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Structural Analysis of High Performance Ion-Gel Comprising Tetra-PEG Network

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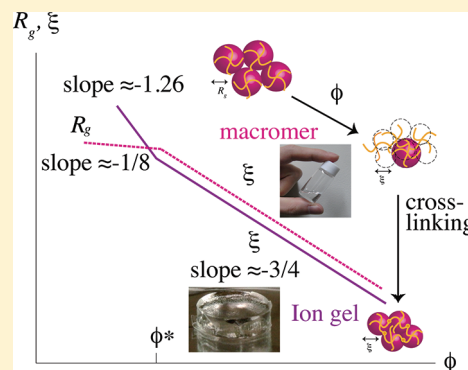
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ABSTRACT: The structure of Tetra-PEG ion gel, which is tetra-arm poly(ethylene glycol) (Tetra-PEG) network in ionic liquid (IL) and has recently established in our group and possesses high ion conductivity and high mechanical properties, was investigated as functions of polymer concentration (ϕ) and molecular weight (M_w) by using small-angle neutron scattering (SANS) measurements. The results were compared with those of Tetra-PEG hydrogel. The macromer solutions of tetra-amine terminated PEG (TAPEG) macromers, which is one of the two constituents forming Tetra-PEG network, were found to interpenetrate each other in IL and exhibited a scaling relationship, $\xi \sim \phi^{-3/4}$, where ξ is the correlation length. The SANS functions, $I(q)$, for the ion gels made by cross-end-coupling of TAPEG and TNPEG (tetra-arm PEG with active ester groups) were represented by the so-called Ornstein–Zernike equation, suggesting absence of frozen inhomogeneities. The same scaling relationship to the macromer solutions, $\xi \sim \phi^{-3/4}$, was also obtained for the ion gels. Furthermore, the SANS curves were superimposed to a single master curve with $I(q)/\xi^{5/3}\phi$ vs ξq irrespective of M_w and ϕ . In contrast, the Tetra-PEG ion gels made by reswelling of a dried hydrogel showed a large upturn, indicating that the ion gels made by the “re-swollen” method caused the network inhomogeneities.



1. INTRODUCTION

Ionic liquids (ILs), which consist only of ions, have unique properties different from not only water but also organic solvents: for example, negligible volatility, nonflammability, thermal and chemical stability, high ion conductivity, and so on.^{1,2} Ion-gel is a gel consisting of a polymeric network as its framework and IL as its solvent, and many kinds of ion gels have been developed in this decade.^{3–6} A representative work is reported by Watanabe et al.⁷ in the system of poly(methyl methacrylate) (PMMA) and 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)amide ([C₂mim][TFSA]), and they successfully made transparent, flexible, and self-standing ion-gels. Such ion gels have been mainly applied to the electrochemical materials such as electrolytes,^{8,9} actuators,^{10–12} and capacitors.^{13–15} Lodge et al. investigated the ion gel with block copolymer based ILs, and they applied not only to the electrochemical devices,¹⁶ but also to the gas separation membrane.¹⁷ The conventional ion-gels, however, have a trade-off problem: As increasing polymer concentration, the mechanical properties of the ion-gel become higher, while the conductivity becomes lower, resulting in the limitation for above-mentioned applications of ion gels. Recently, we reported an ion-gel with excellent toughness by using

Tetra-PEG network and typical ionic liquid.¹⁸ We successfully synthesized the Tetra-PEG ion-gel even with very low polymer concentration (3 wt % Tetra-PEG), which shows high conductivity and mechanical properties. Here, it should be noted that the mechanical properties of a gel is strongly related to its structure. Indeed, it has been established by structural study using small-angle neutron scattering (SANS) that the advanced mechanical properties of Tetra-PEG hydrogel is ascribed to its highly homogeneous network structure.^{19,20}

There have been relatively few reports dealing with the structural studies for polymer in IL by using neutron or X-ray scattering measurements, although it is well-known that small-angle neutron/X-ray scattering experiments are suitable in the structural analysis for gel system.²¹ Triolo et al. studied the conformation of deuterated poly(ethylene oxide) dissolved in ILs by SANS measurements.²² For ion gel system, Sekhon et al. recently reported the effect of polymeric membranes containing ILs in replacement of water on the morphology and the

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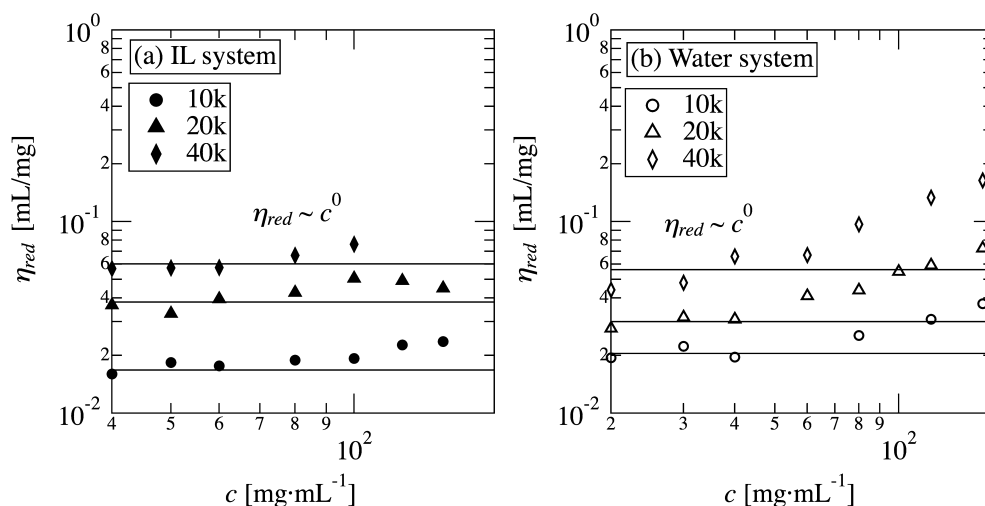


Figure 1. Concentration dependence of the reduced viscosities (η_{red}) of (a) TAPEG/[C₂mIm][TFSA] solutions, and (b) TAPEG/water solutions. By extrapolating η_{red} to $c = 0$, the intrinsic viscosities ($[\eta]$) were obtained.

formation of ionic aggregates by using small-angle X-ray scattering (SAXS) techniques.²³ However, no systematic studies have been reported from the viewpoint of polymer concentration (ϕ) and/or molecular weight (M_w) dependence. In this study, we investigated the structure of Tetra-PEG ion-gels by SANS measurements for the first time. The ϕ and M_w dependences on the structure of Tetra-PEG ion gel are discussed in detail in terms of network structure, which is compared with the corresponding hydrogel system.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. Tetra-amine-terminated PEG (TAPEG) and tetra-NHS-glutarate-terminated PEG (TNPEG) were prepared from tetrahydroxyl-terminated PEG (THPEG) having equal arm lengths. Here NHS represents *N*-hydroxysuccinimide. The details of TAPEG and TNPEG preparation are reported elsewhere.²⁴ The molecular weight (M_w) of TAPEG and TNPEG were matched to be 10 kg/mol, 20 kg/mol, and 40 kg/mol. The IL used in this study was *d*₈-1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (*d*₈-[C₂mIm][TFSA]). The deuteration process of IL is described in our previous paper.¹⁸ The synthesized *d*₈-[C₂mIm][TFSA] was characterized by ¹H NMR, and the deuteration ratio was 96%. In addition, the mass density of *d*₈-[C₂mIm][TFSA] was measured by precision vibrating tube digital density meter (DMA4500, Anton Paar) ($d = 1.55 \text{ cm}^3/\text{g}$). By using the deuteration ratio and mass density, the scattering-length density (SLD) of *d*₈-[C₂mIm][TFSA] was calculated to be $\rho = 4.36 \times 10^{10} \text{ cm}^{-2}$. We used this SLD value for SANS analysis. The preparation method of Tetra-PEG ion gel was described in our previous paper.¹⁸

2.2. Viscosity Measurement. Viscosity measurements were carried out on the TAPEG/IL and TAPEG/H₂O solutions by using a rheometer (MCR501, Anton Paar, Austria) at 25 °C with a cone-plate geometry. The shear rate was 100 s⁻¹.

2.3. Swelling Ratio Measurement. For swelling ratio (Q) measurements, we used 20k 50 mg/mL hydrogels prepared in capillaries 100 μm of diameter, and completely dried them. The Q values were measured as a change of diameters between the dry state and after swelling equilibrium with IL or water.

2.4. Small-Angle Neutron Scattering (SANS). SANS experiments were carried out on High-flux Advanced Neutron Application Reactor (HANARO) located at Korea Atomic Energy Research Institute (KAERI), Korea.²⁵ A monochromated cold neutron beam with an average neutron wavelength 6.00 Å was irradiated to the samples. The scattered neutrons were counted with a 2D detector. The sample-to-detector distances were chosen to be 3 and 17.5 m. After necessary corrections for open beam scattering, transmission, and detector

inhomogeneities, the corrected scattering intensity functions were normalized to the absolute intensity scale.

3. RESULTS AND DISCUSSION

3.1. Determination of Chain-Overlapping Concentration (c^*). Figure 1 shows the variation of the reduced viscosity, $\eta_{red} = (\eta - \eta_0)/c\eta_0$ for (a) IL and (b) water solutions of TAPEG with the molecular weight, $M_w = 10\text{k}$, 20k, and 40k against TAPEG macromer concentration, c . Here, η and η_0 are the viscosities of the solution and the solvent, respectively. In this study, we used only TAPEG macromer for the solution samples. This is because the terminal group of TNPEG macromer is easily decomposed by hydrolysis reaction.²⁶ In addition, it was reported that the size of TAPEG and TNPEG were comparable in aqueous solutions, therefore we skipped the experiments for TNPEG.²⁴ The chain-overlapping concentration (c^*) was determined by the following equation

$$c^* = \frac{3 \times 6^{3/2} \Phi}{4\pi N_A [\eta]} \quad (1)$$

where Φ is the universal constant, and we employed the value of $\Phi = 2.1 \times 10^{23}$.²⁷ The intrinsic viscosities, $[\eta]$, were determined by extrapolating η_{red} to $c = 0$, as shown by solid lines in Figure 1, because they do not depend on c at dilute condition.

The obtained c^* values are plotted against M_w in Figure 2. The c^* values of the IL system are comparable with those of aqueous solutions. In addition, the c^* values of these systems have a relationship, $c^* \sim M_w^{-4/5}$, indicating that they are good solvents for TAPEG.²⁸ We also measured the swelling ratio of both 20k Tetra-PEG gels. The swelling ratio of 20k Tetra-PEG ion-gel (50 mg/mL) was $Q = 23$, which was about a half of that of Tetra-PEG hydrogels ($Q = 48$). These swelling measurement results look inconsistent with the comparable c^* values, because polymer should expand larger in a solvent of which the swelling ratio is larger, leading to a smaller value of c^* . We will discuss this issue in section 3.6.

3.2. TAPEG Macromers in Ionic Liquid. Figure 3 shows the SANS profiles of (a) 10k, (b) 20k, and (c) 40k TAPEG macromer/IL solutions with various polymer concentrations. Note that the samples of 10k were in dilute regime, and those

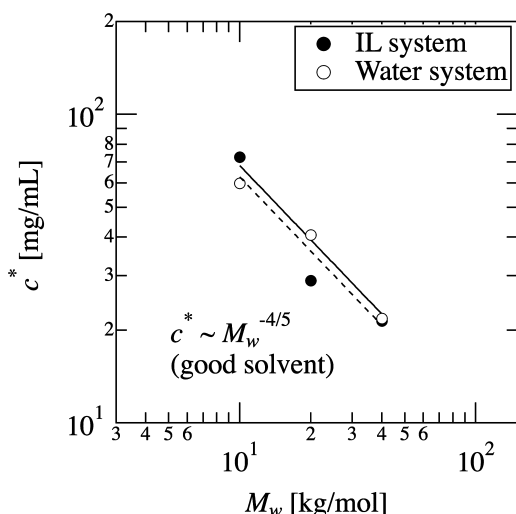


Figure 2. M_w dependence of c^* for IL and water solution system. The c^* values were estimated via eq 1 using $[\eta]$ obtained from Figure 1.

of 20k and 40k were in semidilute regime (refer to the c^* value in Figure 2 and the sample concentration of each M_w). Considering the sample concentrations, we carried out curve fitting by using star-polymer function²⁰ (eq 2 and eq 3) for 10k samples, and by Ornstein–Zernike (OZ) function (eq 4) for 20k and 40k samples. Then we obtained radius of gyration, R_g from the former function and the correlation length, ξ from the latter, respectively. The scattering function, $I(q)$, for star polymers and OZ function are given by

$$I(q) = \frac{(\Delta\rho)^2}{N_A} \frac{V_2 \phi P_{star}(q)}{1 + (1 - 2\chi) \left(\frac{V_2}{V_1} \right) \phi P_{star}(q)} \quad (2)$$

$$P_{star}(q) = \frac{2Z}{fu^2} \left\{ u - [1 - \exp(-u)] + \frac{f-1}{2} [1 - \exp(-u)]^2 \right\} \quad (3)$$

$$I(q) = \frac{(\Delta\rho)^2 RT \phi^2}{N_A K_{os}} \frac{1}{(1 + q^2 \xi^2)} \quad (4)$$

Here, q is the magnitude of the scattering vector, N_A is the Avogadro's number, ϕ is the volume fraction of the solute, and Z

is the degree of polymerization. $\Delta\rho$ is the scattering length density difference between the solute and the solvent ($\Delta\rho = 3.65 \times 10^{10} \text{ cm}^{-2}$ for Tetra-PEG/IL), K_{os} is the osmotic modulus, and V_1 and V_2 are the molar volume of the solvent and solute, respectively. $P_{star}(q)$ is the form factor of f -arm star-polymer chains, and $u \equiv Z a^2 q^2 / 6$. R_g has a relationship, $R_g^2 = (3f - 2) Z a^2 / 6 f^2$. In the low q region, there are upturns in $I(q)$ s. These may be due to a large size but a small fraction of clustered structure of TAPEG macromers via hydrogen bonds between ether oxygens and terminal amine groups.²⁸

Figure 4 shows the variation of obtained R_g and ξ values against ϕ for (a) IL and (b) water solution of TAPEG. The inset shows the corresponding log–log plots. In the 20k and 40k systems of IL solutions (Figure 4a), the ξ values varied as $\xi \sim \phi^{-0.7}$, which was comparable to the relationship of a good solvent system ($\xi \sim \phi^{-3/4}$), where ξ is the blob size.²⁸ On the other hand, the exponent of the R_g in 10k system is smaller than the others ($R_g \sim \phi^{-0.125}$). This should be because the TAPEG solutions of the 10k system are in dilute region (see Figure 2). If TAPEG macromers do not interact each other in dilute region, R_g should scale as $R_g \sim \phi^{-1/8}$. The exponent -0.7 for 20k and 40k TAPEG is close to that of ξ in semidilute region, indicating that TAPEG chains are interpenetrating each other and the size of individual polymer chains, R_g , is not detectable but only mesh size, ξ , is observed by scattering.

In the case of TAPEG/water solutions (Figure 4b), on the other hand, all M_w solutions show a relationship of $R_g \sim \phi^{-1/3}$. This exponent indicates that TAPEG macromers behave like non-interpenetrating “hard spheres”, and they are closely packed.

The difference in the ϕ dependence of the characteristic size of TAPEG between the water and IL solutions are schematically represented in Figure 5. A possible reason for interpenetration of TAPEG macromers in the IL is the absence of electrostatic repulsive interaction. In the case of aqueous solution, it is reported that the most of terminal $-\text{NH}_2$ groups of TAPEG are protonated as $-\text{NH}_3^+$, although the small amount of unprotonated group determine the rate of cross-end-coupling.³⁰ Therefore, the electrostatic repulsive interaction prevents TAPEG macromers from interpenetrating each other. On the other hand, in the case of TAPEG/IL solution, the terminal NH_2 groups of TAPEG are not protonated at all because IL used in this study does not have proton.

3.3. Tetra-PEG Ion Gel. Next, we show the SANS profiles of Tetra-PEG ion-gel for (a) 10k, (b) 20k, and (c) 40K g/mol in Figure 6. All results were well fitted with OZ

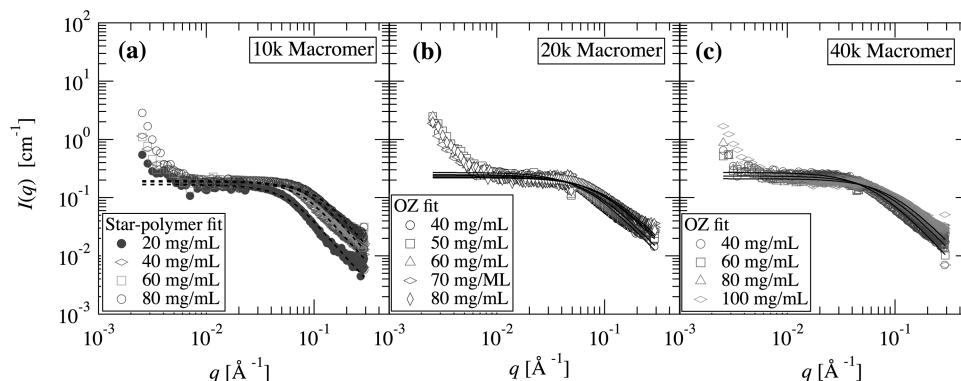


Figure 3. SANS profiles of TAPEG macromer/IL solutions for (a) 10k, (b) 20k, and (c) 40k. The broken lines in part a, and the solid lines in parts b and c indicate the fitting results with star-polymer function (eq 2) and OZ function (eq 4), respectively.

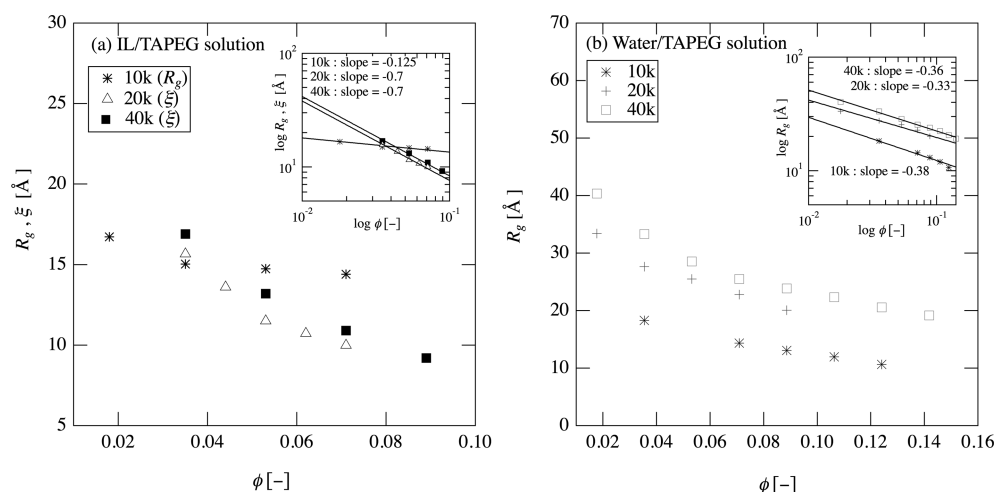


Figure 4. Variation of R_g and ξ of 10k, 20k, and 40k TAPEG macromers against ϕ . The inset shows the corresponding log–log plots.

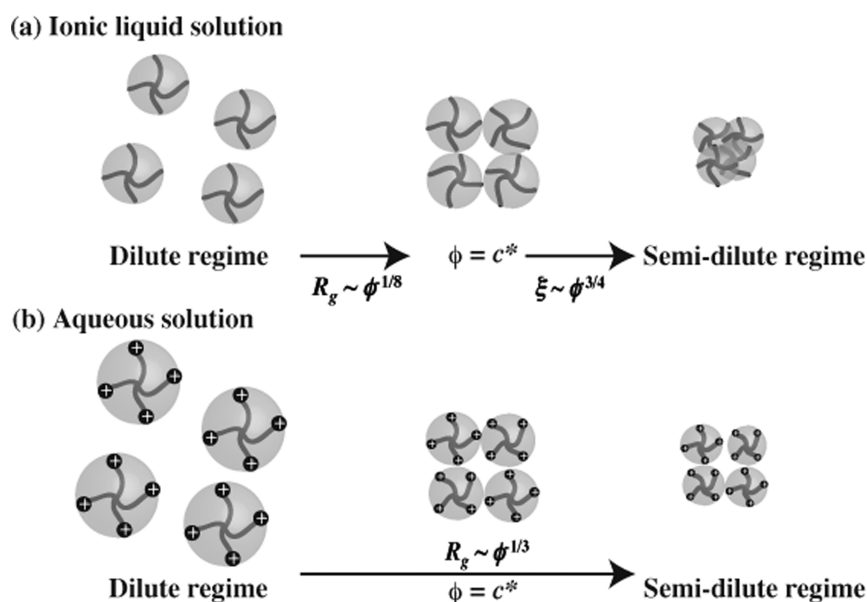


Figure 5. Schematic representation of TAPEG in (a) IL and (b) water.

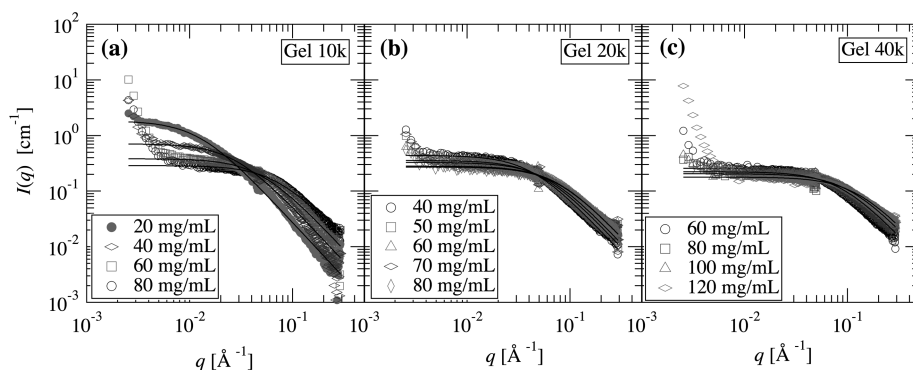


Figure 6. SANS profiles of Tetra-PEG ion-gels for (a) 10k, (b) 20k, and (c) 40k. The solid lines indicate the fitting results by OZ function (eq 5 with $A_{inhom} = 0$).

function (eq 5 with $A_{inhom} = 0$).²⁰

$$I(q) = \frac{(\Delta\rho)^2 RT \phi^2}{N_A M_{os}} \left[\frac{1}{1 + \xi^2 q^2} + \frac{A_{inhom}}{(1 + \Xi^2 q^2)^2} \right] \quad (5)$$

where R and T are the gas constant and absolute temperature, M_{os} is the osmotic modulus, and A_{inhom} is a constant representing the contribution of frozen inhomogeneities. Polymer gels commonly exhibit a strong upturn in small-angle X-ray or neutron scattering intensity functions as a result of frozen-inhomogeneities.^{31,32}

In order to account for it, a squared-Lorentz (SL) function (eq 5) is often used for curve fitting. However, in the Tetra-PEG ion-gel samples, a steep upturn appears only at the lowest few q points. Since the upturn is negligible in our systems, we discuss only the network size of Tetra-PEG ion-gel represented by the parameter ξ .

Figure 7 shows the variation of obtained ξ values for each M_w samples of (a) Tetra-PEG ion gels and (b) Tetra-PEG hydrogels

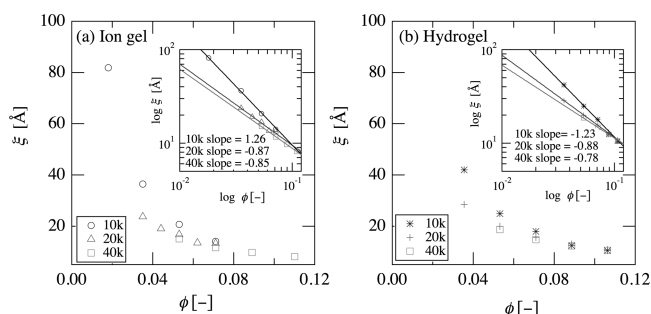


Figure 7. Variation of ξ of Tetra-PEG ion-gels with each M_w against ϕ . The inset shows the corresponding log-log plots.

against ϕ . In the case of the ion gel system in semidilute region (20k and 40k), ξ decreased as polymer concentration increases, with $\xi \sim \phi^{-0.85 \sim -0.87}$. These exponents are near the expected relationship for a gel at swelling equilibrium in good solvent ($\xi \sim \phi^{-3/4}$),²⁸ which is similar to that of R_g (see Figure 4). On the other hand, the exponent of dilute region (10k), $\xi \sim \phi^{-1.26}$, is much larger than that of the semidilute region. Considering that ξ corresponds to the mesh size of network, these results indicate that for the network formed from dilute solution has more defects. Similar behaviors of exponents were also reported in Tetra-PEG hydrogel system (Figure 7b). In the previous

report, we explained this result by the rigidity of PEG chain and the reaction efficiency of gelation: The smaller M_w Tetra-PEG has, the more rigid PEG arms are, resulting in the difficulties of gelation reaction.²⁰ This may be also the reason for the larger exponent in ξ for 10k ion gel samples. Another interesting point is that the ξ values of the ion gel are slightly smaller than those of hydrogel. Considering that TAPEG macromers can interpenetrate in IL (Figure 5), this may be because the interpenetrated macromers are also retained after gelation (cross-linking), resulting in the smaller correlation length of the ion gels.

Figure 8 shows the schematic representation of the structural difference between (a) ion gel and (b) hydrogel guessed from SANS results. As mentioned in Figure 5, the macromers can interpenetrate each other in the IL solution. This interpenetration causes the terminal reactive group of Tetra-PEG macromers to hide in the envelope of the PEG coils, lowering the reaction efficiency of cross-linking. On the other hand, for hydrogel system, the macromers repulsively interact, resulting in the very homogeneous network structure with the active end-group on the envelope of the coils. This structural difference should be one of the reasons for the lower reaction efficiency of Tetra-PEG ion gel even that it is also made by cross-end-coupling of macromers. Note that Tetra-PEG ion gel has homogeneous network structure in this length scale although there are some network defects.

3.4. Master Relationship in SANS Profiles. Next, we tried to normalize the SANS profiles of Tetra-PEG gels. As the scattering intensity of gel is proportional to ϕ and the number of monomers in a blob, g , it can be written as follows:²⁸

$$I(q) = \frac{(\Delta\rho)^2 \phi V_2}{N_A} \frac{g}{1 + \xi^2 q^2} \quad (6)$$

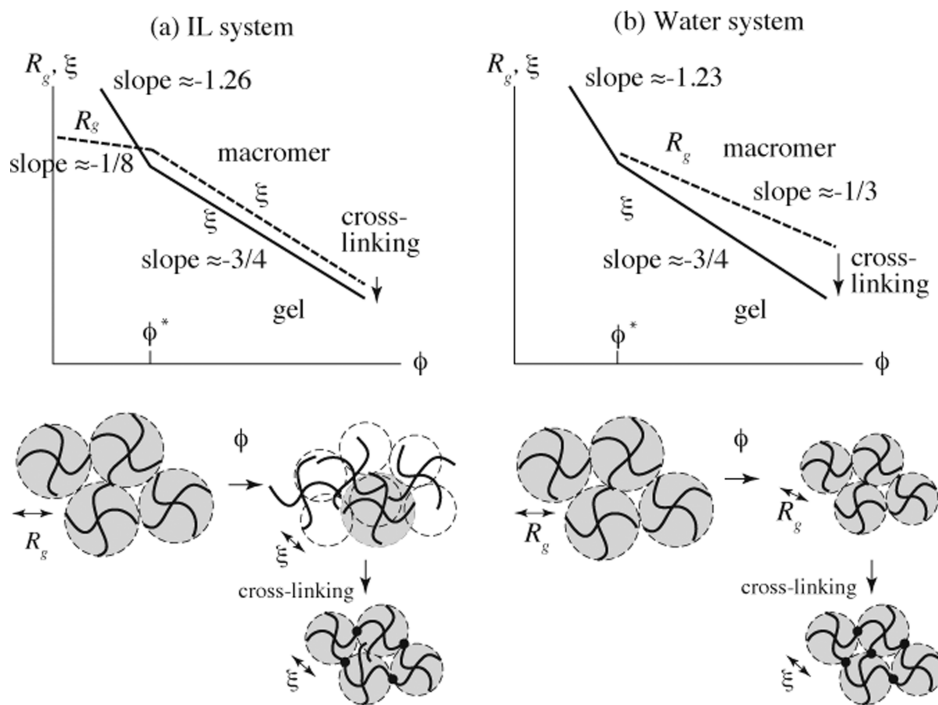


Figure 8. Schematic representation of the structural changes by concentration and by cross-linking for (a) Tetra-PEG ion gel and (b) Tetra-PEG hydrogel. The plots show the changes of power laws between macromer solution and gel. The cartoon explains the process of gelation for each gel system.

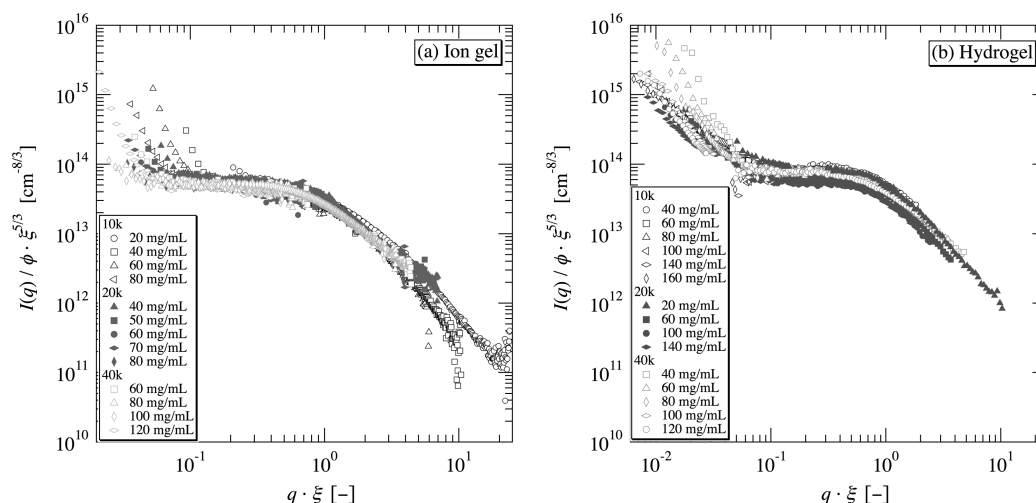


Figure 9. Scaled plots, $I(q)/\phi\xi^{5/3}$, for Tetra-PEG (a) ion gels and (b) hydrogels.

Here, ξ has following relationship with monomer length, a , and g for good solvent system:

$$\xi \approx ag^{3/5} \quad (7)$$

Therefore, from eq 6 and 7, $I(q)$ can be represented by ϕ and ξ as below:

$$I(q) \approx \frac{(\Delta\rho)^2 \phi V_2 \xi^{5/3}}{N_A} \frac{1}{1 + \xi^2 q^2} \quad (8)$$

Equation 8 shows that $I(q)$ can be normalized by ϕ and $\xi^{5/3}$ for good solvent system. Figure 9 shows the normalized SANS profile of (a) ion gel and (b) hydrogel. As shown in these figures, we successfully represent the SANS profiles by a single master curve for each gel system. These master curves mean that the structure of both Tetra-PEG gels have a self-similar structure irrespective of M_w and ϕ . In the hydrogel system, we previously reported a master curve normalized by $\phi\xi^2$ from a phenomenological point of view.^{19,20} However, the master curves shown in Figure 9 are more reasonable as discussed above.

3.5. Examination of the Theory. We examined the validity of the parameters obtained from SANS analysis by comparing with those obtained from theoretical calculation. The osmotic modulus, M_{os} , can be obtained by SANS at $q = 0$ (i.e., the thermodynamic limit) or from the following equation based on the Flory–Huggins and Flory–Rehner theories,³³

$$M_{os} = K_{os}^{gel} + \frac{4}{3}G$$

$$= \frac{RT\phi_0}{N_x V_2} \left[\frac{1}{2} \left(\frac{\phi}{\phi_0} \right) - \frac{1}{3} \left(\frac{\phi}{\phi_0} \right)^{1/3} \right]$$

$$+ \frac{RT}{V_1} (1 - 2\chi + \phi) \phi^2 + \frac{4}{3}G \quad (9)$$

Here, K_{os}^{gel} is the bulk modulus of the gel, N_x is the degree of polymerization between neighboring cross-links. ϕ and ϕ_0 are the polymer volume fraction at measurement and at preparation, respectively, and χ is the Flory–Huggins parameter. For SANS fitting process, we used the OZ function (eq 5 with $A_{inhom} = 0$) with fixed $\Delta\rho$ value between D_2O and PEG as $5.72 \times 10^{10} \text{ cm}^{-2}$. On the other hand, for the calculation with eq 9, we used the following values; $\chi = 0.43$ for linear-PEG/water

system³⁴ and the shear modulus, G , reported in the previous paper.¹⁹ Figure 10 shows the ϕ dependence of M_{os} for 20k

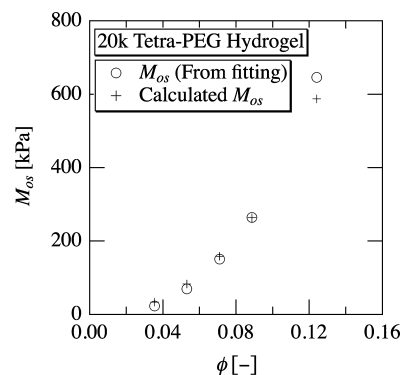


Figure 10. Comparison of the osmotic modulus, M_{os} , obtained from SANS analysis and calculation by eq 9.

Tetra-PEG hydrogel as an example. In this figure, the M_{os} values obtained from SANS fitting results and those from calculation using eq 9 are plotted together. As shown in this figure, the values obtained from SANS and from the calculation were in excellent agreement for the hydrogel system, indicating that the Flory–Huggins theory is valid for this hydrogel system. However, in the case of ion gel system, the M_{os} values from eq 9 were found to be much smaller than those from SANS analysis: for 20k 50 mg/mL ion gel sample, 29.7 kPa from SANS fitting, 4.9 kPa from the calculation. This may be because various types of interactions may have to be considered in the case of ion gels, such as the van der Waals interactions of the cations with anions, of cations with the gel network, and of the anions with the gel network.³⁵ This issue will be discussed elsewhere.

3.6. Tetra-PEG Ion Gel Prepared by Reswollen Method. In the preceding sections, we discussed the structure of Tetra-PEG ion gels, which were prepared by mixing two-types macromer/IL solutions, i.e. as-prepared gel. Here, we discuss Tetra-PEG gels prepared by alternative method. First, we prepared Tetra-PEG hydrogels by cross-end-coupling of the corresponding macromers in water, followed by complete drying and reswelling in IL. We call this preparing method “re-swollen method”. Figure 11 shows the SANS profiles of

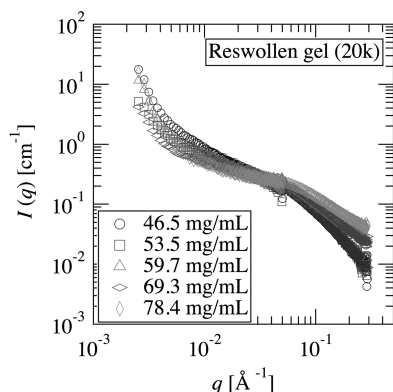


Figure 11. SANS profiles for 20k Tetra-PEG ion gel prepared by reswollen method.

Tetra-PEG ion gels prepared by the reswollen method. The polymer concentrations of reswollen ion gels were calculated from the weight of swollen IL and dried tetra-PEG gels before swelling with the IL. Contrary to the expectations, the reswollen Tetra-PEG ion gels do not reproduce the scattering curves of the corresponding hydrogels although they are made from hydrogels. In addition, they show larger upturns than those of the corresponding as-prepared ion gels, suggesting that larger inhomogeneities are produced during the reswollen process. A possible reason for this inhomogeneity is the crystallization of PEG chains, which are induced during the drying process of the hydrogel.³⁶ Once the PEG chains are crystallized, it may be difficult to dissolve in IL and swell fully, and reproduction of the uniform network may be interrupted. This may be the reason why the swelling ratio of dried tetra-PEG gel in the IL is smaller than that in water, although the c^* or R_g values are comparable for both solvents (section 3.1).

4. CONCLUSION

We investigated the structure of Tetra-PEG ion gel as functions of polymer concentration (ϕ) and molecular weight of macromer (M_w) by using viscosity measurement and small-angle neutron scattering (SANS) measurement. Then we discuss the ϕ and M_w dependence of Tetra-PEG ion gels with those of hydrogels. From the viscosity measurement, it was found that PEG/IL solution was turned to be a good solvent as well as PEG/water solution, which was conjectured from the relationship of $c^* \sim M_w^{-4/5}$ obtained by viscometry.

From the SANS measurements of TAPEG macromer solutions, it was found that TAPEG macromers interpenetrate each other in IL solution above c^* , due to the absence of repulsive electrostatic interaction, resulting in the power law of $\xi \sim \phi^{-3/4}$, which is expected for the good solvent system. This exponent is higher than that of water solution system ($R_g \sim \phi^{-1/3}$), where repulsive electrostatic interaction originated from the protonated terminal amine groups of TAPEG prevents the macromers from interpenetration, and TAPEG macromers act like hard-spheres. After gelation, the ion gel made from the solution of semidilute region shows a similar power law behavior with the corresponding solution, $\xi \sim \phi^{-3/4}$, which is expected for a gel at swelling equilibrium in good solvent. The deviation from this exponent for the 10k gel may come from the network defects due to dilute condition and imperfect reaction of gelation. Such an imperfect reaction may be attributed to the interpenetrated macromers in IL, where the terminal reactive groups of macromers hide in the envelope of the PEG

coils. This may be one of the reasons for the lower reaction efficiency of Tetra-PEG ion gel¹⁸ comparing with the corresponding hydrogel.

In addition, we successfully normalized the SANS profiles of Tetra-PEG gels by $\phi\xi^{5/3}$, which was originated from the scaling theory for good solvent in semidilute regime. The validity of SANS fitting was also examined by comparing the M_{os} values obtained from SANS fitting with those from the Flory–Huggins theory. The M_{os} values for the ion gel obtained from SANS did not match with those from the theory, indicating that the consideration of the interaction between cation, anion, and polymer network may be necessary for IL system.

The preparation method dependence on the structure was also investigated by comparing with the as-prepared ion gel and “re-swollen gel”, which was made by swelling a dried Tetra-PEG hydrogel. Interestingly, the obtained reswollen ion gel showed large inhomogeneity although it was made from a highly uniform Tetra-PEG hydrogel. This may be due to the crystallization of PEG chains, which are induced during the drying process of the hydrogel.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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