

New Lipophilic Polyelectrolyte Gels Containing Quaternary Ammonium Salt with Superabsorbent Capacity for Organic Solvents

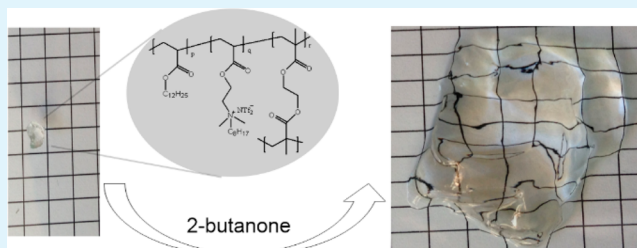
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Supporting Information

ABSTRACT: Water and soil pollution by organic pollutants from petrochemical plants has become one of the major environmental problems in recent years. Lipophilic polyelectrolyte gels with ionic groups dissociable in nonpolar organic solvents show an enhanced swelling ability in a corresponding media attributed to the electrostatic repulsion and osmotic pressure provided by dissociated ionic groups. Here, we synthesized new lipophilic polyelectrolyte gels based on an easily available electrolyte monomer, methacryloxyethyl dimethyloctane ammonium trifluoromethanesulfonimide (MODAT), and a lipophilic neutral monomer, dodecyl acrylate by radiation-induced polymerization and cross-linking. The resultant lipophilic polyelectrolyte gels could absorb plenty of organic solvents with dielectric constants lower than 20 and exhibited a high absorbing ability at a wide range of temperatures (0–40 °C). The maximum swelling degree could reach as high as 200 g/g in some media, such as 1,2-dichloroethane (199.4 g/g) and dichloromethane (204 g/g), which was much higher than that of the nonionic gel without the addition of MODAT. Moreover, the resultant lipophilic polyelectrolyte gels could release most of the absorbed solvents within several hours and then be reused. It is expected that this new type of lipophilic polyelectrolyte gels may be a suitable candidate as organic pollutant absorbents.

KEYWORDS: lipophilic polyelectrolyte gels, radiation-induced polymerization and cross-linking, organic solvents, absorbing ability, swelling, solvent retention



1. INTRODUCTION

Organic pollutant leakage from petrochemical plants or during the transportation and storage has become one of the major environmental problems in recent years. These pollutants will bring adverse impacts to ecosystems and long-term effects of environmental pollution. The RCA (Radio Company of America) pollution incident in 2010 is a typical example of organic solvent pollution with catastrophic impacts on the underground water and the soil. Various methods for solving such contaminations have been reported, such as in situ burning, natural degradation and collection of the organic solvents from water by absorbing materials.^{1–3} Among them, the use of absorbents to collect organic pollutants is one of the most promising techniques. Researchers have developed a great number of absorbent materials, e.g., natural clays, activated carbon, carbon or silicon aerogel, resin, lipophilic gel.^{4–10} Compared with the other materials, lipophilic gel has obvious advantages due to its low cost, easy preparation, reusability and selectivity. However, the absorption capacity of lipophilic gel was not very high until the lipophilic polyelectrolyte gel was developed in 2007 by Ono and his co-workers.¹¹

Polyelectrolyte gels have been widely used as superabsorbent materials due to their superior swelling ability, which originates from the electrostatic repulsion among the ions fixed on the

polymer chains and osmotic pressure between the interior and exterior of the gels.^{12,13} However, they would collapse or shrink in most organic solvents because of the aggregation of the ions, which limited their applications in oil absorption.^{14,15} To overcome this problem, Ono and his co-workers first synthesized a novel class of polyelectrolyte gels bearing tetraalkylammonium tetraphenylborate as a lipophilic and bulky ionic group. Their lipophilic polyelectrolyte gel showed a high absorbing ability in different organic solvents, such as dichloromethane, tetrahydrofuran (THF) and chloroform.^{11,16} The lipophilicity and dissociation abilities in a nonpolar solvent of lipophilic electrolyte are responsible for the high swelling ability. Later, more similar lipophilic polyelectrolyte gels bearing tetraalkylammonium with different hydrophobic counteranions, such as dodecyl sulfate, (μ -(1*H*-imidazolato κ -N1: κ -N3) hexakis (pentafluorophenyl borate)¹⁷ and “albate”,¹⁸ were developed by researchers. However, these lipophilic anions used in the polyelectrolyte gels are either very expensive or difficult to synthesize. Recently, an easily prepared ionic liquid, 3-*n*-dodecyl-1-vinylimidazolium tetra-

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fluoroborate ($[\text{C}_{12}\text{vim}][\text{BF}_4]$), was used as the lipophilic electrolyte to copolymerize with dodecyl methacrylate, but the absorbing ability of the obtained polyelectrolyte gel was not high enough. The highest swelling degree was only 50 g/g.¹⁹ In addition, the absorbing range of the organic solvents is relatively narrow; only these solvents with dielectric constants lower than 10 could be absorbed.^{11,18,19} Therefore, it is still important to find more lipophilic electrolytes that are easily available and cost-effective, and then to develop new lipophilic polyelectrolyte gels with a high absorbing ability in a wider range of organic solvents.

Moreover, all these lipophilic polyelectrolyte gels were synthesized by chemical induced polymerization and cross-linking. The synthesis processes were relatively complicated and energy-consuming, which is not conducive to large-scale industrial production. It has been widely known that γ -ray radiation can initiate polymerization and cross-linking in a wide range of polymers and copolymers without additives during the polymerization process.²⁰ The radiation technique is becoming more and more attractive as it is a rapid, scalable, energy-efficient (can be conducted at ambient temperature) and clean method. A large amount of hydrogels have been fabricated by γ -ray radiation in a water system.^{21–24} Nevertheless, no attempt has been reported to fabricate a lipophilic polyelectrolyte gel in an organic system by using this technique.

In this study, we attempted to synthesize new lipophilic polyelectrolyte gels with a high absorbing ability in a wide range of organic solvents by radiation-induced polymerization and cross-linking. A hydrophobic anion, trifluoromethanesulfonimide anion (NTf_2^-), which is easily available and highly thermal stable,²⁵ was selected to synthesize the lipophilic electrolyte. In our previous work,²⁶ we synthesized an amphiphilic monomer, methacryloxyethyl dimethyloctane ammonium bromide (MODAB), by quaternization of dimethylaminoethyl methacrylate (DMAEMA) with 1-bromooctane, and then prepared amphiphilic gels by radiation technique. Here, NTf_2^- was incorporated to replace bromide anion by anion exchanging reaction with lithium bis-(trifluoromethanesulfonyl)imide (LiNTf_2). The obtained lipophilic monomer, methacryloxyethyl dimethyloctane ammonium trifluoromethanesulfonimide (MODAT), was then copolymerized with dodecyl acrylate and cross-linked in chloroform under γ -radiation. The synthesized lipophilic polyelectrolyte gels showed a high swelling ability in a much wider range of organic solvents, especially those with dielectric constants (ϵ) between 4 and 20. The highest swelling degree reached 204 g/g in dichloromethane. We believe that the resultant lipophilic polyelectrolyte gels will have applications as barriers for spilled organic compounds or as absorbents for organic pollutants.

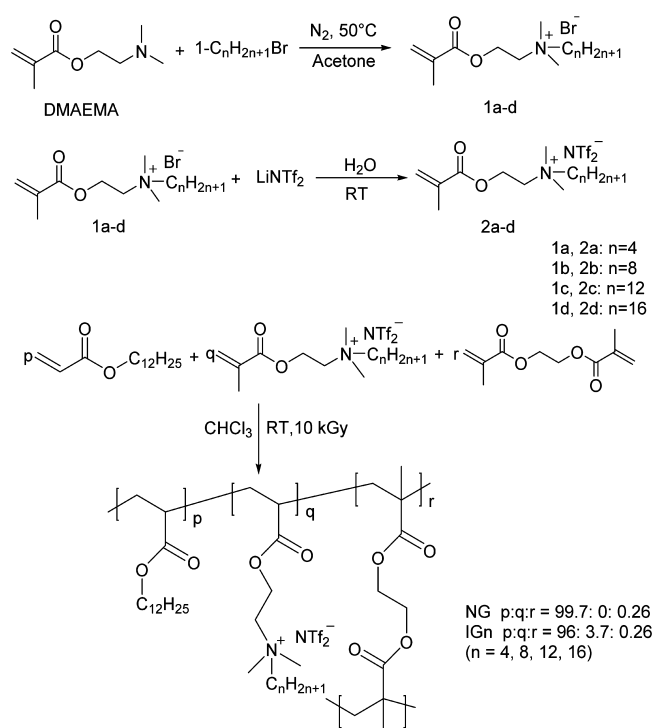
2. EXPERIMENTAL SECTION

Materials. DMAEMA (99%), LiNTf_2 (98%), ethylene glycol dimethacrylate (EGDMA, 98%) and dodecyl acrylate (DDA, 99%) were obtained from J&K and used without further purification. 1-Bromobutane (BB, 98%), 1-bromooctane (BO, 99%), 1-bromododecane (BD, 98%) and 1-bromohexadecane (BH, 98%) were provided by Acros and used as supplied. Other chemicals were analytic-grade reagents obtained from Beijing Chemicals Company and used as received.

Synthesis and Characterization of New Lipophilic Electrolyte Monomers. Four amphiphilic quaternary ammonium salts, methacryloxyethyl dimethylbutane ammonium bromide (MBDAB, 1a), methacryloxyethyl dimethyloctane ammonium bromide

(MODAB, 1b), methacryloxyethyl dimethyldodecane ammonium bromide (MDDAB, 1c) and methacryloxyethyl dimethylhexadecane ammonium bromide (MHDAB, 1d), were first synthesized by modifying dimethylaminoethyl methacrylate with different 1-bromoalkanes ($1\text{-C}_n\text{H}_{2n+1}\text{Br}$, $n = 4, 8, 12, 16$), respectively.²⁶ Then, anion exchange reaction with LiNTf_2 was carried out in water to obtain four new lipophilic monomers, methacryloxyethyl dimethylbutane ammonium trifluoromethanesulfonimide (MBDAT, 2a), methacryloxyethyl dimethyloctane ammonium trifluoromethanesulfonimide (MODAT, 2b), methacryloxyethyl dimethyldodecane ammonium trifluoromethanesulfonimide (MDDAT, 2c) and methacryloxyethyl dimethylhexadecane ammonium trifluoromethanesulfonimide (MHDAT, 2d). The synthesis process is shown in Scheme 1.

Scheme 1. Synthesis Route of the Lipophilic Electrolyte Monomers, Lipophilic Polyelectrolyte Gels and NG



¹H NMR and high resolution electrospray ionization (HR-ESI) were used to characterize the resultant monomers. ¹H NMR spectra were recorded on Bruker AV-400 MHz nuclear magnetic resonance spectrometer apparatus with trichloromethane-*d* (CDCl_3) as the solvent. HR-ESI spectra were recorded on a Bruker APEX IV Fourier transform ion cyclotron resonance (FTIR) mass spectrometer apparatus with chloroform as the solvent.

In a typical example, a mixture of DMAEMA (51 mL, 0.3 mol) and 1-bromooctane (70 mL, 0.4 mol) were stirred at 50 °C for 6 h under N_2 atmosphere. The product was precipitated by adding an excess amount of diethyl ether. Then, the product was filtered and MODAB was obtained as a white powder. ¹H NMR (Figure S1, Supporting Information, 400 MHz, CDCl_3 , TMS standard, r.t.): $\delta = 0.99$ (t, $J = 6.8$ Hz, 3H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.30 (m, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.96 (s, 3H, $\text{CH}_2\text{C}(\text{CH}_3)\text{CO}_2$), 3.53 (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.62 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 4.19 (dd, $J = 5.9, 3.7$ Hz, 2H, $\text{NCH}_2\text{CH}_2\text{O}$), 4.66 (m, 2H, $\text{NCH}_2\text{CH}_2\text{O}$), 5.69 (m, 1H, alkeneH), 6.15 (s, 1H, alkeneH).

MODAB (1.75 g, 5 mmol) and LiNTf_2 (1.45 g, 5 mmol) were then dissolved in 20 mL of deionized water, respectively. $\text{LiNTf}_2(\text{aq})$ was added dropwise into MODAB(aq) over a period of 5 min under stirring conditions. The mixture was further stirred for 24 h at room temperature. The crude product was poured into a separatory funnel

Table 1. Feed Ratios and Swelling Degrees in Solvents with Different Dielectric Constants of the Resultant Gels

sample	electrolytes content (mol %)	EGDMA concentration (mol/L)	Q (g/g)			
			toluene ($\epsilon = 2.4$)	THF ($\epsilon = 7.6$)	1,2-dichloroethane ($\epsilon = 10.3$)	2-butanone ($\epsilon = 18.5$)
NG	0.0	0.005	37.1	46.5	6.3	4.7
IG4	3.7	0.005	42.4	59.4	80.0	22.7
IG8 ₁	3.7	0.005	37.6	107.5	199.4	121.2
IG8 ₁ -Br	3.7	0.005	20.3	17.5	40.0	63.1
IG8 ₂	3.7	0.010	32.0	40.1	87.8	80.2
IG8 ₃	2.7	0.005	44.0	56.7	169.5	90.6
IG8 ₄	5.2	0.005	37.1	76.3	164.0	80.3
IG12	3.7	0.005	33.0	65.3	138.7	75.3
IG16	3.7	0.005	35.1	59.3	135.3	69.3

and the aqueous layer was removed. The obtained viscous liquid was washed 5–10 times with deionized water until no bromide ion was detected by AgNO₃. After removal of water in vacuo, MODAT was obtained as a colorless and viscous liquid. ¹H NMR (Figure S2, Supporting Information, 400 MHz, CDCl₃, TMS standard, r.t.): δ = 0.88 (t, J = 6.7 Hz, 3H, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.29 (m, 12H, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.93 (s, 3H, CH₂C(CH₃)CO₂), 3.16 (s, 6H, N(CH₃)₂), 3.33 (m, 2H, NCH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 3.71 (dd, J = 5.4, 3.2 Hz, 2H, NCH₂CH₂O), 4.56 (s, 2H, NCH₂CH₂O), 5.68 (s, 1H, alkeneH), 6.11 (s, 1H, alkeneH). ESI-MS (Figure S3, Supporting Information): calcd for C₁₆H₃₂NO₂⁺ 270.242 76, found 270.242 76; calcd for C₂F₆NO₄S₂⁻ 279.91 784, found 279.916 74.

Synthesis of the Lipophilic Polyelectrolyte Gels Containing Quaternary Ammonium Salt. A typical protocol for synthesizing the lipophilic polyelectrolyte gels containing quaternary ammonium salt is as follows: 38.5 mg (0.07 mmol) of MODAT, 441.5 mg (1.8 mmol) of DDA and 1.0 mg (0.005 mmol) of EGDMA were placed in a glass tube of 10 mm diameter and dissolved in CHCl₃ to adjust 1.0 mL. The mixture was bubbled with nitrogen for 10 min. Finally, the tube was sealed and irradiated to form the gel with 10 kGy dose at a dose rate of 50 Gy min⁻¹ at room temperature. For comparison, dodecyl acrylate gels (NG) were prepared under the same gelation condition only without the addition of MODAT. A series of gels were prepared by changing the structure and ratio of monomers as well as cross-linking agent concentrations. The obtained transparent gels were washed by swelling in CHCl₃ for 24 h and then dried at room temperature for 1 day, in a vacuum at 40 °C for another 1 day to remove the residual solvents.

Characterization of the Resultant Gels. Micro-FTIR and thermogravimetric analysis (TGA) were used to characterize the composition and thermal stability of the resultant gels. Micro-FTIR analysis was performed using a Nicolet (Magna-IR 750) spectrometer in the range of 4000–600 cm⁻¹. TGA was carried out using a TA Q600 thermal analyzer under a nitrogen atmosphere, over a temperature range of 25–600 °C with a heating rate of 5 °C/min. Elemental analysis (EA) was performed by Elementar Vario MICRO (Germany) in order to determine the component of the resultant lipophilic polyelectrolyte gels after removing the sol part.

Gel Fraction. Sol part of the resultant gels was extracted by chloroform. Then the gels were dried at room temperature for 1 day and then dried in a vacuum oven at 40 °C to constant weight. The gel fraction is defined as

$$\text{gel (\%)} = \frac{W_g}{W_o} \times 100 \quad (1)$$

where W_o and W_g were the weights of the dried gel before and after removing sol, respectively.

Swelling Properties of the Resultant Gels. Swelling kinetics was studied by weighing the resultant gels swelled in different solvents as a function of time. The dried gel was cut into small pieces (about 10 mg). The sliced gel was placed in 20 mL of organic solvents with different polarities at room temperature. After a certain interval of

time, the swollen gel was taken out and weighed. The swelling degree (Q) was calculated by the following formula:

$$Q \text{ (g/g)} = \frac{W_s - W_d}{W_d} \quad (2)$$

where W_d and W_s are weights of the dried gel piece and the swollen gel after immersion in solvent for a certain time, respectively.

The absorbing ability of the resultant gels was studied by swelling the gels in different organic solvents for 2 days. Although less time is sufficient to reach the maximum swelling degree for most solvents at room temperature, we used a standard time of 2 days to get reliable and comparable values for larger pieces of gels.

Effect of temperature on the swelling degree was investigated by immersing the dried gels (about 10 mg) in 20 mL of organic solvents at different temperatures (0, 10, 20, 30, 40 °C) for 2 days.

Solvent Retention of the Resultant Gels. Solvent retention was studied by weighing the fully swelled gel placed in air at room temperature as a function of time.¹⁰ Solvent retention (%) was calculated by the following equation:

$$\text{solvent retention (\%)} = \frac{Q_t}{Q_0} \times 100 \quad (3)$$

where Q_t is the swelling degree of the swollen gel placed in air at different times (t) and Q_0 is the initial swelling degree of the gel.

3. RESULTS AND DISCUSSION

Synthesis of the Lipophilic Polyelectrolyte Gels Containing Quaternary Ammonium Salt. As shown in Scheme 1, the amphiphilic quaternary ammonium salts, MBDAB, MODAB, MDDAB, MHDAB (1a–d), were prepared by quaternization of DMAEMA with BB, BO, BD and BH, respectively. 1a–d were then reacted with LiNTf₂ to yield four new lipophilic electrolyte monomers, MBDAT, MODAT, MDDAT and MHDAT (2a–d). The lipophilic polyelectrolyte gels containing quaternary ammonium salt (IG) were synthesized by irradiating a lipophilic neutral monomer (DDA), lipophilic electrolyte monomer (2a–d) and cross-linker (EGDMA) in a chloroform solvent with an absorbed dose of 10 kGy at a dose rate of 50 Gy min⁻¹ at room temperature. Feed ratios are listed in Table 1. IG_{*n*} ($n = 4, 8, 12, 16$) represents the gels containing lipophilic electrolyte monomers of 2a, 2b, 2c, 2d, respectively, and m ($m = 1, 2, 3, 4$) is the number of IG_{*n*} with various feed ratios. IG8₁-Br is the gel based on MODAB (1b) and DDA, which have the same feed ratios and preparation conditions as IG8₁. For comparison, the nonionic gel (NG) was prepared by DDA and EGDMA in the absence of lipophilic electrolyte monomer. The gel fractions of all the gels were around 35% in this radiation condition (for example, IG8₁, 35.0%; IG8₂, 37.6%; IG8₁-Br, 35.5%; IG16,

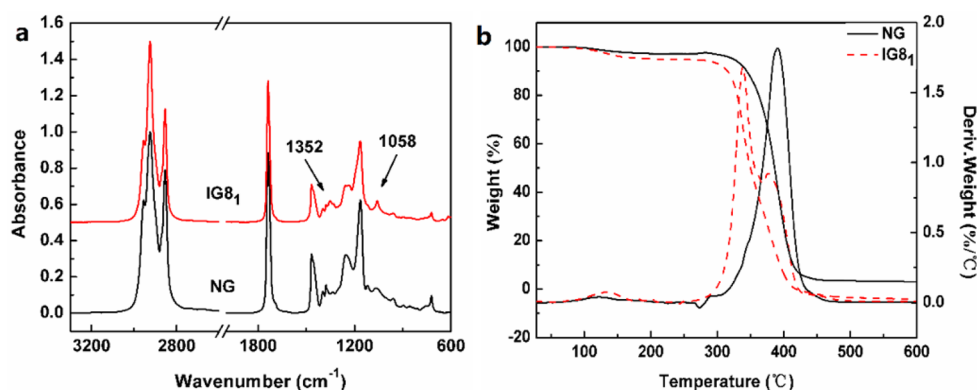


Figure 1. (a) FTIR spectra of IG8₁ and NG; (b) TGA curves of IG8₁ and NG.

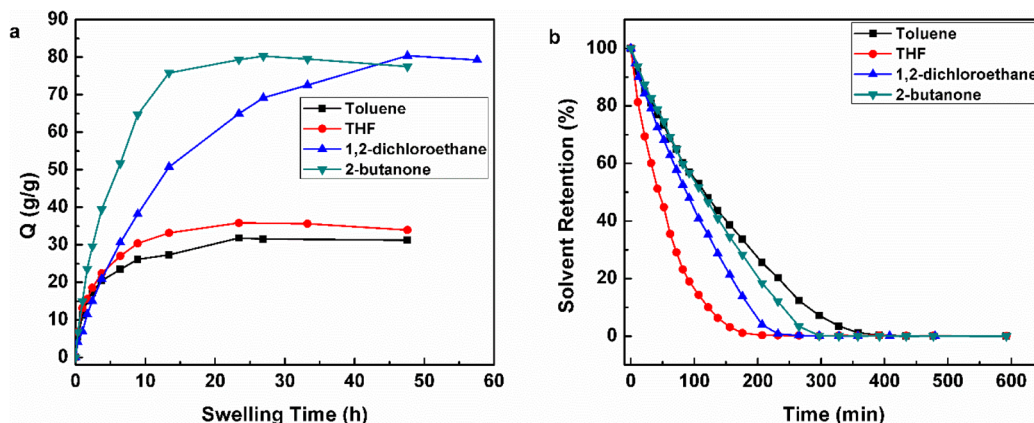


Figure 2. (a) Swelling degree of IG8₂ in toluene, THF, 1,2-dichloroethane and 2-butanone at different swelling times; (b) solvent retention in air at 25 °C for IG8₂ fully swelled in toluene, THF, 1,2-dichloroethane and 2-butanone, respectively.

37.4%; NG, 33.8%), indicating that the addition of electrolyte monomers and the content of cross-linker had little effect on the gel fraction of the gels. The components of the resultant gels (IG8₁ and IG8₃) after removing the sol were determined by elemental analysis. The ratio of MODAT to DDA in the gels is almost the same as their feed ratio, which indicated that the MODAT and DDA have been incorporated into resultant gel networks proportionally (Table S1, Supporting Information). Therefore, the feed ratios were used to represent MODAT content in the gels. Compared with chemical initiating polymerization and cross-linking,^{11,18,19} no initiator was added in our system and the whole synthesis process was conducted at room temperature, which is much easier, safer and cleaner, especially suitable for large-scale production.

FTIR and TGA were carried out to characterize the chemical structure and thermal stability of the resultant gels, respectively. Herein, only the results of IG8₁ and NG are shown in Figure 1, and other polyelectrolyte gels have similar results as IG8₁. Compared with NG, IG8₁ shows two new peaks at 1058 and 1352 cm⁻¹ attributed to the symmetrical stretching vibration and the asymmetric stretching vibration of O=S=O in NTf₂⁻ anion,^{27,28} respectively, and the other peaks are the same as that of NG. The FTIR results indicate that MODAT is successfully copolymerized with DDA and incorporated into the gel network. Figure 1b displays that IG8₁ mainly decomposes in two steps, whereas NG decomposes only in one step, corresponding to the DDA polymer component. The MODAT component is responsible for the first decomposition step of IG8₁ whereas the second step can be attributed to the

DDA polymer component. Although IG8₁ (degradation temperature (T_d) = 320 °C) is thermally less stable than NG (T_d = 360 °C), the degradation temperature was still high enough for the practical use.

Swelling Kinetics and Solvent Retention. IG8₂ was selected to study the swelling kinetics, solvent retention, temperature dependence and reusability of the resultant lipophilic polyelectrolyte gels due to its better dimensional stability during swelling process. Four solvents with different dielectric constants (toluene (ϵ = 2.4), THF (ϵ = 7.6), 1,2-dichloroethane (ϵ = 10.3) and 2-butanone (ϵ = 18.3)) were chosen as the absorbed solvents in the following experiments so that the effects of the solvent could be considered.

Swelling kinetics of IG8₂ in different solvents is shown in Figure 2a. IG8₂ could reach about 50% of the maximum swelling degree within 1.6 h in toluene and THF, 3.7 h in 2-butanone and 9 h in 1,2-dichloroethane. Although it took much more time for IG8₂ to reach the maximum swelling degree (about 24 h in toluene, THF and 2-butanone and 46 h in 1,2-dichloroethane), IG8₂ gel could actually absorb a lot of solvents in several hours due to the high swelling degree. To guarantee that the resultant gels have reached equilibrium swelling in all the solvents, a longer swelling time (2 days) was chosen in the following experiments.

Solvent retention was studied by the solvent evaporation of these four swollen gels in air at room temperature as a function of time (Figure 2b). The solvent release rate was also quite different in these four solvents. IG8₂ could release almost all the absorbed THF within 150 min, whereas in the case of toluene,

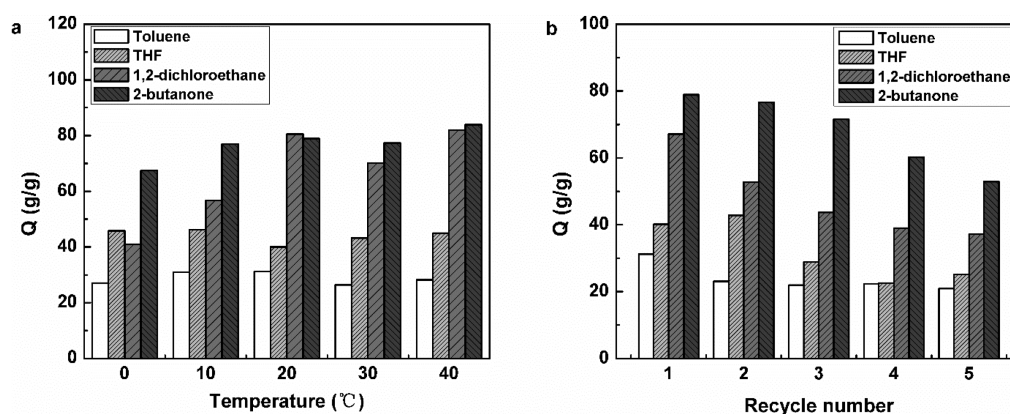


Figure 3. (a) Swelling degree of IG8₂ in toluene, THF, 1,2-dichloroethane, 2-butanone at different temperatures (0, 10, 20, 30, 40 °C); (b) swelling degree of IG8₂ in toluene, THF, 1,2-dichloroethane and 2-butanone during recycling at room temperature.

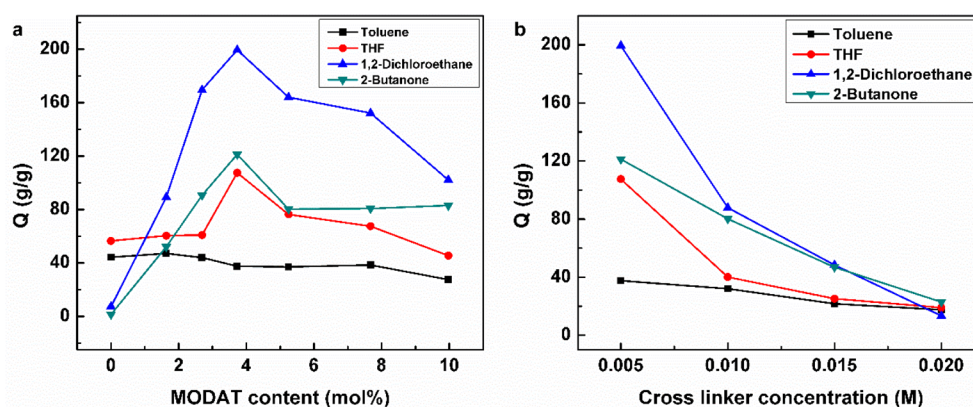


Figure 4. (a) Swelling degrees of IG8 gels with different contents of MODAT after immersion for 2 days in toluene, THF, 1,2-dichloroethane, 2-butanone; (b) Swelling degrees of IG8 with various EGDMA content after immersion for 2 days in toluene, THF, 1,2-dichloroethane and 2-butanone.

400 min was needed. This should be attributed to the better volatility of THF than toluene. For 1,2-dichloroethane and 2-butanone, about 230 and 300 min were needed for the full release, respectively. These results suggest that the absorbed solvents could be quickly released from the swollen gels, which is very important for the reusability of the gel and the recovery of the organic solvents.

Effect of Temperature on the Absorbing Ability and the Reusability. The effect of temperature on the absorbing ability of the resultant lipophilic polyelectrolyte gels was investigated by immersing IG8₂ in toluene, THF, 1,2-dichloroethane and 2-butanone for 2 days at 0, 10, 20, 30 and 40 °C, respectively. As shown in Figure 3a, IG8₂ could absorb these four solvents at all the selected temperatures. Moreover, the swelling degree did not change much as the temperature changed from 0 to 40 °C in most solvents, indicating that temperature has only a small impact on the absorbing ability of IG8₂. Ion dissociation of electrolytes is generally insensitive to temperatures of media at low temperatures.^{29,30} Therefore, dissociation of the ionic pairs in IG8₂ is still working at low temperatures for expansion of the network. It should be noted that the swelling degree of IG8₂ in 1,2-dichloroethane at low temperatures (0, 10 °C) decreased much. Because the swelling rate of the resultant gels in 1,2-dichloroethane was much slower than that in toluene, THF and 2-butanone, as shown in Figure 2a, the decrease of swelling

degree in 1,2-dichloroethane might be attributed to the poorer diffusivity of 1,2-dichloroethane at lower temperatures.

Reusability of absorbents is becoming important for solvents spill cleanup procedures. All the resultant gels can be reused after full release of absorbed organic solvents at room temperature. The reusability of IG8₂ was investigated by repeated absorption-release cycles in toluene, THF, 1,2-dichloroethane and 2-butanone, and the results are shown in Figure 3b. IG8₂ still showed a strong absorbing ability to these four solvents after five absorption-release cycles. Compared with the maximum swelling degree, although a little decrease of swelling degree was found after several cycles, IG8₂ still maintained a relatively high swelling degree. The possible reason for the swelling degree decrease of IG8₂ might be the change in gel network structure during the absorption-release process. These results indicated that the resultant gels could be used as recyclable absorbents for organic solvents.

Effects of Electrolyte Content and Cross-Linker Concentration on the Absorbing Ability. Swelling degrees of the IG8 gels with different MODAT contents in various solvents were investigated by immersing the gels in each solvent for 2 days at room temperature. As shown in Figure 4a, the MODAT content had different effects on the absorbing ability of IG8 in organic solvents with different polarities. In nonpolar solvents with very low dielectric constants, such as toluene, the addition of MODAT did not affect the swelling degree of IG8 at all. Dissociation of the ionic groups of

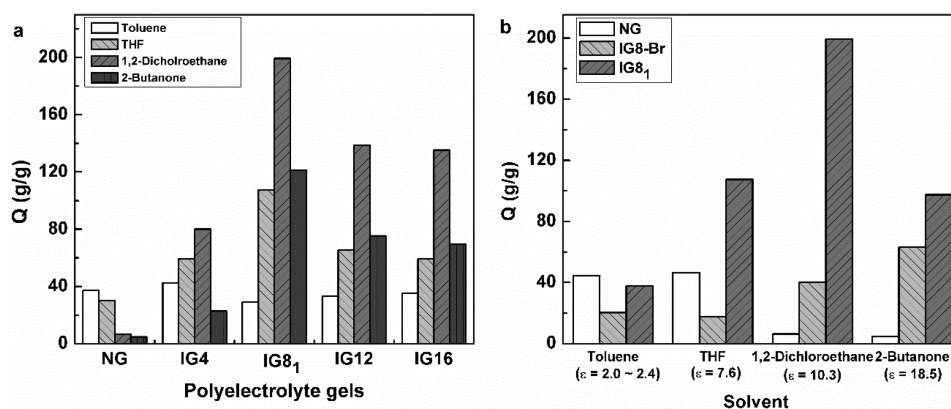


Figure 5. (a) Swelling degrees of NG, IG4, IG8₁, IG12 and IG16 after immersion for 2 days in toluene, THF, 1,2-dichloroethane and 2-butanone. (b) Swelling degrees of NG, IG8₁ and IG8₁-Br after immersion for 2 days in toluene, THF, 1,2-dichloroethane and 2-butanone.

MODAT in IG8 was completely suppressed due to the low polarity. As a result, the absorbing ability of IG8 was similar to that of the nonionic gel (NG). However, in solvents with higher polarity, such as THF, 1,2-dichloroethane and 2-butanone, the swelling degree of IG8 was significantly affected by the content of MODAT due to the dissociation of ionic groups in these solvents. The swelling degree first increased with increasing content of MODAT due to the increment of the dissociated ionic group amount, and the maximum swelling degree was observed at the MODAT content of 3.7 mol %. Then, the swelling degree began to decrease with further increase of the MODAT content, because incorporating too many ionic groups would cause physical cross-linking by higher aggregation of the ionic groups and consequently collapse of the gels.^{14,31} Thus, it can be found there is an optimum content of the electrolyte monomer for the lipophilic polyelectrolyte gel, which is around 3.7 mol % for preparing IG8.

Furthermore, the cross-linker concentration has a great effect on the absorbing ability of the lipophilic gels. IG8 gels with different concentrations of EGDMA (from 0.005 to 0.02 M) were prepared under the same conditions. The swelling degrees of IG8 gels with various cross-linker concentrations in toluene, THF, 1,2-dichloroethane and 2-butanone were also studied by immersing the gels in each solvent for 2 days at room temperature. As shown in Figure 4a, the swelling degrees of IG8 gels decreased significantly with increasing content of EGDMA in all four solvents. This is attributed to the fact that increasing the content of the cross-linking agent will increase the cross-linking density and reduce the chain length between cross-linking points, causing a drastic decrease in the mobility of the polymer chains.³² Although the absorbing capacity of the IG8 gels decreased with increase of the cross-linker concentration, the mechanical strength of the gels was enhanced dramatically. Although IG8 gels with EGDMA concentrations lower than 0.005 M showed higher swelling degrees, the mechanical strength of swollen IG8 was so bad that it was hard to be used. IG8₁ could absorb an organic solvent up to hundreds of times, but the swollen IG8₁ could not retain its original shape and was brittle, as shown in Figure 7. Although the swollen IG8₂ could still keep the original shape and maintain some elasticity, the swelling degree of IG8₂ was then much lower than that of IG8₁. Therefore, choosing an optimum cross-linker content is necessary to balance the absorbing capacity and mechanical strength of gel in practical application.

Effect of the Quaternary Ammonium Salt Structure on the Absorbing Ability. Dissociation ability of the

electrolyte monomer in the absorbed solvents has a huge impact on the absorbing ability of the polyelectrolyte gel.¹⁷ Therefore, the structure of the quaternary ammonium salt, which is closely related to the dissociation ability, should affect the absorbing ability of the resultant gels. The swelling degrees of four different lipophilic polyelectrolyte gels (IG4, IG8₁, IG12, IG16) prepared by incorporating MBDAT (2a), MODAT (2b), MDDAT (2c) and MHDAT (2d) electrolyte monomers into the gels, respectively, are shown in Figure 5a.

In toluene, the four lipophilic polyelectrolyte gels (IG4, IG8₁, IG12 and IG16) showed similar absorbing abilities to that of NG due to lack of enhancement induced by ionic dissociation in a nonpolar solvent. However, in solvents with a relatively higher polarity, such as THF, 1,2-dichloroethane and 2-butanone, the swelling degree increased first with the increase of alkyl chain length of the quaternary ammonium salts, and then decreased slightly until it leveled off. The maximum swelling degree was found in IG8₁. As mentioned above, the ionic groups in the polyelectrolyte gels could be dissociated by THF, 1,2-dichloroethane or 2-butanone; therefore, the absorbing ability of all the polyelectrolyte gels was enhanced. Increasing the alkyl chain length weakened the electrostatic attraction between the cation and anion,³³ which facilitated the dissociation of the quaternary ammonium salt. As a result, the swelling degree increased with the increase of alkyl chain length. At last, the slight decrease in the swelling degree was probably attributed to the higher physical cross-linking by chain entanglement.

To investigate the effect of the anion of electrolyte monomer on the absorbing ability of the resultant lipophilic polyelectrolyte gels, another lipophilic polyelectrolyte gel (IG8₁-Br) with MODAB (1b) as the electrolyte monomer instead of MODAT (2b) was also synthesized under the same condition as IG8₁. The swelling degrees of NG, IG8₁ and IG8₁-Br in toluene, THF, 1,2-dichloroethane and 2-butanone are shown in Figure 5b. Unlike IG8₁, the swelling degree of IG8₁-Br was much lower than that of NG in toluene and even in THF. Although the swelling degree of IG8₁-Br became higher than that of NG in 1,2-dichloroethane and 2-butanone, it is still much lower than that of IG8₁. The differences of the absorbing ability between IG8₁-Br and IG8₁ should be attributed to differences in size and hydrophobicity between Br⁻ and NTf₂⁻. The dissociation degrees were closely related to the molecular structure of ion pairs. Increase of the bulkiness around counteranions reduced Coulomb interactions between the oppositely charged ions and promoted dissociation of ion

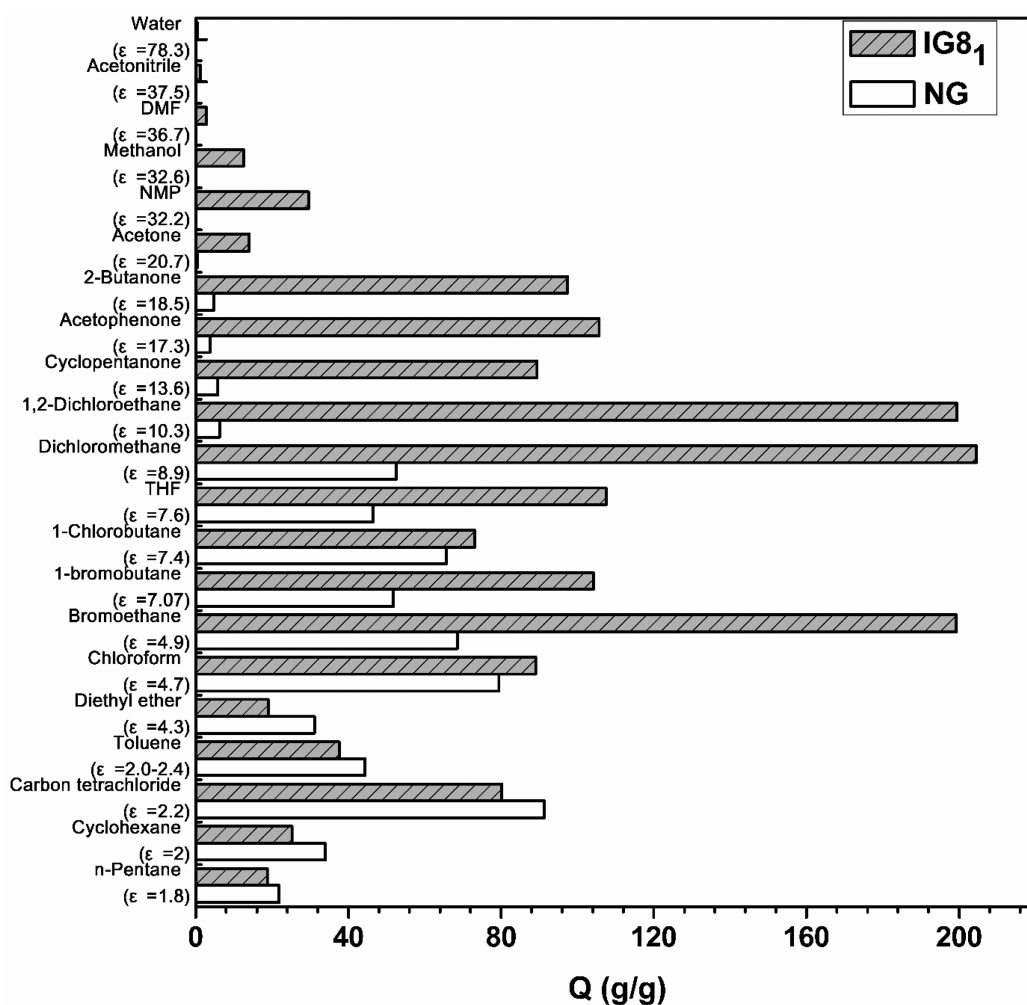


Figure 6. Swelling degrees of NG and IG8₁ after immersion for 2 days in solvents with various dielectric constants.

pairs.^{17,34} Br⁻ is much smaller and less hydrophobic than NTf₂⁻. Therefore, the association of ammonium cations (N⁺) and Br⁻ is much tighter than N⁺ and NTf₂⁻. The compatibility between MODAB with nonpolar organic solvents is also worse than that between MODAT and nonpolar solvents due to the hydrophilic property of Br⁻. As a result, even in THF, N⁺ and Br⁻ ion pairs could not be separated to free ions while N⁺ and NTf₂⁻ have been dissociated so that the swelling degree in THF is as follows: IG8₁ > NG > IG8₁-Br. In 1,2-dichloroethane or 2-butanone, N⁺ and Br⁻ ion pairs could be dissociated successfully, owing to higher polarity of the solvents. Thus, the absorbing ability of IG8₁-Br exceeded that of NG. These results suggest that the structure of the added electrolyte monomer, which is closely related to the dissociation ability of the ionic groups, has a great impact on the absorbing ability of the lipophilic polyelectrolyte gel.

Absorbing Ability of IG8 to Different Organic Solvents. Here, IG8₁ was selected to study the maximum absorbing ability of the resultant lipophilic polyelectrolyte gels to various organic solvents. The swelling degrees of IG8₁ and NG in different organic solvents with various polarities from *n*-pentane ($\epsilon = 1.8$) to methanol ($\epsilon = 32.6$) are summarized in Figure 6. As shown in Figure 6, IG8₁ could absorb a wide range of organic solvents, especially those with the dielectric constants between 4 and 20, such as bromoethane ($Q = 199.3$), THF ($Q = 107.5$), dichloromethane ($Q = 204.5$) and

1,2-dichloroethane ($Q = 199.4$). The maximum swelling degree of IG8₁ reached 204 g/g in CH₂Cl₂. The excellent absorbing ability of IG8₁ to a wide range of organic solvents has made it possible to be used as organic pollutant absorbents.

Furthermore, the absorbing ability of IG8₁ in solvents with different polarities is quite different. The absorbed organic solvents can be roughly divided into 3 types: (1) the extremely nonpolar organic solvents ($\epsilon < 4$), in which the dissociation of ionic groups was suppressed by the solvents and the swelling degree was mainly contributed by the compatibility between the solvents and polymer chains. Therefore, IG8₁ showed moderate swelling degrees (except in CCl₄ ($Q = 80$)), such as cyclohexane ($Q = 25$), *n*-pentane ($Q = 18$) and toluene ($Q = 37$), which was similar to that of NG. (2) The intermediate polar solvents ($4 < \epsilon < 20$), in which the ionic groups could be dissociated by the solvents and the swelling degree of IG8₁ began to exceed that of NG. The enhancement of the absorbing ability was more and more obvious with increasing the polarity of the solvents. IG8₁ showed an excellent absorbing ability to these intermediate polar organic solvents, such as bromoethane ($Q = 199.3$), THF ($Q = 107.5$), 1-bromobutane ($Q = 104.2$), dichloromethane ($Q = 204.5$) and 1,2-dichloroethane ($Q = 199.4$), which was much better than that of NG. Especially in the solvents with dielectric constants larger than 10, NG could only absorb a little amount of the solvents, such as cyclopentanone ($Q = 5.8$), acetophenone ($Q = 3.7$), 2-

butanone ($Q = 4.7$), whereas IG8₁ still kept a high absorbing ability (cyclopentanone ($Q = 89.4$), acetophenone ($Q = 105.7$), 2-butanone ($Q = 97.4$)), which was also much better than the reported lipophilic polyelectrolyte gels.^{11,18,19} The high absorbing ability of IG8₁ should be attributed to electrostatic repulsion between the N⁺ ions in the polymer chains as well as the ionic osmotic pressure provided by the free NTf₂⁻. (3) The highly polar solvents ($\epsilon > 20$), which are almost completely incompatible with the poly(dodecyl acrylate) polymer chain. Little solvent could enter the gel due to the incompatibility. As a result, even though the ion pairs in IG8₁ would be easily dissociated in these solvents, almost no swelling was observed in IG8₁, such as water ($Q = 0.4$), *N,N*-dimethylformamide (DMF, $Q = 2.8$), acetonitrile ($Q = 1.2$). Surprisingly, IG8₁ could still absorb some organic solvents with dielectric constants higher than 20 (acetone ($Q = 14$), *N*-methyl-2-pyrrolidone (NMP, $Q = 29.6$), methanol ($Q = 12.5$)) even though NG could not absorb these solvents at all. Figure 7 is

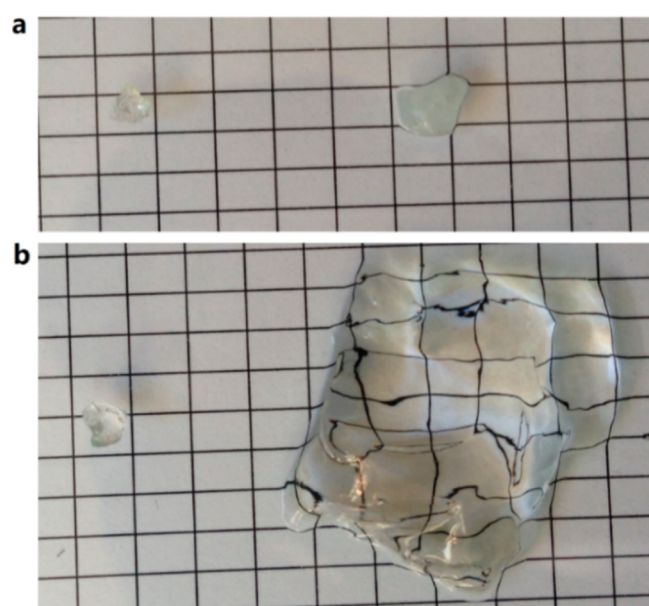


Figure 7. Digital pictures of NG (a) and IG8₁ (b) before and after swelling in 2-butanone for 2 days.

the digital picture of NG and IG8₁ before and after swelling in 2-butanone for 2 days, which clearly shows that NG could not absorb 2-butanone ($\epsilon = 18.5$) whereas IG8₁ could still maintain a high swelling ability in 2-butanone.

4. CONCLUSIONS

Lipophilic polyelectrolyte gels based on easily available lipophilic quaternary ammonium salts and dodecyl acrylate were prepared successfully by γ -ray induced polymerization and cross-linking at a mild condition. Incorporation of quaternary ammonium salts containing the NTf₂⁻ anion into gel networks can drastically enhance the absorbing ability of the gels. The resultant polyelectrolyte gel showed a good absorbing ability to a wide range of organic solvents with dielectric constants between 4 and 20 ($4 < \epsilon < 20$), such as THF, dichloromethane, chloroform and 2-butanone. The highest swelling degree of the polyelectrolyte gel (IG8₁) could reach 204 g/g. Moreover, this kind of lipophilic polyelectrolyte gel, e.g., IG8₂, kept its high absorbing ability in most solvents at a wide range of temperatures (0–40 °C) and showed good reusability. It is

expected that this new type of lipophilic polyelectrolyte gel may be a suitable candidate as a protective barrier for spilled organic compounds or organic pollutant absorbents.

■ ASSOCIATED CONTENT

Supporting Information

¹H NMR and ESI-MS spectra of monomers; EA data of IG8₁ and IG8₃. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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