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PAPER

Counter anion dependent swelling behaviour of poly(octadecyl acrylate)-based lipophilic polyelectrolyte gels as superabsorbent polymers for organic solvents†

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Molecular design of superabsorbent materials for organic solvents has attracted much attention due to their superior applications for the removal of hazardous leakages or spillages of volatile organic compounds (VOCs) and waste oils. One approach for preparing such soft matter is loosely crosslinked lipophilic polyelectrolytes. Here, we demonstrate the counter anion effect for superabsorbency for various organic solvents in a series of poly(octadecyl acrylate)-based lipophilic polyelectrolyte gels bearing tetraalkylammonium with relatively hydrophobic counter-anions: dodecyl sulfate (DS), tetrakis(3,5-bis(trifluoromethyl)phenyl) borate (TFPB) and (μ -(1*H*-imidazolato κ -N1: κ -N3) hexakis(pentafluorophenyl) borate) (IM). The benefit of high-swelling abilities due to dissociation of ionpairs was observed in less- and non-polar media ($3 < \epsilon < 13$), when TFPB and IM were selected as counter anions. These results indicate that molecular design of superabsorbent materials requires that the ionic groups have sufficient bulkiness and lipophilicity for ionic dissociation in nonpolar solvents.

Introduction

Superabsorbent polymers are prepared by loosely crosslinked polyelectrolytes and can retain a large amount of solvent within their three-dimensional polymer networks without dissolving. They are increasingly used for a variety of applications such as diapers, filters in cosmetics, separation media, drug delivery systems, biomedical devices, sensors, inks and display devices.^{1–4} Their high swelling abilities originate from the electrostatic repulsion among the ions fixed on the polymer chains and osmotic pressure between the interior and the exterior of the gel networks induced by freely mobile counter ions in the crosslinked polyelectrolytes.^{5,6} In less- or non-polar solvents ($\epsilon < 10$), however, the conventional polyelectrolyte gels such as cross-linked poly(acrylic acid sodium salt) and poly(allylamine hydrochloride) collapse or shrink due to strong aggregation of the ionic groups.^{7–11} Therefore, preparation of superabsorbent materials for volatile organic compounds (VOCs) including high-oil absorbents is rare, and exploration has been limited to non-ionic polymer gels that have relatively low swelling abilities.^{12–22}

In order to address these limitations, we have recently demonstrated a new class of polyelectrolyte gels as

superabsorbent materials. They exhibited high swelling abilities in a wide range of non-polar to polar organic solvents.^{23,24} Our design was simply based on incorporation of a small amount of tetraalkylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl) borate (TFPB) as dissociable ionic groups into poly(alkyl acrylate) and polystyrene gels, and we confirmed that they act as polyelectrolyte gels in these media. These results indicated that the superabsorbent materials for organic solvents could be achieved by appropriate selection of both the polymer chains that control compatibility to the media and the ionic groups that dissociate in them.

In the present study, we focused on the effect of ionic groups incorporated into the polyelectrolyte chains, and investigated the counter-ion effects on the swelling behaviours by introducing two new ionic acrylate monomers with different counter anions as shown in Fig. 1. Among the poly(alkyl acrylate)s, poly(octadecyl acrylate) was selected as the main polymer chain due to the high compatibility to less- or non-polar organic solvents. Dodecyl sulfate (DS) is known as an anionic surfactant consisting of a long alkyl chain attached to a sulfate group, providing amphiphilic properties and enhancing solubility in organic solvents. TFPB, which we had used in previous papers,^{23,24} is now widely recognized as an excellent example of weakly coordinating anions (WCAs)²⁵ and chemically more inert in nature, whose anionic center is tetrahedrally covered by four bulky aryl groups with many trifluoromethyl groups. (μ -(1*H*-Imidazolato κ -N1: κ -N3) hexakis(pentafluorophenyl) borate) (IM) is recently developed as a WCA obtained by the simple reaction of two equivalents of $B(C_6F_5)_3$ with

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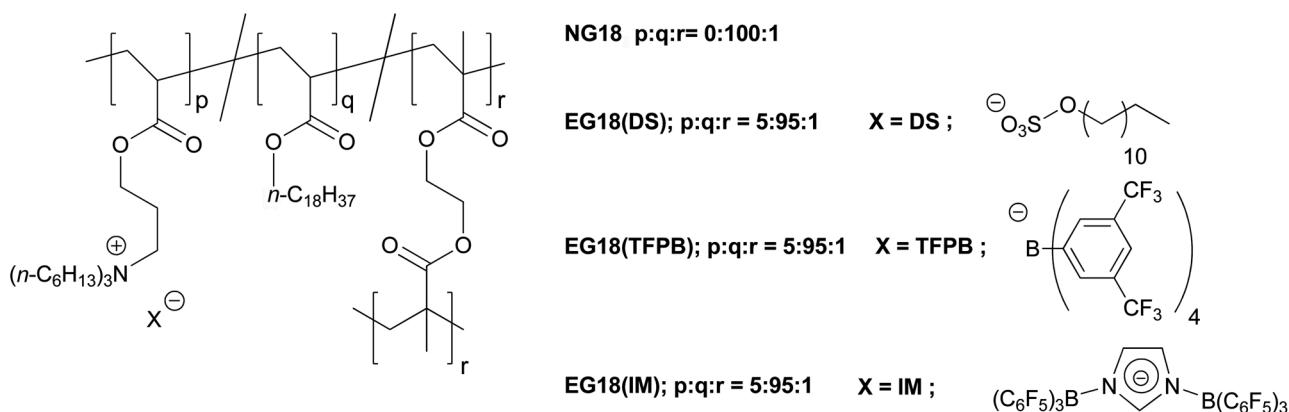


Fig. 1 Ionic gels (EG18(X)) and non-ionic gel (NG18).

a $C_3N_2H_3^-$ (imidazolate) and is expected to have higher dissociation ability due to the extraordinarily large size and widely delocalized negative charge by two borate fragments.²⁶ Here, we describe preparation of new poly(octadecyl acrylate)-based lipophilic polyelectrolyte gels with various counter anions, and compare their swelling behaviours in a wide variety of organic solvents from non-polar to polar, including hydrocarbons, halogenated hydrocarbons, aromatics, ethers, ketones, nitriles, alcohols, and so on, in order to understand the rational design for superabsorbent materials in those media.

Experimental

Materials and measurements

All solvents and chemicals are commercially available, and used without purification. Alkyl acrylates are purified through alumina. 1H NMR spectra were recorded on a Bruker Biospin 300 MHz NMR. MALDI-TOF spectra were recorded on a Perspective Voyager RP.

Monomer synthesis

Syntheses of (*N*-(3-acryloyloxy)propyl)-*N,N,N*-triethylammonium bromide (**E-Br**) and **E-TFPB** were carried out as previously reported.²⁴ Other two ionic acrylates monomers, **E-DS** and **E-IM**, were prepared by simple counter anion exchange from **E-Br** as described below.

Preparation of (*N*-(3-acryloyloxy)propyl)-*N,N,N*-triethylammonium dodecyl sulfate (**E-DS**)

Sodium dodecyl sulfate (348 mg, 1.21 mmol) and **E-Br** (531 mg, 1.15 mmol) were dissolved in methanol (6 mL). Water was added dropwise to the stirring solution, and a white solid gradually precipitated. The resulting precipitate was extracted with dichloromethane and evaporated to dryness to obtain **E-DS** as a viscous liquid (570 mg, 76%). 1H NMR (300 MHz, $CDCl_3$, TMS standard, rt) δ = 0.86–0.91 (m, 12H, $NCH_2CH_2CH_2CH_2CH_2CH_3$ and $SOCH_2CH_2(CH_2)_9CH_3$), δ = 1.24–1.34 (m, 36H, $NCH_2CH_2CH_2CH_2CH_2CH_3$ and $SOCH_2CH_2(CH_2)_9CH_3$), δ = 1.60–1.65 (br, 8H, $NCH_2CH_2CH_2CH_2CH_2CH_3$ and $SOCH_2CH_2(CH_2)_9CH_3$), δ = 2.17 (m, 2H, $NCH_2CH_2CH_2O$), δ = 3.29 (t, J = 8.1 Hz, 6H, $NCH_2CH_2CH_2CH_2CH_2CH_3$), δ = 3.45

(t, J = 7.8 Hz, 2H, $NCH_2CH_2CH_2O$), δ = 4.00 (m, 2H, $SOCH_2CH_2(CH_2)_9CH_3$), δ = 4.34 (t, J = 5.3 Hz, 2H, $NCH_2CH_2CH_2O$), δ = 5.88 (d, J = 10.2 Hz, 1H, alkene-*H*), δ = 6.10 (dd, J = 10.2, 17.3 Hz, 1H, alkene-*H*), δ = 6.43 (d, J = 17.3 Hz, 1H, alkene-*H*). Elemental analysis: calcd (%) $C_{36}H_{73}NO_6S$: C 66.72, H 11.35, N 2.16; found C 65.62, H 10.88, N 2.08.

Preparation of (*N*-(3-acryloyloxy)propyl)-*N,N,N*-triethylammonium (μ -(1*H*-imidazolato κ -N1: κ -N3) hexakis(pentafluorophenyl) borate) (**E-IM**)

Potassium (μ -(1*H*-imidazolato κ -N1: κ -N3) hexakis(pentafluorophenyl) borate)²⁶ (409 mg, 0.885 mol) and **E-Br** (1000 mg, 0.885 mmol) were dissolved in methanol (40 mL). Water was added dropwise to the stirring solution, and a white solid gradually precipitated. The solid was extracted with dichloromethane and evaporated to dryness and purified by flash column chromatography (SiO_2 , dichloromethane) to obtain **E-IM** as a white solid (780 mg, 60%). 1H NMR (300 MHz, $CDCl_3$, TMS standard, rt) δ = 0.86 (t, J = 5.9 Hz, 9H, $NCH_2CH_2CH_2CH_2CH_2CH_3$), δ = 1.29 (m, 18H, $NCH_2CH_2CH_2CH_2CH_2CH_3$), δ = 1.54 (m, 6H, $NCH_2CH_2CH_2CH_2CH_2CH_3$), δ = 2.02 (m, 2H, $NCH_2CH_2CH_2O$), δ = 3.08 (t, J = 8.4 Hz, 6H, $NCH_2CH_2CH_2CH_2CH_2CH_3$), δ = 3.22 (t, J = 8.3 Hz, 2H, $NCH_2CH_2CH_2O$), δ = 4.21 (t, J = 5.5 Hz, 2H, $NCH_2CH_2CH_2O$), δ = 5.92 (d, J = 10.5 Hz, 1H, alkene-*H*), δ = 6.06 (dd, J = 10.2, 15.4 Hz, 1H, alkene-*H*), δ = 6.43 (d, J = 17.1 Hz, 1H, alkene-*H*), δ = 6.76 (s, 2H, imidazole-*H*), δ = 7.47 (s, 1H, imidazole-*H*). Elemental analysis: calcd (%) for $C_{56}H_{60}BF_{24}NO_2$: C 51.35, H 3.49, N 2.85; found C 53.39, H 3.50, N 2.92.

Preparation of polymer gels

Gelation conditions are summarized in Table 1. A typical protocol is as follows: 125 mg (0.1 mmol) of **E-TFPB**, 617 mg (1.9 mmol) of octadecyl acrylate (ODA), 3.96 mg (0.02 mmol) of ethylene glycol dimethacrylate (EGDMA), and 6.57 mg (0.04 mmol) of azobis(isobutyronitrile) (AIBN) were placed in a glass tube of 7.0 mm diameter and dissolved in benzene to adjust to 1.0 mL. The solution was degassed and polymerized by heating at 70 °C for 24 hours. The feed ratio was adjusted to **E-X** : ODA : EGDMA = 5 : 95 : 1 and the obtained gels denoted as **EG18(X)**. As a reference, the octadecyl acrylate gel (**NG18**) was prepared under the same copolymerization conditions

Table 1 Gelation conditions

Sample	$E/\text{mol L}^{-1}$	ODA/ mol L^{-1}	EGDMA/ mol L^{-1}	AIBN/ mol L^{-1}
NG18		2.00	0.020	0.040
EG18(DS)	E-DS(0.10)	1.90	0.020	0.040
EG18(TFPB)	E-TFPB(0.10)	1.90	0.020	0.040
EG18(IM)	E-IM(0.10)	1.90	0.020	0.040

(ODA : EGDMA = 100 : 1) without E-X. The formed gels were washed by soaking in benzene for 10 hours, and air-dried at room temperature. The sample was cut into cylinders of length *ca.* 1.0 mm, and the cylinders were dried *in vacuo* at 40 °C.

Measurement of swelling degrees

A sliced gel was placed in the following typical organic solvents with various polarities at room temperature:²⁷ hexane (dielectric constant $\epsilon = 1.9$), toluene ($\epsilon = 2.4$), chloroform ($\epsilon = 4.8$), tetrahydropyran ($\epsilon = 5.6$), chlorobenzene ($\epsilon = 5.6$), ethyl acetate ($\epsilon = 6.0$), 1-chlorobutane ($\epsilon = 7.4$), tetrahydrofuran (THF) ($\epsilon = 7.6$), 2-octanol ($\epsilon = 8.2$), dichloromethane ($\epsilon = 8.9$), 1,2-dichloroethane ($\epsilon = 10.4$), 2-octanone ($\epsilon = 10.4$), 2-heptanone ($\epsilon = 12.0$), 4-methyl-2-heptanone ($\epsilon = 12.0$), cyclopentanone ($\epsilon = 13.6$), cyclohexanone ($\epsilon = 16.1$), 1-butanol ($\epsilon = 17.5$), 2-butanone ($\epsilon = 18.5$), acetone ($\epsilon = 20.6$), butyronitrile ($\epsilon = 24.8$), propionitrile ($\epsilon = 28.9$), *N*-methyl-2-pyrrolidinone (NMP) ($\epsilon = 32.2$), methanol ($\epsilon = 32.7$), acetonitrile ($\epsilon = 35.9$), *N,N*-dimethylformamide (DMF) ($\epsilon = 36.7$), and dimethylsulfoxide (DMSO) ($\epsilon = 46.5$). After immersion for 2 days, we measured the weights of the wet gels, and evaluated the swelling degrees (Q) of the gels defined by the following equation:

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

where W_{dry} and W_{wet} are weights of the dried gel and the wet gel, respectively. The Q indicates the weight ratio of the amount of the solvent entrapped in the gel over that of the dried gel.

Normalized swelling ratios were defined by the following equation: $Q' = Q/Q_0$, where Q_0 is the swelling degree of NG18 in each solvent. If Q' is approximate to 1 ($Q' \approx 1$), dissociation of the ionic groups is not enough to enhance the swelling degrees, and the swelling behaviours are attributed to good compatibility between the media and the polymer chains. However, if Q' is larger than one ($Q' \gg 1$), ionic dissociation plays a key role in enhancement of the swelling degrees due to the expansion of the polymer network (polyelectrolyte effect). On the other hand, if Q' is less than one ($Q' \ll 1$), dissociation of the ionic groups is completely suppressed and should lead to aggregation of ions and ion-pairs (ionomer effect).

Results and discussion

Swelling behaviour of lipophilic polyelectrolyte gels (EG18(X)) and non-ionic gel (NG18) in organic solvents

The swelling abilities of polyelectrolyte gels, EG18(DS), EG18(TFPB), and EG18(IM), and a non-ionic gel (NG18) as a non-ionic analogue in organic solvents with various polarities

from hexane ($\epsilon = 1.9$) to DMSO ($\epsilon = 46.5$) were investigated. The swelling degrees are summarized in Table S1 in the ESI†. As described in the previous report, compatibility of the poly(octadecyl acrylate) polymer chains plays the primary role in swelling behaviour.²⁴ The strong association of the octadecyl groups largely suppresses the swelling degrees in the polar organic solvents. Thus, some of the swelling degrees, in particular in less- and non-polar solvents, are shown in Fig. 2. In extremely non-polar solvents ($\epsilon < 3$) such as hexane ($\epsilon = 1.9$) and toluene ($\epsilon = 2.4$), the swelling degrees (Q) of polyelectrolyte gels (EG18(X)) and the non-ionic gel (NG18) were moderate regardless of the kinds of counter-anions. For example, the swelling degrees of NG18, EG18(DS), EG18(TFPB) and EG18(IM) were 11, 11, 12, and 16 in hexane and 25, 19, 24, and 31 in toluene. In these solvents, dissociation of the ionic groups was completely suppressed owing to low polarity, and they would act as tightly bound ion pairs or highly aggregated species. As a result, incorporation of ionic groups did not affect the swelling behaviours, and the swelling degrees were attributed mainly to compatibility between the media and the poly(octadecyl acrylate) polymer chains. On the other hand, EG18(TFPB) and EG18(IM) swelled and absorbed large amounts of the organic solvents with dielectric constants ranging from three to ten ($3 < \epsilon < 10$) except ethyl acetate and 2-octanol. The swelling degrees of EG18(TFPB) and EG18(IM) were 99 and 122 in chloroform, 93 and 79 in tetrahydropyran, 70 and 109 in chlorobenzene, 89 and 104 in 1-chlorobutane, 121 and 119 in tetrahydrofuran, 128 and 224 in dichloromethane and 157 and 181 in 1,2-dichloroethane. These high swelling degrees were caused by dissociation of the ion-pairs into free ions or loosely bound ion-pairs, which significantly expanded the polymer network. In more polar organic solvents ($10 < \epsilon < 13$), EG18(IM) had the moderate swelling degrees in 2-octanone ($Q = 29$) and 2-heptanone ($Q = 29$), but the other gels collapsed or shrank in these media. Moreover, more polar solvents ($\epsilon > 13$), all

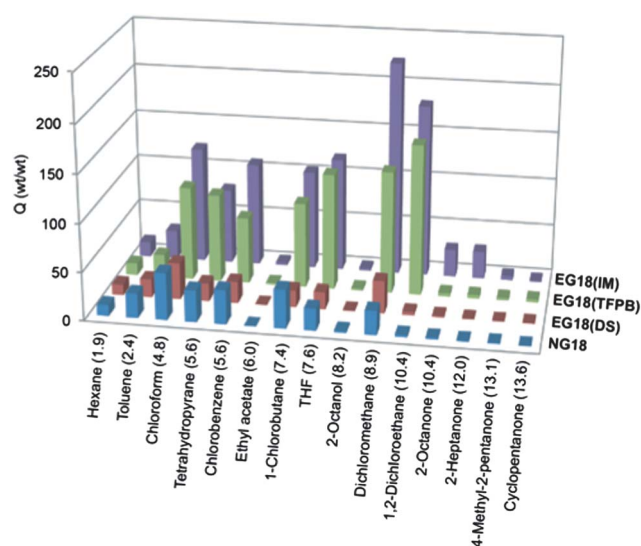


Fig. 2 Swelling behaviours of NG18, EG18(DS), EG18(TFPB), and EG18(IM) in various organic solvents that possess different dielectric constants, increasing from left to right. Dielectric constants of these solvents are shown in the parentheses.

polyelectrolyte gels (**EG18(X)**) and the non-ionic gel (**NG18**) collapsed and had low swelling degrees. For example, the swelling degrees of **NG18**, **EG18(DS)**, **EG18(TFPB)**, and **EG18(IM)** were 0.6, 0.4, 1, and 2 in 1-butanol, 1.2, 0.7, 2, and 2 in acetone, 0.4, 0.7, 2, and 2 in butyronitrile, 0.1, 0.9, 0.3, and 1 in methanol, 0.3, 0.7, 0.7, and 1 in DMSO and 0.8, 0.8, 3, and 1 in DMF. The poly(octadecyl acrylate) polymer chains were completely incompatible with them and the swelling degrees were suppressed low, even though the ion-pairs in the polyelectrolyte gels could dissociate.²⁴ Finally, in ethyl acetate and 2-octanol, both **EG18(X)** and **NG18** collapsed owing to a mechanism similar to that in the polar solvents.

Counter anion dependent swelling behaviour of **EG18(X)**

In order to evaluate the counter anion effects on the swelling behaviours of **EG18(X)**, we calculated normalized swelling ratios (Q'). Fig. 3 shows Q' of **EG18(X)** in less- and non-polar media ($\epsilon < 13$). In the case of **EG18(DS)**, Q' values were constant around 1 regardless of the change in all the solvents, for example, hexane ($Q' = 1.0$), toluene ($Q' = 0.7$), chloroform ($Q' = 0.8$), THF ($Q' = 0.8$), dichloromethane ($Q' = 1.3$) and 1,2-dichloroethane ($Q' = 1.4$). This result indicated that DS was difficult to dissociate in these media and the obtained gel behaved as non-ionic gels. On the other hand, in the case of **EG18(TFPB)** and **EG18(IM)**, the Q' values depended primarily on solvent polarity. Starting from non-polar ones, in extremely non-polar solvents ($\epsilon < 3$) such as hexane and toluene, the Q' values of **EG18(TFPB)** (1.1 in hexane and 0.9 in toluene) and **EG18(IM)** (1.4 in hexane and 1.2 in toluene) were similar to **EG18(DS)**. Therefore, the counter anion effect in these media ($\epsilon < 3$) could be $DS \approx TFPB \approx IM$. On the other hand, in non-polar solvents with dielectric constants ranging from three to ten ($3 < \epsilon < 10$), they increased with increasing the solvent polarity: 2.0 in chloroform, 2.8 in tetrahydropyrene, 5.3 in THF, 5.1 in dichloromethane and 64 in 1,2-dichloroethane for **EG18(TFPB)**,

and 2.5 in chloroform, 2.4 in tetrahydropyrene, 5.2 in THF, 8.9 in dichloromethane and 74 in 1,2-dichloroethane for **EG18(IM)**. This result strongly suggested that dissociation of the ion-pairs contributed to swelling behaviours, and the degree of dissociation increased with increasing the dielectric constant of the solvents. The counter anion effect on the swelling ability in the media ($3 < \epsilon < 10$) could be $DS \ll TFPB \approx IM$. On the other hand, for more polar solvents with the dielectric constant ranging from ten to thirteen ($10 < \epsilon < 13$), the Q' value of **EG18(IM)** was much higher than **EG18(TFPB)**, for example, 1.9 in 2-octanone and 2.9 in 2-heptanone for **EG18(TFPB)** and 16.5 in 2-octanone and 24.6 in 2-heptanone for **EG18(IM)**. The counter anion effect in these media ($10 < \epsilon < 13$) could be expressed as $DS \approx TFPB \ll IM$.

Effect of solvent polarity on swelling behaviours

With respect to solvent polarity, the swelling behaviours of these ionic gels could be divided roughly into three types. Firstly, in extremely non-polar solvents whose dielectric constants were less than three ($\epsilon < 3$), no counter-anion specificity was observed; $DS \approx TFPB \approx IM$. The swelling degrees of all the polyelectrolyte gels (**EG18(X)**) were similar to the non-ionic gel (**NG18**), even though strong aggregation of ions and ion-pairs formation could occur²⁸ and induce gel deswelling (ionomer effect). This was because of their low contents (5 mol %) and ion-pairs hindered spatially by surrounding long alkyl chains to avoid further aggregation of the ionic groups among the polymer chains. In these media, compatibility of the polymer chains governed their swelling ability. Secondly, in non-polar solvents whose dielectric constants ranged from three to ten ($3 < \epsilon < 10$), the counter-anion specificity was observed; $DS \ll TFPB \approx IM$. In these media, the swelling degrees of **EG18(TFPB)** and **EG18(IM)** were much higher than those of **EG18(DS)** and non-ionic **NG18**. This indicated that TFPB and IM acted as dissociated counter anions compared to DS. The dissociation degrees were closely related to the molecular structure of ion-pairs, because increase of the bulkiness around counter anions reduced Coulomb interactions between the oppositely charged ions and promoted dissociation of ion-pairs.²⁵ Moreover, the negative charges in TFPB and IM anions were delocalized to phenyl rings, and their sizes were relatively large due to bulky phenyl groups surrounding the anion center. By contrast, the negative charge of DS was localized on the sulfate group and the anion size was much smaller. This difference led to the counter-anion effect on swelling of these polyelectrolyte gels. Third, in more polar solvents with dielectric constants ranging from ten to thirteen ($10 < \epsilon < 13$), the counter-anion effect was observed; $DS \approx TFPB \ll IM$. In these media, enhancement of gel swelling was observed only for **EG18(IM)**. The swelling degrees of **EG18(TFPB)** and **EG18(DS)** were low and similar to the non-ionic gel (**NG18**) ($Q < 3$). In these solvents, the poly(octadecyl acrylate) polymer chains were completely incompatible and the swelling degrees were largely suppressed, even though they have enough high polarity to dissociate the ion-pairs in the polyelectrolyte gels. Only **EG18(IM)** could overcome the attractive force among the polymer chains in the media because of the large size which enhances ionic dissociation of IM.

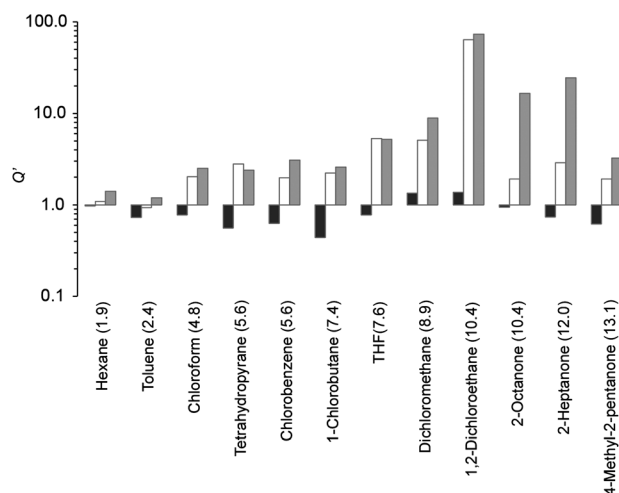


Fig. 3 Normalized swelling degrees ($Q' = Q/Q_0$, Q_0 is the swelling degree of **NG18**) of **EG18(DS)** (black bars), **EG18(TFPB)** (open bars), and **EG18(IM)** (gray bars) in various organic solvents that possess different dielectric constants, increasing from left to right. Dielectric constants of these solvents are shown in the parentheses.

Conclusions

In conclusion, we demonstrated preparation of poly(octadecyl acrylate)-based lipophilic polyelectrolyte gels with three counter anions (DS, TFPB and IM) to investigate the counter anion effect on the swelling ability of the polyelectrolyte gels. It was shown that the benefit of the high swelling ability due to incorporation of the ion-pair was observed when TFPB and IM were selected as counter anions in less- and non-polar media ($3 < \epsilon < 13$). More hydrophilic counter anions such as halides, sulfonates, phosphates, and carboxylates should be similar to DS, due to exposure of polarized charges to cause the formation of ion-pairs and their aggregates. Therefore, our results indicated that designing superabsorbent polymers for organic solvents requires appropriate ionic groups that have both good solubility and high dissociation ability to the media. Exploration for crosslinked polymer networks based on non-polar polymer chains and ionic groups is under current investigation to understand rational design for superabsorbent materials for organic solvents.

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Notes and references

- 1 T. Tanaka, *Sci. Am.*, 1981, **244**, 124–138.
- 2 Y. Osada and S. B. Ross-Murphy, *Sci. Am.*, 1993, **268**, 82–87.

- 3 F. L. Buchholz and A. T. Graham, *Modern Superabsorbent Polymer Technology*, Wiley-VCH, New York 1998.
- 4 T. Okano, *Biorelated Polymers and Gels: Controlled Release and Applications in Biomedical Engineering*, Academic Press, Boston 1998.
- 5 I. Ohmine and T. Tanaka, *J. Chem. Phys.*, 1982, **77**, 5725–5729.
- 6 P. J. Flory and J. Rehner, Jr, *J. Chem. Phys.*, 1943, **11**, 521–526.
- 7 A. R. Khokhlov and E. Y. Kramarenko, *Macromol. Theory Simul.*, 1994, **3**, 45–59.
- 8 S. G. Starodoubtsev, A. R. Khokhlov, E. L. Sokolov and B. Chu, *Macromolecules*, 1995, **28**, 3930–3936.
- 9 D. Kawaguchi and M. Satoh, *Macromolecules*, 1999, **32**, 7828–7835.
- 10 Y. Nishiyama and M. Satoh, *J. Polym. Sci., Part B: Polym. Phys.*, 2000, **38**, 2791–2800.
- 11 N. Yasumoto, Y. Hata and M. Satoh, *Polym. Int.*, 2004, **53**, 766–771.
- 12 Z. Hrnjak-Murčić, J. Jelenčić and M. Bravar, *Angew. Makromol. Chem.*, 1996, **242**, 85–96.
- 13 O. Okay, S. Durmaz and B. Erman, *Macromolecules*, 2000, **33**, 4822–4827.
- 14 M. H. Zhou and W. J. Cho, *Polym. Int.*, 2001, **50**, 1193–1200.
- 15 M. H. Zhou and W. J. Cho, *J. Appl. Polym. Sci.*, 2002, **85**, 2119–2129.
- 16 M. H. Zhou and W. J. Cho, *J. Appl. Polym. Sci.*, 2003, **89**, 1818–1824.
- 17 A. M. Atta, R. A. El-Ghazawy, R. K. Farag, A. F. El-Kafrawy and A. A. Abdel-Azim, *Polym. Int.*, 2005, **54**, 1088–1096.
- 18 A. M. Atta and K. F. Arndt, *J. Appl. Polym. Sci.*, 2005, **97**, 80–91.
- 19 A. M. Atta, S. H. El-Hamouly, A. M. Al Sabagh and M. M. Gabr, *J. Appl. Polym. Sci.*, 2007, **105**, 2113–2120.
- 20 A. M. Atta, S. H. El-Hamouly, A. M. Al Sabagh and M. M. Gabr, *J. Appl. Polym. Sci.*, 2007, **104**, 871–881.
- 21 J. Jang and B. S. Kim, *J. Appl. Polym. Sci.*, 2000, **77**, 903–913.
- 22 J. Jang and B. S. Kim, *J. Appl. Polym. Sci.*, 2000, **77**, 914–920.
- 23 T. Ono, T. Sugimoto, S. Shinkai and K. Sada, *Nat. Mater.*, 2007, **6**, 429–433.
- 24 T. Ono, T. Sugimoto, S. Shinkai and K. Sada, *Adv. Funct. Mater.*, 2008, **18**, 3936–3940.
- 25 I. Krossing and I. Raabe, *Angew. Chem., Int. Ed.*, 2004, **43**, 2066–2090.
- 26 R. E. LaPointe, G. R. Roof, K. A. Abboud and J. Klosin, *J. Am. Chem. Soc.*, 2000, **122**, 9560–9561.
- 27 J. A. Riddick, W. B. Bunger and T. K. Sakano, *Organic Solvents*, Wiley-VCH, New York, 4th edn, 1986.
- 28 B. Endeward, P. Brant, R. D. Nielsen, M. Bernardo, K. Zick and H. Thomann, *J. Phys. Chem. C*, 2008, **112**, 7818–7828.