Physical Gelation of Organic Solvents by Low Molecular Weight Gelators and Preparation of Organogel Electrolytes

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ABSTRACT: Three low molecular weight gelators, *i.e.*, *N*-carbobenzyloxy-L-isoleucylaminooctadecane, *N*-carbobenzyloxy-L-valyl-L-valylaminooctadecane, and 1,12-bis(*N*-carbobenzyloxy-L-valyl)diaminododecane, were chosen and organogel electrolytes were prepared by physical gelation of polar solvents containing supporting electrolytes. γ -Butyrolactone (γ -BL), propylene carbonate (PC), and 3-methoxypropionitrile (3-MPN) were used as polar solvents. The supporting electrolytes used were LiClO₄, LiBF₄, and (CF₃SO₂)₂NLi. The gel strength of the prepared organogel electrolytes markedly increased with increasing concentration of gelator, whereas the ionic conductivity decreased very slightly with increasing concentration. The ionic conductivity of organogel electrolytes increased in order 3-MPN < PC < γ -BL, while the order with respect to supporting electrolytes was (CF₃SO₂)₂NLi < LiBF₄ < LiClO₄. Arrhenius plots of ionic conductivities of organogel electrolytes indicated that the behavior of supporting electrolytes in the organogels is essentially similar to that in the isotropic solution.

KEY WORDS Gels / Gelation / Physical Gelation / Gelators / Organogels / Gel Electrolytes / Solid Electrolytes / Ionic Conductivity /

When a mixture of low molecular weight compound and liquid is heated to form a homogeneous fluid and then allowed to cool to room temperature, physical gelation sometimes takes place instead of crystallization. Such low molecular weight compounds capable of hardening organic fluids is called “gelators” and they are of special interest for potential applications as hardeners of spilled fluids and cooking oils, as thickeners for paints, and as cosmetic materials.^{1–22} Since the physical gelation occurs with cooperating noncovalent interactions of gelator molecules as hydrogen bonding, hydrophobic interaction, π – π interaction, and electrostatic interaction, the low molecular weight gelators have the following unique properties; (i) good solubility upon heating and inducement of smooth gelation of organic fluids, (ii) gelation at low concentration of gelator less than 50 g dm^{–3}, and (iii) thermally reversible sol-to-gel phase transition. However, the study on gelation of organic solvents by low molecular weight gelators is carried out on a limited number of compounds, because low molecular weight compounds usually tend to precipitate as thermodynamically stable crystals. We have proposed the three features for development of gelators; (i) the existence of intermolecular interactions to build up macromolecule-like aggregate, (ii) the occurrence of intertwining of the aggregates, and (iii) the presence of some factor for preventing the crystallization of the metastable gel.²³ We have developed some all-powerful gelators²⁴ on the basis of these features, and recently we are interested in application of the gelators to functional materials. In fact, the gelators were used for quasi-solidification of liquid crystals^{25,26} and for gelation of electrolytes for solar cells²⁷ by our co-workers.

In the last decade many different battery systems were found to meet the requirements of electric vehicle batteries, among which the lithium-ion battery is thought to be most promising due to the safety in handling and the high oxidation potential. The high oxidation potential of lithium ion may cause decomposition and leakage of organic solvents used as electrolyte. Therefore, the replacement of the liquid electrolyte with a polymer film is desired eagerly. Solid polymer electrolytes (SPE) which are solid solutions of alkali

metal salts in polymers, crosslinked SPE, and molecularly reinforced SPE have been special attention owing to their excellent characteristics, such as high reliability, nonleakage of electrolyte solution, thin film formation, and flexibility.²⁸ However, radical polymerization, ring-opening polymerization, or polycondensation is indispensable to the preparation, and the tedious process may make a difficulty to use SPEs, which is a personal view though.

The proven gelation abilities obtained in our study prompted us to make use of gelators for gel electrolytes. To our knowledge, only a paper was reported as organogel electrolyte based on the gelator, which was gelled by 1,3:2,4-di(*p*-methoxycarbonylbenzylidene)sorbitol.²⁹ In the present paper, we describe the fabrication of organogel electrolytes using gelators and the characterization of the obtained organogel electrolytes.

EXPERIMENTAL

Instrumentation

The strength of the gels was measured with a Sun Science RHEO TEX SD-305. Transmission electron microscope (TEM) was done with a Jeol JEM-1200. Impedance spectra were measured with a Yokogawa-Hewlett-Packard 4192A impedance analyzer between 5 Hz and 13 MHz at an oscillation level of 0.5 V.

Gelation Test and Gel Strength

The preparation of gelators are described elsewhere.^{24,30,31} A typical procedure for gelation test: a weighed gelator was mixed with an organic liquid (2.0 cm³) 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 “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 g dm^{-3} (gelator/liquid).

The strength of gels containing LiClO_4 (0.10 M) was measured and evaluated as the strength necessary to sink a cylinder bar (10 mm in diameter) 4 mm deep in the gel.

Electrical Measurements

γ -Butyrolactone (γ -BL) and 3-methoxypropionitrile (3-MPN) were freshly distilled over CaH_2 under reduced pressure. Propylene carbonate (PC) was dried over 4A molecular sieves for several days and distilled under reduced pressure. Supporting electrolytes, LiClO_4 , LiBF_4 , and $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ (supplied from Central Glass Co., Ltd.) were dried under reduced pressure for several days. The viscosity of γ -BL was calculated by corrected density and kinematic viscosity determined using Ubbelohde viscometer. Two indium-tin-oxide electrodes (ITO) were cut into the size of 3 mm x 50 mm and fixed by a silicone-rubber stopper. The interval of two ITO electrodes was 6 mm. The weighed gelator and supporting electrolyte were mixed with 2 cm^3 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 a silicone-rubber stopper equipped with ITO electrodes, and then kept at the prescribed temperature for 1h to form gels. The real resistance of gel electrolytes was estimated from the resistance Z' at which the resistance Z'' had its minimum value.³²

Transmission Electron Microscopy

For TEM of the sample, the gelator **2** was dissolved in cyclohexane (0.1 wt-%) and a droplet of the loose gel was put on a collodion- and carbon-coated grid (copper, 400 mesh). The sample dried by vacuum pump overnight was negatively stained by osmium tetroxide (2 wt-% cyclohexane solution) vapor for 10 h.

RESULTS AND DISCUSSION

Gelation Ability and Gel Strength

It is difficult to design all-powerful gelators that can gelate a wide variety of liquids from protic polar solvents to aprotic nonpolar ones. Because the physical gelation by low molecular gelator brings about through the process of the self-aggregation of gelator molecules in solvent, followed by the gathering of self-aggregates. Especially, there are not so many gelators which can gelate polar solvents with high dielectric constant, since the self-aggregation of molecules strongly depends on polarity of solvents.

In this study, we chose the following gelators; *N*-carbobenzyloxy-L-isoleucylaminooctadecane³⁰ (**1**), *N*-carbobenzyloxy-L-valyl-L-valylaminooctadecane³¹ (**2**), and 1,12-bis(*N*-carbobenzyloxy-L-valyl)diaminododecane²⁴ (**3**).

The MGC of **1-3** obtained in the gelation test are summarized in Table I. It should be emphasized that these gelators can gelate up polar solvents with high dielectric constant such as 3-MPN, PC, γ -BL, and acetonitrile. These solvents are widely used for electrolytes owing to the good solubility toward inorganic salts.

Table I. Gelation test of **1-3** and MGC necessary for gelation^a

organic liquid	MGC in g dm^{-3} (gelator/organic liquid)		
	1	2	3
ethanol	13	15	10
ethyl acetate	18	8	6
acetone	7	5	7
1,4-dioxane	40	18	15
toluene	36	14	2
3-MPN	5	5	8
DMF	20	18	soln.
DMSO	10	3	soln.
PC	10	7	7
γ -BL	13	7	7
acetonitrile	7	8	6
tetrachloromethane	20	18	3
kerosene	11	4	2
silicone oil	5	4	1
soybean oil	23	2	2

^asoln.=solution. Temperature of gelation test for **1**, **2**, and **3** are 25 °C, 20 °C, and 25 °C, respectively.

Figure 1. Effect of gelator concentration on the strength of gel electrolytes containing LiClO_4 (0.10 M): PC gel electrolyte by **2** (●), γ -BL gel electrolyte by **2** (▲), 3-MPN gel electrolyte by **2** (■), hydrogel electrolyte by agar (◇).

Considering the practical use of organogel electrolytes, it is assumed that the gel strength is one important factor. Figure 1 shows the plots of the strength of three gels containing LiClO_4 (0.10 M) vs. the concentration of **2**. Since absolute gel strength is not determined, the strength of hydrogel prepared by commercial agar is also plotted in

Figure 1 for comparison. The strength of gel increases with increasing gelator concentration and competes with the strength of hydrogel by agar, and the strength of PC, γ -BL, and 3-MPN gel electrolytes prepared at the concentration of 45 g dm^{-3} of **2** were 943, 818, and 610 g cm^{-2} . In Figure 2 are shown the strength of PC and γ -BL gel electrolytes containing $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ prepared by gelator 1-3. From Figure 2, it can be said that the high strength of gel electrolytes are achieved by using gelators 1-3 except for γ -BL gel by 3.

Figure 2. Effect of gelator concentration on the strength of PC and γ -BL gel electrolyte containing $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ (0.10 M). PC gel electrolyte by gelator 1 (●), PC gel electrolyte by gelator 2 (▲), PC gel electrolyte by gelator 3 (■), γ -BL gel electrolyte by gelator 1 (○), γ -BL gel electrolyte by gelator 2 (△), γ -BL gel electrolyte by gelator 3 (□).

Observation of TEM

When gels are formed by low molecular gelators, images of molecular aggregates can be very often observed by electron microscope³³, because gelation is firstly caused by self-aggregation of molecules. The TEM of gels formed by **2** in cyclohexane, negatively stained by osmic acid, is shown in Figure 3. Fibrous aggregates juxtaposed by several well-defined nano-fibers whose diameter is 6 nm were observed. The three-dimensional structures responsible for the immobilization of fluid may be formed by gathering of fibrous aggregates juxtaposed by several nano-fibers.

Figure 3. TEM image of loose gel by **2** in cyclohexane, negatively stained by osmic acid.

Ionic Conductivity of Organogel Electrolytes

The cell apparatus for conductivity measurements is illustrated in Figure 4. 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 a silicone-rubber stopper equipped with ITO electrodes, and then kept at room temperature for 1h.

Figure 4. Cell apparatus for conductivity measurements.

Table II. Ionic conductivities of organogel electrolytes made by **2** at 25 °C

Electrolyte 0.10 M	Solvent	2/solvent g dm^{-3}	$\log \sigma$
LiClO_4	γ -BL	10	-2.525
LiClO_4	PC	10	-2.803
LiClO_4	3-MPN	20	-2.632
LiBF_4	γ -BL	10	-2.591
LiBF_4	PC	10	-2.608
LiBF_4	3-MPN	20	-2.611
$(\text{CF}_3\text{SO}_2)_2\text{NLi}$	γ -BL	10	-2.868
$(\text{CF}_3\text{SO}_2)_2\text{NLi}$	PC	10	-3.161
$(\text{CF}_3\text{SO}_2)_2\text{NLi}$	3-MPN	20	-2.923

Ionic conductivities of the different gel electrolytes made by **2** are summarized in Table II. It is clear from Table II that the ionic conductivities increase in the order $\text{LiClO}_4 > \text{LiBF}_4 > (\text{CF}_3\text{SO}_2)_2\text{NLi}$. This behavior can be explained by taking into account the dissociation constant of electrolytes and/or the Stokes radii of anionic species. In general, supporting electrolytes having a relatively large dissociation constant, containing ionic species with a small Stokes radius, are suitable for achieving the high ionic conductivity of electrolyte solutions. Since the degree of dissociation in 1:1 mixture of PC and 1,2-dimethoxyethane were reported to be $\text{LiClO}_4, (\text{CF}_3\text{SO}_2)_2\text{NLi} > \text{LiBF}_4$,³⁴ the above order of $\text{LiBF}_4 > (\text{CF}_3\text{SO}_2)_2\text{NLi}$ may be explained by the Stokes radii of anionic species rather than the dissociation constant. In addition, the anionic species of $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ may interact with the gelator through hydrogen bonding, so that the ionic conductivity of the gel electrolytes containing $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ is relatively low. With respect to solvents, the ionic conductivity seems to decrease in the order γ -BL $>$ 3-MPN $>$ PC. It is well-known that the Walden rule³⁵ is described in equation 1

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

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 solvent. The eq. 1 indicates that the carrier mobility μ is proportional to the reciprocal of viscosity η . The viscosity of γ -BL,³⁶ 3-MPN, and PC³⁶ are 1.73, and 1.06, and 2.53 cP; therefore, 3-MPC with the low viscosity is expected to reveal high ionic conductivity according to the Walden rule. However, the order of ionic conductivity is not agreement with that of the reciprocal of viscosity. The high ionic conductivity of γ -BL gel electrolyte as compared to 3-MPN gel electrolyte is attributed to the high dielectric constant of γ -BL, in fact, the dielectric constants of γ -BL, 3-MPN, and PC are 42, 53, and 36. It can be said that the order of ionic conductivity for gel electrolytes is best interpreted by considering both viscosity and dielectric constant of solvent.

Effect of Gelator Concentration on Ionic Conductivity

Plots of ionic conductivity at room temperature vs. gelator concentration, using LiClO_4 or $(\text{CF}_3\text{SO}_2)_2\text{NLi}$, are shown in Figure 5. The ionic conductivity decreased very slightly with increasing concentration of gelator, although the gel strength drastically increased (see Figure 1 and 2). The similar behavior to that in Figure 5 was also observed for the 3-MPN gel electrolyte and γ -BL gel electrolyte containing $(\text{CF}_3\text{SO}_2)_2\text{NLi}$. We can moderately say that the gelator scarcely interferes with the ionic mobility of supporting electrolyte.

Figure 5. Effect of gelator concentration on ionic conductivity. γ -BL gel electrolyte containing LiClO_4 (0.10 M) of 1 (●), γ -BL gel electrolyte containing LiClO_4 (0.10 M) of 2 (▲), γ -BL gel electrolyte containing LiClO_4 (0.10 M) of 3 (■), PC gel electrolyte containing $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ (0.10 M) of 1 (○), PC gel electrolyte containing $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ (0.10 M) of 2 (Δ), PC gel electrolyte containing $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ (0.10 M) of 3 (□).

Polymer gel electrolyte; for example, polyacrylonitrile,^{37,38} polymers based on poly(methyl methacrylate),¹⁸ poly(oligooxyethylene methacrylate),⁴⁰⁻⁴² poly(ethylene oxide),⁴³⁻⁴⁵ or poly(dimethylsiloxane),⁴⁶ contain polymers of several tens of weight percent to immobilize electrolyte

solution, and an increase of added polymers leads to a significant decrease in ionic conductivity. On the other hand, the gel electrolytes based on low molecular weight gelators are characterized by two facts; the ionic conductivity is almost independent of the amount of gelator, and the content of gelator necessary to make gel electrolytes is several weight percent. Actually, the contents of gelator in Table II are 1.1 wt-% for γ -BL, 0.8 wt-% for PC, and 2.1 wt-% for 3-MPN.

Arrhenius-type Behavior of Ionic Conductivity

Figure 6 and 7 show the plots of conductivity against $1/T$ for gel electrolytes containing LiClO_4 , prepared by gelator 2 and 1. Transition temperatures from gel to sol for these gels, determined visually on heating process, are 35–36 °C for γ -BL gel by 2, 38–40 °C for DMF gel by 1, 56–58 °C for DMSO gel by 1, and 58–60 °C for PC gel by 1. The transition regions are marked in Figure 6 and Figure 7, where the low temperature zone across the transition region is gel and the high temperature one is sol. The plots of conductivity for electrolyte solutions without the gelator are also shown in Figure 6. The temperature dependence exhibits a classical Arrhenius plot, as indicated by the Arrhenius equation below:

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

where σ is the ionic conductivity, E_A is the activation energy, and k is Boltzmann's constant. The conductivity of organogel electrolytes is essentially similar to that of the corresponding electrolyte solutions without gelator and the activation energy of the organogel electrolyte and the electrolyte solution is ca. 13.6 kJ/mol. These results indicate that the behavior of supporting electrolytes in the organogels is similar to that in the isotropic solution, and the ionic mobility of supporting electrolytes is scarcely affected by the gelator molecules.

Figure 6. Arrhenius plots for ionic conductivity of gel electrolyte and electrolyte solution of γ -butyrolactone containing LiClO_4 (0.10 M). γ -BL gel electrolyte prepared by 2 of 10 g dm^{-3} (■), γ -BL electrolyte solution without 2 (○).

The straight relationship between $\log \sigma$ and $1/T$ was also observed for DMF, DMSO, and PC gel electrolytes by **1** (Figure 7). The relationship indicates that the activation energy is unchanged, regardless of whether the system is a gel phase or a sol one. The activation energy of these organogel electrolytes were found from the equation 2 to be 4.3 kJ/mol (DMF gel electrolyte), 11.0 kJ/mol (DMSO gel electrolyte), and 10.4 kJ/mol (PC gel electrolyte). It should be noted that the present activation energy for organogel electrolytes is significantly low in comparison with that for polymer electrolytes.^{37,47-49} Considering these results that the activation energy observed for organogel electrolytes is very low and constant irrespective of the gel and sol phase, we can 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.

Figure 7. Arrhenius plots for ionic conductivity of gel electrolyte containing LiClO_4 (0.05 M).

DMF gel electrolyte prepared by **1** of 20 g dm^{-3} (■),
DMSO gel electrolyte prepared by **1** of 10 g dm^{-3} (●),
PC gel electrolyte prepared by **1** of 10 g dm^{-3} (▲).

CONCLUDING REMARKS

By physical gelation using low molecular weight gelators, gel electrolytes were easily prepared from supporting electrolyte and polar solvents. The gel strength of the prepared organogel electrolytes increased with increasing concentration of gelator, and usually reached to several hundreds of g cm^{-2} at the concentration of 45 g dm^{-3} (gelator/solvent). On the contrary, the ionic conductivity of gel electrolytes, which was in the range of 3.0×10^{-3} to $4.0 \times 10^{-4} \text{ S cm}^{-1}$, decreased very slightly with increasing concentration of gelator. The organogel electrolytes from LiClO_4 and $\gamma\text{-BL}$ exhibited the highest ionic conductivity (ca.

$3.0 \times 10^{-3} \text{ S cm}^{-1}$) among the organogel electrolytes prepared from LiClO_4 , LiBF_4 , and $(\text{CF}_3\text{SO}_2)_2\text{NLi}$ as supporting electrolytes and $\gamma\text{-BL}$, PC, 3-MPN as solvents. The Arrhenius-type behavior between $\log \sigma$ and $1/T$ indicates that the activation energy for organogel electrolytes is constant irrespective of the gel and sol phase. 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.

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