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Palmitoylated amino acids as low-molecular-weight gelators for ionic liquids

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Abstract

We report palmitoylated amino acids (Gly, L-Val, L-Ile, L-Asp, L-Glu, L-Met, L-Phe, L-Lys) as low-molecular-weight gelators for ionic liquids (ILs). The palmitoylated amino acids gelate ammonium- and imidazolium-based ILs, at gelation concentrations of 0.3–1.6 wt.%, despite their simple molecular structures. Eight types of gelators are synthesized, with palmitoylated methionine (Pal-Met) and palmitoylated phenylalanine (Pal-Phe) exhibiting high gelation ability towards the tested ILs. Scanning electron microscopy and confocal laser scanning microscopy observations suggest that the gelator molecules self-assemble into nanofibers within the ILs, which leads to gelation. The ionogels exhibit reversible thermal transition and viscoelastic properties, which are typical of gels. Fourier-transform

infrared spectra recorded at various temperatures reveal that hydrogen bonding and van der Waals interactions between gelator molecules are important in the self-assembly. Incorporating gelators of varying concentrations do not affect the intrinsic conductivities of the ILs.

Keywords: palmitoylated amino acids, self-assembly, ionic liquids, gels

Introduction

Ionic liquids (ILs) exhibit high ionic conductivities and ultralow vapor pressures, are non-flammable and thermally stable, and have wide operating temperature and electrochemical stability ranges [1,2]. These characteristics make them ideal as electrolytes in batteries [3-5], capacitors [6-7], fuel cells [8] and photovoltaic devices [9]. The use of ILs in organic synthesis, chemical separation, cleaning operations, and catalysis has been extensively studied [10-11]. The demand for safety and high performance has led to much interest in immobilizing ILs as electrolytes in electrochemical devices [12]. Ionogels consist of an IL immobilized in a polymer matrix, and gelation to form ionogels is an effective strategy in immobilizing ILs. Ionogels have been synthesized using organic polymer-based gelation [13-17], inorganic polymer-based gelation [18-20] and low-molecular-weight gelators (LMWGs) or supramolecular gelators [21-31].

Supramolecular gelators have potential in materials and biomimetic engineering, because their useful properties can be tailored to a potential application. LMWGs are representative supramolecular gelators. LMWGs can self-assemble into fibrous or sheet-like structures, because of their non-covalent hydrogen bonding, π - π stacking, hydrophobic and / or van der Waals interactions [24,26,32-34]. Non-covalent interactions between gelator molecules create a three-dimensional network, and provide flexibility to the gel network. The molecular structures of LMWGs can be designed to respond to stimuli such as pH, sonication, the presence of redox, ligand and enzyme species [35-41]. The first example of an ionogel using a LMWG was reported by Kimizuka and Nakashima in 2001. They

demonstrated the thermoreversible molecular self-assembly of a synthetic glycolipid in an IL and the resulting ionogel had a bilayer membrane structure [21]. They demonstrated that amide bonds were important in the molecular self-assembly in the IL. Hanabusa et al. reported cyclo(dipeptides) gelators for ILs which yielded thermally stable ionogels [24]. Cyclo(dipeptides) gelators from aspartame formed ionogels with many different kinds of ILs, including imidazolium, pyridinium, pyrazolidinium, piperidinium, morpholinium and ammonium salts with gelator concentrations of <1.0 wt.%. The ionogels exhibited wide electrochemical windows and their ionic conductivities were not significantly affected by the gelator concentration. Tu et al. reported the first organometallic gelator, a pyridine-bridged bis(benzimidazolylidene)-palladium complex, that could gelate various ILs. They demonstrated that π - π stacking, van der Waals interactions and metal-metal bonding contributed to the gelation of the ILs [26].

There are numerous reports of the LMWGs used to form ionogels. However, many of LMWGs suitable for ionogels have relatively complicated molecular structures. The difficulty in their syntheses and their limited availability inhibit further studies of ionogels in a broad range of fields, especially by those who are not experts in organic synthesis. Herein, we report LMWGs with simple molecular structure based on palmitoylated amino acids which can act as LMWGs for ILs. The gelation properties of various palmitoylated amino acids and the characteristics of the resulting ionogels are discussed.

Experimental

Materials

Fatty acids, *N*-hydroxysuccinimide (NHS), amino acids (L-aspartic acid (L-Asp), glycine (Gly), L-glutamic acid (L-Glu), L-isoleucine (L-Ile), L-methionine (L-Met), L-phenylalanine (L-Phe), L-valine (L-Val)), sodium chloride, potassium carbonate, ethyl acetate, *n*-hexane, hydrochloric acid and tetrahydrofuran (THF) were purchased from Wako Pure Chemical Industries (Osaka, Japan). *N*^α-(tert-butoxycarbonyl)-L-lysine (L-Lys) was purchased from Tokyo Chemical Industry (Tokyo, Japan). *N,N*-

Dimethylformamide (DMF) was purchased from Watanabe Chemical Industries (Hiroshima, Japan) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) was purchased from Dojindo Molecular Technologies (Kumamoto, Japan). Full names and molecular structures of the ILs are listed in the ESM (Fig. 1 and S1). [BuMeIm][TFSA] was synthesized from [BuMeIm][Br] and [Li][TFSA] as described below. [EtMeIm][TFSA] was purchased from Sigma Aldrich (St. Louis, MO, USA). [BuMeIm][CF₃SO₃] and [EtMeIm][CF₃SO₃] were purchased from Merck KGaA (Darmstadt, Germany). [TMPA][TFSA] was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). Water used was produced by a Millipore water purification system.

Synthesis of Ionic liquid [BuMeIm][TFSA]

1-Buthyl-3-methylimidazolium bromide ([BuMeIm][Br]) (0.079 mol), lithium bis(trifluoromethanesulfonyl)imide ([Li][TFSA]) (0.087 mol) and deionized water (170 ml) were mixed in an eggplant-shaped flask for 3 h at room temperature. The resultant lower phase was washed with deionized water several times. The obtained IL was freeze-dried overnight and stored in a desiccator until use.

Instrumentation

¹H NMR spectra were obtained using a 500 MHz Bruker AV-500 spectrometer (Bruker BioSpin AG, Fällanden, Switzerland). Fourier transform infra-red (FTIR) spectra for characterization of synthesized gelators were recorded on a Bruker Alpha-E equipped with an attenuated total reflection unit (Bruker Optik GmbH, Ettlingen, Germany). Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF/MS) measurements were carried out using an UltrafleXtreme TM mass spectrometer (Bruker, Billerica, MA, USA).

Field emission-scanning electron microscopy (FE-SEM) observations were carried out using a field emission scanning electron microscope (JSM-7500F, JEOL, Japan), operated at an accelerating voltage

of 7 kV. For sample analysis, ionogels were converted to xerogels using the procedure reported by Hanabusa et al. [24]. Briefly, the ionogels were immersed in water for 3 days (water was refreshed each day) to exchange the ILs in the gels with water. The obtained gels were freeze-dried. The resulting xerogels were mounted on an aluminum stub and coated with osmium by vapor deposition.

Confocal laser scanning microscopy (CLSM) observations (Nikon Corp., Tokyo, Japan) were carried out at room temperature with excitation by a He-Ne laser at 543 nm and an emission bandpass at 605–1000 nm. Ionogels were stained with rhodamine B (30 μ M) prior to observation.

Rheology measurements were carried out using a rheometer (Anton Paar Physica MCR301, Graz, Austria) with a parallel plate (diameter of 5.0 cm) in a rotation mode, a strain of 0.1% and gap of 0.5 mm. For sample measurements, the gelator-containing IL solution (0.7 wt.%) was loaded on a sample plate whose temperature was set at 90 °C. The sample plate was then gradually cooled to 25 °C and the measurement was started.

The gel-sol transition temperatures (T_{gel}) of the ionogels were measured using a Thermoplus Evo instrument DSC8230 (Rigaku, Tokyo, Japan) in aluminum pans with a heating rate of 3 °C/min.

FTIR spectra were recorded under vacuum at temperatures of 30, 60, 100 and 120 °C, using a FT/IR-660 plus spectrometer (Jasco, Tokyo, Japan). Spectra were recorded from 1024 scans at a resolution of 4 cm^{-1} . The sample ionogel was sandwiched between two pieces of silicon wafer (1.5 $\times$ 1.5 cm) and detected by a mercury cadmium telluride detector.

The conductivities of ionogels were measured at 25 °C using a Hioki 3532-80 Chemical Impedance Meter (Japan). The isotropic hot solution of the IL containing the gelator was injected into the U-tube, followed by gelation. The cell constant was determined by measuring the conductivity of KCl solution (7.44 g/L).

Results and Discussion

Gelation of ILs

LMWGs with simple palmitoylated amino acid structures were synthesized, as shown in Fig. 2. All gelators consisted of an amino acid that are conjugated to palmitic acid. The amino acids used were Gly, L-Val, L-Ile, L-Asp, L-Glu, L-Met, L-Phe and L-Lys. The alkyl chain and amide bonds are expected to play important roles in the formation of the fibrous structures, by promoting self-assembly of the gelator molecules in the ILs. Long alkyl chains can provide hydrophobic interactions and amide bonds can provide intermolecular hydrogen bonding [30,34]. The ionogels were prepared by heating the ILs containing the gelators to 120 °C and subsequent cooling to room temperature. All gelators were dissolved in all tested ILs at 120 °C.

Table 1 shows the results of the gelation tests for the imidazolium and ammonium-based ILs. The synthesized gelators were effective gelators for many of the tested ILs, in which the minimum gelation concentration (MGC) varied over the range 0.3–1.6 wt.%. Gelator **1** had the simplest amino acid structure (Gly) and resulted in the translucent gelation of [TPMA][TFSA] at 0.7 wt.%. Gelators **2** and **3** had L-Val and L-Ile residues, respectively, and showed higher gelation ability for [TPMA][TFSA]. Their MGC values were 0.5 and 0.4 wt.%, respectively. These gelators also showed good gelation ability for the imidazolium-based ILs. [BuMeIm][TFSA] with 0.4 wt.% gelator **3** yielded a translucent gel, as shown in Fig. 2b. Gelators **4** and **5** exhibited similar MGC values. Gelator **6** showed high gelation ability for many of the tested ILs. Their MGC values were below 1.0 wt.%. Table 1 shows that the critical gelation concentrations were generally <1.0 wt.%, for the four different ILs. Gelator **7** had an aromatic ring side chain and exhibited gelation ability toward all ILs except for [BuMeIm][TFSA]. High MGC values tended to be associated with opaque gels, for example [BuMeIm][TFSA] with 1.4 wt.% gelator **7**, as shown in Fig. 2b. This probably resulted from relatively large structures, such as thick fibers, forming during self-assembly. Gelator **8** also gelled [TPMA][TFSA] at a low concentration, yielding a translucent gel. These results demonstrate that many palmitoylated amino acids act as LMWGs for ionic liquids. The present LMWGs contained acidic, basic, and neutral amino acid residues. This suggests that any repulsion between the amino acid side

chains was negligible in ILs.

We also tested gelation of non-fluorinated ionic liquids using gelators **6** and **7**. Amino acid-based ionic liquids ([EtMeIm][Gly] and [EtMeIm][Ileu]) and [EtMeIm][acetate] were used as non-fluorinated ionic liquid (Fig. S1). [EtMeIm][Gly] and [EtMeIm][Ileu] were gelated by 2.0 wt/vol. % gelator **6** but not by gelator **7**. [EtMeIm][acetate] was gelated by 1.9 wt.% gelator **6** and not by gelator **7**. These results suggest that the present gelators work for a wide variety of ionic liquids.

Solubility and gelation tests were carried out for gelators **1–8** (1.5 wt.%) in several solvents. All gelators were soluble in acetonitrile, ethyl acetate, tris-HCl buffer and Hepes buffer at high temperature (i.e. near the solvent boiling point). Many of the gelators were also soluble in ethanol, toluene, 1,4-dioxane and dichloromethane. None of the tested solvents containing gelators hardened after cooling to room temperature. Thus, the present gelators are suitable for ILs [31].

Microscopy observations of ionogels

In many gels formed using LMWGs, gelator molecules self-assemble to form fibrous structures because of non-covalent interactions among the molecules [21,24,30,31]. To confirm this for the current gelators, we selected the ionogels of [EtMeIm][TFSA] with gelator **6** and [TMPA][TFSA] with gelator **7** and observed the morphologies of these ionogels by FE-SEM and CLSM because these ionogels were translucent and were prepared with relatively low gelator concentrations (high gelation ability). FE-SEM images of the ionogels show three-dimensional fibrous network structures. This probably resulted from the self-assembly of gelator molecules in [EtMeIm][TFSA] and [TMPA][TFSA], as shown in Fig. 3a and b, respectively. The diameters of the fibers were about 1.0–5.0 and 0.5–1.0 μm , respectively. Gelator **7** formed fibers with diameters of $<1\ \mu\text{m}$ in [TMPA][TFSA], which explains why the ionogel of [TMPA][TFSA] with gelator **7** was translucent (Table 1).

CLSM observations were carried out to observe the in-situ morphologies of the ionogels (Fig. 3 c and d). Rhodamine B (30 μM) was used to stain the ionogels prior to observation. Rhodamine B is

highly soluble in ILs, so was thought to be localized between nanofibers where the gelator resided [30,31]. Dark fibrous regions were observed in CLSM images of [EtMeIm][TFSA] containing 0.5 wt.% gelator **6** and [TMPA][TFSA] containing 0.7 wt.% gelator **7**. These indicated fibrous structures within the ionogels.

Rheological and calorimetric measurements of the ionogels

Rheological measurements with dynamic frequencies were carried out approximately 1 h after sample cooling on the three different ionogels, [EtMeIm][TFSA] and [EtMeIm][CF₃SO₃] with 0.7 wt.% gelator **6** and [TMPA][TFSA] with 0.7 wt.% gelator **7** (Fig. 4a–c). The values of the storage modulus (G') for the ionogels [EtMeIm][TFSA] and [EtMeIm][CF₃SO₃] with 0.7 wt.% gelator **6** were about twelve and six times higher, respectively, than those of the loss modulus (G'') over the entire angular frequency range (0.1–100 rad/s) at 25 °C (Fig. 4a and b, respectively). These results indicated that [EtMeIm][TFSA] and [EtMeIm][CF₃SO₃] containing 0.7 wt.% gelator **6** exhibited gel-like characteristics. The values of G' for the ionogel [TMPA][TFSA] containing 0.7 wt.% gelator **7** were also higher than those of G'' over the entire angular frequency range, as shown in Fig. 4c. This trend is typical of gels.

A thermoreversible gel-sol transition is a characteristic of supramolecular gels. The gel-sol transition temperatures (T_{gel}) of the ionogels [EtMeIm][TFSA] containing gelators **6** and **7** were observed by differential scanning calorimetry (DSC). Endothermic peaks were observed at 78 °C for the ionogel containing 1.3 wt.% gelator **6** (Fig. 5a) and at 86 °C for the ionogel containing 1.3 wt.% gelator **7** at the second heating (Fig. 5b). Observations by the naked eye confirmed that these ionogels were in the liquid state above the observed T_{gel} and in the gel state below the T_{gel} . These T_{gel} values were comparable to those reported by Das et al [29], but lower than those of our gelators previously reported [30,31]. These T_{gel} values might be affected by the number of intermolecular interaction sites in their molecular structures and to the interaction strength. It should be noted that a pristine ionic

liquid [EtMeIm][TFSA] does not show an exothermic or exothermic in the present measurement temperature range [42,43].

FTIR spectra of ionogels

FTIR spectra were recorded at various temperatures to evaluate the interactions between the gelator molecules. The FTIR spectrum of [EtMeIm][TFSA] containing 0.7 wt.% gelator **6** is shown in Fig. 6a. The typical peptide bonds in the absorption regions of amide I and II were observed [44,45]. Peaks in the regions of 1600–1690 and 1480–1590 cm^{-1} were assigned to the amide I and II bands, respectively (Fig. 6b). Amide I is attributed to the C=O bond stretching vibration while amide-II band is to C-N stretching and N-H bending. These peaks can be also used to evaluate the hydrogen bonding in peptide gelator studies [46,47]. Although the peak 1573-1576 cm^{-1} is also attributed to C-N stretching from the ionic liquid [48-50], there is overlapping of two types of bonding in this region. Fig. 6b shows that the amide I peak at 1647 cm^{-1} shifted into 1645 cm^{-1} with increasing temperature up to 60 °C and disappeared for the further increasing temperature, which coincided with the gel-sol transition at 78 °C (T_{gel}). The amide I band is predominantly C=O stretching in character. It is associated with the backbone conformation, thus is affected by the number and strength of the hydrogen bonding [44-47]. The shift and disappearance of these peaks were caused by a change in hydrogen bonding during the gel-sol transformation of the ionogel. The increasing temperature perturbed the hydrogen bonding due to some changes in a longer hydrogen bond and incline number of disrupted intermolecular hydrogen bonding, so that it resulted in the shift and disappearance of the peaks. These results confirmed that hydrogen bonding is important in the self-assembly of the gelator molecules in the IL [30,31].

We also observed peaks at 3000–2700 cm^{-1} at 30 °C. These were assigned to C–H vibrations and are often used to evaluate interactions between alkyl chains [51]. The peaks at around 2849 and 2915 cm^{-1} corresponded to the C–H symmetric and asymmetric stretching vibrations, respectively (Fig. 6c). The C–H symmetric stretching peak shifted to 2850 cm^{-1} at temperature of 60 °C and to 2857 cm^{-1} for

the temperature of 100 and 120 °C. While the peak of C–H asymmetric stretching shifted to 2917 cm⁻¹ at 60 °C and disappeared for higher temperature, which are also consistent with T_{gel} of [EtMeIm][TFSA] containing 0.7 wt.% gelator **6**. These indicated that the interactions between alkyl chains in the gel state were probably van der Waals forces [51].

There also observed peaks at 3300–3000 cm⁻¹ at 30 °C, which would be derived from hydrogen bonding. However, we did not find a remarkable change in the absorption when increasing temperature.

Conductivity of ionogels

The ionic conductivities of the ILs and the ionogels of [EtMeIm][TFSA], [BuMeIm][CF₃SO₃], [EtMeIm][CF₃SO₃] and [TMPA][TFSA] using gelator **6** are shown in Fig. 7. The conductivity of the [EtMeIm][TFSA] ionogel decreased slightly with increasing gelator concentration. However, there was only an 18% decrease in conductivity at 3.0 wt.% of gelator **6**, compared with that of [EtMeIm][TFSA]. The ionogels of [BuMeIm][CF₃SO₃], [EtMeIm][CF₃SO₃] and [TMPA][TFSA] retained the ionic conductivities of their respective ILs, even at gelator concentrations of 3 wt.%. These results agree well with previous reports, in which the ionic conductivities of ionogels were not affected by LMWG concentrations [17,24,30,31]. The constant conductivity may have resulted from the vacant space between nanofibers, in which ions could move as freely in the gel state as in the liquid state [17,24,30,31].

Conclusions

A simple molecular structure of supramolecular gelator composed of fatty acid and an amino acid is studied specifically toward ionic liquids. The palmitoylated amino acids L-Asp, Gly, L-Glu, L-Ile, L-Lys, L-Met, L-Phe and L-Val self-assemble into fibrous networks at relatively low concentrations and result in ionogels. FTIR measurements suggest that these fibrous network structures are formed by self-assembly of the gelator molecules, because of non-covalent interactions including hydrogen

bonding between amide bonds and hydrophobic interactions between alkyl chains. The ionogels prepared using the palmitoylated amino acids retain the high intrinsic conductivities of the ILs, even at high gelator concentrations. The new LMWGs have simple structures and are easily synthesized, so that they can be used as gelators in a broad range of fields thus extending the potential of ionogels.

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Conflict of Interest

The authors declare that they have no conflict of interest.

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Table and Figures

Table 1 Gelation properties of gelators 1–8*

Gelator	Ionic liquid				
	[BuMeIm][TFSA]	[EtMeIm][TFSA]	[BuMeIm][CF ₃ SO ₃]	[EtMeIm][CF ₃ SO ₃]	[TMPA][TFSA]
1. Pal-Gly	TG(1.0)	TG(1.2)	TG(0.9)	vS	TG(0.7)
2. Pal-Val	OG(1.0)	OG(0.8)	OG(1.3)	TG(0.4)	TG(0.5)
3. Pal-Ileu	TG(0.4)	OG(0.5)	OG(1.6)	vS	TG(0.4)
4. Pal-Asp	TG(1.0)	TG(0.8)	TG(1.2)	TG(0.7)	TG(0.7)
5. Pal-Glu	TG(0.7)	TG(0.8)	TG(1.6)	TG(0.7)	TG(0.8)
6. Pal-Met	TG(0.5)	TG(0.5)	TG(1.3)	TG(0.5)	TG(0.5)
7. Pal-Phe	OG(1.4)	TG(0.3)	TG(0.9)	TG(0.5)	TG(0.5)
8. Pal-Lys	vS	TG(0.7)	TG(0.9)	TG(1.1)	TG(0.4)

*TG, OG and vS indicate translucent gel, opaque gel and viscous solution, respectively. Minimum gelation concentrations (MGCs) in wt.% are given in parentheses.

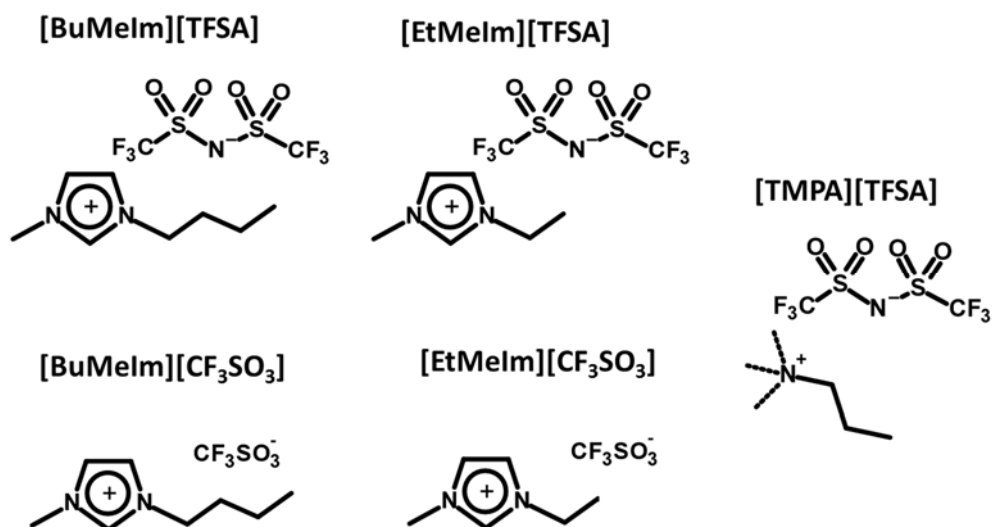


Fig. 1 Molecular structure of the ionic liquids used in gelation test.

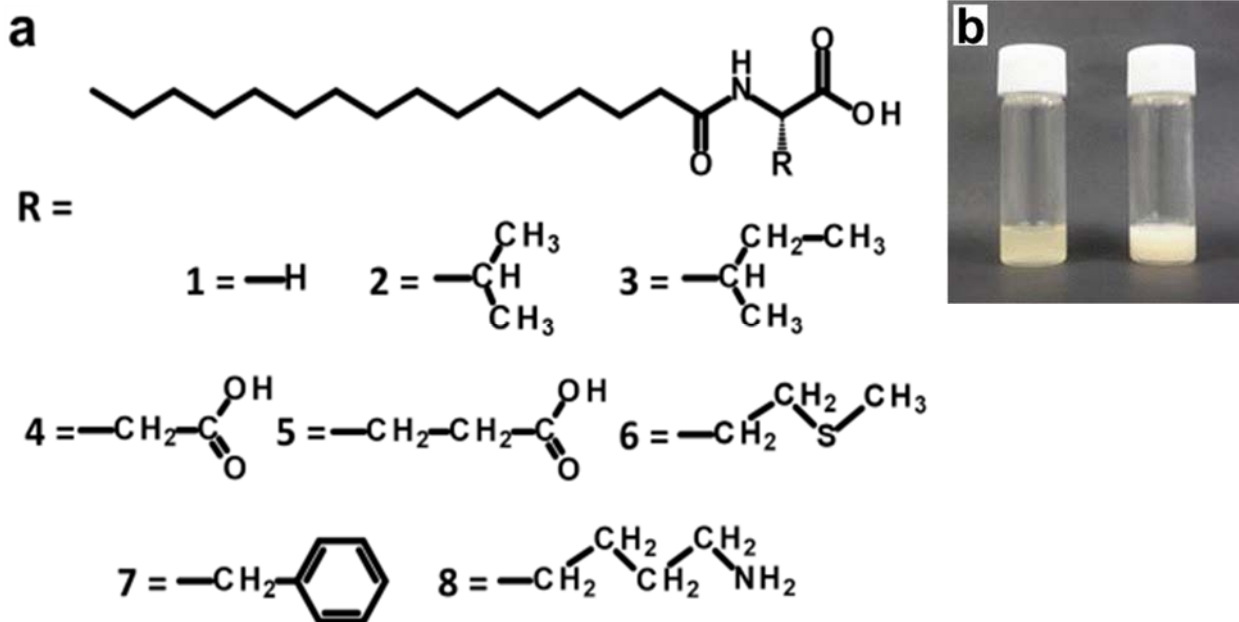


Fig. 2 (a) Molecular structures of gelators 1–8. (b) Digital photographs of the translucent ionogel of [BuMeIm][TFSA] with 0.4 wt.% gelator 3 (left), and opaque ionogel of [BuMeIm][TFSA] with 1.4 wt.% gelator 7 (right).

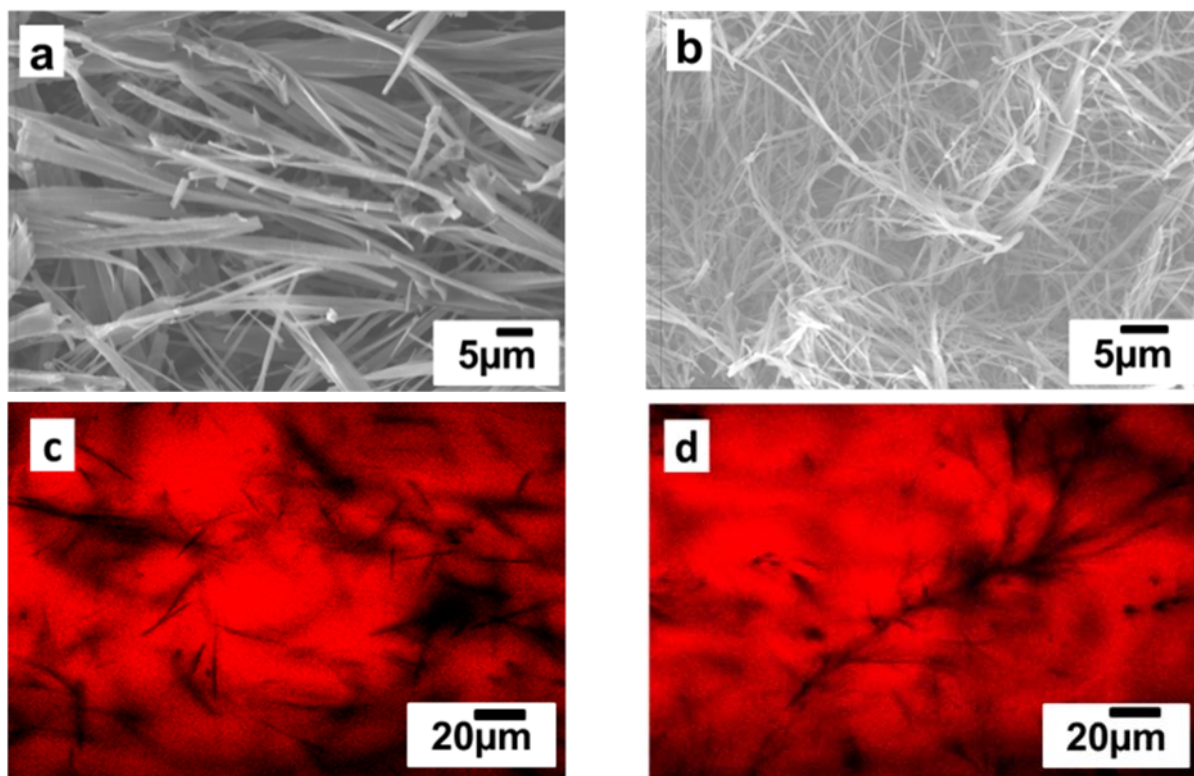


Fig. 3 FE-SEM and CLSM images of ionogels. (a, c) [EtMeIm][TFSA] with 0.5 wt.% gelator 6. (b) [TMPA][TFSA] with 0.5 wt.% gelator 7. (d) [TMPA][TFSA] with 0.7 wt.% gelator 7.

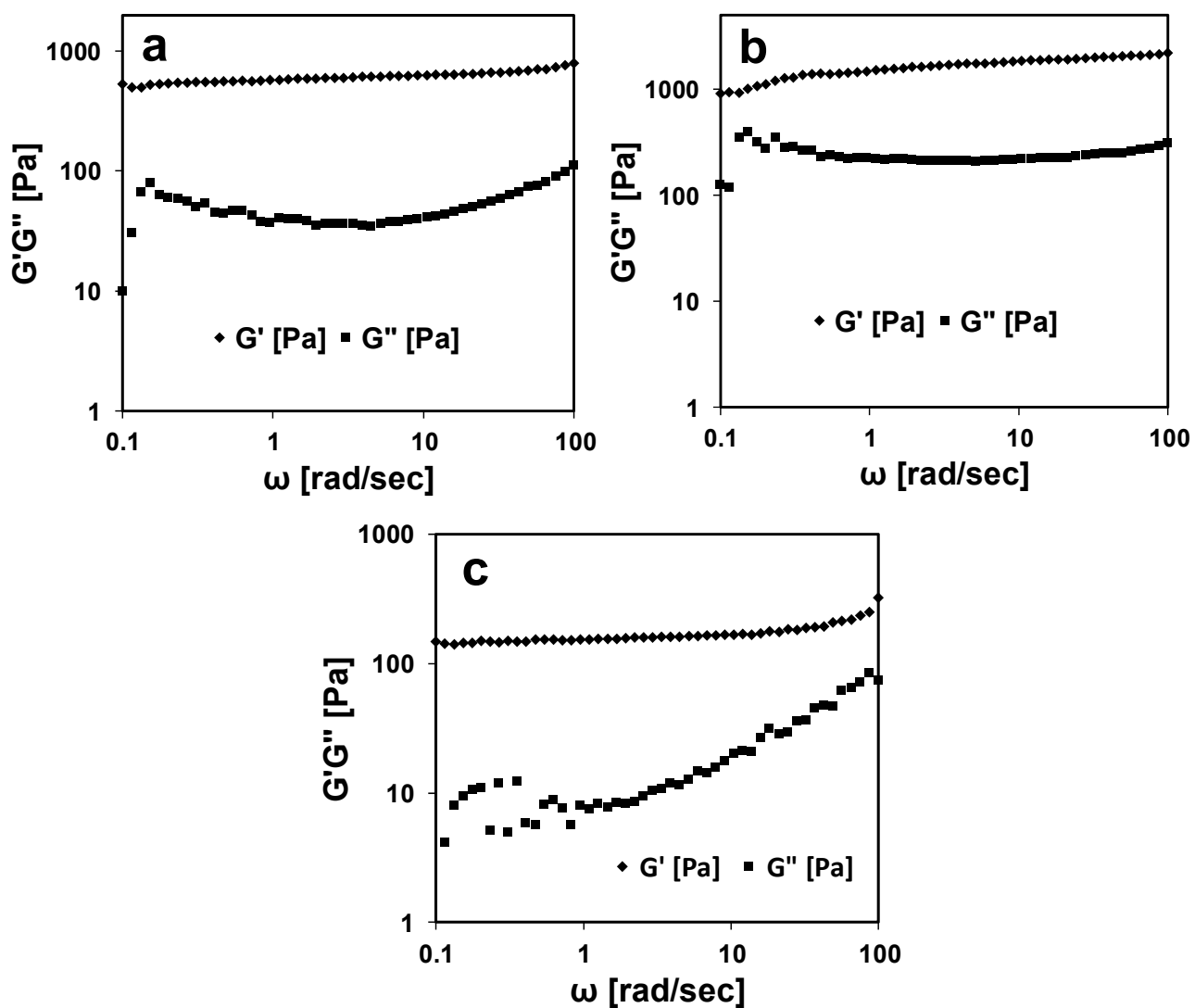


Fig. 4 Rheological properties of ionogels. (a) [EtMeIm][TFSA] with 0.7 wt.% gelator 6. (b) [EtMeIm][CF₃SO₃] with 0.7 wt.% gelator 6. (c) [TPMA][TFSA] with 0.7 wt.% gelator 7.

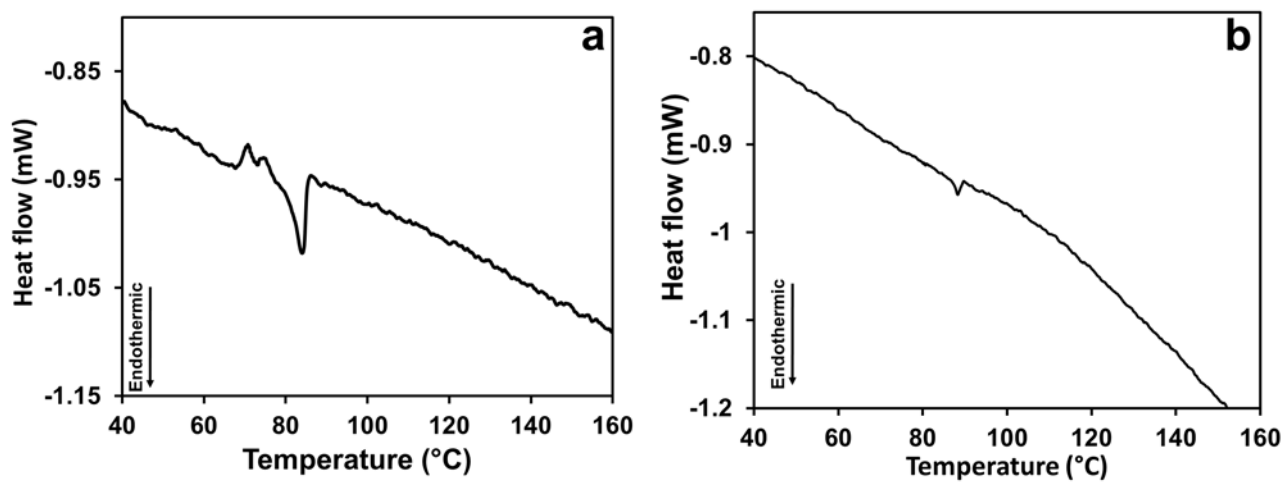


Fig. 5 Calorimetric properties of the ionogels as determined by DSC. (a) [EtMeIm][TFSA] with 1.3 wt.% gelator 6. (b) [EtMeIm][TFSA] with 1.3 wt.% gelator 7.

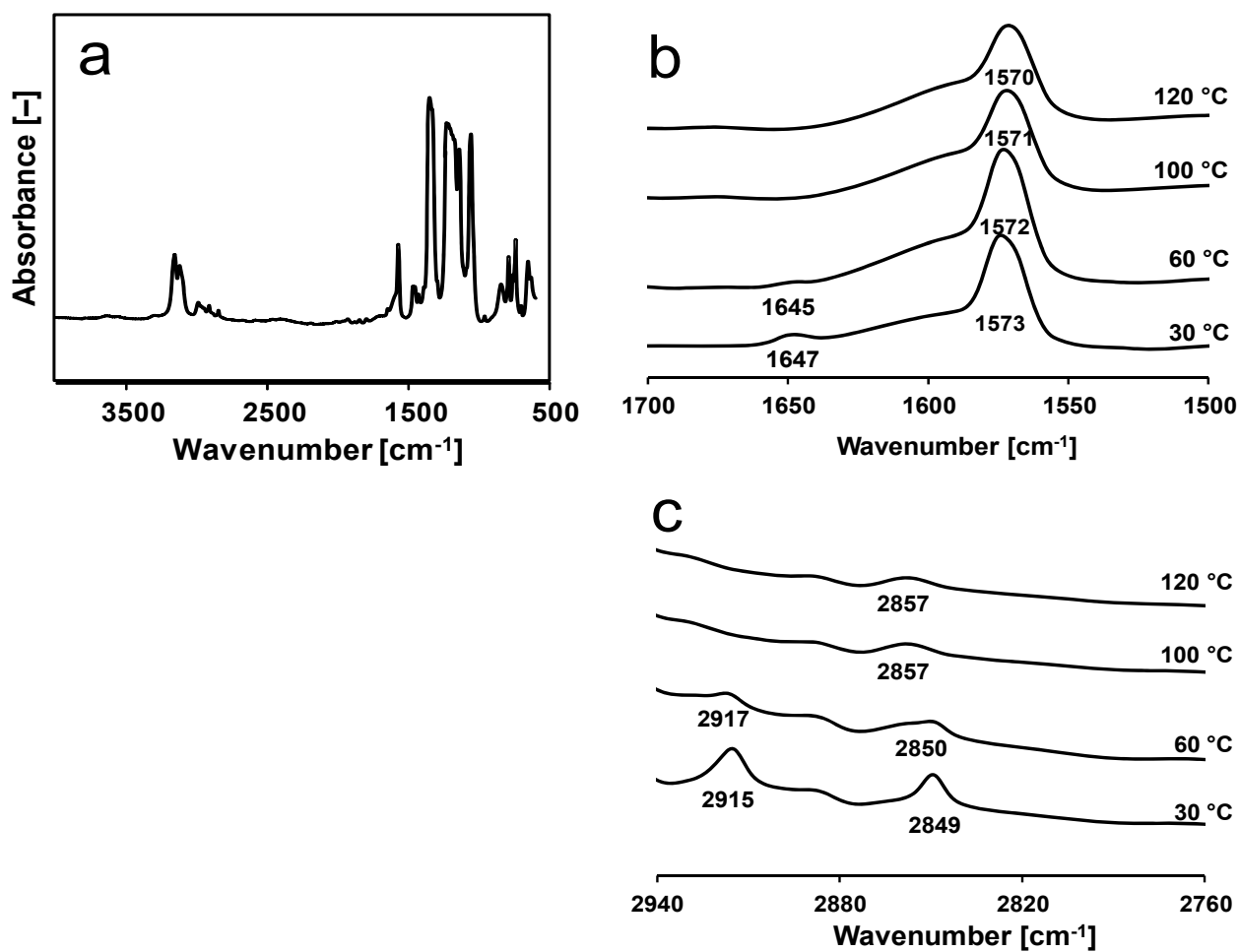


Fig. 6 (a) FTIR spectra of the ionogel [EtMeIm][TFSA] containing 0.7 wt.% gelator 6 at 30 °C.
 (b, c) Magnified spectra at various temperatures.

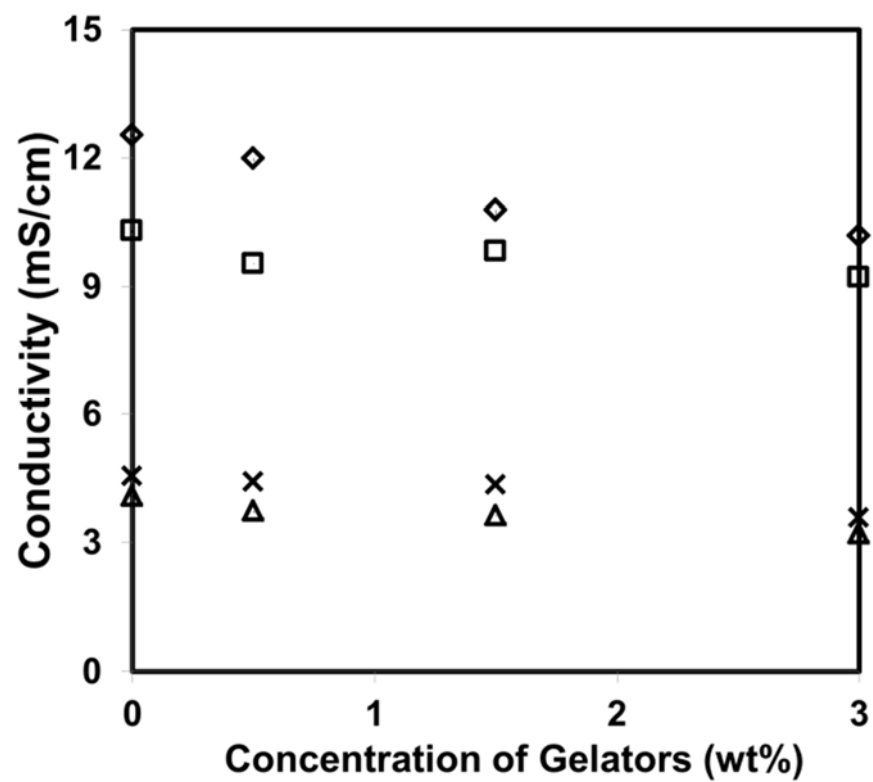


Fig. 7 Ionic conductivities of ILs and ionogels at 25 °C. Gelator 6 was used at concentrations of 0–3.0 wt.%. ($\diamond$)[EtMeIm][TFSA], ($\square$)[EtMeIm][CF₃SO₃], (x) [BuMeIm][CF₃SO₃], (Δ)[TMPA][TFSA].