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Easy Preparation and Useful Character of Organogel Electrolytes Based on Low Molecular Weight Gelator

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Using *N*-carbobenzyloxy-L-isoleucylaminooctadecane as a low molecular weight gelator for polar solvents, organogel electrolytes were prepared from supporting electrolyte and a polar solvent such as DMF, DMSO, and PC by physical gelation. The ionic conductivity of the prepared organogel electrolytes decreased very slightly with increasing concentration of gelator, while the gel strength drastically increased with increasing concentration. The organogel prepared from DMF exhibited relatively high ionic conductivity, interpreted due to the high mobility of carrier ions in the low-viscosity DMF. Arrhenius plots of ionic conductivities of organogel electrolytes indicate that the behavior of supporting electrolytes in the organogels is essentially similar to that in the isotropic solution, and the ionic mobility of supporting electrolytes is scarcely affected by the gelator molecules. The optimal concentration of supporting electrolytes in organogel electrolytes to achieve both high conductivity and high gel strength was 0.05−0.2 M. The addition of PEG to organogel electrolytes markedly raised the gel strength without decreasing ionic conductivity.

Introduction

Solid electrolytes, which are electrically conductive solids with ionic carriers, have received special attention, because of their potential use in the fields of solid-state batteries, fuel cells, energy storage, and chemical sensors.[1−5] In particular, polymer solid electrolytes are of special interest for applications owing to their excellent characteristics, such as high reliability, nonleakage of electrolyte solution, thin film formation, and flexibility.[6−14] For instance, three-component-type of polymer solid electrolytes which consist of highly polar polymers such as polyacrylonitrile and poly(vinylidene fluoride), alkali metal salts, and high dielectric solvents such as ethylene carbonate and propylene carbonate were prepared, and the conductivity was reported to be 10^{-5}−10^{-3} S/cm at ambient temperature.[15] It is also noteworthy that a composite electrolyte using low molecular weight poly(ethylene glycols) and fumed silica as a filler materials had a high conductivity ($\sim 10^{-4}$ S/cm) without significant degradation of conductivity.[16] Gel-type polymer solid electrolytes, which consist of $LiBF_4$, a mixture of propylene carbonate and 1,2-dimethoxyethane, and a mixture of ethoxypolyoxyethyleneacrylate and trimethylolpropanetriacrylate, were also prepared by photopolymerization, and their ionic conductivity was clarified.[17] However, radical polymerization is essential for the preparation, and the tedious process reduces the utility of polymer solid electrolytes.

Very recently, low molecular weight compounds used to harden organic liquids, which are called “gelators”, have received considerable attention[18] due to the fact that they are potentially useful for several applications: environmentally, as hardeners of spilled fluids and cooking oils; industrially, as thickeners for paint; and medically as drug-delivery materials. Gelators of low molecular weight compounds have unique characteristics of both good solubility upon heating and inducement of smooth gelation of organic fluids at low concentration. We have been developing new gelators and studying gelation behavior,[19−23] and their proven gelation abilities prompted us to make use of gelators

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for solid electrolytes. Actually, little is known about applications of low molecular weight gelators as functional materials. To our knowledge, the only example is that in which 1,3:2,4-dibenzylidene-D-sorbitol was used to harden DMF containing $(n\text{-Bu})_4NBF_4$ for a salt bridge.[24]

In this paper, we report on the preparation and useful character of organogel electrolytes based on physical gelation of electrolyte solution by a low molecular weight gelator.

Experimental Section

Instrumentation. Elemental analysis was performed with a Perkin-Elmer 240B analyzer. Infrared spectra were recorded on a Jasco FTIR-7300 spectrometer using cells of KRS-5 (thallium halide; Jasco) plates. NMR spectra were obtained with a JEOL JNM-LA400 spectrometer. The strength of the gels was measured with a Sun Science RHEO TEX SD-305. Transmission electron microscopy (TEM) was done with a JEOL JEM-1200. Impedance spectra were measured with a Yokogawa-Hewlett-Packard 4192A multifrequency LCR meter between 5 Hz and 1.3 MHz at an oscillation level of 0.5 V. The purity of the gelator was determined by HPLC (Jasco PU-980) equipped with a Finepack SIL-5 column, with $CHCl_3$: MeOH (8:2, v/v) as the eluent at 1 mL min^{-1} and detection at 250 nm.

Synthesis of Gelator. *N*-Carbobenzyloxy-L-isoleucylaminooctadecane, which is referred to as Z-L-Ile-$NHC_{18}H_{37}$, was prepared from *N*-carbobenzyloxy-L-isoleucine and 1-aminooctadecane using *N,N′*-dicyclohexylcarbodiimide (DCC) as the coupling reagent. To a solution of *N*-carbobenzyloxy-L-isoleucine (26.53 g, 0.10 mol) in 300 mL of distilled ethyl acetate was added DCC (22.70 g, 0.11 mol) at 0 °C. After the mixture was stirred for 1 h, 1-aminooctadecane (26.95 g, 0.10 mol) was added and the mixture stirred for 1 h at 0 °C and then for 12 h at room temperature, followed by stirred for 10 h at 45 °C. The formed *N,N′*-dicyclohexylurea was filtered off and the filtrate was allowed to stand at ambient temperature. The gel-like matter was filtered off, dissolved in 300 mL of ethyl acetate, and then cooled to room temperature. The gel-like matter was suction filtered and dried. The gelator Z-L-Ile-$NHC_{18}H_{37}$ was obtained in a yield of 38.24 g (74%): mp 113−114 °C. ^1H NMR ($CDCl_3$) δ 7.36 (m, 1H), 7.35 (s, 5H), 7.33 (m, 1H), 5.10 (s, 2H), 3.93 (d, $J = 6.8$ Hz, 1H), 3.23 (m, 2H), 1.91 (m, 2H), 1.69 (m, 1H), 1.48 (brt, 2H), 1.25 (s, 28H), 1.11 (m, 2H), 0.90 (m, 9H). Elemental analysis calculated for $C_{32}H_{56}N_2O_3$: C, 74.37; H, 10.92; N, 5.42. Found: C, 74.21; H, 10.99; N, 5.61.

Gelation Test and Gel Strength. A typical procedure for gelation testing is as follows: a weighed Z-L-Ile-$NHC_{18}H_{37}$ was mixed with an organic liquid (2.0 mL) in a test tube with a screw cap (inside diameter; 14 mm), and the mixture was heated until the solid was dissolved. The resulting solution was cooled at 25 °C for 2 h and then the gelation was checked visually. When upon inversion of the test tube no fluid ran down the walls of the tube, we judged it “successful gelation”. When the gel was formed, we evaluated quantitatively the gel-forming ability by determining the minimum gel concentration (MGC), which is the minimum concentration of gelator necessary for gelation at 25 °C. The unit of MGC is grams/liter (gelator/liquid).

The strength of gels containing $LiClO_4$ (0.05 M) was measured and evaluated as the strength necessary to sink a cylinder bar (10 mm in diameter) 4 mm deep in the gel.

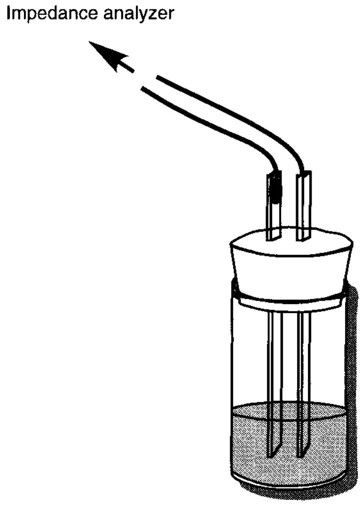

Figure 1. Cell apparatus for conductivity measurements.

Transmission Electron Microscopy. For TEM of the sample, the gelator was dissolved in DMSO (2 mg mL^{-1}) and a droplet of the loose gel was put on a collodion- and carbon-coated grid (copper, 400 mesh). The sample was allowed to stand at room temperature for 2 h, and then dried by vacuum pump overnight. The sample was negatively stained by osmium tetroxide (5 wt % methanol solution) vapor for 10 h.

Electrical Measurements. DMF and DMSO were freshly distilled over CaH_2 under reduced pressure. Poly(ethylene glycol) (PEG), whose number-average molecular weight was 400, and propylene carbonate (PC) were dried over 4A molecular sieves for several days. Supporting electrolytes, $LiClO_4$, $KClO_4$, $LiBF_4$, $LiCF_3SO_3$, $(n\text{-Bu})_4NClO_4$, and $(n\text{-Hex})_4NClO_4$, were dried under reduced pressure for several days.

The cell apparatus for conductivity measurements is illustrated in Figure 1. Two indium-tin-oxide electrodes (ITO) were cut to the size of 3 mm × 50 mm and fixed by a silicone rubber stopper. The interval of two ITO electrodes was 6 mm. The weighed gelator and electrolyte were mixed with 2 mL of solvent in a sample vial (inside diameter, 19 mm), and the mixture was heated until the solids were dissolved. The resulting vial was stoppered with silicone rubber stopper equipped with ITO electrodes and then kept at the prescribed temperature for 1 h to form gels. The real resistance of gel electrolytes was estimated from the resistance Z' at which the resistance Z'' had its minimum value.[25]

Results and Discussion

Gelation Ability. In general, physical gelation by low molecular weight gelators occurs when a heated homogeneous mixture of gelator and liquid is allowed to cool to room temperature. The physical gelation by low molecular weight compounds occurs not only because of self-aggregation of gelator molecules in solvent but most importantly because of the gathering of self-aggregates. The gathering of self-aggregates seems absolutely necessary to build up a huge three-dimensional network structure for the gel formation. There are not so many all-powerful gelators which can gelate a wide variety of liquids from protic polar solvents to aprotic nonpolar ones, since the self-aggregation of molecules strongly depends on the polarity of solvents. In fact, the almost all-powerful gelators are limited to some compounds.[26] Although we have discovered strong

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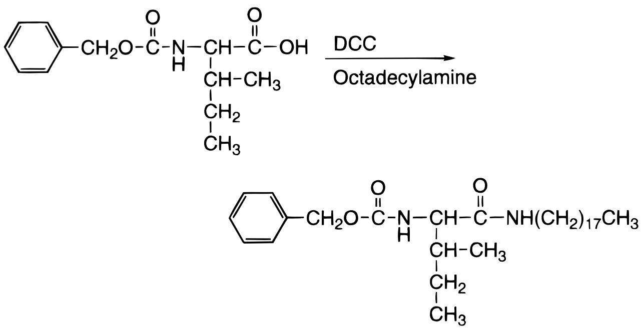
Scheme 1



Z-L-Ile-NHC$_{18}$H$_{37}$

Table 1. Gelation Test of Z-L-Ile-NHC$_{18}$H$_{37}$ and Minimum Gel Concentration [in g L^{-1} (gelator/orgainic fluid)] Necessary for Gelation at 25 °C

organic fluid	MGC	organic fluid	MGC
DMF	20	cyclohexanone	35
DMSO	10	THF	crystallization
PC	10	1,4-dioxane	40
PEG(400)	7	cyclohexane	9
γ-butyrolactone	13	benzene	10
acetonitrile	7	toluene	36
MeOH	19	chlorobenzene	30
EtOH	13	nitrobenzene	22
1-PrOH	20	CCl$_4$	20
2-PrOH	10	kerosene	11
1-BuOH	19	light oil	10
ethyl acetate	18	silicone oil	5
acetone	7	salad oil	15
2-butanone	crystallization	soybean oil	23

gelation abilities in a family of amino acid derivatives,[27] we here turned our attention to Z-L-Ile-NHC$_{18}$H$_{37}$ as gelator for the following reasons: (i) it can be easily obtained in moderate yield by one step reaction from commercially available reagents, (ii) it can gelate high polar solvents as well as nonpolar aprotic ones. The synthesis path of Z-L-Ile-NHC$_{18}$H$_{37}$ is shown in Scheme 1. The purity of Z-L-Ile-NHC$_{18}$H$_{37}$ used for this study was found by HPLC to be 97%.

The results of the gelation test and the MGC are summarized in Table 1. The gelator, Z-L-Ile-NHC$_{18}$H$_{37}$, is characterized by the fact that it can gelate polar solvents with high dielectric constant such as DMF, DMSO, PC, PEG, γ-butyrolactone, and acetonitrile. These solvents are widely used as electrolytes owing to their ability to solubilize inorganic salts. For example, the amounts of Z-L-Ile-NHC$_{18}$H$_{37}$ necessary to harden 1 L of DMF, DMSO, PC, PEG, γ-butyrolactone, and acetonitrile are 20, 10, 10, 7, 13, and 7 g, respectively. The present MGC values are in the range of 0.9 to 2.1 wt % (gelator/solvent). It is important to note that the MGC values are almost independent of the presence of supporting electrolytes when the concentration of supporting electrolytes is less than 0.1 M, in other words, each MGC is unchanged regardless of whether supporting electrolyte is added to the solvent or not.

Gel Strength. Gel strength is one important factor in view of application of gel electrolytes. The strength of gel containing LiClO$_4$ (0.05 M) is plotted vs the concentration of gelator in Figure 2. The strength of hydrogel prepared by commercial agar is also plotted in Figure 2. The strength of gel increases with increasing gelator concentration and competes with the strength of hydrogel by agar. The strength of gel depends on the concentration of supporting electrolytes as well as solvents (see Figure 3). In general, the addition of supporting electrolytes more than 0.2 M decreases considerably the strength of organogel prepared by Z-L-Ile-NHC$_{18}$H$_{37}$.

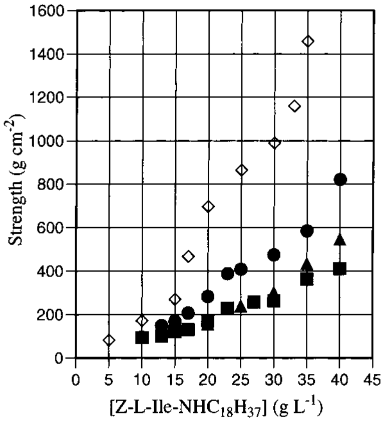


Figure 2. Effect of gelator concentration on the strength of gel electrolytes containing LiClO$_4$: DMSO gel electrolyte by Z-L-Ile-NHC$_{18}$H$_{37}$ (●), DMF gel electrolyte by Z-L-Ile-NHC$_{18}$H$_{37}$ (▲), PC gel electrolyte by Z-L-Ile-NHC$_{18}$H$_{37}$ (■), hydrogel electrolyte by agar (◇). [LiClO$_4$] = 0.05 M.

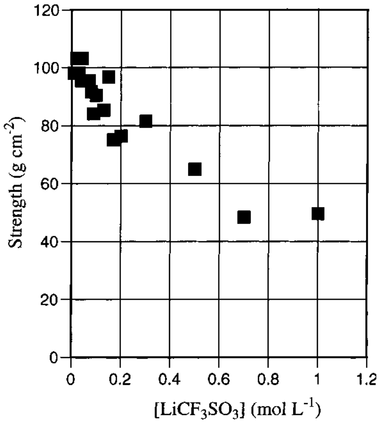


Figure 3. Effect of the concentration of LiCF$_3$SO$_3$ on the strength of DMSO gel at room temperature. [Z-L-Ile-NHC$_{18}$H$_{37}$] = 10 g L^{-1}.

Transmission Electron Microscope. Considering that the gelation mechanism by low molecular weight compounds is primary by self-aggregation of molecules, followed by the gathering of self-aggregates, it is reasonable to assume that images of molecular aggregates are observed by electron microscope. Actually, electron microscopic images of molecular aggregates formed by gelators have been reported,[18,20,21,23,27−33]

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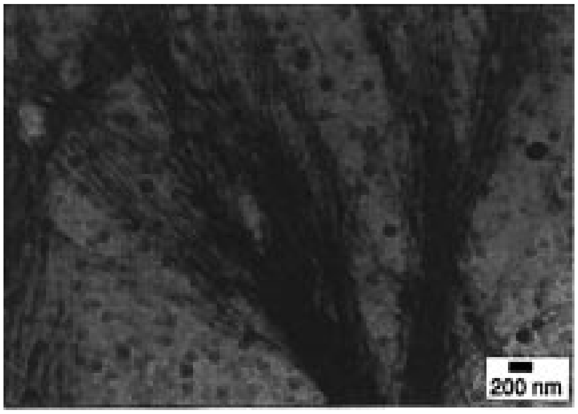

Figure 4. Transmission electron micrograph of loose gel by Z-L-Ile-$NHC_{18}H_{37}$ in DMSO, negatively stained by osmic acid.

though the xerogels may not be the same as the superstructure of the gels. The TEM of a loose gel formed by Z-L-Ile-$NHC_{18}H_{37}$ in DMSO, negatively stained by osmic acid, shows the gathering of numerous well-defined fibers whose diameter is 16−24 nm (Figure 4). Some of the wide fibers seem to be helix twined by two slender fibers. Images very similar to the molecular aggregates shown in Figure 4 were obtained with a loose gel of Z-L-Ile-$NHC_{18}H_{37}$ in DMSO containing $(n\text{-Hex})_4NClO_4$ (0.01 M). It is thought that the presence of supporting electrolytes in solvents has no influence on formation of molecular aggregates. It is also in agreement with the fact that the MGC values are almost independent of the presence of supporting electrolytes when the concentration of supporting electrolytes is less than 0.1 M.

Effect of Gelator on Ionic Conductivity. Figure 1 shows the cell apparatus for conductivity measurements. The gel electrolytes are easily made up by the following procedure: a mixture of gelator, supporting electrolyte, and solvent in a sample vial is heated until it becomes a homogeneous solution, stoppered with silicone rubber stopper equipped with ITO electrodes, and then kept at room temperature for 1 h to form gels. Ionic conductivity was evaluated by alternating-current measurements from 5 Hz and 1.3 MHz at 0.5 V.

Plots of ionic conductivity vs gelator concentration, using $(n\text{-Bu})_4NClO_4$ or $LiClO_4$, are shown in parts a and b of Figure 5. The ionic conductivity decreased very slightly with increasing concentration of gelator, while the gel strength drastically increased (see Figure 2). It is clear that the gelator hardly interferes with the ionic mobility of supporting electrolyte. We chose DMF, DMSO, and PC as polar solvents with high dielectric constants for preparation of organogel electrolytes. The ionic conductivities in Figure 5 decrease in the order DMF > DMSO > PC. Considering the fact that the viscosity of DMF, DMSO, and PC are 0.802, 1.99, and 2.53 cP at 25 °C,[34] these results are best interpreted by the Walden rule,[35] as described in eq 1

$$\mu = e/6\pi r\eta \qquad (1)$$

where μ is the carrier mobility, e is the carrier charge, r is the radius of the carrier ion, and η is the viscosity of the solvent. Equation 1 indicates that the carrier mobility μ is proportional to the reciprocal of viscosity η. The relatively high ionic conductivity of DMF gel electrolyte can be attributed to the high mobility of carrier ions in the low viscosity. This behavior, observed for organogel electrolytes, is quite similar to that of electrolyte solutions.

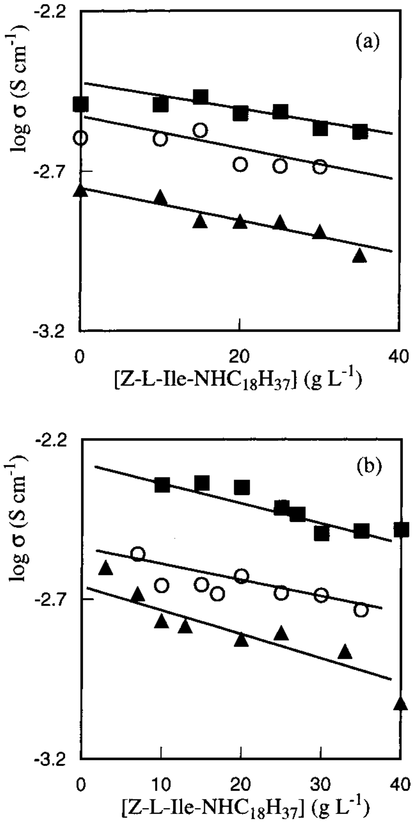

Figure 5. Effect of the concentration of gelator on ionic conductivity for gel electrolytes at room temperature: DMF gel electrolyte (■), DMSO gel electrolyte (○), PC gel electrolyte (▲). (a) [$(n\text{-Bu})_4NClO_4$] = 0.05 M. (b) [$LiClO_4$] = 0.05 M.

Polymer solid electrolytes, for example, poly(methyl methacrylate) or poly(ethylene oxide), contain polymers of several tens of weight percent to immobilize the electrolyte solution, and an increase of added polymers leads to a significant decrease in ionic conductivity.[36−38] On the other hand, the organogel electrolytes based on Z-L-Ile-$NHC_{18}H_{37}$ are characterized by two facts: the ionic conductivity is almost independent of the amount of gelator, and the content of gelator necessary to make organogel electrolytes is several weight percent. Actually, the contents of gelator in this study are 2.1−4.1 wt % for DMF, 0.9−3.5 wt % for DMSO, and 0.83−3.2 wt % for PC.

Temperature Dependence of Ionic Conductivity. Figures 6 and 7 show the plots of conductivity against 1/T for organogel electrolytes containing $(n\text{-Bu})_4NClO_4$ and $LiCF_3SO_3$, respectively. The plots of conductivity for electrolyte solutions without the gelator

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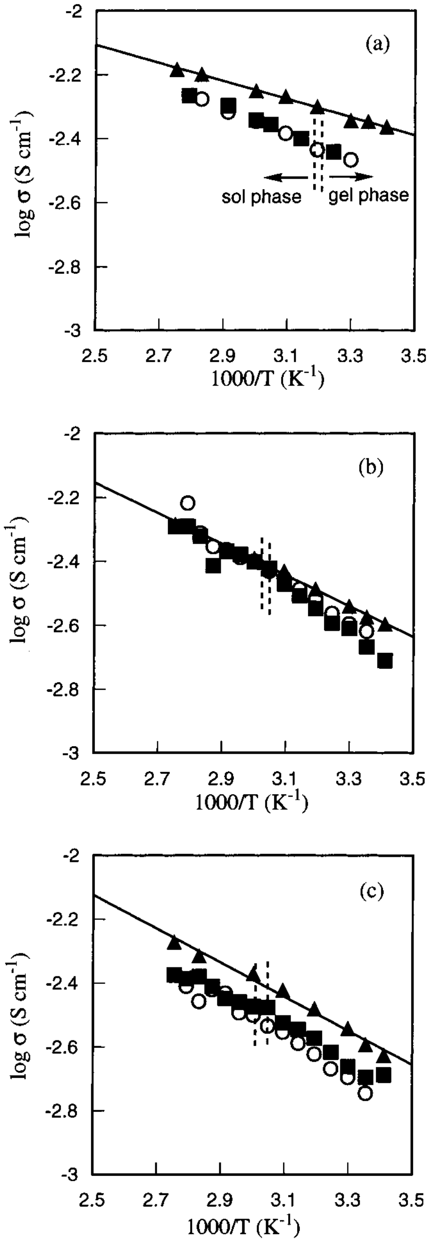

Figure 6. Arrhenius plots for ionic conductivity of gel electrolytes containing $(n\text{-Bu})_4NClO_4$ and electrolyte solution. Ascending process of gel electrolyte (■); descending process of gel electrolyte (○); electrolyte solution without Z-L-Ile-$NHC_{18}H_{37}$ (▲). (a) Solvent is DMF. [Z-L-Ile-$NHC_{18}H_{37}$] = 20 g L^{-1}. [$(n\text{-Bu})_4NClO_4$] = 0.05 M. (b) Solvent is DMSO. [Z-L-Ile-$NHC_{18}H_{37}$] = 10 g L^{-1}. [$(n\text{-Bu})_4NClO_4$] = 0.05 M. (c) Solvent is PC. [Z-L-Ile-$NHC_{18}H_{37}$] = 10 g L^{-1}. [$(n\text{-Bu})_4NClO_4$] = 0.05 M.

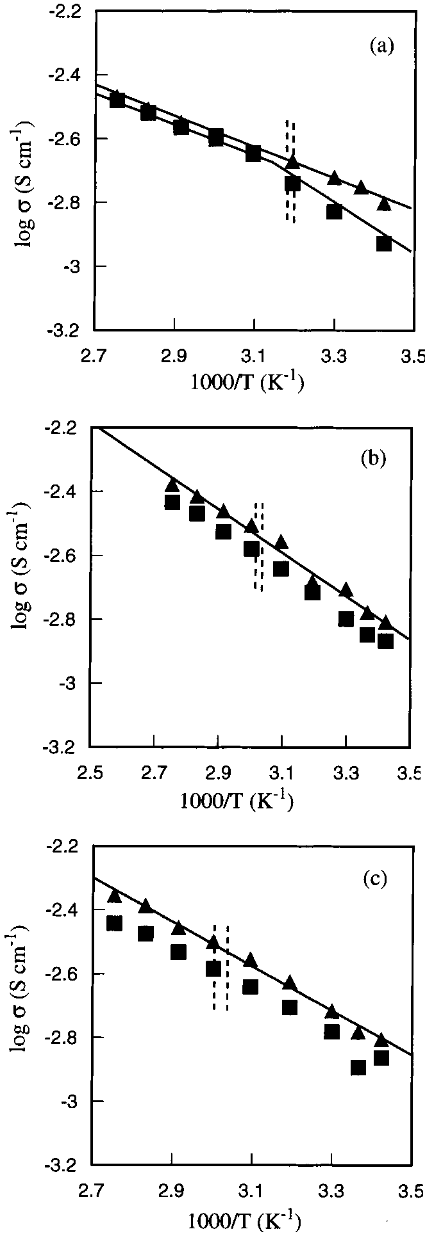

Figure 7. Arrhenius plots for ionic conductivity of gel electrolytes containing $LiCF_3SO_3$ and electrolyte solution. Ascending process of gel electrolyte (■); electrolyte solution without Z-L-Ile-$NHC_{18}H_{37}$ (▲). (a) Solvent is DMF. [Z-L-Ile-$NHC_{18}H_{37}$] = 20 g L^{-1}. [$LiCF_3SO_3$] = 0.05 M. (b) Solvent is DMSO. [Z-L-Ile-$NHC_{18}H_{37}$] = 10 g L^{-1}. [$LiCF_3SO_3$] = 0.05 M. (c) Solvent is PC. [Z-L-Ile-$NHC_{18}H_{37}$] = 10 g L^{-1}. [$LiCF_3SO_3$] = 0.05 M.

are also shown in these figures. The temperature dependence exhibits a classical Arrhenius plot, as indicated by the Arrhenius equation below:

$$\sigma = \sigma_0 \exp(-E_A/kT) \qquad (2)$$

where σ is the ionic conductivity, E_A is the activation energy, and k is Boltzmann's constant. In some instances, the conductivity of organogel electrolytes is a little low compared to that of the corresponding electrolyte solutions without gelator. However, there is almost no difference between the activation energy of organogel electrolytes and electrolytes solutions, which lie in the range of 5.4−10.1 kJ/mol for Figure 6 and 12.2−13.4 kJ/mol for Figure 7. It is important to note that the present activation energy for organogel electrolytes is significantly low in comparison with that for polymer electrolytes.[15,38−40]

The gelator concentrations for organogels in Figures 6 and 7 are 20 g L^{-1} for DMF gel, 10 g L^{-1} for DMSO gel, and 10 g L^{-1} for PC gel. Transition temperatures from gel to sol for these gels, determined visually on heating, are 38−40 °C for DMF gel, 56−58 °C for DMSO gel, and 58−60 °C for PC gel. The transition regions

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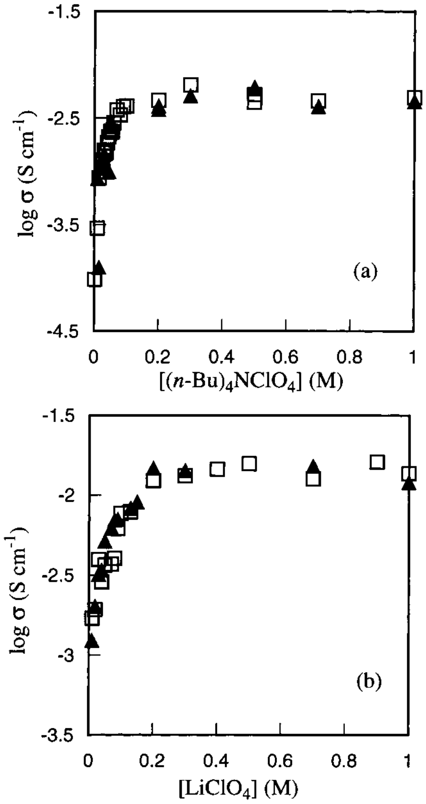

Figure 8. Dependence of ionic conductivity on electrolyte for gel electrolytes and electrolyte solution at room temperature. Gel electrolyte (□); electrolyte solution without Z-L-Ile-NHC$_{18}$H$_{37}$ (▲). (a) Electrolyte is [(n-Bu)$_4$NClO$_4$]; solvent is DMSO; [Z-L-Ile-NHC$_{18}$H$_{37}$] = 10 g L^{-1}. (b) Electrolyte is LiClO$_4$; solvent is DMF; [Z-L-Ile-NHC$_{18}$H$_{37}$] = 20 g L^{-1}.

are marked in Figures 6 and 7, where the low-temperature zone across the transition region is gel and the high-temperature one is sol. The straight relationship between log σ and $1/T$, except for Figure 7a, indicates that the activation energy is unchanged, regardless of whether the system is a gel phase or a sol one. From these results that the activation energy observed for organogel electrolytes is very low and constant irrespective of the gel and sol phase, we conclude that the supporting electrolytes in the organogel electrolytes are dissolved in the solvent which are located in the three-dimensional networks built up by gelator molecules. Namely, the behavior of supporting electrolytes in the organogels is almost similar to that in the isotropic solution, and the ionic mobility of supporting electrolytes is scarcely restricted to the three-dimensional network structure by the gelator. The change in the slope for log σ at the gel point in Figure 7a may suggest that there is some slight interaction between electrolyte and gelator in DMF.

Effect of Supporting Electrolytes on Ionic Conductivity. The effect of the concentration of supporting electrolytes on ionic conductivity was studied separately in the low and high concentration regions. The effects of supporting electrolyte in the low concentration region (less than 1.0 M) on ionic conductivity are shown in Figure 8. Ionic conductivity vs supporting electrolyte concentration profiles, as exemplified by (n-Bu)$_4$NClO$_4$ and LiClO$_4$, have a rise region followed by a plateau. It should be mentioned that the concentration dependence of electrolyte solution without gelator, which is also shown in Figure 8, is essentially similar to that of the organogel electrolytes. The same behavior described above was observed for organogel electrolytes containing LiCF$_3$SO$_3$ or LiBF$_4$. The initial increasing of ionic conductivity in the concentration less than 0.2 M is due to the increasing number of carrier ions.

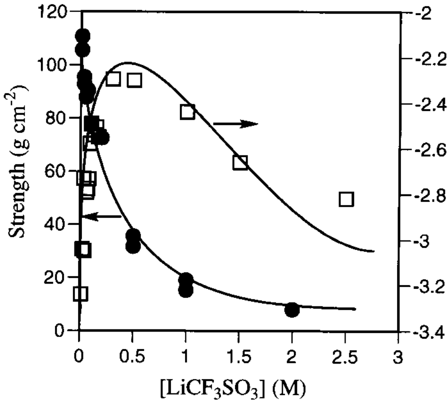

Figure 9. Effect of the concentration of LiCF$_3$SO$_3$ on ionic conductivity and strength for PC gel electrolytes at room temperature. [Z-L-Ile-NHC$_{18}$H$_{37}$] = 10 g L^{-1}.

The results of Figure 8 led us to conclude that the gelator molecules have no influence on the dissociation constant of supporting electrolytes.

The effect of LiCF$_3$SO$_3$ on ionic conductivity throughout the high concentration region is shown in Figure 9, which includes the plots of gel strength. The gel strength decreases with increasing concentration of LiCF$_3$SO$_3$, while the ionic conductivity increases till [LiCF$_3$SO$_3$] = 0.3 M and then declines. The drastic decrease of conductivity over 0.3 M is interpreted by the dominant formation of higher aggregates such as triple ions through electrostatic interaction.[41] We have already revealed that the intermolecular hydrogen bondings of urethane and amide segments play a critical role for physical gelation by amino acid derivatives.[26,27] The decrease of gel strength can be explained by taking into account the breakage of intermolecular hydrogen bondings of Z-L-Ile-NHC$_{18}$H$_{37}$ by supporting electrolytes of high concentration. A concentration of LiCF$_3$SO$_3$ over 1.0 M is sufficient to interact with the polar N−H and C=O of Z-L-Ile-NHC$_{18}$H$_{37}$, so that the intermolecular hydrogen bonding, crucial to the self-aggregation of gelator molecules, is no longer formed. Actually, the gel fails to form when the concentration of LiCF$_3$SO$_3$ is over 1.0 M. This is supported by the fact that the FT-IR spectrum of PC gel containing 0.05 M LiCF$_3$SO$_3$ is characterized by bands attributed to intermolecular hydrogen bonding, i.e. 3294 cm^{-1} (νN−H of urethane and amide), 1690 cm^{-1} (νC=O of urethane), and 1646 cm^{-1} (νC=O of amide), while the spectrum of PC gel containing 1.0 M LiCF$_3$SO$_3$ reveals the non-hydrogen-bonding bands, 3440, 1720, and 1670 cm^{-1}.

We conclude that the optimal concentration of supporting electrolytes for organogel electrolytes with high conductivity and high gel strength is 0.05−0.2 M.

Effect of Cation Species on Ionic Conductivity. The effect of cation species on ionic conductivities was studied by organogel electrolytes containing alkali metal

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(41) Cameron, G. G.; Ingram, M. D.; Sorrie, G. A. *J. Chem. Soc., Faraday Trans.* **1987**, *83*, 3345.

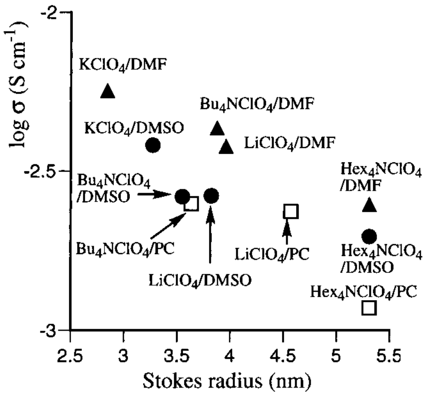

Figure 10. Effect of Stokes radius of cations on ionic conductivity. DMF (▲); DMSO (●); PC (□). [supporting electrolyte] = 0.05 M. [Z-L-Ile-$NHC_{18}H_{37}$] = 20 g L^{-1}, 10 g L^{-1}, and 10 g L^{-1} when the solvent is DMF, DMSO, and PC.

and tetraalkylammonium perchlorates. In Figure 10 are shown plots of log σ vs Stokes radii of cation species of supporting electrolytes. Walden products ($\lambda_0\eta$) and Stokes radius are defined by eq 3

$$\lambda_0\eta = 0.820|z_i|/r_s \qquad (3)$$

where λ_0 is the limiting molar conductivity, η is the viscosity of solvent, $|z_i|$ is the charge of the ion, and r_s is the Stokes radius. The values of Stokes radius listed in Figure 10 were calculated from eq 3 using λ_0 from the literature.[42] It is clear from Figure 10 that the ionic conductivity of organogel electrolytes decreases upon increasing the Stokes radius of the cation. It is reasonable to assume that the solvated cations having large Stokes radii are hard to move in organogel electrolytes.

The effect of anionic species on ionic conductivity was also examined in DMF, DMSO, and PC by using $LiClO_4$, $LiBF_4$, or $LiCF_3SO_3$. However, the ionic conductivities were virtually independent of the anionic radii. The ionic conductivity increased in the order $LiClO_4 > LiBF_4 > LiCF_3SO_3$. Since the association constants[43] of $LiClO_4$, $LiBF_4$, and $LiCF_3SO_3$ in PC were reported to be 2.8, 8.4, and 16.1, the above ionic conductivity is explained by the association constant of the supporting electrolytes. It seems to us that supporting electrolytes having a relatively small association constant, containing cation with a small Stokes radius, are suitable for high ionic conductivity of organogel electrolytes.

Table 2. Ionic Conductivity and Gel Strength of Organogel Electrolytes at Room Temperature

solvent	amount gelator, g L^{-1}	electrolyte (0.05 M)	log σ, S cm^{-1}	gel strength, g cm^{-2}
PEG	10	$(n\text{-Bu})_4NClO_4$	−4.41	64
DMF	20	$(n\text{-Bu})_4NClO_4$	−2.49	172
DMSO	10	$(n\text{-Bu})_4NClO_4$	−2.60	102
PC	10	$(n\text{-Bu})_4NClO_4$	−2.76	56
PEG + DMF (1:1)	20	$(n\text{-Bu})_4NClO_4$	−2.89	239
PEG + DMSO (1:1)	10	$(n\text{-Bu})_4NClO_4$	−3.21	112
PEG + PC (1:1)	10	$LiClO_4$	−3.42	98
PEG	10	$LiClO_4$	−4.32	62
DMF	20	$LiClO_4$	−2.36	148
DMSO	10	$LiClO_4$	−2.65	97
PC	10	$LiClO_4$	−2.76	94
PEG + DMF (1:1)	20	$LiClO_4$	−3.12	239
PEG + DMSO (1:1)	10	$LiClO_4$	−3.41	112
PEG + PC (1:1)	10	$LiClO_4$	−3.29	98

Organogel Electrolytes of Mixed Solvents. When polymer solid electrolytes are composed of high molecular weight PEG and supporting electrolyte, their carrier ions are strongly solvated by ether segments in PEG; consequently, they move along with the segmental motions of the PEG backbone.[41] The fact that the carrier ions are solvated by PEG prompted us to prepare organogel electrolyte from PEG whose number-average molecular weight is 400. The ionic conductivities of organogel electrolytes from PEG are considerably lower than those from DMF, DMSO, or PC (Table 2). The low conductivity is ascribed to the high viscosity of PEG in the microscopic domain; in fact, the PEG used is a highly viscous liquid at room temperature and the viscosity is 8.23 cP, even at 98 °C. To reduce the viscosity in the microscopic domain, we prepared organogel electrolytes from mixed solvents containing PEG and others. The ionic conductivity and gel strength are summarized in Table 2. The $(n\text{-Bu})_4NClO_4$-containing organogel electrolyte from a mixture of PEG and DMF exhibited ionic conductivity nearly comparable to that of organogel electrolyte from only DMF. However, it is noteworthy that the gel strength of the organogel electrolyte is improved compared with that from DMF. For example, the gel strength of the organogel electrolyte from a mixture of PEG and DMF (1:1 by volume) is 239 g cm^{-2}. This is 3.7 times larger than 64 g cm^{-2}, measured for the gel strength of the organogel electrolyte from PEG, and 1.4 times larger than 172 g cm^{-2}, that from DMF. From the results in Table 2, we can conclude that the addition of PEG to another solvent for organogel electrolytes raises markedly the gel strength, though the ionic conductivity decreases even slightly.

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