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COMMUNICATION

High swelling ability of polystyrene-based polyelectrolyte gels at low temperature[†]

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Molecular design of polymer gels that exhibit high swelling degrees at low temperature was demonstrated with the aid of repulsive interaction among the polymer chains in the ionic polymer gels and the utility of organic solvents with relative low melting points. A small amount of tetraalkylammonium tetraphenylborate as ionic groups was incorporated into cross-linked polystyrene to yield novel ionic polymer gels. The swelling degrees at room temperature (23 °C) were about 100 times as much as their dried weights in various organic solvents. Moreover, they swelled and absorbed some organic solvents such as THF and dichloromethane at low temperature (-80 °C), and the swelling degrees were similar to those at room temperature.

The most characteristic property of polymer gels as functional materials is swelling, the drastic increase of their 3D network in volume or weight due to absorption of solvent molecules. The swelling properties of the polymer gels are generally evaluated by the volume or weight ratios before and after soaking in them and should be governed mainly by interaction of the polymer chains in the media and rubber elasticity due to cross-linking of the polymer chains. Good compatibility of the polymer chains to the media expands the network and a poor one collapses. Densely cross-linked polymer gels should be tough and their swelling abilities should be low, while sparsely cross-linked ones should be soft and high. In addition to these two factors, in the case of ionic polymer gels, osmotic pressure and electrostatic repulsion generated by dissociation of the ionic moieties in the polymer chains largely expand their network hugely, and association of the ions and ion pairs collapses them. Therefore, investigation of swelling abilities under the similar cross-linking densities should be a good indicator for both the compatibility of the polymer chain to the media and ionization of the ionic groups in the media.¹ The swelling abilities of the polymer gels have been mostly studied under ambient conditions. The polymer gels based on poly(acrylic acid sodium salts), polyNIPAM, polystyrene and polydimethylsiloxane were investigated at room temperature for superabsorbent polymers, thermal stimuli-sensitive polymers,²⁻⁵ polymer supports⁶⁻⁸ and microfluidic devices,⁹ respectively. However, the swelling abilities under other extreme conditions such as high or low temperature are still in their infancy. Watanabe *et al.* investigated the swelling abilities and LCST behaviour of poly(benzyl methacrylate) above 100 °C by using non-volatile ionic liquids, as a pioneer work at higher temperature (>100 °C).¹⁰ On the other hand, swelling properties of polymer gels at low temperatures below 0 °C have been scarcely investigated, because polymer–polymer interactions should be much stronger than at room temperature and suppress swelling abilities in any media.

As molecular design for the high swelling polymer gels at low temperature, we focused on the utility of ionic groups. It is because ion dissociation of electrolytes is generally insensitive to temperatures of the media at low temperature,11-13 and dielectric constants of less polar organic solvents increase with decreasing temperature.14 These two features strongly suggest that dissociation of ionic polymer gels is useful even at low temperature for large expansion of the network against strong polymer-polymer interactions. Moreover, most of the known ionic polymer gels are highly hydrophilic and their swelling abilities have been investigated mainly in water, and the swelling properties at low temperatures below 0 °C have been never investigated. Recently, we reported a new class of poly(alkyl acrylate) gels with tetraalkylammonium tetraphenylborate as a lipophilic ionic group, and they exhibited high swelling abilities in various non- or less-polar organic solvents due to ion dissociation and we confirmed that they act as polyelectrolyte gels in them.15,16 This result prompted us to explore the ionic polymer gels that exhibit high swelling abilities at relatively low temperatures (=-20, -80 °C) by similarly designed polyelectrolyte gels and organic solvents with low melting points such as THF, acetone and dichloromethane. In this report, we demonstrate preparation of polystyrene-based polyelectrolyte gels bearing a small amount of tetraalkylammonium tetraphenylborate as dissociable ionic groups and swelling abilities at room temperature and at low temperature in various organic solvents.

A quaternary alkylammonium salt with a styrene group was prepared from alkylation of tri(*n*-hexyl)amine by 4-(chloromethyl)styrene. The resulting quaternary alkyl-ammonium halide was treated with sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (TFPB) to yield 1. Lipophilic polyelectrolyte gels (EG) were prepared by radical polymerization initiated by AIBN in the presence of 1,

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divinylbenzene (DVB) as a crosslinker, and styrene as a comonomer, as shown in Scheme 1. As a reference, nonionic gels (NG) were prepared by the same procedure in the absence of 1. The feed ratios were adjusted to 1 : styrene : DVB 3 : 97 : 1 for EG, and 0 : 100 : 1 for NG, respectively.

The swelling abilities of polyelectrolyte gels EG(PS) and nonionic gels NG(PS) in organic solvents with various polarities from toluene ($\varepsilon = 2.4$) to dimethylsulfoxide (DMSO: $\varepsilon = 47$) were investigated at room temperature (23 °C). The swelling degrees (Q) of EG(PS) and NG(PS) were calculated as the following equation, and are summarized in Fig. 1; $Q = (W_{wet} - W_{dry})/W_{dry}$ (w/w). In extremely nonpolar solvents ($\varepsilon < 5$), the swelling degrees of EG(PS) were smaller than those of NG(PS). For example, the swelling degrees of EG(PS) in toluene and in chloroform were 5 and 30, respectively, whereas those of NG(PS) were 27 and 45, respectively. In these solvents, dissociation of the ionic groups was completely suppressed owing to their low polarity, and they would act as tightly bound ion pairs or highly aggregated species. As a result, collapse of the polymer network was observed for EG(PS), and the swelling degrees were much lower than NG(PS). On the other hand, in more polar solvents with dielectric constants $6 < \varepsilon < 40$, except for a series of aliphatic alcohols, the swelling degrees of EG(PS) were larger than those of NG(PS). In these solvents, the polystyrene backbone had enough good miscibility to expand the polymer chains, and the higher polarity promoted dissociation of the ion-pairs, which enhanced significantly the swelling degrees. For example, the swelling degrees for EG(PS) in THF, dichloromethane and 1,2-dichloroethane were 68, 109 and 113, and those of NG(PS) were 23, 35 and 32, respectively. The former were several times as large as the latter. Moreover, it is noteworthy that EG(PS) swelled in some ketones, such as 2-octanone (Q = 75) and acetone (Q = 92), and in more polar solvents such as DMF, EG (PS) took the largest swelling degree (Q = 166), whereas NG(PS) did not at all, 2-octanone (Q = 9), acetone (Q = 1). The enhancement effect on the swelling degrees for EG(PS) tended to increase with increasing solvent polarity owing to an increase in the number of dissociated ionic groups. These results clearly indicated that EG(PS) should act as the super-absorbent polymer for organic solvents.

We further investigated the swelling behaviours of **EG(PS)** at low temperatures. Fig. 2 shows the swelling degrees at various low temperatures in THF. The swelling degrees of **EG(PS)** after 48 h incubation at 23 °C, 2 °C, -16 °C, and -30 °C were 71, 82, 67 and 74, respectively. At -80 °C, the swelling degree was about half. However, prolonged incubation for 96 h to the equilibrium swelling

 $\begin{array}{c} (\stackrel{(r-C_{\theta}H_{13})_{3}N}{DMF} \xrightarrow{(r-C_{\theta}H_{13})_{3}N} \xrightarrow{(r-C_{\theta}H_{13})$

Scheme 1 Synthesis of 1, EG(PS) and NG(PS).



Fig. 1 Swelling degrees of EG(PS) (grey bar) and NG(PS) (open bar) in various organic solvents at room temperature (23 $^{\circ}$ C). In parentheses, their dielectric constants are shown.



Fig. 2 (Left) Swelling degrees of EG(PS) (grey bar) and NG(PS) (open bar) in THF at various low temperatures after 48 h and at -80 °C after 96 h incubation. (Right) Photographic images of (a) dried EG(PS) and (b) wet EG(PS) in THF at -30 °C.

degree increased the swelling degree similar to that at 23 °C. They were nearly constant against temperature. The rate of swelling became much slower because of the slower kinetics of expansion of the polymer network. Therefore, the swelling degrees of EG(PS) kept high even at the low temperatures and were independent of the incubation temperatures. Comparison of the swelling degrees between EG(PS) and NG(PS) provided fruitful information for understanding the role of the ionic groups for swelling. After the same incubation time, the swelling degrees of NG(PS) at 23 $^{\circ}$ C, 2 $^{\circ}$ C, -16°C, -30 °C and -80 °C, were 23, 29, 27, 30 and 14, respectively. They were all of a similar magnitude and were about one-third as large as those of EG(PS). This decrease in the swelling degrees was attributed simply to the absence of electrostatic repulsion and osmotic pressure originated from the dissociated ionic groups in the polymer chain. Even at -80 °C, ion dissociation of EG(PS) played a key role for the enhancement of the swelling ability. Moreover, this result supported that the polystyrene polymer chains had enough good compatibility to THF in this range of temperatures, due to the absence of attractive force among them.

The swelling behaviour of **EG(PS)** in the other solvents, such as dichloromethane and acetone, was investigated. The swelling degrees are summarized in Fig. 3. In dichloromethane, the swelling degree at



Fig. 3 Swelling degrees of **EG(PS)** at -80 °C (grey bar) and at room temperature (23 °C) (open bar) after 48 h incubation in THF, CH₂Cl₂ and acetone. In parentheses, their dielectric constants are shown. *The swelling degree at -80 °C in THF was after 96 h incubation.

-80 °C was similar to that at room temperature (23 °C) like in THF. In acetone, however, the swelling degree at -80 °C was much lower than at room temperature. In the latter solvent, although the ionic groups could dissociate into free ions due to much higher dielectric constant, compatibility of the polymer chains to the media became much poorer, and the polymer–polymer interaction should be much stronger at -80 °C, which significantly suppressed the swelling ability.

In conclusion, we demonstrated a new class of polyelectrolyte gels on the basis of polystyrene as a polymer backbone. This gel swelled and absorbed various organic solvents from low dielectric media $(\varepsilon = 6)$ to highly polar solvents ($\varepsilon = 40$). High swelling degrees are attributed to ionic dissociation of tetraalkylammonium tetraphenylborate. Moreover, this polyelectrolyte gel could swell largely at low temperature (-80 °C) in some organic solvents. To the best of our knowledge, this is the first example of super-absorbent polymers working at low temperature, and this material should be the first step for development of absorbent materials or actuators¹⁷ under extreme conditions. Moreover, high swelling abilities in THF at -80 °C should provide a potent solid support for chemical reactions.¹⁸ Finally, our results clearly indicate that electrostatic repulsion by ionic dissociation of polyelectrolytes should be a powerful tool to generate a repulsive force among the polymer chains at low temperature as well as at room temperature, although the other intermolecular interactions such as hydrogen bonds, and π - π interaction should act as an attractive force at low temperature.

Combining these repulsive and attractive groups in the polymer gels should enable us to develop various stimuli-sensitive polymer gels working at low temperature. Development of super-absorbent polymers for various environments is also under current investigation.

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