Control of ionic conductivity of ionic liquid/photoresponsive poly(amide acid) gels by photoirradiation

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1,3-Dibutylimidazolium bromide was soaked into a polymer network prepared by condensation of 4-4′-diaminoazobenzene, pyromellitic dianhydride and 1,3,5-tri(4-aminophenyl)benzene to form photoresponsive ion conductive gels.

Ionic liquids (ILs) are composed of only ions and show melting point below 100 °C.[1] Due to their distinguishing properties, ILs have been expected to develop electrolyte solution substituents.[2] Such IL-based ion conductive materials are expected to be safe electrolyte solutions. However, electrolyte solutions always need to be contained and there is the possibility of leakage toward physical stress. There is inevitable development of solid-state and flexible ion conductors for a variety of mobile energy sources. Combination of polymers and ILs is one of potential strategies for these purposes. Especially, polymerization of ILs[2,3] and simple mixing of polymers and ILs[2,4] are receiving interest from industry.

On the other hand, "stimulus-responsive polymer gels" have been investigated.[5] In these systems, photochemical reactions have been used reversibly for the following reasons; precise control by photoirradiation at the nanometer level, and rapid and remote manipulation without wiring between the device and energy source. Azobenzene is known to show a reversible photochemical reaction. Azobenzene typically exists in the *trans* form. When exposed to UV light, the stable *trans* form photoisomerizes to the *cis* form. On the contrary, *cis*-to-*trans* isomerization occurs by irradiation with visible light or heating. Gels containing azobenzene units in the polymer network have been prepared, and their photoresponse has been evaluated.[6]

Horie and co-workers prepared rigid oligo(amide acids) (Fig. 1(a)) containing azobenzene groups as photoresponsive main chains and then crosslinked by a trifunctional amine, 1,3,5-tri(4-aminophenyl)benzene (TAPB; Fig. 1(b)), in DMF.[7] The thus obtained rigid network poly(amide acid) gels have already been analyzed.[7] Hereafter, the photoresponsive poly(amide acid) gel composed of azobenzene is abbreviated as P-Gel.† The P-Gel was expected to show a change in shape upon the photoisomerization of azobenzene. Photoisomerization of the azobenzene group from *cis* to *trans* resulted in local shrinkage of the irradiated site in the P-Gel (Fig. 2, (d) to (e)). The initial state of P-Gel was recovered by visible light irradiation (Fig. 2, (e) to (d)). Heating of the P-Gel is also helpful to change the *cis* azobenzene to the *trans* form. This result was attributed to the photoisomerization of azobenzene groups containing the rigid poly(amide acid) structure. As shown in Fig. 2, photoisomerization induces changes in distance between crosslinking points in P-Gels. This should affect the diffusion coefficient of small molecules and ions in the P-Gel. We reported that the P-Gel was impregnated in suitable ILs and the thus obtained P-Gel containing IL was able to be actuated under air atomosphere.[8] One of suitable ILs for these purposes was 1,3-dibutylimidazolium bromide ([bbim][Br]; Fig. 1(c)) because highly polar [bbim][Br] solubilized the starting materials for the P-Gel[8] and other appropriate polyimides were synthesized in [bbim][Br].[9]

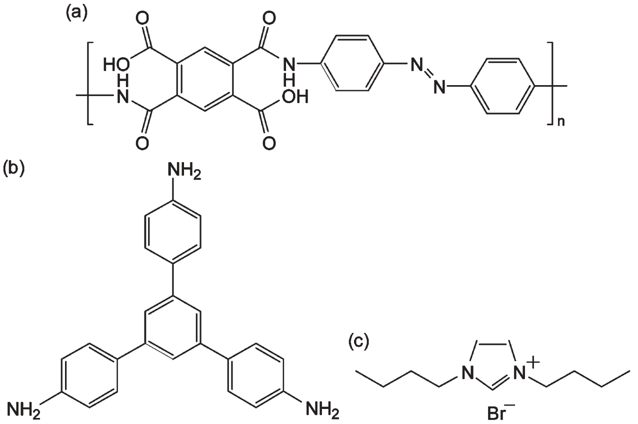

Fig. 1 Structure of oligo(amide acid) (a) and TAPB (cross-linker; (b)) and 1,3-dibutylimidazolium bromide ([bbim][Br]; (c)).

In the present study, we aimed to control the ionic conductivity of P-Gel containing IL by photoirradiation. This is the first report on the evaluation of reversible change in ionic conductivity of the

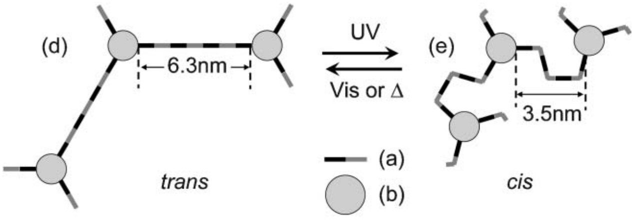

Fig. 2 Scheme of photoresponsive poly(amide acid) gel (swollen state: (d), contraction state: (e)). The distance between crosslinking points is a calculated value.

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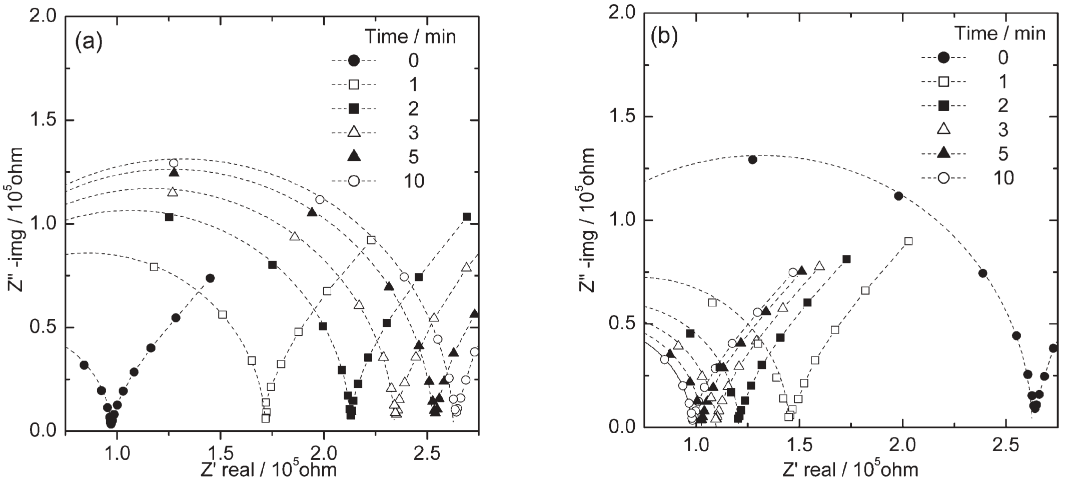

Fig. 3 Nyquist plot of the poly(amide acid) gel containing [bbim][Br] after UV irradiation (a) and visible light irradiation (b).

P-Gels containing IL by photoirradiation.† Hereafter, P-Gels containing [bbim][Br] is abbreviated as P-Gel/IL.

The Nyquist plots of P-Gel/IL with time after UV light irradiation are shown in Fig. 3(a). The semicircle represents a typical equivalent circuit of a resistor and a capacitor connected in parallel corresponding to the bulk electrical properties. In the Nyquist plot, the intersection of the semicircle with the real axis shows the bulk resistance of the sample. Fig. 3 shows the enlarged view of the intersection of the semicircles with the real axis. As clearly seen in Fig. 3(a), the resistance (R_b = Z' value at the minimum Z'' value for every measurement) of the P-Gel/IL increased by successive UV irradiation. This increase in the resistance is easily explained by the decreased lattice size in the shrunk gel. However, even though the P-Gel/IL ideally shrank after UV light irradiation, the average distance between cross-linking points in the amide acid gel was larger than the diameter of both [bbim]$^+$ and [Br]$^-$. The ionic conductivity of the P-Gel/IL decreased after UV light irradiation. This decrease was comprehensible in terms of an increase of "local viscosity". Shrinkage of the network corresponds to an increase in the polymer fraction per unit volume. This should elevate the viscosity of IL inside the gel. This may suppress diffusion of the component ions in the gels.

On the contrary, Fig. 3(b) shows the Nyquist plot of the P-Gel/IL, shrunk by UV light, with time after visible light irradiation. The R_b of the P-Gel/IL decreased upon irradiation with visible light. The average distance between crosslinking points in the P-Gel was recovered by visible light irradiation resulting in a decrease of the local viscosity of [bbim][Br] in the gel. As a consequence, mobility of ions was recovered and R_b decreased. This directly related to the recovery of the ionic conductivity.

It is interesting to evaluate the kinetics of the change. However, since the power of irradiation of UV light was not the same as that of visible source in previous studies, the rate of shrinkage could not directly be compared to that of recovery. In the present study, we used the same light source with two light filters, and the difference of light power could be reduced. From the conductivity change shown in Fig. 3, it is obvious that the change in the resistance by UV light irradiation was slower than the recovery by visible light irradiation. The reason for faster recovery is attributable to the kinetics. Shrinkage of the network should be followed by the release of incorporated ILs. Taking the excluded volume in the gel into account, the initial rate of shrinkage of the gel should be slow. Against this, swelling should be a thermodynamically more favorable process. Also, *trans*-azobenzene is known to be more stable than *cis*-azobenzene. Taking this different stability also into account, faster recovery of resistance as seen in Fig. 3 can be understood.

Change of ionic conductivity of the P-Gel/IL alternately irradiated by UV and visible light is shown in Fig. 4. The ionic conductivity (σ) is expressed by the following formula:

$$\sigma = d/R_bA \tag{1}$$

In eqn (1), R_b, d and A are the resistance and thickness of sample, and effective area of electrode, respectively. For eqn (1), lower resistance corresponds to higher ionic conductivity. Ionic conductivity was switched repeatedly by alternating irradiation of UV and visible light. When the P-Gel/IL was first irradiated by UV light, the ionic conductivity remained low. The P-Gel/IL showed sufficient shrinkage by UV light after the second cycling. The ionic conductivity of the P-Gel/IL was reversibly changed by

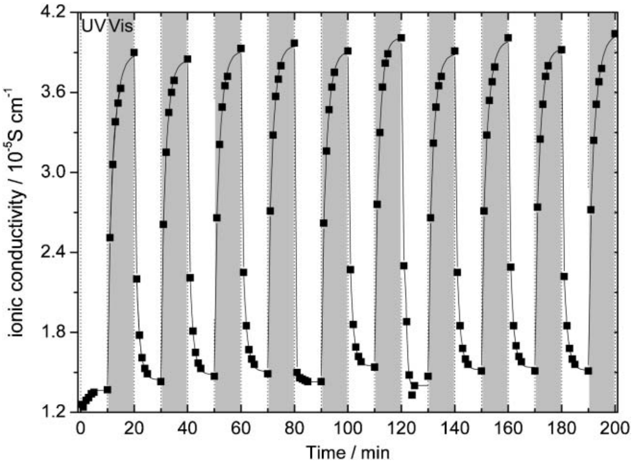

Fig. 4 Ionic conductivity of the poly(amide acid) gel containing ionic liquid after photoirradiation.

alternating irradiation of UV and visible light without attenuation. When the P-Gel containing volatile organic solvents was examined under the same condition, namely under air, change of ionic conductivity was attenuated due to vaporization of the solvent during the irradiation. Stable switching of ionic conductivity of P-Gel/IL under air is supported by the negligibly small volatility of the ILs. Since ILs have almost no vapor pressure at ambient temperature, switching can be carried out for a long time.

Until now, there is no report on the control of ionic conductivity by photoirradiation. The present system requires no wiring for switching. Since the conductivity can be remote-controlled, this may relate to a new ion conductive device. Selective ion transport may be realized by the selection of ions with different size as well as the design of the polymer matrix.

In conclusion, a gel containing azobenzene units was synthesized in DMF solution and then the DMF in P-Gel was replaced with [bbim][Br] to prepare P-Gel/IL. After irradiation with UV light, the ionic conductivity of the P-Gel/IL decreased. Against this, the ionic conductivity of the P-Gel/IL increased by visible light irradiation. These changes were carried out repeatedly without attenuation.

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Notes and references

† *Synthesis* of [bbim][Br]. ILs used in this study were prepared by applying the method as reported previously.[10] 1-Butylimidazole (Aldrich) (2.0 g, 1.6×10^{-2} mol) was dissolved in toluene (100 ml). Then *n*-butyl bromide (TCI) (3.0 g, 2.21×10^{-2} mol) was added to the solution. The solution was stirred under dry dinitrogen at room temperature for 3 days. After removing toluene by decantation, the obtained transparent viscous liquid was washed with dehydrated toluene twice and dried at 45 °C under reduced pressure for 1 day; yield 85%.

Preparation of P-Gel/IL. P-Gel containing IL was obtained by the similar procedure as reported previously.[8] 4,4′-Diaminoazobenzene (DAA) (Lancaster, recrystallized from water–DMF, 2.5×10^{-2} g, 1.2×10^{-4} mol) and pyromellitic dianhydride (PMDA) (Aldrich, recrystallized from 1,4-dioxane, 3.4×10^{-2} g, 1.6×10^{-4} mol) were mixed in anhydrous DMF (0.83 ml) and stirred for 1 day at 25 °C. The thus prepared oligo(amide acid) with terminal acid anhydride groups was added to an anhydrous DMF (0.14 ml) solution of the crosslinker TAPB (1.0×10^{-2} g, 2.8×10^{-5} mol) with a stoichiometric ratio of amino groups to terminal acid anhydride groups. Brown transparent photoresponsive poly(amide acid) was obtained by the reaction at room temperature. P-Gel synthesized in DMF solution was soaked in a large excess of [bbim][Br]. Since DMF is miscible with [bbim][Br], DMF is expected to be replaced by this IL after sufficient incubation. The P-Gel in the IL was then dried *in vacuo* at room temperature for 5 days in order to remove volatile DMF. The obtained P-Gel/IL gave a brown transparent self-standing film.

Measurement of ionic conductivity by photoirradiation: Measurement of ionic conductivity was carried out by the complex impedance method. The cell was composed of stainless steel and ITO electrodes with two Teflon® plates with different hole radius as spacers. The Teflon® spacer with the smaller hole was attached to the stainless steel electrode and the other spacer with the larger hole was fixed on the above ITO electrode. The P-Gel/IL was cast on the stainless steel with spacers, and then covered and clipped with the ITO electrode under N_2 atmosphere. The P-Gel/IL was set in the cell and change of ionic conductivity under light irradiation was dynamically analyzed. A system of ionic conductivity measurement was previously built in our laboratory.[11] Using this system, ionic conductivity measurement was completed within 20 s for every complex impedance plot (Nyquist plot), depending on the frequency of the given ac potential. In order to prevent change of sample temperature, and accordingly, ionic conductivity with light irradiation, the temperature of the sample was kept at 20 °C using a Peltier device. Light was irradiated from the ITO electrode side. During light irradiation, ionic conductivity was measured at 1, 2, 3, 5 and 10 min after the irradiation.

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