetraPEG-based polymer network with metal-coordination cross-links.

In summary, we established a facile one-step synthesis of a metal ion-complexation-induced homogeneous TetraPEG network ion gel. First, TetraPEG–MA was fully end-functionalized using catecholamine (Cat–NH_2) in IL-based solutions, and the resulting TetraPEG–Cat prepolymers were cross-linked via the complexation of the metal ions and Cat terminals. Employing this TetraPEG–Cat/IL system, we easily controlled and varied the mechanical properties of the ion gels using various metal ion species. Notably, a higher mechanical strength was obtained with transition metal ions owing to the stronger coordination bond of the M^{n+}–Cat complexes acting as a cross-linking point, whereas lower mechanical strengths were obtained with the alkaline-metal ions owing to their weaker complexation based on the electrostatic interactions. Conversely, the ion-conducting properties of the ion gels did not depend on the utilized metal ion species, indicating the good conductivity of the ion gels for application as gel electrolytes for electrochemical devices, such as LIBs and EDLCs.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publication website at DOI:

IR spectra of the ion gel (Figure S1); UV–vis spectra of the Ni–Cat complexes (Figure S2); UV–vis spectra of the ion gel (Figure S3); Ionic conductivities of the ion gel and IL solution (Figure S4); Fitting parameters (Vogel–Tammann–Fulcher equation, Table S1).

AUTHOR INFORMATION

Corresponding Author

*E-mail: k-fujii@yamaguchi-u.ac.jp

Author Contributions

S.T. and T.I. conducted the synthesis, measurements, and data analysis. T.U. contributed to the discussion. K.F. conceived the idea, designed the experiments and analysis, and supervised the project. The manuscript was written through the contributions of all the authors. All the authors have approved the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

This study was financially supported by JSPS KAKENHI (Grant No. JP23H02066, JP23K26759, and JP22H00340. The authors are grateful to Ms. Koyuki Fujita (Yamaguchi University, Japan) for her experiments at the initial stage of this study.

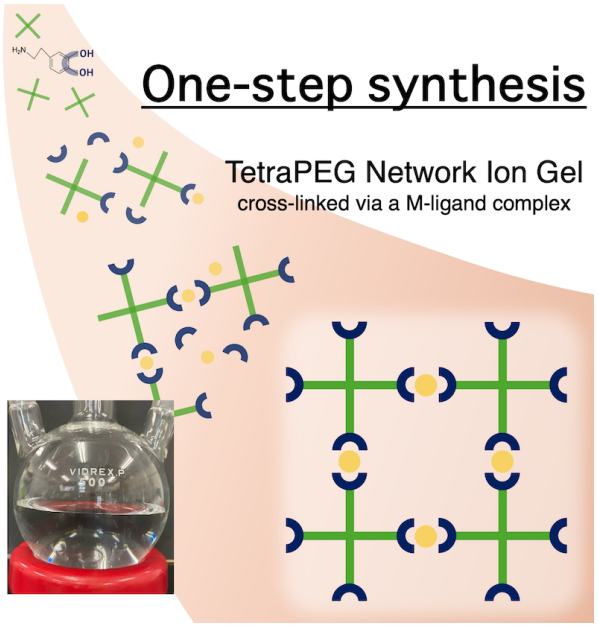
REFERENCE

(1) MacFarlane, D. R.; Tachikawa, N.; Forsyth, M.; Pringle, J. M.; Howlett, P. C.; Elliott, G. D.; Davis, J. H.; Watanabe, M.; Simon, P.; Angell, C. A. Energy Applications of Ionic Liquids. *Energy. Environ. Sci.* **2014,** *7*, 232-250.
(2) Kitazawa, Y.; Ueno, K.; Watanabe, M. Advanced Materials Based on Polymers and Ionic Liquids. *Chem. Rec.* **2018,** *18*, 391-409.
(3) Tamate, R.; Ueki, T. Adaptive Ion‐Gel: Stimuli‐Responsive, and Self‐Healing Ion Gels. *Chem. Rec.* **2023,** *23*, e202300043.
(4) Moghadam, F.; Kamio, E.; Yoshioka, T.; Matsuyama, H. New approach for the fabrication of double-network ion-gel membranes with high CO_2/N_2 separation performance based on facilitated transport. *J. Membr. Sci.* **2017,** *530*, 166-175.

(5) Shahzadi, K.; Xiong, W.; Shekh, M.; Stadler, F. J.; Yan, Z. C. Fabrication of Highly Robust and Conductive Ion Gels Based on the Combined Strategies of Double-Network, Composite, and High-Functionality Cross-Linkers. *ACS Appl. Mater. Interfaces* **2020,** *12*, 49050-49060.
(6) Samitsu, S.; Araki, J.; Kataoka, T.; Ito, K. New solvent for polyrotaxane. II. Dissolution behavior of polyrotaxane in ionic liquids and preparation of ionic liquid‐containing slide‐ring gels. *J. Polym. Sci., Part B: Polym. Phys.* **2006,** *44*, 1985-1994.
(7) Sugihara, N.; Nishimura, K.; Nishino, H.; Kanehashi, S.; Mayumi, K.; Tominaga, Y.; Shimomura, T.; Ito, K. Ion-Conductive and Elastic Slide-Ring Gel Li Electrolytes Swollen with Ionic Liquid. *Electrochim. Acta* **2017,** *229*, 166-172.
(8) Fujii, K.; Asai, H.; Ueki, T.; Sakai, T.; Imaizumi, S.; Chung, U.-i.; Watanabe, M.; Shibayama, M. High-performance ion gel with tetra-PEG network. *Soft Matter* **2012,** *8*, 1756-1759.
(9) Hashimoto, K.; Fujii, K.; Nishi, K.; Sakai, T.; Shibayama, M. Nearly Ideal Polymer Network Ion Gel Prepared in pH-Buffering Ionic Liquid. *Macromolecules* **2016,** *49*, 344-352.
(10) Yoshitake, M.; Han, J.; Sakai, T.; Morita, M.; Fujii, K. TetraPEG Network Formation via a Michael Addition Reaction in an Ionic Liquid: Application to Polymer Gel Electrolyte for Electric Double-layer Capacitors. *Chem. Lett.* **2019,** *48*, 704-707.
(11) Han, J.; Takano, S.; Fujii, K. Tetra-arm Poly(ethylene glycol)-based Ion Gels with Controlled Polymer Network Defects: Application to Lithium-ion Battery Gel Electrolytes. *Chem. Lett.* **2021,** *50*, 1508-1511.
(12) Matsuura, S.; Shibata, M.; Han, J.; Fujii, K. Polymer Gel Electrolyte Prepared by "Salting-In" Poly(ethylene glycol) into a Phosphonium-Based Ionic Liquid with a Lithium Salt. *ACS Appl. Polym. Mater.* **2020,** *2*, 1276-1282.
(13) Han, J.; Osugi, M.; Ikeda, N.; Fujii, K. Lithium salt-concentrated organogels prepared via one-step polymer network formation in acetonitrile-based solutions. *Polymer* **2022,** *262*, 125426.
(14) Tamate, R.; Hashimoto, K.; Horii, T.; Hirasawa, M.; Li, X.; Shibayama, M.; Watanabe, M. Self-Healing Micellar Ion Gels Based on Multiple Hydrogen Bonding. *Adv. Mater.* **2018**, e1802792.
(15) Chen, Y.; Kushner, A. M.; Williams, G. A.; Guan, Z. Multiphase design of autonomic self-healing thermoplastic elastomers. *Nat. Chem.* **2012,** *4*, 467-472.
(16) Shafiq, Z.; Cui, J.; Pastor-Perez, L.; San Miguel, V.; Gropeanu, R. A.; Serrano, C.; del Campo, A. Bioinspired underwater bonding and debonding on demand. *Angew. Chem., Int. Ed.* **2012,** *51*, 4332-5.
(17) Xu, H.; Nishida, J.; Ma, W.; Wu, H.; Kobayashi, M.; Otsuka, H.; Takahara, A. Competition between Oxidation and Coordination in Cross-Linking of Polystyrene Copolymer Containing Catechol Groups. *ACS Macro Lett.* **2012,** *1*, 457-460.
(18) Holten-Andersen, N.; Harrington, M. J.; Birkedal, H.; Lee, B. P.; Messersmith, P. B.; Lee, K. Y.; Waite, J. H. pH-induced metal-ligand cross-links inspired by mussel yield self-healing polymer networks with near-covalent elastic moduli. *Proc. Natl. Acad. Sci. USA* **2011,** *108*, 2651-5.
(19) Krogsgaard, M.; Hansen, M. R.; Birkedal, H. Metals & polymers in the mix: fine-tuning the mechanical properties & color of self-healing mussel-inspired hydrogels. *J. Mater .Chem. B* **2014,** *2*, 8292-8297.
(20) Lu, L.; Tian, T.; Wu, S.; Xiang, T.; Zhou, S. A pH-induced self-healable shape memory hydrogel with metal-coordination cross-links. *Polym. Chem.* **2019,** *10*, 1920-1929.

(21) Ishikawa, A.; Sakai, T.; Fujii, K. An ionic liquid gel with ultralow concentrations of tetra-arm polymers: Gelation kinetics and mechanical and ion-conducting properties. *Polymer* **2019,** *166*, 38-43.
(22) Ishikawa, A.; Ikeda, N.; Maeda, S.; Fujii, K. Polymer network formation mechanism of multifunctional poly(ethylene glycol)s in ionic liquid electrolyte with a lithium salt. *Phys. Chem. Chem. Phys.* **2021,** *23*, 16966-16972.
(23) Ishiguro, S.-i.; Ozutsumi, K.; Ohtaki, H. Calorimetric and spectrophotometric studies of chloro complexes of nickel (II) and zinc (II) ions in *N*, *N*-dimethylformamide. *Bull. Chem. Soc. Jpn.* **1987,** *60*, 531-538.

TOC


One-step synthesis
TetraPEG Network Ion Gel
cross-linked via a M-ligand complex