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Highly Efficient and Specific Gelation of Ionic Liquids by Polymeric Electrolytes to Form Ionogels with Substantially High Gel–Sol Transition Temperatures and Rheological Properties Like Self-Standing Ability and Rapid Recovery

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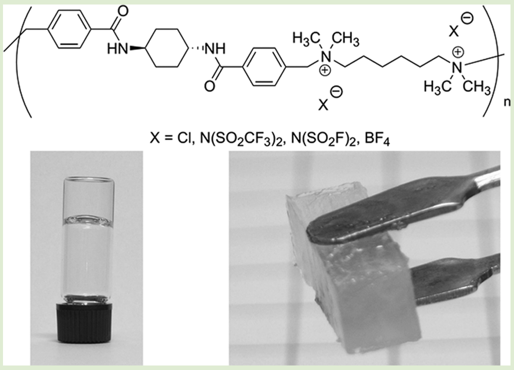
Supporting Information

ABSTRACT: We synthesized gel-forming polyelectrolytes having *N*,*N*′-(*trans*-cyclohexane-1,4-diyl)dibenzamide linkages, with chloride, bis(trifluoromethanesulfonyl)amide, bis(fluorosulfonyl)amide, or tetrafluoroborate anions that could gelatinize a variety of ionic liquids at very low concentrations. The temperatures at which these ionogels transitioned into isotropic fluids were greater than 100 °C even at concentrations as low as 5 g/L. In addition, the ionogels exhibited high mechanical strength without a significant loss in their ionic conductivities, along with the rapid recovery.



Ionic liquids (ILs) have attracted much attention because of their unique properties such as low volatility, thermal stability, nonflammability, intrinsic ionic conductivity, and electrochemical stability.[1] Although one of the most important features of ILs is their high ionic conductivity with respect to their use as fluidic organic electrolytes, solid or quasi-solid electrolytes are often preferred in practical applications to avoid electrolyte leakage. If gelation of the ILs does not change their intrinsic ionic conductivity, the gelation procedure may become a convenient method to obtain conductive quasi-solid electrolytes. Indeed, ionogels[2] have been prepared by several procedures, including in situ polymerization[3] or blending with polymeric materials,[4] by using low-molecular-weight (LMW) gelators,[5] and from solid materials such as carbon nanotubes[6] and inorganic particles.[7] It has also been reported that the ionogels performed well in applications in electrochemical devices, including in organic field-effect transistors.[8] However, a noticeable decrease in the ionic conductivity of the ILs after gelation has often been observed.[3a,c,4a−e,i] In addition, the mechanical strength of ionogels is usually low, and the storage modulus has been typically reported to be in the order of 10^3–10^4 Pa even when the concentration of the gel-forming additives is greater than 10 wt %.[4d−g,j] Finally, a number of processes used to prepare ionogels involve extra steps such as the evaporation of a cosolvent,[4a−c,e−j,5a,7b] centrifugation,[6] and degassing.[7a] Recently, Shibayama et al. reported the ionogels based on the tetra-arm poly(ethylene glycol) (tetra-PEG) network, showing high ionic conductivity and high mechanical properties.[9] In this study, we report new gel-forming polymeric electrolytes that can be used for various ILs (see Chart S1 in the Supporting Information), and the ionogels can be efficiently prepared through gelation by simple thermal dissolution and subsequent cooling. The resulting gel exhibits relatively high mechanical strength and has a storage modulus that is on the order of 10^5 Pa for an additive concentration of only 5 wt %.

We have already reported that linear oligomeric and polymeric electrolytes with both ammonium and benzamide backbones can undergo physical gelation.[10] Some of these electrolytes could be used for ionogel preparation.[10c] In this study, we have prepared a novel ionic gel-forming compound. It is a polymer with *N*,*N*′-(*trans*-cyclohexane-1,4-diyl)-dibenzamide linkages as the key structural moieties and is shown as **CDBA6·X** in Chart 1, where **X** represents a monoanion that is either chloride, bis(trifluoromethanesulfonyl)amide (**TFSA**), bis(fluorosulfonyl)amide (**FSA**), or tetrafluoroborate (**BF$_4$**). **CDBA6·Cl** was synthesized by copolymerization based on the intermolecular quaternization of dielectrophilic and dinucleophilic monomers in a manner similar to that reported in a previous study.[10b]

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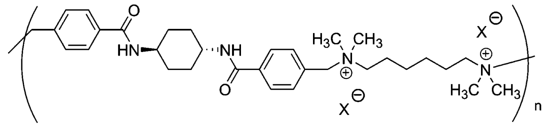
Chart 1. Structures of CDBA6·X



X = Cl, $N(SO_2CF_3)_2$, $N(SO_2F)_2$, BF_4

CDBA6•X

CDBA6·TFSA, **CDBA6·FSA**, and **CDBA6·BF_4** were then prepared by anion exchange reactions of **CDBA6·Cl** with the corresponding anion salts. The weight-averaged molecular weight of the present polymer was 6.81 × 10^4 Da, which was determined by size exclusion chromatography for **CDBA6·TFSA** (see SI). It was found that **CDBA6·X** exhibited a low ability to form a gel in the case of common polar solvents, and only a few of the solvents were gelatinized. For example, **CDBA6·Cl** formed a hydrogel and a methanol gel, and **CDBA6·FSA** produced a propionitrile gel at a concentration of 3 wt % (Table S1). On the other hand, **CDBA6·X** specifically led to the formation of a variety of physical gels of ILs at concentrations that are lower than those of the electrolytes that we had reported previously,[10c] as summarized in Table 1.

Table 1. Gelation Properties of CDBA6·X in Ionic Liquids

polymer	ionic liquids	state at 10 g/L	min gelation concn (g/L)
CDBA6·Cl	[EMI][TFSA]	G	10
CDBA6·TFSA	[EMI][TFSA]	G	3
	[BMI][TFSA]	G	3
	[P13][TFSA]	G	10
	[PP13][TFSA]	G	4
	[PTMP][TFSA]	G	6
	[DEME][TFSA]	G	10
	[EMPy][TFSA]	G	4
	[TMPA][TFSA]	P	
	[SEt_3][TFSA]	P	
	[TBMEP][TFSA]	I	
	[BMI][Tf]	G	5
	[BMI][BF_4]	S	20
	[EMI][BF_4]	P	
	[EMI] [I]	S	
	[BMI][Ac]	S	
CDBA6·FSA	[EMI][FSA]	G	0.9
	[BMI][FSA]	G	2
	[P13][FSA]	G	2
CDBA6·BF_4	[BMI][BF_4]	G	10

[a]Abbreviations: G, gel; S, solution; P, precipitates; I, insoluble.

CDBA6·TFSA gelatinized seven of the representative TFSA anion-based ILs, along with 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([BMI][Tf]) and [BMI][BF_4]. The minimum gelation concentrations were determined by the reversed vial method and found to be in the range of 3–20 g/L, clearly suggesting a very high efficiency. **CDBA6·FSA** also gelatinizes three FSA anion-based ILs at concentrations much lower than 0.2 wt % such as 0.9–2 g/L. To the best of our knowledge, 0.9 g/L (<0.1 wt %) is the lowest concentration at which gelation can occur for any ILs.[5] It is interesting to note that the viscosities of FSA anion-based ILs are about 40% lower than that of the corresponding TFSA anion-based ILs.[11] Therefore, the high efficiency observed in ILs with FSA is not related to the differences in the viscosities, but derived from very effective self-assembly of the polyelectrolytes with FSA in ILs, as similar to the nature of highly efficient LMW gelators.[5] Note that among the other derivatives, **CDBA6·BF_4** gelatinizes [BMI][BF_4] and **CDBA6·Cl** does [EMI][TFSA] (EMI: 1-ethyl-3-methylimidazolium) with moderately high concentrations. All the ionogels with TFSA, FSA, and Tf anions prepared by **CDBA6·TFSA** and **CDBA6·FSA** are colorless and transparent at a concentration of 10 g/L or less in contrast to our previous results to give turbid ones because of the much lower gelation concentrations (Figure S1). The structure of *N*,*N*′-(*trans*-cyclohexane-1,4-diyl)dibenzamide appears important for gelation of ILs, as we have already shown that similar compounds containing the benzene ring instead of the cyclohexane ring of **CDBA6** could form hydrogels but cannot form gels with ILs.[10b]

The gel network structure was analyzed by scanning electron microscopy (SEM) after the removal of the IL from the gel surface in a manner similar to those reported in previous studies.[5c,10c] The SEM image of the low-concentration (3–5 g/L) gel samples of **CDBA6·TFSA**/[EMI][TFSA] after washing of the IL by an appropriate procedure (see SI) is shown in Figure 1. As a result, nanosized fibrous structures with a width of 10–50 nm are observed. The transparency of the ionogel seems to be due to these nanoscale fine structures. A sample stored under high vacuum (6 × 10^{-5} Pa) for 4 d resulted in an image similar to that of the washed one (Figure S2). The film-like structure instead of fibrous one has been observed by SEM for our previous gel systems based on the related oligo- and poly electrolytes.[10] It has been known that both morphologies were observed, reflecting a very small difference of the gelator structures.[12] In the present study, the difference of morphology might be caused by the similar reason of the structural effect on the morphology. Although three-dimensional network structures were generally observed in a variety of gels, the fibrous structures were reported only in a few studies on the ionogel using LMW gelators.[5a,c] To the best of our knowledge, this is the first observation of a fibrous network structure in an ionogel with polymers and is likely due to the noncovalent interactions based on the electrostatic, hydrogen-bond and amide−anion interactions as similar to our previous studies.[13] Actually, the FTIR spectra of **CDBA6·FSA** were measured in solid state, in an acetonitrile solution, and in a [P13][FSA] gel states (10 g/L), respectively (Figure S3). Although N−H stretching vibration was difficult to detect in this condition, the amide-I band was shifted to a lower wavenumber in the gel state (1630

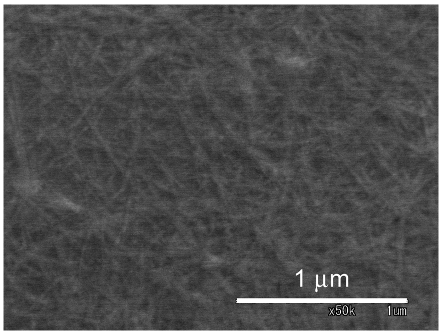


Figure 1. SEM images of the **CDBA6·TFSA**/[EMI][TFSA] gel washed with toluene.

cm^{-1}) than in the solution (1659 cm^{-1}). This result should suggest some interaction of amide carbonyl groups such as hydrogen-bond interaction and electrostatic interaction at carbonyl part may exist in the gel state.

A typical characteristic of physical ionogels is the gel–sol phase transition, because the gel network is based on noncovalent interactions. To discuss the thermal properties of the ionogels, the effect of the concentration on the gel–sol phase transition temperatures (T_{gel}) upon heating are examined, as shown in Figure 2. Obviously, T_{gel} increased with the concentration of the gel-forming electrolytes. Although T_{gel} was affected by the choice of cations and anions, the effect of the anions on T_{gel} was generally greater than that of the cations. For example, in the case of a concentration of **CDBA6·X** at 100 g/L, the range of T_{gel} was narrowly distributed between 69 and 95 °C for the systems having the TFSA anion (Figure 2a). On the other hand, it was widely distributed between 84.5 and 141 °C for the ionogel systems having the BMI cation with different anions and the highest T_{gel} was observed for [BMI][Tf] (Figure 2b). It was also found that T_{gel} for the three ionogels of the FSA anion-based ILs was 33–44 °C higher than that for the corresponding ionogels of the TFSA anion-based ILs for the same concentration of 100 g/L. This result suggests a unique effect of the anions on the thermal properties of the ionogels. T_{gel} was also greater than 100 °C for several FSA anion-based ionogels, such as 5 g/L of **CDBA6·FSA** in [P13][FSA] (P13: 1-methyl-1-propylpyrrolidinium), 20 g/L in [BMI][FSA], and 50 g/L in [EMI][FSA] (Figure S4). The thermal stability above 100 °C suggests that these gels can be used as quasi-solid ionic materials under conditions that include relatively high temperatures.

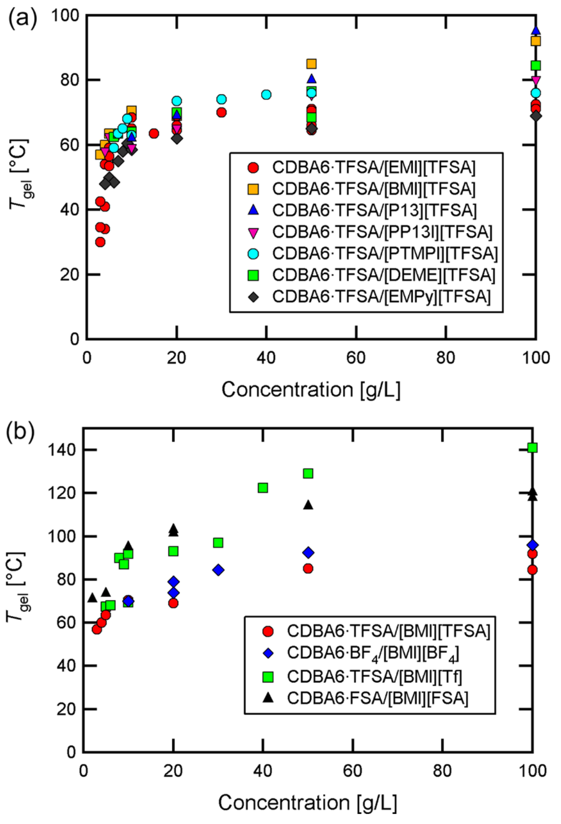


Figure 2. Thermal transition of ionogels on heating. Multiple measurements were performed on several concentrations and each individual value was plotted without averaging. (a) **CDBA6·TFSA** gels of TFSA anion-based ionic liquids having different cations. (b) Ionogels of BMI cation-based ionic liquids having different anions.

The mechanical properties of ionogels are one of the most important factors considered for their practical and sustainable applications. The rheological properties of the ionogel consisting of **CDBA6·TFSA** and [EMI][TFSA] were also investigated. The thermal transition temperature was reconfirmed by the rheological measurements. The point where the storage moduli (G') and the loss moduli (G'') cross was determined at a heating rate of 1 °C/min. The transition temperatures were 70.5 and 73.0 °C for 10 and 20 g/L of **CDBA6·TFSA** in [EMI][TFSA], respectively. These values were fairly consistent with those obtained visually (Figure S5b). In Figure 3a, G' and G'' are plotted against the angular frequency. The data showed that G' was greater than G'' for the entire range of frequencies; this indicates that the elastic component of the dynamic modulus was greater, suggesting that the ionogel acted like a quasi-solid. The strain amplitude sweeps also showed the elastic response of the ionogel (Figure 3b). The value of G' decreased rapidly above the critical strain regions, indicating a strain-induced collapse of the gel state. The value of G' increased with an increase in the concentration of **CDBA6·TFSA** and eventually reached 1 × 10^5 Pa at 50 g/L (Figure S6a). This value is exceptionally high but still comparable with the G' values of the hydrogel based on triblock protein copolymers, in which the cross-linked protein fibers should be the origin of the high moduli.[14] Although we also observed the fibers of xerogels in SEM, more detailed analysis was necessary to clarify the origin of the present high rigidity. Unfortunately, we could not determine G' at higher concentrations because we could not avoid the high compressive pressure, which causes the gel to collapse, when

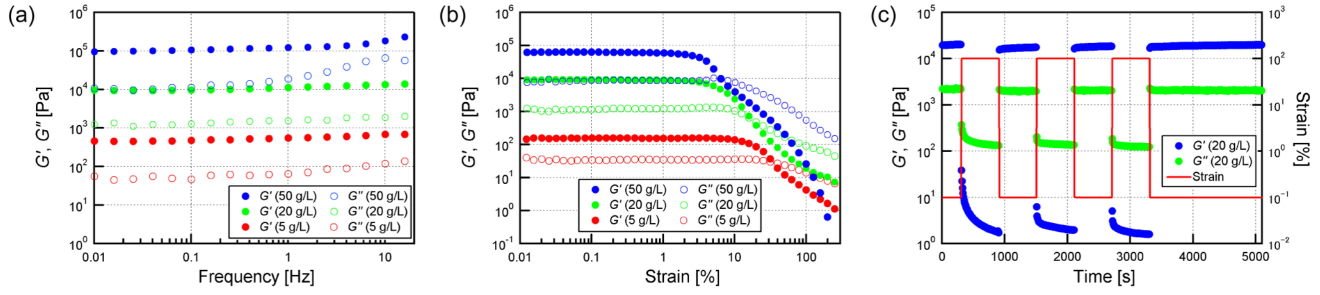


Figure 3. Rheological data of the **CDBA6·TFSA**/[EMI][TFSA] and **CDBA6·FSA**/[EMI][FSA] ionogels. (a) Frequency sweeps of three samples of the ionogels with different concentrations. (b) Strain amplitude sweeps. (c) Step strain measurement (0.1% ↔ 100%) of the **CDBA6·FSA**/[EMI][FSA] ionogel (20 g/L). Step strain measurement was a continuous one (three cycles).

setting the appropriate gap distance between the plates for the experiment; nevertheless, the observed value was almost an order of magnitude greater than that reported for conventional ionogels in previous studies.[4d−g,j] At 50 g/L, the **CDBA6·TFSA**/[EMI][TFSA] ionogel finally became moldable and self-standing, and the gel could be lifted by tweezers (Figure 4).

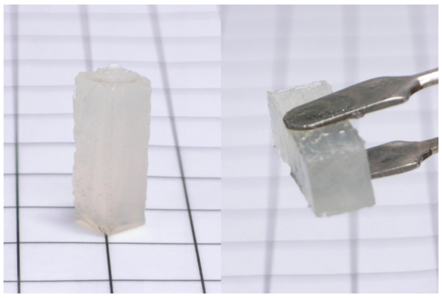


Figure 4. Photographs of a 50 g/L **CDBA6·TFSA**/[EMI][TFSA] ionogel. The gel size is 6 × 6 × 18 mm.

Superior mechanical strength in spite of the noncovalent physical gel network is an additional characteristic of the ionogels investigated in the present study. Except for the recovery behavior, the rheological properties of the **CDBA6·FSA**/[EMI][FSA] ionogel were similar to those of the **CDBA6·TFSA**/[EMI][TFSA] ionogel. The gel consisting of **CDBA6·FSA**/[EMI][FSA] demonstrated a very rapid recovery in its mechanical strength after a breakdown at oscillations of a large amplitude (Figure 3c). The recovery was fully reproducible for at least three cycles. To the best of our knowledge, this is the first observation of a quick, complete recovery and thixotropy in an ionogel, although a similarly rapid recovery has been previously reported by us for hydrogels based on oligomeric and polymeric electrolytes.[10a,b] We have observed that the local gel network was not disrupted under large strain, but that only the interconnects between gel domains were broken, similar to the other rapid recovery gels.[15] We consider the rapid recovery should be mainly caused by the electrostatic interaction at the interconnects, as we have proposed previously,[10a,b] because the phenomenon has been typically observed in several polyelectrolyte-based gels.[10a,b,16] The electrostatic interaction was a long-range force in comparison with the other ones such as hydrogen bond interaction, which can effectively contribute a rapid reconstruction of the gel network. It should be interesting that the electrostatic interaction is still effective on the gel nature of ILs. It is likely to consider that, therefore, the IL solvents could be involved in the present gel network. In the same experiment, the **CDBA6·TFSA**/[EMI][TFSA] gel showed an incomplete recovery of G' when the amplitude of the oscillations was reduced (Figure S8). Therefore, the choice of anion definitely affects the ability to recover rapidly.

The ionic conductivity (σ) of the **CDBA6·TFSA**/ [EMI]-[TFSA] ionogels was measured by the alternating-current impedance method, as shown in Figure S9. For reference, we confirmed that the ionic conductivity of the neat ionic liquid was consistent with the values reported in literature.[17] For the ionogels, although the ionic conductivity decreased slightly with increasing amounts of the gelator, the conductivities were almost identical to the intrinsic ones of the ILs at each temperature. The ionic conductivity increased with increasing temperature, as with the neat ILs, without any apparent change due to the quasi-solid nature. Compared with the ionic conductivities of the ILs before and after gelation, it was found that the ionic conductivities were closely constant ($\sigma_{gel}/\sigma_{neat}$ = 0.91 at 49 g/L on average) in the gel state over a wide range of temperatures. For the **CDBA6·FSA**/[EMI][FSA] ionogels, the ionic conductivities were also constant at concentrations lower than 30 g/L ($\sigma_{gel}/\sigma_{neat}$ = 0.96 at 30 g/L and 0.82 at 50 g/L, on average; see Figure S10). These values are comparable with those reported for ionogels with good conductivity, prepared by LMW gelators,[5c−e] silica particles,[7a] and tetra-PEG.[9a]

In conclusion, we succeeded in improving the ability of polymeric electrolytes to gelate ILs, by introducing *N*,*N*′-(*trans*-cyclohexane-1,4-diyl)dibenzamide linkages and modifying the main chain structure of the polymeric gelators. These ionic gelators gelatinize a variety of ILs at very low concentrations without the need for complicated procedures. The thermal gel−sol transition temperatures of these ionogels were greater than 100 °C when FSA and Tf were used as the IL anions. The ionogels exhibited high mechanical strength without a significant loss in their ionic conductivities, along with the rapid recovery. We believe that these novel polymeric gelators have the potential to provide gel electrolytes for various electrochemical devices such as Li-ion batteries, electric double-layer capacitors, and dye-sensitized solar cells.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, compound characterization data, abbreviations of the structures of the ILs, gelation properties, photographs of the ionogels, SEM images, IR spectra, T_{gel} data, rheological data, and conductivity data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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