

Lipophilic polyelectrolyte gels as super-absorbent polymers for nonpolar organic solvents

TOSHIKAZU ONO¹, TAKAHIRO SUGIMOTO¹, SEIJI SHINKAI^{1,2} AND KAZUKI SADA^{1*}

¹Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

²Center for Future Chemistry, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

*e-mail: sadatcm@mbox.nc.kyushu-u.ac.jp

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Polyelectrolyte gels that are known as super-absorbent polymers swell and absorb water up to several hundred times their dried weights and have become ubiquitous and indispensable materials in many applications^{1,2}. Their superior swelling abilities originate from the electrostatic repulsion between the charges on the polymer chains and the osmotic imbalance between the interior and exterior of the gels³. However, no super-absorbent polymers for volatile organic compounds (VOCs), and especially for nonpolar organic solvents ($\epsilon < 10$) have been reported, because common polyelectrolyte gels collapse in such solvents^{4–6} owing to the formation of a higher number of aggregates of ions and ion pairs^{7,8}. Here, we report that a novel class of polyelectrolyte gels bearing tetra-alkylammonium tetraphenylborate^{9,10} as a lipophilic and bulky ionic group swell in some nonpolar organic solvents up to 500 times their dry size. Dissociation of the ionic groups even in low-dielectric media ($3 < \epsilon < 10$) enhances the swelling ability by expansion of the polymer networks³. This expands the potential of polyelectrolytes that have been used only in aqueous solutions or highly polar solvents¹¹, and provides soft materials that swell in a variety of media. These materials could find applications as protective barriers for VOCs spilled in the environment and as absorbents for waste oil.

The observation of swelling of neutral polymer gels in organic solvents dates back to the discovery of the swelling behaviour of rubber in oil¹². The swelling is caused by the imbalance between the repulsive forces among the polymer chains and the contractile forces due to stretching of elastically active networked structures¹³. Thus, both the compatibility of the polymer chains with the organic solvents and the crosslinking density of the networked structures play a key role in the swelling and collapsing of neutral polymer gels. Reducing the amount of crosslinker increases the swelling ability, but stable networks cannot form if the crosslinking density is too low. Consequently, improvement of the swelling ability is limited in practice, and swelling degrees, defined as the weight ratio of the amount of absorbed solvent over that of the gel in the dried state, of up to 100 have been reported^{14–20}. On the other hand, hydrogels prepared by crosslinked polyelectrolytes swell in water, to a degree of several hundred or more. They are used in a wide range of applications such as nappies, fillers in cosmetics, separation media, drug-delivery systems, biomedical

devices, sensors, inks and display devices^{1,2}. The high swelling abilities originate from the electrostatic repulsion between the ions fixed on the polymer chains and osmotic pressure induced by freely mobile counter-ions in the networked polyelectrolytes³. However, the gels collapse owing to aggregation of the ions in most organic solvents except highly polar ones. Moreover, amphiphilic polymer gels with lipophilic polymer chains bearing common ionic groups such as carboxylate anions and ammonium cations result in similar collapse of the gels^{4,21}. Only one example of charge-transfer gels has been reported for discontinuous volume phase transition in hydrocarbons, but the swelling abilities were of a similar magnitude to those of common neutral polymer gels²². Thus, we attempted to synthesize super-absorbent polymers that swell with high swelling degrees in nonpolar organic solvents ($\epsilon < 10$). Our design relies simply on the incorporation of a small amount of the ionic groups dissociable in the media into the lipophilic polymer gels. Substituted tetraphenylborate as a lipophilic anion and tetraalkylammonium with long alkyl chains as a lipophilic cation were selected as the lipophilic ionic groups. Both the anion and the cation are large and covered with lipophilic functional groups. In particular, the anion belongs to the class of 'weakly coordinating anions' (ref. 23). As a low-molecular-weight model salt, tetra(*n*-butyl)ammonium tetraphenylborate is easily dissolved and dissociates slightly to free ions or loosely bound ion pairs even in nonpolar organic solvents such as chloroform and tetrahydrofuran^{9,10} (THF). For the polymer chains in the gels, we selected poly(octadecyl acrylate) owing to its easy synthesis and good compatibility to the media. Then, we prepared a new lipophilic ionic acrylate monomer (**1**), which was copolymerized with octadecyl acrylate (ODA) using azobisisobutyronitrile (AIBN) as the initiator in the presence of ethylene glycol dimethacrylate (EGDMA) as a crosslinker to yield lipophilic polyelectrolyte gels (**1G**) as shown in Fig. 1. The content of the ionic groups in the polymer chains was suppressed to less than 5%, because incorporation of too many ionic groups would cause physical crosslinking by higher aggregation of the ionic groups and consequently collapse of the gels^{7,8}.

The swelling behaviour of the lipophilic polyelectrolyte gel (**1G**) in organic solvents with various polarities from hexane ($\epsilon = 1.9$) to dimethyl sulphoxide (DMSO; $\epsilon = 46$) was investigated. Figure 2 shows the wet gels swollen in THF, and the swelling degrees of **1G**

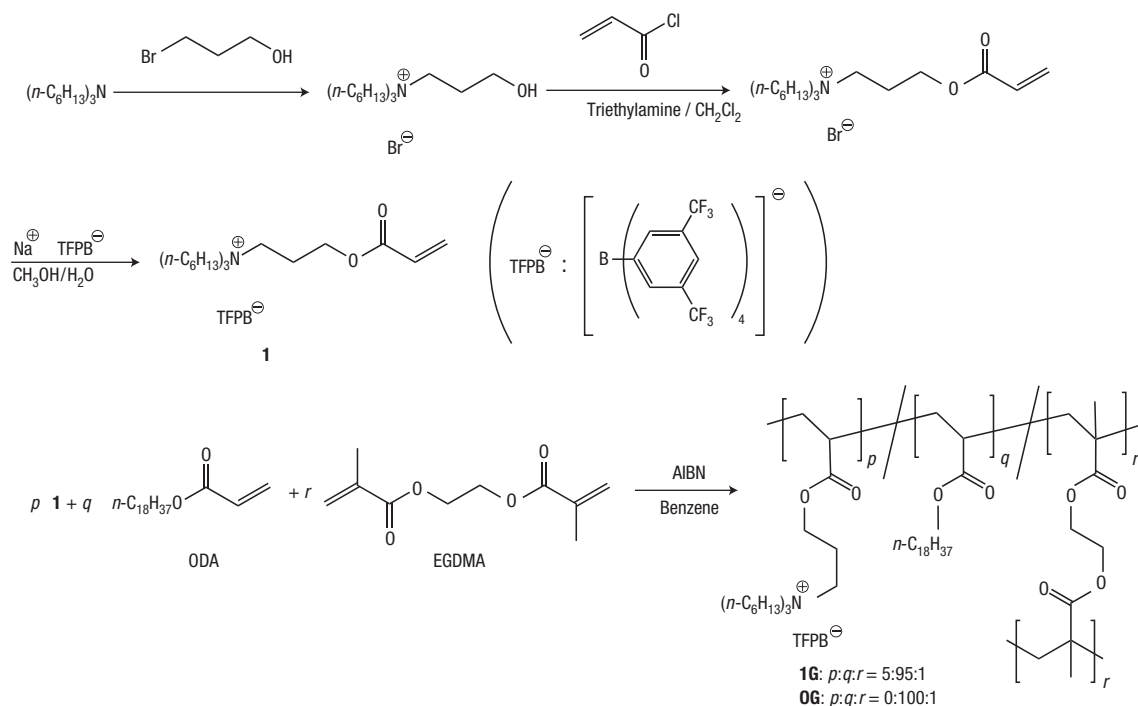


Figure 1 Preparation of monomer (**1**), lipophilic polymer gels (**1G**) and octadecyl gel (**OG**). A quaternary alkylammonium salt with an acrylate group was prepared from alkylation of tri(*n*-hexyl)amine by 3-bromo-1-propanol, followed by esterification of the hydroxyl group using acryloyl chloride in the presence of triethylamine. The resulting quaternary alkylammonium halide was treated with sodium TFPB to yield **1**. Lipophilic polyelectrolyte gels (**1G**) were prepared by radical polymerization initiated by AIBN in the presence of EGDMA as a crosslinker and ODA as a comonomer.

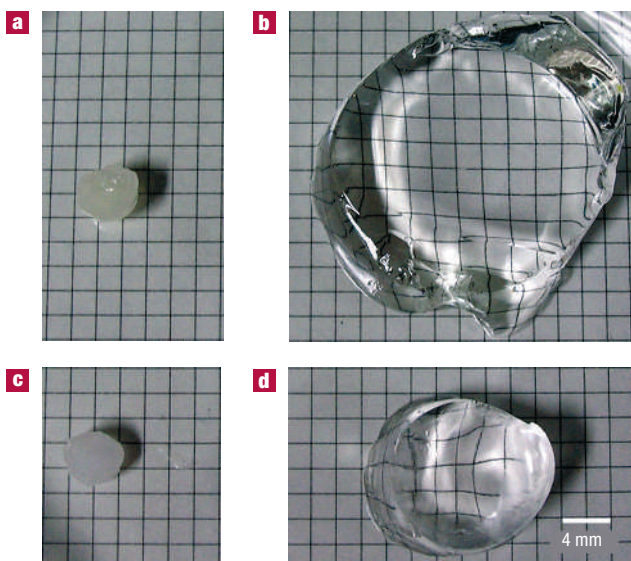


Figure 2 Swelling of **1G** and **OG**. **a**, Dried **1G**. **b**, Wet **1G** swollen in THF for 48 h. **c**, Dried **OG**. **d**, Wet **OG** swollen in THF for 48 h.

are summarized in Fig. 3a. Starting from the nonpolar solvents, the swelling increased with increasing dielectric constant, and the maximum swelling degree was observed in dichloromethane

($\epsilon = 8.9$) as shown in Fig. 3a. Then, the swelling decreased with increasing solvent polarity, and the gels collapsed in the more polar solvents ($\epsilon > 10$). In particular, **1G** swelled and absorbed large amounts of nonpolar organic solvents with dielectric constants between three and ten ($3 < \epsilon < 10$) such as THF (swelling degree, $Q = 122$), dichloromethane ($Q = 128$), chloroform ($Q = 99$) and chlorobenzene ($Q = 70$). Moreover, **1G** absorbed moderate amounts of solvent even in extremely nonpolar solvents ($\epsilon < 3$), such as hexane ($Q = 12$), carbon tetrachloride ($Q = 44$) and toluene ($Q = 24$). In more polar organic solvents, such as 1-hexanol ($Q = 0.7$), acetone ($Q = 0.8$), methanol ($Q = 0.3$), DMSO ($Q = 2.5$) and *N,N*-dimethylformamide (DMF; $Q = 0.7$), **1G** did not absorb solvent at all. Comparison of **1G** with neutral octadecyl gels (**OG**) without lipophilic ionic groups provided explanations for the high swelling abilities of **1G** and useful information for designing super-absorbent polymers in organic solvents, because swelling behaviour depends on both the compatibility of the polymer chains with the media and the ionic dissociation of the ionic groups in the media. The swelling behaviour of **OG** demonstrates the compatibility of the polymer chains to the media. In the nonpolar solvents ($\epsilon < 3$) and in the polar solvents ($\epsilon > 10$), **OG** and **1G** exhibited similar swelling behaviour. For example, the swelling degrees in hexane were 12 and 11 for **1G** and **OG**, and those in DMF were 0.7 and 0.3, respectively. In the polar solvents, the lipophilic polymer chains with long alkyl groups of ODA had poor solvent compatibility and did not allow penetration of the solvent molecules into the polymer networks of the gels. As a result, both the gels collapsed, even though the ion pairs in **1G** would be easily dissociated. In the nonpolar media, dissociation of the ion pairs was completely suppressed owing to the low dielectric

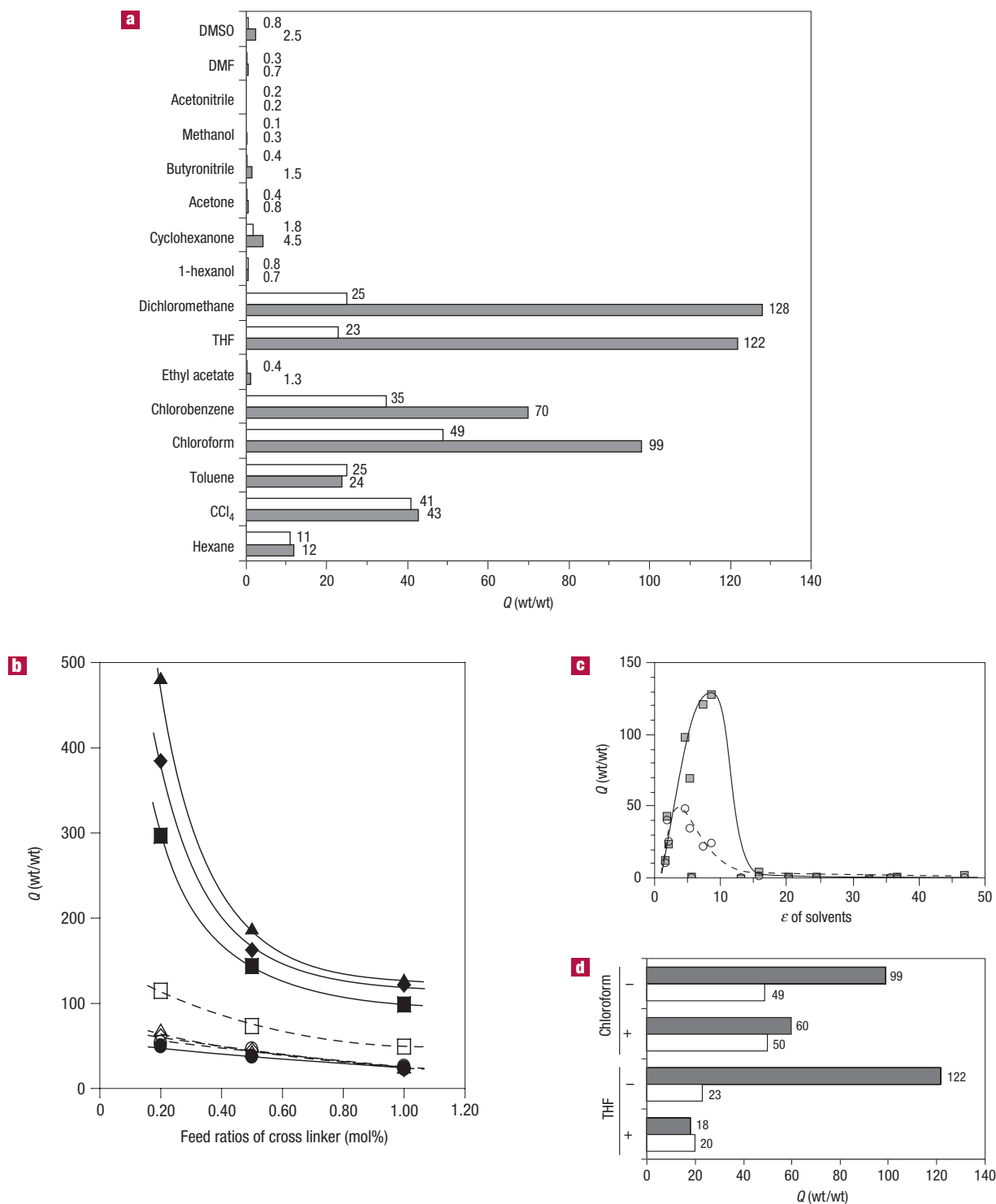


Figure 3 Swelling behaviours of **1G** and **OG** in various organic solvents. **a**, Swelling degrees (Q) of **1G** (grey bars) and **OG** (open bars) after immersion for 48 h. The values beside the bars are swelling degrees. **b**, Swelling degrees (Q) of **1G** (filled symbols) and **OG** (open symbols) in some nonpolar organic solvents: toluene (circles), chloroform (squares), THF (diamonds) and dichloromethane (triangles) versus feed ratios of the crosslinker to the monomers. **c**, Plot of the swelling degrees of **1G** (grey squares) and **OG** (open circles) versus polarity (ϵ) of the solvents. **d**, Swelling degrees in THF and chloroform of **1G** (grey bars) and **OG** (open bars) in the presence (+) and absence (-) of tetra(*n*-butyl)ammonium TFPB (1.0 mM). The values beside the bars are swelling degrees.

constants; the ionic groups acted as tightly bound ion pairs. Thus, incorporation of the ionic groups into the polymer chains did not affect the swelling degree. On the other hand, in the nonpolar

solvents with intermediate dielectric constants ($3 < \epsilon < 10$) except ethyl acetate, the polymer chains have good compatibility, and the more polar nature of the solvents promoted dissociation of the ion

pairs into free ions or loosely bound ion pairs, which significantly enhanced the swelling degree. The swelling degrees of **1G** (122 in THF and 128 in dichloromethane) were several times large than those of **OG** (25 and 23). Enhancement of the swelling degrees decreased gradually with decreasing media polarity, as shown in Fig. 3c, owing to the decrease in the number of dissociated ions. These results indicate that the swelling behaviour of the lipophilic polyelectrolyte gels is controlled primarily by the compatibility of the polymer chains with the media, and that incorporation of the dissociable ionic groups enhances the swelling abilities in more polar compatible solvents.

To clarify the role of dissociation of the ionic groups, we investigated the salt effect in swelling as shown in Fig. 3d. In the 1 mM solution of tetra(*n*-butyl)ammonium tetra(3,5-bis(trifluoromethyl))phenylborate (TFPB) in THF, the swelling degree of ionic **1G** decreased significantly from 12 to 18 compared with the mixture without TFPB. This latter value is similar to those of the neutral **OG** in THF in the presence (20) or absence (23) of the salt. A similar salt effect was also observed in chloroform. The salt effects of **1G** in these solvents were the same as those of ionic hydrogels in water³. As a result, the lipophilic polyelectrolyte gels swell and absorb nonpolar organic solvents using the same mechanism as that of the ionic hydrogels. Dissociation of the ionic groups on the polymer chains seems to play an important role in swelling even in nonpolar media. Next, we attempted to prepare super-absorbent polymers based on the lipophilic polyelectrolyte by reducing the crosslinking density as shown in Fig. 3b. Reducing the feed ratios of the crosslinker to the monomers from 1 mol% to 0.2 mol% enhanced the swelling abilities. In the case of **1G**, the swelling degrees in chloroform, THF and dichloromethane, increased to 296, 384 and 481, respectively. These values are much larger than those of **OG** prepared under the same conditions; the swelling degrees were 114, 61 and 69. Such high swelling degrees are well known in polyelectrolyte hydrogels in water but have never been achieved in nonpolar organic solvents. To the best of our knowledge, these are the highest swelling degrees in polymer gels that have ever been reported in these organic solvents.

Up to now, discussion about the swelling of polyelectrolyte gel has been restricted to aqueous solutions or mixtures with highly polar organic solvents ($\epsilon > 30$). Thus, the lipophilic polyelectrolyte gels described here represent a breakthrough. Our results indicate that super-absorbent polymers for desirable organic solvents could be prepared by appropriate selection of both the polymer chains that control the compatibility with the media and the ionic groups that are dissociable in them. At this stage, the swelling degrees of **1G** are not satisfactory in the extremely low-dielectric solvents ($\epsilon < 3$) such as toluene and hexane. However, more weakly coordinating anions²³ and more lipophilic polymer chains such as polystyrenes and polybutadienes should enable the design of oil super-absorbents. Polymer chains with perfluoroalkyl groups might provide super-absorbent polymers for chlorofluorocarbons and fluorocarbons. These would be key materials for the removal of hazardous leakages or spillages of VOCs. Moreover, lipophilic polyelectrolyte gels are expected to exhibit volume phase transitions towards stimulus-responsive actuators working in organic media^{24,25}. Finally, our results indicate that polyelectrolytes can expand or swell in a wide range of media including nonpolar organic solvents. Therefore, various unique properties of polyelectrolytes can be realized in a range of media as soft materials, such as low-friction surfaces lubricated by polyelectrolyte brushes²⁶, lipophilic layer-by-layer composites²⁷ and double-network gels with the high mechanical strength of common organic polymers²⁸.

METHODS

PREPARATION OF GELS

A typical protocol is as follows: 125 mg (0.1 mmol) of **1**, 617 mg (1.9 mmol) of ODA, 3.96 mg (0.02 mmol) of EGDMA, and 6.57 mg (0.04 mmol) of AIBN were placed in a capillary of 7.0 mm in diameter and dissolved in benzene adjusted to 1.0 ml. The solution was degassed and polymerized by heating at 60° for 24 h. The feed ratio was adjusted to **1**:ODA:EGDMA = 5:95:1. As a reference, **OGs** were prepared under the same copolymerization conditions (ODA:EGDMA = 100:1) without **1**. Gels with low crosslinking densities were prepared in a similar manner by reducing the feed ratios of EGDMA. The formed gels were washed by swelling in benzene for 10 h, then air-dried at room temperature. The sample was cut into cylinders of about 1.0 mm in length, and the cylinders were dried *in vacuo* at 40°.

MEASUREMENT OF SWELLING DEGREES

A sliced gel was placed in the following organic solvents with various polarities at room temperature²⁹: hexane ($\epsilon = 1.9$), carbon tetrachloride ($\epsilon = 2.2$), toluene ($\epsilon = 2.4$), chloroform ($\epsilon = 4.8$), chlorobenzene ($\epsilon = 5.6$), ethyl acetate ($\epsilon = 6.0$), THF ($\epsilon = 7.6$), dichloromethane ($\epsilon = 8.9$), 1-hexanol ($\epsilon = 13$), cyclohexanone ($\epsilon = 16$), acetone ($\epsilon = 21$), butyronitrile ($\epsilon = 25$), methanol ($\epsilon = 33$), acetonitrile ($\epsilon = 36$), DMF ($\epsilon = 37$) and DMSO ($\epsilon = 46$). After immersion for 2 days, we measured *Q* of the gels, which is defined by the following equation:

$$Q = (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}} \text{ (wt/wt)}$$

where W_{dry} and W_{wet} are the weights of the dried gel and the wet gel, respectively.

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Competing financial interests

The authors declare no competing financial interests.

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