

ORIGINAL ARTICLE

Tuning of solubility and gelation ability of oligomeric electrolyte by anion exchange

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To tune the miscibility of the gel-forming oligomeric electrolyte, we examined anion exchange reactions using appropriate ammonium or alkali-metal salts. Nine oligomeric electrolytes with different anions were obtained in high yields by the reactions. The solubility of these oligomeric electrolytes in organic solvents was carefully tested. Although the starting material with chloride as a counter anion was not soluble in any organic solvents, excellent miscibility and gelation ability of the oligomeric electrolytes with different anions were consequently observed with dipolar protophilic and aprotic solvents such as *N,N*-dimethylformamide, dimethylsulfoxide and *N,N*-dimethylacetamide. Furthermore, ionogels based on aliphatic ionic liquids were readily formed using the oligomer with bis(trifluoromethanesulfonyl)amide anion at a 40 g l⁻¹ concentration. It is remarkable that the ionic conductivity of the above-mentioned ionogels is almost identical to that of neat ionic liquids, despite the significant increase in the apparent viscosity. This study shows a novel and convenient approach to gelators for multiple solvents.

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Keywords: anion exchange; ionic conductivity; physical gels

INTRODUCTION

The gel is a typical soft matter consisting of an excess of adequate liquid (for example, water or organic solvent) and a relatively small amount of gel-forming compounds. The material often shows both quasi-liquid and quasi-solid natures; thus, many potential applications have been pointed out.^{1–3} Regarding the physical gels, their main feature is a reversible thermal-phase transition between gel and sol states, reflecting the driving force of the gelation based on weak interactions such as hydrogen bonding, π - π stacking, van der Waals forces, charge transfer interactions and electrostatic forces among the gelator molecules.^{4–7}

Although the gel-forming materials based on natural compounds (for example, agar, gelatin) are commercially and inexpensively available in large amounts, they cannot be used for organic solvents because of poor solubility. Difficulty in chemical modification was also observed for such common gel-forming materials. On this account, synthetic gelators promise to improve on the properties of natural gelators by chemical modification of their molecular structure. For instance, when functional groups able to respond to external stimuli are introduced into artificial gelators, the gel–sol transition can be induced by light,^{8–11} pH change¹² or chemical triggers.^{13,14} Despite such an advantage of the artificial functional gels, large-scale production of synthetic gelators is often limited because of multistep syntheses and tedious purifications.

Solvents also control the gel properties. Gels are generally classified into hydrogels and organogels on the basis of the used solvents, that is,

water and organic solvents. Recently, ionic liquids have attracted a great deal of attention as a different type of solvent because of their distinctive properties, including chemical and thermal stability, non-volatility, lower flammability and high ionic conductivity.^{15–18} Owing to these significant characteristics, there has been extensive research on ionic liquids to clarify their fundamental properties and plausible applications. Several low-molecular-weight^{19–21} or polymeric^{22,23} gelators have been developed for ionic liquids to form ionogels, and the applications of ionogel electrolytes for dye-sensitized solar cells showing long-time stability have been reported.^{24–27}

Although there have been reports of amphiphilic gelators for multiple solvents, they are still limited in number.^{28–30} Recently, we reported a new oligomeric physical gelator, poly[pyridinium-1,4-diyl-iminocarbonyl-1,4-phenylene-methylene chloride] **1-Cl**, having pyridinium and amide moieties in its main chain (Scheme 1).³¹ The novel oligomeric gelator **1-Cl** was synthesized by a one-pot synthesis involving condensation and subsequent intermolecular quaternization reaction. The ionic gelator **1-Cl** showed many unique physical properties, especially rheological behavior, showing self-healing after mechanical collapse.^{31–33} In our previous report, we have preliminarily shown that the solubility and gelation ability of the oligomeric electrolyte can be tuned by an anion exchange reaction with fluorinated anions such as hexafluorophosphate (PF₆) or bis(trifluoromethanesulfonyl)amide (TFSA).³¹ Although the initial oligomeric electrolyte **1-Cl** was soluble only in hot water, the products of the

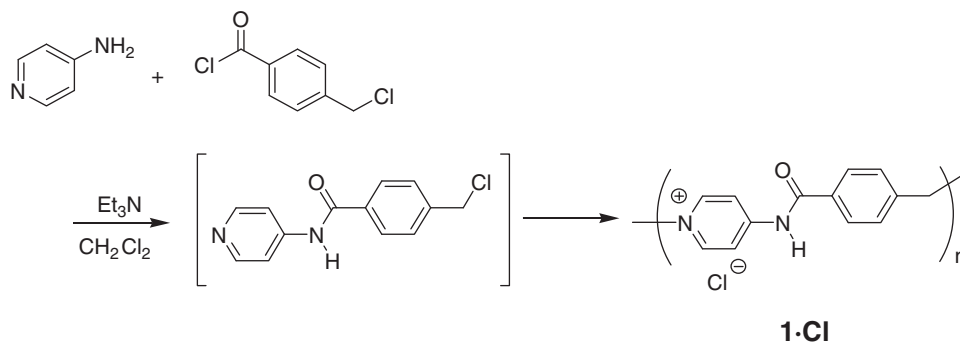
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Scheme 1 Synthesis of oligomeric electrolyte **1-Cl**.

anion exchange reactions were eventually insoluble in water but readily soluble in polar organic solvents. The gelation ability of oligomeric electrolytes **1-PF₆** and **1-TFSA** was also briefly shown for several organic solvents and ionic liquids. The results prompted us to further research multisolvent gelators on the basis of chemical tuning by anion exchange using different types of salts. Herein, we report a number of oligomeric electrolytes with other anions, prepared from **1-Cl** as a structural scaffold, to prove the usefulness of the anion exchange method. The miscibility and gelation property of the oligomeric electrolytes for several organic solvents and ionic liquids are also described.

EXPERIMENTAL PROCEDURE

General procedure

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance-400 (Bruker, Karlsruhe, Germany) (¹H: 400 MHz, ¹³C: 100 MHz). Chemical shifts are denoted in δ-units (p.p.m.) relative to DMSO-*d*₆. ¹⁹F NMR was recorded on a JEOL ECA300 (JEOL, Tokyo, Japan) (¹⁹F: 300 MHz) with CFCl₃ as an internal standard. The solvents were distilled and dried, if necessary, by standard methods. The reagents, including ionic liquids, were purchased from Aldrich (St Louis, MO, USA), Wako (Tokyo, Japan), Kanto Chemical (Tokyo, Japan), TCI (Tokyo, Japan) and Merck (Darmstadt, Germany). Field-emission scanning electron microscope images were obtained using a Topcon DS-720 (Topcon, Tokyo, Japan). Elemental analyses (only for nonfluorinated derivatives to avoid the generation of hydrogen fluoride) were performed by a CE Instruments EA 1110 automatic elemental analyzer (CE Instruments, Wigan, UK). Because of difficulty in completely drying oligomeric electrolyte samples even *in vacuo*, the calculated numbers at the elemental analysis have accounted for the hydration water. Size-exclusion chromatography was conducted on a Shimadzu system (Shimadzu, Kyoto, Japan), comprising an LC-10ADvp pump unit, an SPD-10Avp UV detector (λ=280 nm), a CTO-10Avp column oven and an SCL-10Avp controller, on the Asahipak column (GF-310 HQ (Shodex, Tokyo, Japan), polyvinyl alcohol gel, upper *M_w* limit: 40 000 kDa) in dimethylformamide eluent containing 5 or 30 mM of lithium bis(trifluoromethanesulfonyl)imide at 40 °C. Thermal gravimetric analysis (TGA) was performed on a thermal analysis system (Seiko Instruments, Chiba, Japan, TG/DTA 6200) by placing an average sample weight of 3 mg in a platinum pan and heating at 10 °C min⁻¹ under a flow of nitrogen.

Anion exchange reaction

The oligomer **1-Cl** (*M_w*=2.80, PDI=1.66, polystyrene standard) was prepared in a manner similar to that described in the previous report.³¹ To a solution of oligomer **1-Cl** (1 eq) in hot water was added an aqueous solution of an excess amount (5–20 eq) of appropriate salt. The reaction mixture was then refluxed for 30 min. After cooling to room temperature, precipitates were formed. The product was filtered off, washed with water and dried under vacuum to obtain the corresponding oligomer with the exchanged anion in over 90% yield. Using

1-Cl (292 mg) and ammonium tetrafluoroborate (NH₄BF₄, 6.20 g) as starting materials, **1-BF₄** was obtained as a white powder (343 mg, 97%); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.66 (NH, 1H), 8.96 (2H), 8.35 (2H), 8.08 (2H), 7.68 (2H), 5.83 (CH₂, 2H), ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.0, 153.0, 145.7, 139.8, 133.7, 129.4, 129.0, 116.5, 61.5. ¹⁹F NMR (300 MHz, DMSO-*d*₆) δ -147.66 (¹⁰B-F), -147.72 (¹¹B-F). Using **1-Cl** (860 mg) and ammonium hexafluorophosphate (NH₄PF₆) as starting materials, **1-PF₆** was obtained as a white powder (1.24 g, >99%); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.70 (NH, 1H), 8.96 (2H), 8.35 (2H), 8.08 (2H), 7.67 (2H), 5.84 (CH₂, 2H), ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.0, 153.0, 145.7, 139.8, 133.7, 129.5, 128.9, 116.5, 61.5. ¹⁹F NMR (300 MHz, DMSO-*d*₆) δ -69.6 (J_{P-F}=757 Hz). Using **1-Cl** (277 mg) and lithium bis(trifluoromethanesulfonyl)amide (LiTFSA) as starting materials, **1-TFSA** was obtained as a white powder (343 mg, 97%); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.73 (NH, 1H), 8.96 (2H), 8.35 (2H), 7.67 (2H), 5.84 (CH₂, 2H), ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.0, 153.1, 145.6, 139.8, 133.7, 129.4, 128.9, 121.3, 118.1, 116.5, 61.4. ¹⁹F NMR (300 MHz, DMSO-*d*₆) δ -78.3. Using **1-Cl** (106 mg) and sodium tetraphenylborate (NaBPh₄) as starting materials, **1-BPh₄** was obtained as a white powder (215 mg, 94%); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.72 (NH, 1H), 8.83 (2H), 8.34 (2H), 8.10 (2H), 7.64 (2H), 7.25 (8H), 6.96 (8H), 6.81 (4H), 5.73 (CH₂, 2H), ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.0, 163.6 (q, ¹J_{C-B}=49.3 Hz), 153.0, 145.5, 139.7, 135.8, 133.7, 129.4, 128.8, 125.5 (q, ²J_{C-B}=2.6 Hz), 121.8, 116.4, 61.4. Anal calcd for (C₃₇H₃₁BN₂O(H₂O))_n: C, 81.02; H, 6.06; N, 5.11. Found: C, 80.98; H, 5.91; N, 5.00. Using **1-Cl** (150 mg) and ammonium iodide (NH₄I) as starting materials, **1-I** was obtained as a yellow powder (192 mg, 93%); ¹H NMR (400 MHz, DMSO-*d*₆, at 373 K) δ 9.02 (2H), 8.39 (2H), 8.11 (2H), 7.71 (2H), 5.89 (CH₂, 2H), ¹³C NMR (100 MHz, DMSO-*d*₆, at 373 K) δ 166.2, 152.5, 144.8, 138.6, 133.1, 128.7, 128.4, 115.9, 61.0. Anal calcd for (C₁₃H₁₁N₂IO(H₂O))_n: C, 43.84; H, 3.68; N, 7.87. Found: C, 43.52; H, 3.80; N, 7.49. Using **1-Cl** (257 mg) and sodium thiocyanate as starting materials, **1-SCN** was obtained as a white powder (268 mg, 95%); ¹H NMR (400 MHz, DMSO-*d*₆, at 353 K) δ 11.51 (NH, 1H), 8.95 (8H), 8.35 (2H), 8.09 (2H), 7.69 (2H), 5.86 (CH₂, 2H), ¹³C NMR (100 MHz, DMSO-*d*₆, at 353 K) δ 166.4, 152.7, 145.1, 138.9, 133.3, 128.8, 128.5, 116.1, 61.3. Anal calcd for (C₁₄H₁₁N₃OS(H₂O)_{0.7})_n: C, 59.64; H, 4.43; N, 14.90; S, 11.37. Found: C, 59.99; H, 4.46; N, 15.01; S, 10.57. Using **1-Cl** (321 mg) and sodium dicyanoamide as starting materials, **1-DCA** was obtained as a white powder (326 mg, 94%); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.67 (NH, 1H), 8.96 (2H), 8.34 (2H), 8.08 (2H), 7.67 (2H), 5.84 (CH₂, 2H), ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.0, 153.0, 145.6, 139.8, 133.7, 129.4, 128.9, 119.3, 116.4, 61.4. Anal calcd for (C₁₅H₁₁N₅O(H₂O)_{0.7})_n: C, 62.15; H, 4.31; N, 24.16. Found: C, 62.47; H, 4.17; N, 23.14. Using **1-Cl** (296 mg) and lithium perchlorate (LiClO₄) as starting materials, **1-ClO₄** was obtained as a white powder (352 mg, 94%); ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.66 (NH, 1H), 8.96 (2H), 8.34 (2H), 8.08 (2H), 7.67 (2H), 5.84 (CH₂, 2H), ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.0, 152.9, 145.7, 139.8, 133.7, 129.4, 128.9, 116.4, 61.5. Anal calcd for (C₁₃H₁₁ClN₂O₅(H₂O)_{0.7})_n: C, 48.30; H, 3.87; N, 8.66. Found: C, 48.65; H, 3.85; N, 8.44. Using **1-Cl** (382 mg) and lithium trifluoromethanesulfonate (LiSO₃CF₃) as starting materials, **1-SO₃CF₃** was obtained as a white powder (525 mg, 94%);

^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 11.66 (NH, 1H), 8.96 (2H), 8.35 (2H), 8.08 (2H), 7.68 (2H), 5.84 (CH_2 , 2H), ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$) δ 167.0, 153.0, 145.7, 139.8, 133.7, 129.4, 128.9, 122.5, 116.4, 61.5. ^{19}F NMR (300 MHz, $\text{DMSO}-d_6$) δ -77.3.

Preparation of gels

A typical preparation method of gels was as follows: weighed amounts of gelator and solvent were sonicated in a screw-cap bottle for a short time using a cleaning bath to form a suspension. The suspension was then heated until a clear solution was formed. The solution was cooled at room temperature overnight, and the gelation was then checked visually by inverting the bottle. Regarding the units of concentration of the gels, 'wt%' was used for the comparison between the conventional organic solvents. On the other hand, g l^{-1} was used for the ionic liquids with or without electrolyte additives because their density data to calculate 'wt%' were not always available.

Ionic conductivity measurements

The ionic conductivity (σ) of the ionogels was measured by a conductivity meter (Radiometer Analytical, Lyon, France, CDM-230) in a sealed conductivity cell (Radiometer Analytical, CDC-749) at an appropriate temperature controlled by an incubator. Ionogels were typically prepared with a gelator by heating, and then allowed to stand at room temperature. A conductivity cell was set into the initial hot solution of an ionic liquid containing the gelator before solidification, and the entire system was then cooled at room temperature to form an ionogel.

RESULTS AND DISCUSSION

Syntheses of oligomeric electrolytes by the anion exchange reaction

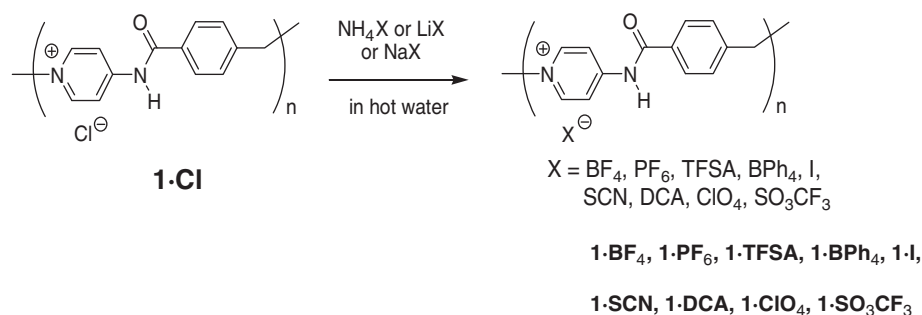
The anion exchange reaction of **1-Cl** ($M_w=2.80$, $\text{PDI}=1.66$, polystyrene standard)³¹ was carried out by the addition of an excess of an appropriate salt in a hot aqueous solution of **1-Cl** (Scheme 2). Ammonium hexafluorophosphate (NH_4PF_6), ammonium tetrafluoroborate (NH_4BF_4), ammonium iodide (NH_4I), sodium thiocyanate, sodium dicyanoamide, sodium tetraphenylborate (NaBPh_4), lithium perchlorate (LiClO_4), LiTfSA or lithium trifluoromethanesulfonate (LiSO_3CF_3) was used for the anion exchange reaction. After the anion exchange reaction, a white or yellowish (in the case of an iodide anion) precipitate was formed. After cooling to room temperature, the precipitate was filtered and dried *in vacuo* to obtain the corresponding oligomer with an exchanged anion. In each case, the conversion yield was fairly high, estimated by a mass balance between the reactant and the product. The thermal properties of the new oligomeric electrolytes were evaluated by TGA. All the compounds were thermally decomposed without melting under the heating condition with nitrogen gas atmosphere (see Supplementary Figure S1). The apparently high char yields (18–40%) should reflect the oligomeric structure of the materials in contrast to the conventional imidazolium ionic liquids, which typically show low char yields (<10%) after pyrolysis in TGA.³⁴ The highest thermal stability was observed for the TGA profile of **1-SO₃CF₃**, in which the decomposition start temperature reached

approximately 350 °C. It is noteworthy that the preference of the SO_3CF_3 anion for the thermal property of the oligomeric electrolytes was also characteristic, in contrast to the common nature of the typical imidazolium ionic liquids.³⁵

Solubility and gelation ability of oligomeric electrolytes in organic solvents

To examine the miscibility and gelation properties of the oligomeric electrolytes in various organic solvents, we referred to the categorization of solvents proposed by Kolthoff,³⁶ which has been commonly used in the area of electrochemistry. According to the classification, general solvents are roughly divided into two main categories: amphiprotic and aprotic solvents. Amphiprotic solvents are subdivided into three categories, neutral, protogenic and protophilic solvents, on the basis of the strength of acidity and basicity compared with water in terms of the Brønsted concept. For aprotic solvents, there are also three subdivided categories, protophilic, protophobic and inert solvents, by the strength of basicity compared with water. Both amphiprotic and aprotic solvents are further divided by the strength of the dielectric factor (ϵ). We tested 13 representative solvents, categorized as 1a, 4a, 4b, 5a and 5c (water, methanol (MeOH), ethanol (EtOH) (category 1a), dimethylsulfoxide (DMSO), dimethylformamide, dimethylacetamide (category 4a), dimethoxyethane, anisole (category 4b), acetone, acetonitrile, propylene carbonate (PC) (category 5a), chloroform and chlorobenzene (category 5c)) in Kolthoff's definition, to investigate the miscibility and gelation abilities of the oligomeric electrolytes for general solvents in organic chemistry and electrochemistry. The results are summarized in Table 1.

It was found that the anion exchange reaction dramatically changed the solubility of the oligomeric electrolyte. Although the oligomeric electrolyte **1-Cl** is not soluble in any organic solvent, the products with an exchanged anion, such as BF_4^- , PF_6^- and TfSA, dissolved well in several organic solvents. In the case of the solvents categorized as 1a, a translucent hydrogel was obtained using **1-BF₄** at 1 wt% concentration, whereas the other oligomers did not dissolve in water. The solubility of **1-BF₄** in water was much lower than that of **1-Cl**; thus, 1 wt% was the maximum concentration of **1-BF₄** even in hot water. **1-TfSA** and **1-SO₃CF₃** were not soluble in water, but sparsely soluble in MeOH. Using **1-TfSA**, a MeOH gel was available at 5 wt% concentration. The oligomers except for **1-Cl** were miscible in the solvents categorized as 4a with moderate basicity and a high dielectric factor ($\epsilon > 20$), such as dimethylformamide, DMSO and dimethylacetamide, while being insoluble in the solvents categorized as 4b, with a low dielectric factor ($\epsilon < 20$). Therefore, the dielectric factor should strongly affect the miscibility of the oligomers, and the intrinsic solubility increased with an increase in the dielectric factor. In addition, organogels of the solvents in category 4a were obtained



Scheme 2 Anion exchange reaction of oligomeric electrolyte **1-Cl**.

Table 1 Solubility and gelation ability of oligomeric electrolytes 1·X (X: anion)^a

Solvent (ϵ) ^b	1·Cl	1·BF ₄	1·PF ₆	1·TFSA	1·BPh ₄	1·I	1·SCN	1·DCA	1·ClO ₄	1·SO ₃ CF ₃
<i>1a</i>										
H ₂ O (78.4)	G	G	I	I	I	P	PG	P	I	I
	G	G ^c	—	—	—	—	—	—	—	—
MeOH (32.7)	I	I	I	S	I	I	I	I	I	S
	—	—	—	G	—	—	—	—	—	P
EtOH (24.6)	I	I	I	I	I	I	I	I	I	I
	—	—	—	—	—	—	—	—	—	—
<i>4a</i>										
DMF (36.7)	I	S	S	S	S	G (0.5)	S	S	S	S
	—	G	S	S	S	G ^c	G (2)	PG	G	PG
DMSO (46.5)	I	S	S	S	S	S	S	S	S	S
	—	S	S	S	PG	G (2)	PG	S	S	S
DMA (37.8)	I	S	S	S	S	G	S	I	S	S
	—	G	S	S	S	G ^c	G	—	G	G
<i>4b</i>										
DME (7.20)	I	I	I	I	I	I	I	I	I	I
	—	—	—	—	—	—	—	—	—	—
Anisole (4.33)	I	I	I	I	I	I	I	I	I	I
	—	—	—	—	—	—	—	—	—	—
<i>5a</i>										
Acetone (20.6)	I	I	I	P	I	I	I	I	I	I
	—	—	—	—	—	—	—	—	—	—
AN (35.9)	I	P	S	S	S	I	I	I	I	I
	—	—	S	S	P	—	—	—	—	—
PC (64.9)	I	S	S	S	S	I	I	PG	S	S
	—	S	S	S	S	—	—	G (1.5)	PG	PG
<i>5c</i>										
CHCl ₃ (4.81)	I	I	I	I	I	I	I	I	I	I
	—	—	—	—	—	—	—	—	—	—
Cl-Bz (5.62)	I	I	I	I	I	I	I	I	I	I
	—	—	—	—	—	—	—	—	—	—

Abbreviations: AN, acetonitrile; Cl-Bz, chlorobenzene; DMA, dimethylacetamide; DME, dimethoxyethane; DMF, dimethylformamide; DMSO, dimethylsulfoxide; EtOH, ethanol; G, gel; I, insoluble; MeOH, methanol; P, precipitate; PC, propylene carbonate; PG, partial gel; S, solution.

^aThe concentration of each oligomeric electrolyte was 1 wt% (above) and 5 wt% (below). First, we tried to test the solubility at 1 wt% concentration; next, when dissolved, the solubility was investigated at 5 wt% concentration. The number in parentheses indicates the minimum gel concentration.

^bDielectric factor of the solvent.

^cThe gel became heterogeneous due to the precipitation of the gelator compound.

with 1·I and 1·SCN at 0.5–2 wt% concentrations. The use of 1·ClO₄ and 1·SO₃CF₃ also resulted in organogels at higher concentrations (5 wt%). The solvents categorized as 5a have a high dielectric factor ($\epsilon > 20$), as do the category-4a solvents, but have a lower basicity than that of water. Despite the high dielectric factor of the solvents of 5a, the oligomers 1·Cl, 1·I and 1·SCN were insoluble even in PC. In contrast, the oligomeric electrolytes 1·PF₆, 1·TFSA and 1·BPh₄ show good solubility in the solvents of 5a, except for acetone. PC is the best solvent to dissolve these oligomeric electrolytes, and a PC gel was obtained using an oligomer 1·DCA at 1.5 wt% concentration. In the solvents categorized as 5c, chloroform and chlorobenzene, all the oligomers were insoluble.

Preparation of ionic liquid gels (ionogels)

Previously, we preliminarily reported that the oligomeric electrolyte 1·PF₆ gelatinized several ionic liquids, that is, 1-ethyl-1-methylimidazolium tetrafluoroborate (EMIm-BF₄) and 1-butylpyridinium

tetrafluoroborate (1-BuPy-BF₄).³¹ As depicted in Figure 1 and Table 2, we further investigated the gelation abilities of oligomeric electrolytes 1·PF₆, 1·BF₄ and 1·TFSA for several ionic liquids on the basis of the imidazolium and tetraalkylammonium structures, which are expected to be useful for electronic devices because of high ionic conductivities and wide electrochemical windows. Although an ionogel of EMIm-BF₄ using 1·PF₆ was obtained at the minimum concentration of 12 g l⁻¹, it was difficult to obtain ionogels on the basis of imidazolium ionic liquids with a longer alkyl chain or the TFSA anion, that is, 1-butyl-3-methylimidazolium tetrafluoroborate (BMIm-BF₄), 1-butyl-3-methylimidazolium hexafluorophosphate (BMIm-PF₆), 1-hexyl-3-methylimidazolium tetrafluoroborate (HMIm-BF₄) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (EMIm-TFSA), by oligomeric electrolytes 1·PF₆, 1·BF₄ and 1·TFSA. It was therefore presumed that the size of cationic moieties or the hydrophobicity of ionic liquids was very important to match the miscibility and gelation property of the oligomeric electrolytes.

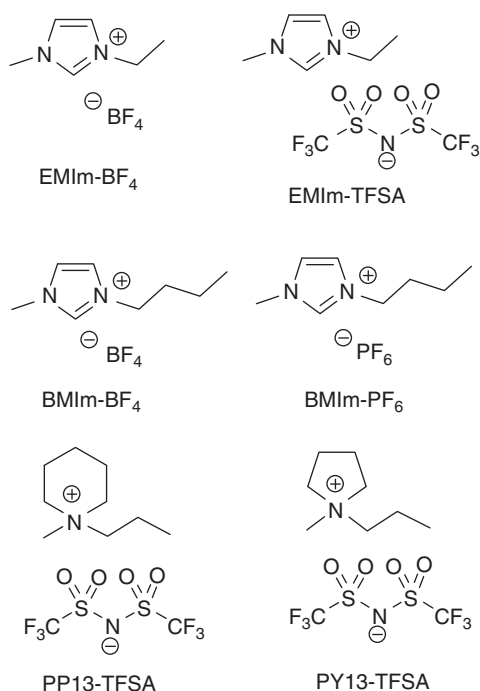


Figure 1 Chemical structures of typical ionic liquids.

Table 2 Gelation ability of **1**·PF₆, **1**·BF₄ and **1**·TFSA in several ionic liquids^a

Ionic liquids	1 ·PF ₆	1 ·BF ₄	1 ·TFSA
EMIm-BF ₄	G (12)	PG	P
EMIm-TFSA	P	P	P
BMIm-BF ₄	P	P	P
BMIm-PF ₆	P	P	—
PP13-TFSA	—	—	G (40)
PY13-TFSA	—	—	G (40)

Abbreviations: G, gel; P, precipitate; PG, partial gel.

^aThe general concentration of each oligomeric electrolyte was 20 g l⁻¹. The number in parentheses indicates the minimum gel concentration (g l⁻¹).

We tried to prepare the dried gel (xerogel) of an ionogel to examine the morphology of the assembled gelator molecules in an ionic liquid. Although the freeze-dry method for preparation of xerogels is generally used, it is very difficult for an ionic liquid to be evaporated by continuous vacuum pumping. Therefore, we obtained dried ionogel after a thorough rinsing of the ionogel based on EMIm-BF₄ with **1**·PF₆ by water to remove the ionic liquid, followed by drying *in vacuo*. As shown in Figure 2, the multilayer film structure was observed in the field-emission scanning electron microscope measurement to be similar to the morphology of a xerogel prepared from a hydrogel based on **1**-Cl.³¹ It is presumed that the liquid medium would be trapped between the layers to be gelatinized, although the multilayer structure is different from that of the known ionogels based on the low-molecular-weight gelators with a three-dimensional fibrous network.²¹ As discussed in the previous section, the solubility of oligomeric electrolytes **1**·TFSA in organic solvents is slightly better than that of **1**·PF₆. Indeed, the oligomeric electrolyte **1**·TFSA was well soluble in several imidazolium-type ionic liquids at a high temperature: EMIm-BF₄, EMIm-TFSA and BMIm-PF₆. Precipitates of

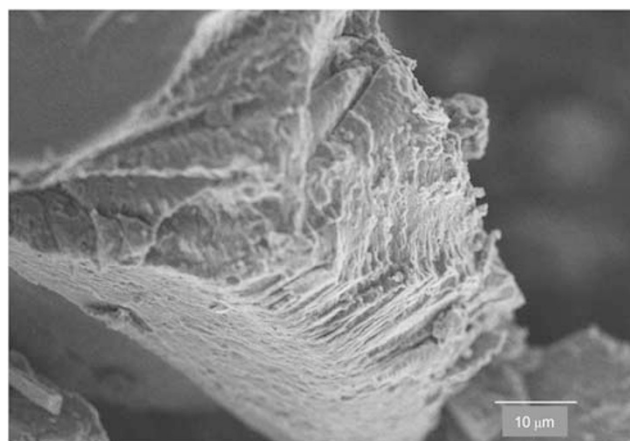


Figure 2 Field-emission scanning electron microscope image of EMIm-BF₄ xerogel formed by **1**·PF₆.

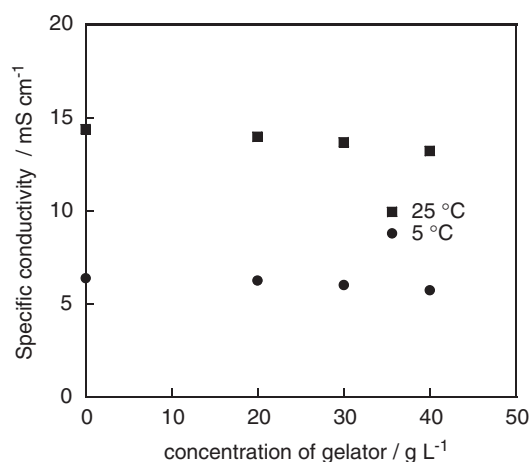


Figure 3 Dependence of the ionic conductivities of the EMIm-BF₄ ionogel on the concentration of **1**·PF₆ at 5 and 25 °C.³¹

1·TFSA, however, were formed in these ionic liquids on cooling. On the other hand, several tetraalkylammonium-type ionic liquids, for example, *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)amide (PP13-TFSA) and *N*-methyl-*N*-propylpyrrolidinium bis(trifluoromethanesulfonyl)amide (PY13-TFSA), were gelatinized using **1**·TFSA at 40 g l⁻¹ concentration. These aliphatic ionic liquids are expected to be useful as the electrolyte for a Li-ion secondary battery because of a wide electrochemical window and the relatively high ionic conductivity among the ammonium-type ionic liquids.³⁷

Ionic conductivities of ionogels

Although one of the most important features of ionic liquids is the high ionic conductivity with respect to the application as a novel organic electrolyte, solid or quasi-solid electrolytes are often preferable in practical uses to prevent electrolyte leakage. If the gelation does not change the intrinsic ionic conductivity of the ionic liquid, the procedure may become a convenient method to obtain quasi-solid electrolytes with high conductivity. However, a decrease in ionic conductivity after gelation of ionic liquids was often observed.^{19–23} We initially reported the ionic conductivities of the EMIm-BF₄ gel formed by the oligomeric gelator **1**·PF₆ at 0–40 g l⁻¹ concentrations at 5 and 25 °C.³¹ Although the ionic conductivity slightly decreased with

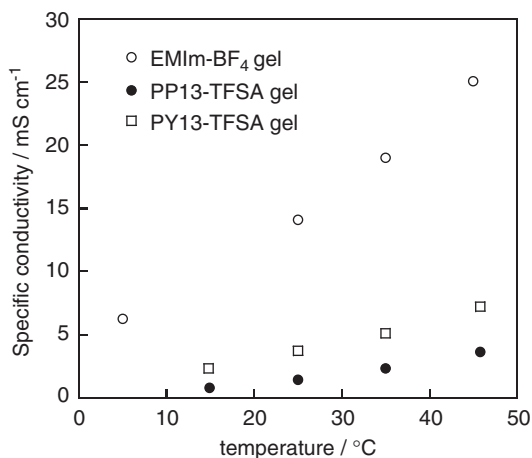


Figure 4 Temperature dependency of the ionic conductivities of ionogels: EMIm-BF₄ gel with **1**-PF₆, PP13-TFSA gel with **1**-TFSA and PY13-TFSA with **1**-TFSA.

Table 3 Comparison of ionic conductivity of ionic liquids and the corresponding gels at room temperature (25 °C)^a

Ionic liquid	Gelator	Temperature (°C)	σ_l (mS cm ⁻¹)	σ_g (mS cm ⁻¹)	σ_g/σ_l
EMIm-BF ₄	1 -PF ₆ ^b	25	14.4	14.1	0.98
		35	19.7	19.0	0.96
		45	25.9	25.1	0.97
PP13-TFSA	1 -TFSA ^c	15	0.85	0.77	0.91
		25	1.6	1.4	0.88
		35	2.6	2.3	0.88
		45	3.8	3.6	0.95
		55	5.3	5.0	0.94
PY13-TFSA	1 -TFSA ^c	15	2.5	2.3	0.92
		25	3.8	3.7	0.97
		35	5.7	5.1	0.89
		45	7.6	7.2	0.95
		55	9.8	9.3	0.95
PP13-TFSA+ 10% LiTFSA	1 -TFSA ^c	15	0.38	0.33	0.89
		25	0.75	0.66	0.88
		35	1.4	1.2	0.86
		45	2.3	2.0	0.87
		55	3.4	3.0	0.88

^a σ_l , conductivity of ionic liquids, σ_g , conductivity of ionogels.

^bThe concentration of gelator **1**-PF₆ was 20 g l⁻¹.

^cThe concentration of gelator **1**-TFSA was 40 g l⁻¹.

increasing amounts of the gelator, the conductivities were almost identical to the intrinsic conductivity of the ionic liquid at each temperature, as shown in Figure 3. The temperature dependencies of the ionic conductivities of the ionogels, namely, the EMIm-BF₄ gel with **1**-PF₆ at 20 g l⁻¹ concentration, PP13-TFSA and PY13-TFSA gels with **1**-TFSA at 40 g l⁻¹ concentration, are described in Figure 4. The ionic conductivity increased with increasing temperature, as with neat ionic liquids, without any apparent change due to the quasi-solid nature. Compared with the ionic conductivities of ionic liquids before and after gelation, it was found that the ionic conductivities were well maintained in a wide range of temperatures in the gel state (Table 3). Although the slight decrease in ionic conductivities is mostly consistent with the observation in the previous study,²¹ the conductivities



Figure 5 Ionogel of PP13-TFSA with **1**-TFSA at 40 g l⁻¹ concentration (right) and ionogel of PP13-TFSA+10% LiTFSA with **1**-TFSA at 40 g l⁻¹ concentration (left) in upturned vials.

observed ($\sigma \sim 10^{-2}$ – 10^{-3} S cm⁻¹) in this study are higher than those in the past report, especially in the case of EMIm-BF₄. We also confirmed that the activation energy (E_a) of the ionic conductivity estimated by an Arrhenius plot did not change after gelation ($E_a=11$, 15, 11 kJ mol⁻¹ for EMIm-BF₄, PP13-TFSA and PY13-TFSA, respectively). Regarding the application for electronic devices, a supporting electrolyte has often been added to the ionic liquids. It is thus worth noting that the oligomeric electrolyte **1**-TFSA gelatinized the mixed solution of an ionic liquid PP13-TFSA, containing 10 wt% concentration of a supporting electrolyte LiTFSA, at the same concentration (40 g l⁻¹) as the original gelation condition without the lithium salt (Figure 5). The ionic conductivity of the ionogel of PP13-TFSA with a LiTFSA salt was maintained at the 86–89% level of the intrinsic values even after gelation, as shown in Table 3.

CONCLUSIONS

The following nine oligomeric electrolytes, **1**-BF₄, **1**-PF₆, **1**-TFSA, **1**-BPh₄, **1**-I, **1**-SCN, **1**-DCA, **1**-ClO₄ and **1**-SO₃CF₃, were prepared by the facile anion exchange reaction using **1**-Cl (poly[pyridinium-1,4-diyl-iminocarbonyl-1,4-phenylene-methylene chloride]) as a starting material. Eventually, we succeeded in tuning the solubility of the oligomeric electrolytes for organic solvents by the anion exchange method from chloride into hydrophobic ones. Several organic solvents with a high dielectric factor, such as dimethylformamide, DMSO, dimethylacetamide and PC, showed excellent miscibility with the oligomers. In addition to organic solvents, several ionic liquids were gelatinized by these oligomeric electrolytes. The ionic conductivities of the ionogels were adequately maintained in comparison with the intrinsic one of neat ionic liquids. The gelator **1**-TFSA also gelatinized an ionic liquid containing lithium salt as a supporting electrolyte. These gelators have the potential to provide gel electrolytes for various electronic devices, such as Li-ion batteries, dye-sensitized solar cells and electric double-layer capacitors.

TGA curves of the oligomeric electrolytes with different anions. This material is available free of charge via the *Polymer Journal* website.

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