NUCL SCI TECH (2016) 27:50
DOI 10.1007/s41365-016-0039-0

# New methacrylic imidazolium poly(ionic liquid) gel with super swelling capacity for oil-in-water emulsions

Xing Zhang[1] · Shuo-Jue Wang[1] · Jing Peng[1] · Jiu-Qiang Li[1] · Ling Xu[2] · Mao-Lin Zhai[1]

Received: 17 March 2015 / Revised: 26 April 2015 / Accepted: 27 April 2015 / Published online: 21 April 2016

**Abstract** A new polymeric ionic liquid gel was prepared with 1-[(2-methacryloyloxy)ethyl]-3-methylimidazolium bromide (MEMImBr) via radiation-induced polymerization and cross-linking at room temperature. The resultant PMEMImBr gel exhibits high strength and flexibility as well as special swelling behavior in oil-in-water (O/W) emulsions. The swelling behavior of PMEMImBr gel in emulsions is similar to that in water except that the swelling rate in emulsions is slightly smaller than that in water. The organic solvents with higher polarity in the emulsions contribute to the swelling of PMEMImBr gels, and the O/W proportion of emulsion in the swollen gel equals approximately that of original emulsion when the concentration of organic solvent is lower than 0.2 g/g.

**Keywords** Poly(ionic liquid)s · PMEMImBr gel · Radiation cross-linking · Swelling · Emulsion

## 1 Introduction

As a new class of green solvents, ionic liquids (ILs) have stirred great interest over the last decade due to their unique properties, such as low flammability, negligible vapor pressure, and good chemical and electrochemical stability [1–3]. Polymeric forms of ionic liquids (PILs), or poly(ionic liquid)s, belong to a subclass of polyelectrolytes, which bear an ionic liquid species in each monomer repeating unit. They are of enhanced mechanical stability, improved processability, durability, and spatial controllability over the IL species [4].

PILs can be dissolved in some solvents, which is a problem for some applications like absorption. Cross-linked PIL gels, as a kind of insoluble material with definite shape, were prepared by polymerization and cross-linking of ionic liquids monomers or by chemically linking of PILs molecules. PIL gel materials combine the characteristics of the polymer with those of the ILs, often resulting in new hybrid materials with interesting properties [5, 6]. Sui et al. [7] reported a new cross-linkable redox-responsive poly(ferrocenylsilane)-based poly(ionic liquid)s (PFS-PILs) which can self-cross-link at low concentrations into nanogels or form macroscopic hydrogel networks at higher concentrations. Batra et al. [8] reported the polymerization of a methylimidazolium-based ionic liquid, forming an elastic, self-supporting hydrogel that can swell to nearly 200 times of its original volume.

Gels are excellent support for biotechnology applications, especially as a support for active pharmaceutical ingredient in the form of oil-in-water (O/W) type emulsion. Recently, O/W type emulsions have aroused great interest in biotechnology, pharmaceutical, cosmetics, food, and

---

**Electronic supplementary material** The online version of this article (doi:10.1007/s41365-016-0039-0) contains supplementary material, which is available to authorized users.

✉ Mao-Lin Zhai
mlzhai@pku.edu.cn

[1] Beijing National Laboratory for Molecular Sciences, Radiochemistry and Radiation Chemistry Key Laboratory of Fundamental Science, The Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

[2] Department of Energy and Resources Engineering, College of Engineering, Peking University, Beijing 100871, China

agricultural industries. In particular, they have been studied as unique microenvironment for controlled release, e.g., in drug delivery to biological targets, and as nanocarriers [9–11]. A lot of polymer gels are highly hydrophilic or highly lipophilic. Their swelling abilities have been investigated mainly in pure water [12, 13], alcohol/water mixture solutions [14, 15], and pure nonpolar organic solvents [16, 17]. However, the swelling and adsorption properties in O/W emulsion have never been explored. In this work, a new PIL gel was demonstrated to swell in O/W emulsion with a large swelling ratio similar to that in pure water. To the best of our knowledge, this is the first report about such property of PIL gels.

Some groups reported polymerization of a polymerizable ionic liquid with 1-[(2-methacryloyloxy)ethyl]-3-alkylimidazolium (MEAIm) cation [18–22], but the reports about the study of the correlative gel are rare. Compared with traditional chemical cross-linking reactions which needs initiators at higher temperatures, radiation-induced polymerization and cross-linking is a facile, clean, and effective route, without any initiators. However, to the authors' knowledge, no attempt has been reported on the radiation synthesis of PIL gels.

In an attempt to build a new perspective of using the new poly(ionic liquid) gel in emulsion adsorption, we prepared a new gel of poly[1-[(2-methacryloyloxy)ethyl]-3-methylimidazolium bromide] (PMEMImBr) via γ-ray irradiation at room temperature. The effects of dose, concentration of monomer and cross-linker on gel fraction, mechanical compression strength, and equilibrium degree of swelling (EDS) of the radiation-synthesized PMEMImBr gels were studied. The PMEMImBr gel was used in adsorption of O/W emulsions. The swelling behavior and the content of organic solvent of PMEMImBr gel in emulsions were investigated.

## 2 Experimental section

### 2.1 Materials

N-methylimidazole (99 %), methacryloyl chloride (99 %), 2-bromoethanol (99 %), polyethylene glycol sorbitan monolaurate (Tween-20), and 2-(dimethylamino)ethyl methacrylate (DMAEMA, 99 %) were purchased from J&K Chemical. Benzene, toluene, p-xylene, dichloromethane, chloroform, tetrachloromethane, and other common chemical reagents were analytical pure and purchased from Sinopharm Chemical Reagent Beijing Co. Ltd. Polyethylene glycol dimethacrylate (PEGDMA, average molecular weight = 875) was obtained from Acros. All materials were used without further purification.

### 2.2 Synthesis of ionic liquid monomer

The 2-bromoethanol was added dropwise to N-methylimidazole dissolved in methanol in nitrogen atmosphere. The reaction solution was stirred for 24 h at room temperature. A white solid (1-(2-hydroxyethyl)-3-methyimidazolium bromide) was formed after removing the solvent. The solid was suspended in certain amount of anhydrous acetonitrile. Methacryloyl chloride diluted with acetonitrile was added dropwise at 0 °C in nitrogen atmosphere. After stirring for 48 h, the solvent was removed, and the residue was extracted with diethyl ether to obtain 1-[(2-methacryloyloxy)ethyl]-3-methylimidazolium bromide (MEMImBr).

### 2.3 Procedure of gel synthesis

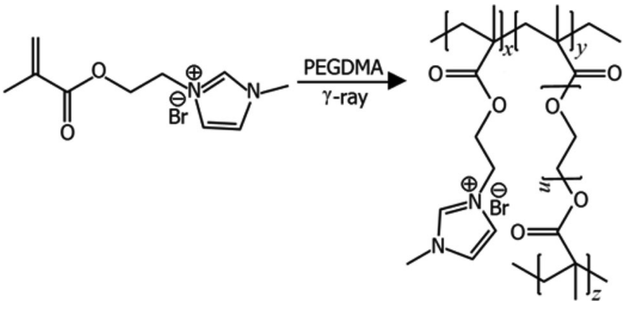
MEMImBr ionic liquid monomer and cross-linker PEGDMA were dissolved in deionized water to form a homogeneous solution, which was transferred into a glass tube. After bubbling with $N_2$ gas for 30 min, the tube was sealed and irradiated to 0.3–15 kGy by $^{60}$Co γ-rays at 50 Gy/min to form the poly(N, N-dimethylaminoethyl methacrylate) (PDMAEMA) gel (Scheme 1). Poly(N, N-dimethylaminoethyl methacrylate) (PDMAEMA) gel used in this work was prepared with 1.0 M DMAEMA monomer, 0.01 M PEGDMA cross-linker, and irradiated to 3 kGy at 50 Gy/min (Scheme S1). The gel fraction was 75 %, close to that of PMEMImBr gel with 1.0 M monomer, 0.01 M cross-linker, and 5 kGy irradiation.

### 2.4 Gel fraction

Unreacted monomers and cross-linkers were removed by soaking the gels in deionized water for 10 days (the water was changed 2 times a day). Finally, all gels were dried in vacuum at room temperature to constant weight.

Gel fraction of the gel is defined as

$$\text{Gel fraction}\,(\%) = \left[W_g/W_0\right] \times 100, \tag{1}$$



**Scheme 1** Synthesis route of PMEMImBr gel

where $W_0$ and $W_g$ are the weights of dried samples before and after extraction, respectively.

### 2.5 Swelling ratio by gravimetric method

Swelling ratio of the gels was studied gravimetrically at room temperature. After their swelling in the solvent for a certain time, the gels were taken out, placed on a tissue paper to remove excess solvent, and weighed. Swelling ratio was determined by

$$\text{Swelling ratio (SR)} = \left(W_s - W_g\right)/W_g, \tag{2}$$

where $W_g$ and $W_s$ are the mass of the dried and swollen gels, respectively. When $W_s$ is the mass of the equilibrium swollen gel, the corresponding SR is equilibrium degree of swelling (EDS). Each SR was averaged from three measurements, with an error of less than 4.5 %.

### 2.6 Mechanical compression strength test

The as-prepared PMEMImBr gels were cut into cylindrical pieces of $\Phi$ 8.0 mm × 10.0 mm. The gel samples were stressed by compression. Measurements were performed at ca. 22 °C with two-column testing machine Instron 3365 (Instron Co. Ltd, US) and a 500 N load cell and jaw inserts. The resulting specimens were subsequently compressed in a speed of 1.00 mm/min. All measurements were performed in triplicate.

### 2.7 Microstructure observation

Morphology of the freeze-dried specimens was investigated with scanning electron microscope (SEM, Model S-3400, Hitachi, Japan). The samples were sputter-coated with gold on Denton Vacuum Desk IV Cold Sputter/Etch unit to reduce surface charging by the electron beams.

### 2.8 Emulsion preparation and swelling of PMEMImBr gels in O/W emulsions

The organic solvent was mixed with water, and a certain amount of emulsifier (9 % of organic solvent) was added. The mixture was fully oscillated and stirred until homogeneous emulsion was formed. To create an initial stabilized O/W emulsion, the liquid was blended at 2000 rpm for 2 min with a high speed blender (IKA Co. Ltd, Germany) to form a coarse emulsion, which was homogenized with vortex turbulence mixing homogenizer (IKA Co. Ltd, Germany) for 10 min to form a fine emulsion. The prepared emulsions are stable during the period of swelling experiment of PMEMImBr gels.

In order to minimize influence of volatilization of the organic solvent on the authenticity of organic content obtained by the subsequent experiment method, the same amount of emulsion was transferred into two tubes, each containing 20.0 g emulsion. The dried PMEMImBr gel of 60 mg was added into each of the tubes, which was sealed adequately. They were placed on the table con centrator with 240 r/min overnight at 25 °C to avoid the emulsion from being unstable. After removing the gel, the emulsion was fully homogenized with vortex turbulence mixing homogenizer again to ensure the homogeneity of the oil-in-water proportion. For each O/W emulsion with a certain concentration, the amount of organic solvent absorbed by gels was obtained by calculating and comparing the organic solvent concentration of the residual emulsion in the two tubes. Changes in concentration of the organic solvent in the emulsion were obtained by analyzing the $^1$H NMR characteristic peak of the emulsion. The $^1$H NMR experiments were performed on a Bruker AVANCE III spectrometer at 500 MHz. Measurements were performed at room temperature in deuterated dimethyl sulfoxide (DMSO-$d_6$). The concentration of tetrachloromethane in the residual emulsion was obtained by weighing method after the ultrasonic emulsion-breaking process (small amount of calcium chloride and isopropanol were added as demulsifiers) and centrifugalization process.

## 3 Results and discussion

When the monomer aqueous solution containing cross-linker is irradiated, the hydroxyl free radicals and hydrogen atom generated by the radiolysis of $H_2O$ induce polymerization and cross-linking of monomers, hence the formation of the gel network [23–26]. The MEMImBr monomer is a kind of polymerizable ionic liquid with methacrylic group, and the MEMImBr solution turned into gels after irradiation. Unlike other methods of PIL gels synthesis [27–31], the irradiation method needs no initiator, and the whole preparation process is conducted at room temperature, being easier, cleaner, and more energy-saving. Gel fraction plays an important role in swelling and mechanical property of gels. Gel fractions of PMEMImBr gel as a function of absorbed dose are shown in Fig. 1a. Similar to many other gels, the formation of PMEMImBr gel starts at a critical absorbed dose (gelation dose = 0.3 kGy); the MEMImBr monomers did not cross-link into gel network below the critical absorbed dose, but the gel fraction increases sharply with the increasing absorbed dose in a narrow range and then levels off.

The maximum gel fraction of PMEMImBr gel decreases with increasing concentrations of MEMImBr at 0.01 M of the cross-linker concentration. PMEMImBr gel with 0.5 M MEMImBr monomer gives a maximum gel fraction of 85.9 % at 10 kGy of absorbed dose, where the maximum

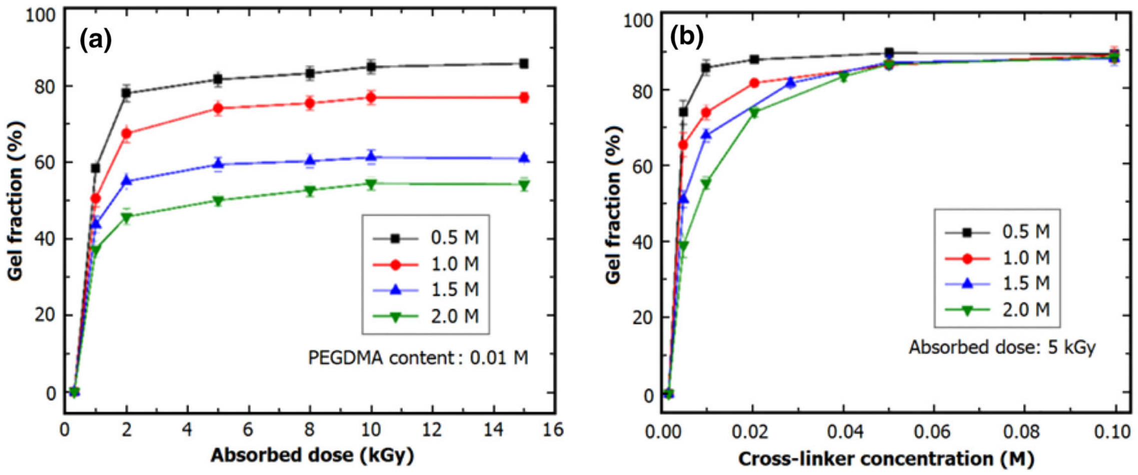


**Fig. 1** Gel fraction of PMEMImBr gels prepared with 0.5–2.0 M MEMImBr, as a function of **a** the dose and **b** cross-linker content

gel fraction of PMEMImBr gel with 2.0 M monomer is just 54.5 %. The weak cross-linking property of PMEMImBr gel comes from the space charge repulsion interaction of large unshieldable imidazolium ions. The gel fraction changes little after 6 kGy. So PMEMImBr gels prepared at 5 kGy were used for further investigation.

The effect of cross-linker content on the gel fraction is shown in Fig. 1b. The gel fraction increases sharply with the cross-linker concentration in a narrow range at first, while it changes little when the amount of cross-linker is over 0.05 M. With the increase of monomer amount, more cross-linker is needed to reach similar gel fraction. The gel fraction of PMEMImBr gel with 0.5 M monomer is 85.9 % at 0.01 M cross-linker, while PMEMImBr gel with 2.0 M monomer needs more than 0.06 M cross-linker to reach the gel fraction of over 85 %.

The basic feature of gel is its ability to absorb and hold amount of solvent in its network structure. The equilibrium swelling of gels is a result of the balance of internal cause (e.g., the hydrophily of the polymer chain and the network elasticity of the gel) and external cause (e.g., solvent property). PMEMImBr gels belong to superhydrophilic gels. The superhydrophility of PMEMImBr gel comes from the fully dissociation of ions in water. Figure 2 shows swelling dynamics behavior of PMEMImBr gels (PMEMImBr-**1**–**4**) of different IL monomer contents, of similar gel fractions (70–75 %), though. They differ in EDS value due to different cross-linking density.

The SEM images (Fig. 3) of PMEMImBr gels show that the pore size of gels decreases from PMEMImBr-**1** to PMEMImBr-**4** in spite of the same proportion of monomer to cross-linker. In similar gel fractions, the mean pore size is 120 μm for PMEMImBr-**1**, while it is 20 μm for PMEMImBr-**4**, hence its higher cross-linking density. The SR curve of PMEMImBr gels with different concentration of cross-linker PEGDMA as a function of time is shown in Fig. S1. More cross-linker leads to denser network structure of the gels, which reduces the absorption ability.

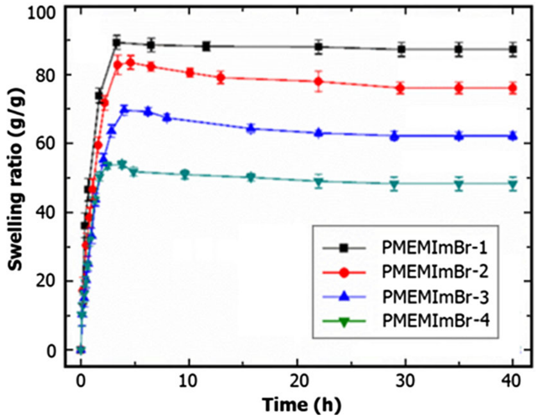


**Fig. 2** Swelling ratio (in water) of PMEMImBr gels of similar gel fractions, as a function of time

Good mechanical capacity of gels is of great importance for their applications. Compression test was performed to investigate the mechanical behavior of synthesized gels. Deformation can be used to fully characterize the mechanical stability of a material and is essential for use in biomedical applications, cosmetic application, and pharmaceutical sciences [32]. The stress-compression curves (Fig. 4) for gels are of similar shapes. In the initial linear region of the curves, the gels follow Hooke's law, where they deform elastically and return to their initial length when the stress is removed. Above a specified point, a specimen cannot return to its original length (rupture-fracture point). As shown in Fig. 4 and Table 1, both the maximum compression strain and stress of gels increase from PMEMImBr-**1** to PMEMImBr-**4**.

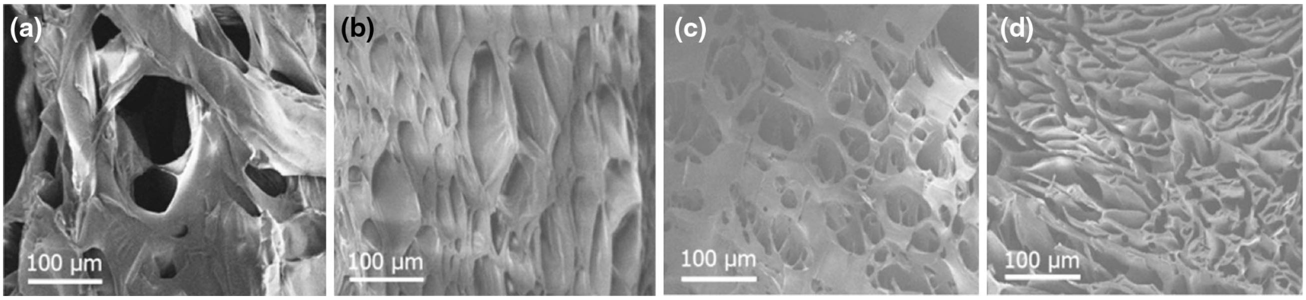


**Fig. 3** SEM images of **a** PMEMImBr-**1**, **b** PMEMImBr-**2**, **c** PMEMImBr-**3**, **d** PMEMImBr-**4** gels when swollen to EDS

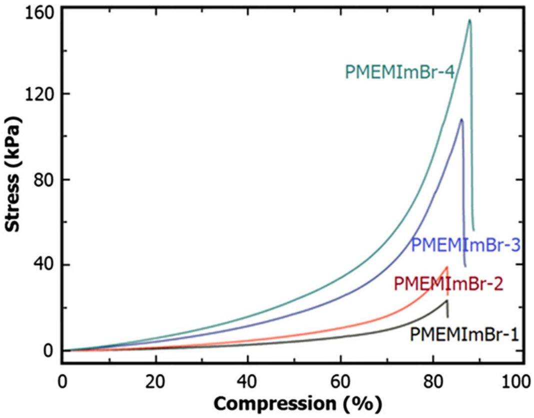


**Fig. 4** Compression curves of as-prepared PMEMImBr gels of similar gel fraction

Of all the specimens, PMEMImBr-**2** gel is the best in strength and flexibility. It can be compressed 83.2 ± 0.6 % of its original length and can fully recover to its original state after pressure removal, and it can be bent 180° without breakage (Fig. 5). It has large EDS in water and good mechanical properties for swelling in O/W emulsions.

O/W type emulsions have attracted much attention recently because of their potential in the pharmaceutical, biotechnology, and agriculture. Gels have special uses as emulsion-type substrates. The swelling and adsorption properties of gels in the O/W emulsions are yet to be explored. Swelling behavior of the PMEMImBr gels in emulsion was investigated for the first time. Solvent polarity plays an important role in many chemical processes in solution. According to Ref. [33], solvent polarity can be defined as the overall solvation capability of solvents, which depends on actions of all possible intermolecular interactions between solutes and solvents. There are different definitions of solvent polarity and several ways to measure it. Solvent polarity index (SPI) is a common parameter to measure polarities of solvents and high SPI value corresponds to high solvent polarity.

Polarity of solvent influences the swelling of gels. Most hydrophilic gels collapse when organic solvents exist, and lipophilic gels deswell when high polar solvents (like water) exist because their chains stretching is blocked in aquatic environment [34–36]. PMEMImBr gels show large EDS and similar swelling kinetic curves in different O/W emulsions (Fig. 6). EDS of PMEMImBr-**2** in dichloromethane (or chloroform)/water emulsion is larger than that in pure water, whereas EDS in tetrachloromethane/water emulsion and other benzene series/water emulsion is lower than that in pure water. The polarity order of solvents is water (W) > chloroform (C) > dichloromethane (D) > benzene (B) > p-xylene (P) > toluene (T) > tetrachloromethane (TC) (Table 2).

According to Ref. [37], second-order kinetics model can be used to describe the swelling procedure of gels:

$$\mathrm{d}W/\mathrm{d}t = k_s(W_\infty - W)^2, \tag{3}$$

where $k_s$ ($h^{-1}$) is the rate constant of swelling and $W_\infty$ is the theoretical maximum swelling degree. With initial condition of $t = 0$ and $W = 0$, Eq. (4) can be deduced:

$$t/W = A + Bt, \tag{4}$$

**Table 1** Preparation conditions and properties of PMEMImBr gels (Nos. 1–4) irradiated to 5 kGy

| No. | Concentration of MEMImBr (M) | Concentration of PEGDMA (M) | Gel fraction (%) | Maximum compression stress (kPa) | Maximum compression strain (%) | EDS (g/g) in water |
|---|---|---|---|---|---|---|
| **1** | 0.5 | 0.005 | 74.3 | 23.4 ± 1.5 | 83.0 ± 0.7 | 87.3 |
| **2** | 1.0 | 0.010 | 74.0 | 39.3 ± 0.9 | 83.2 ± 0.6 | 80.5 |
| **3** | 1.5 | 0.015 | 73.0 | 107.6 ± 1.3 | 86.3 ± 0.6 | 67.4 |
| **4** | 2.0 | 0.020 | 72.2 | 154.8 ± 1.0 | 88.1 ± 0.8 | 51.7 |

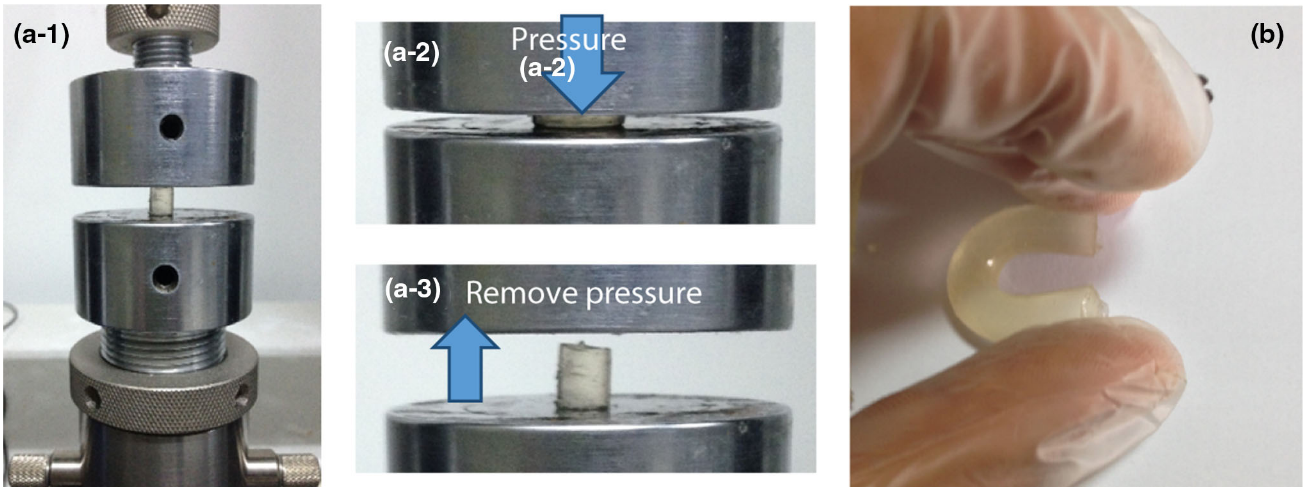


**Fig. 5** Photographs of as-prepared PMEMImBr-**2** gel compressed on a mechanical strength tester (**a-1**), under pressure (**a-2**), removal of pressure (**a-3**), and its excellent elasticity to 180° bending (**b**)

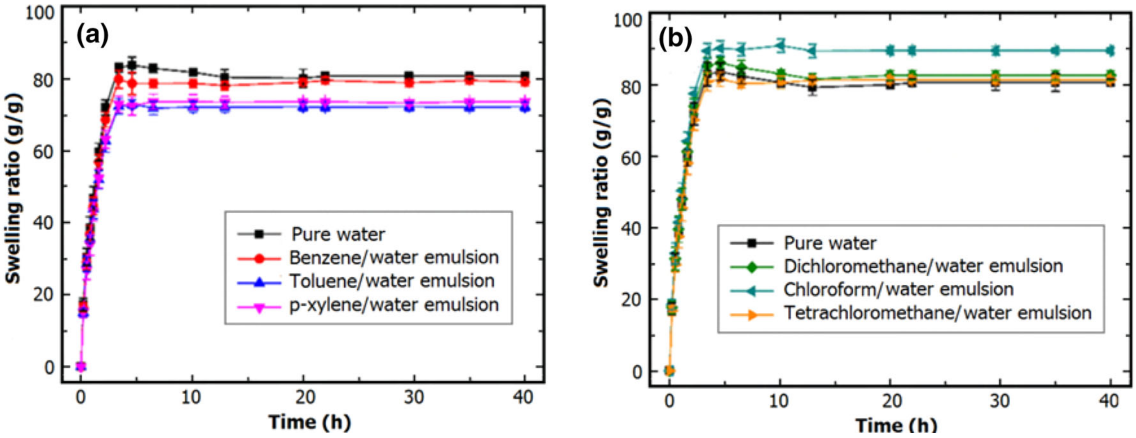


**Fig. 6** Swelling kinetic curves of PMEMImBr-**2** gel in benzene series/water (**a**) and chloromethane series/water (**b**) emulsions (temperature = 25 °C; the concentration of organic solvents in O/W emulsions is 0.2 g/g)

**Table 2** The impact of solvent parameters on EDS of the gel obtained in different emulsions

| Solvents | SPI [39–41] | $D^a$ (g/mL) | EDS (g/g) |
|---|---|---|---|
| Benzene (B) | 3.0 | 0.879 | 79.3 |
| Toluene (T) | 2.4 | 0.867 | 72.0 |
| p-Xylene (P) | 2.5 | 0.861 | 73.4 |
| Dichloromethane (D) | 3.4 | 1.327 | 82.5 |
| Chloroform (C) | 4.4 | 1.483 | 89.4 |
| Tetrachloromethane (TC) | 1.6 | 1.594 | 81.3 |
| Water (W) | 10.2 | 0.997 | 80.5[b] |

[a] *D* densities measured at 25 °C

[b] EDS (g/g) in pure water

where $A = 1/\left(k_s W_\infty^2\right) = 1/(\mathrm{d}W/\mathrm{d}t)_0$, which is the reciprocal of initial swelling rate ($r_0$), and $B = 1/W_\infty$. $W_\infty$ and $k_s$ can be calculated with the curve of $t/W \sim t$. The results are presented in Table 3.

The $W_{\infty,\mathrm{cal}}$ values of PMEMImBr gels calculated by Eq. (4) in O/W emulsions are almost the same as the measured $W_{\infty,\mathrm{exp}}$ values. This indicates that the swelling behavior of PMEMImBr gels follows second-order kinetics (correlation coefficients $R^2 > 0.99$), which is controlled by stress relaxation of PMEMImBr gels. The swelling behavior of PMEMImBr gel exhibits a slight overshooting effect, and the EDS value of PMEMImBr gel is slightly lower than the corresponding maximum swelling ratio value. From Fig. 6 and Table 3, it can be seen that the $k_s$ values of the PMEMImBr swelling in pure water are slightly larger than those in benzene series/water and chloromethane/water emulsions, which indicates that the swelling rates in emulsions are a bit slower than those in water added with hydrophobic organic solvents.

**Table 3** Data of the swelling kinetics of PMEMImBr gel in O/W emulsions

| Solvent/water emulsion | $k_s$ ($h^{-1}$) | $W_{\infty,cal}$ | $W_{\infty,exp}$ | $R_4^{2a}$ | $k$ | $n$ | $R_5^{2a}$ |
|---|---|---|---|---|---|---|---|
| Pure water | 0.030 | 80.3 | 83.5 | 0.9938 | 0.53 | 0.58 | 0.9973 |
| Benzene/water (B/W) | 0.022 | 79.9 | 79.6 | 0.9966 | 0.55 | 0.58 | 0.9974 |
| Toluene/water (T/W) | 0.026 | 73.7 | 72.7 | 0.9969 | 0.58 | 0.62 | 0.9914 |
| p-Xylene/water (P/W) | 0.024 | 73.6 | 73.4 | 0.9968 | 0.55 | 0.60 | 0.9960 |
| Dichloromethane/water (D/W) | 0.023 | 85.0 | 86.0 | 0.9959 | 0.56 | 0.58 | 0.9974 |
| Chloroform/water (C/W) | 0.016 | 94.4 | 90.8 | 0.9972 | 0.53 | 0.58 | 0.9961 |
| Tetrachloromethane/water (TC/W) | 0.017 | 85.8 | 81.3 | 0.9978 | 0.53 | 0.58 | 0.9974 |

[a] $R_4^2$ and $R_5^2$, correlation coefficients from Eqs. (4) and (5), respectively

The swelling model in the whole process cannot be used to totally describe the initial stages of swelling precisely. Peppas and co-workers [38] proposed the following equation to describe the initial stages of swelling ($W/W_\infty \leq 0.6$),

$$F = \frac{W}{W_\infty} = kt^n \quad \text{or} \quad \ln F = \ln k + n \ln t, \tag{5}$$

where $F$ denotes the amount of solvent fraction at time $t$, $k$ is a constant related to the structure of the network, and the exponential $n$ is a number indicative of the type of diffusion.

The results calculated by Eq. (5) are also presented in Table 3. The diffusion exponent ranges from 0.58 to 0.62. For the gels swelling in emulsions, the $n$ values are found to be over 1/2. Hence, the diffusion of solvent molecules into the gels can be regarded as non-Fickian diffusion, which is generally explained as a consequence of slow relaxation rate of the polymer matrix. That means the relaxation rate of the PMEMImBr gels is slower than the diffusing rate of emulsion particles in gels because of the entanglement of polymer chains in gels. From Table 3 and the initial stage of swelling in Fig. 6, it can be seen that $k$ values of PMEMImBr gels in benzene series/water and chloromethane/water emulsions are similar (from 0.53 to 0.58) to those in water. This proves that the swelling rates on the initial stage of swelling in emulsions are close to that in water, and the polarity of organic solvents does not affect much on swelling rates in the initial stage when small amount of hydrophobic organic solvents exists.

Figure 7 shows EDS of the PMEMImBr gel in O/W emulsion systems compared with common superhydrophilic PDMAEMA gel. The PMDAEMA and PMEMImBr gels are both superhydrophilic gels with similar EDS values in pure water. The EDS of PMEMImBr gels is 72.0–79.3 g/g in 0.2 g/g benzene series/water emulsions and 81.3–89.4 g/g in 0.2 g/g chloromethane series/water emulsions, while it is just 4.6–30.1 for PDMAEMA gels.

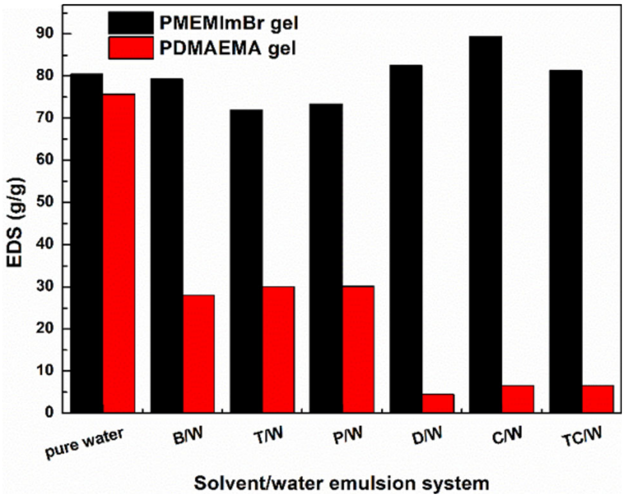


**Fig. 7** Equilibrium degree of swelling of PMEMImBr and PDMAEMA gel in O/W emulsions, temperature = 25 °C, the concentration of organic solvents in O/W emulsions is 0.2 g/g, and the gel used here was PMEMImBr-**2**

The special swelling behavior of PMEMImBr gel in O/W emulsions should attribute to the structure of PMEMImBr gel. PMEMImBr polymer chains in water can be dissociated from the polymer chains with free negative bromide ions and positive imidazolium ions which contributes to the stretch of polymer chains in water. When small amount of hydrophobic organic solvents exists, the dissociation of imidazolium positive ions and free negative bromide ions in water and the electrostatic repulsion of polymer chains with imidazolium positive ions avoid the collapse of the gels. In addition, the extra osmotic pressure from the dissociation also facilitates the PMEMImBr gel to keep a large EDS value in emulsions.

It is important to know the amount of organic composition in the swollen PMEMImBr gel. In order to figure out the composition of emulsion absorbed in PMEMImBr gel, we investigated the composition of organic solvent in the O/W emulsions by $^1$H NMR. The results are given in Table 4.

When the initial concentration of organic solvent is lower than 0.2 g/g, the absorbed ratio of organic solvent to water is similar with the ratio of organic solvent to water in the original emulsion. This means the O/W emulsion is

**Table 4** The concentration analysis of organic solvent in swollen PMEMImBr gel in different emulsions

| Emulsions | Organic solvent contents (g/g) | | EDS (g/g) |
|---|---|---|---|
| | Original[a] | Swollen PIL | |
| B/W | 0.20 ± 0.010 | 0.19 ± 0.019 | 79.3 |
| B/W | 0.44 ± 0.012 | 0.27 ± 0.037 | 59.3 |
| T/W | 0.20 ± 0.010 | 0.19 ± 0.009 | 72.0 |
| T/W | 0.47 ± 0.013 | 0.36 ± 0.033 | 69.3 |
| P/W | 0.20 ± 0.011 | 0.18 ± 0.016 | 73.4 |
| P/W | 0.49 ± 0.014 | 0.34 ± 0.024 | 60.9 |
| D/W | 0.20 ± 0.009 | 0.20 ± 0.009 | 82.5 |
| D/W | 0.49 ± 0.021 | 0.40 ± 0.083 | 80.5 |
| C/W | 0.20 ± 0.014 | 0.18 ± 0.029 | 89.4 |
| C/W | 0.57 ± 0.020 | 0.30 ± 0.040 | 71.7 |
| TC/W | 0.20 ± 0.011 | 0.19 ± 0.012 | 81.3 |
| TC/W | 0.63 ± 0.023 | 0.24 ± 0.022 | 61.4 |

[a] The original emulsion is the emulsion without gels added but treated in the same way of the emulsion with gels added

absorbed completely. The PMEMImBr gel swells hardly in organic solvents, and the EDS in pure organic solvents is less than 0.3 g/g (Fig. S2). The amount of organic solvent absorbed into the gels increases with concentration of the initial organic solvent, but the concentration of organic solvent in swollen PMEMImBr gel is lower than that in original emulsion. This is because that low-polarity organic solvent hinders the swelling process of PMEMImBr gel when its organic solvent concentration becomes too high. O/W emulsions obtained by flow shearing force are usually polydisperse in droplets sized at 0.1–10 μm [42–44]. Being smaller than the pore size of PMEMImBr gels, the emulsion droplets can be absorbed easily into the gel network. In emulsions of lower organic solvent concentration, the droplets are even smaller, which is helpful to the absorption of emulsion droplets. As concentration of organic solvent increase, the emulsion droplets shall become too large to be absorbed into the gel network. Therefore, the concentration of organic solvent in swollen PMEMImBr gel is usually lower than that in original emulsion at organic solvent concentrations of greater than 0.2 g/g.

In order to investigate the influence of emulsifier on the EDS, PMEMImBr gels and PDMAEMA gels were used to swell in aqueous solution of Tween-20 emulsifier without other organic solvents added. The maximum concentration of Tween-20 was 0.06 g/g, and the EDS in emulsion changed less than 1 % compared with that in pure water. Therefore, it proves that the few amount of Tween-20 emulsifier does not affect the swelling ratio of PMEMImBr and PDMAEMA gels.

In general, drug concentration in the substrate for controllable release is lower than 1 wt% [45], so the absorption ability of the PMEMImBr gel can be developed as drug containing soft substrate by adjusting the initial active drug ingredients concentration. Given such emulsion absorption property, the PMEMImBr gels can also be used as potential adsorption separation materials for emulsion–wastewater remediation [46], carrying materials in agricultural, cosmetics, biomedical application, or as actuators [47] for controlled protein and DNA delivery.

## 4 Conclusion

In this work, a new PIL gel based on MEMImBr monomer has been successfully synthesized by using radiation technique for the first time. The resultant PIL gel shows good flexibility, mechanical strength, and high equilibrium swelling ratio in benzene series/water emulsions and chloromethane series/water emulsions, and the EDS in chloroform/water O/W emulsion reaches as high as 89.4 g/g at 25 °C which is similar to the EDS in pure water. O/W emulsions containing the organic solvents with higher polarity contribute to the swelling of PMEMImBr gels, and the O/W proportion of emulsion in the swollen gel equals approximately that of original emulsion when the concentration of organic solvent is lower than 0.2 g/g. This material should be the first step for development of absorbent materials in heterogeneous environment. This work provides a simple and efficient way to synthesize PIL gels and emphasizes the application of PIL gels for emulsion absorption.

**Acknowledgments** This work was supported by the National Natural Science Foundation of China (No. 11375019).

## References

1. R.D. Rogers, Materials science—reflections on ionic liquids. Nature **447**, 917–918 (2007). doi:10.1038/447917a
2. D. Mecerreyes, Polymeric ionic liquids: broadening the properties and applications of polyelectrolytes. Prog. Polym. Sci. **36**, 1629–1648 (2011). doi:10.1016/j.progpolymsci.2011.05.007
3. A.F.M. Cláudio, C.F. Marques, I. Boal-Palheiros et al., Development of back-extraction and recyclability routes for ionic-liquid-based aqueous two-phase systems. Green Chem. **16**, 259–268 (2014). doi:10.1039/C3GC41999A
4. J.Y. Yuan, M. Antonietti, Poly(ionic liquid)s: polymers expanding classical property profiles. Polymer **52**, 1469–1482 (2011). doi:10.1016/j.polymer.2011.01.043
5. J. Le Bideau, L. Viau, A. Vioux, Ionogels, ionic liquid based hybrid materials. Chem. Soc. Rev. **40**, 907–925 (2011). doi:10.1039/C0CS00059K
6. T. Ueki, M. Watanabe, Macromolecules in ionic liquids: progress, challenges, and opportunities. Macromolecules **41**, 3739–3749 (2008). doi:10.1021/ma800171k

7. X.F. Sui, M.A. Hempenius, G.J. Vancso, Redox-active cross-linkable poly(ionic liquid)s. J. Am. Chem. Soc. **134**, 4023–4025 (2012). doi:10.1021/Ja211662k
8. D. Batra, D.N.T. Hay, M.A. Firestone, Formation of a biomimetic, liquid-crystalline hydrogel by self-assembly and polymerization of an ionic liquid. Chem. Mater. **19**, 4423–4431 (2007). doi:10.1021/Cm062992z
9. J.C. Leroux, Injectable nanocarriers for biodetoxification. Nat. Nanotechnol. **2**, 679–684 (2007). doi:10.1038/nnano.2007.339
10. A.S. Utada, E. Lorenceau, D.R. Link et al., Monodisperse double emulsions generated from a microcapillary device. Science **308**, 537–541 (2005). doi:10.1126/science.1109164
11. B.D. Klugherz, P.L. Jones, X.M. Cui et al., Gene delivery from a DNA controlled-release stent in porcine coronary arteries. Nat. Biotechnol. **18**, 1181–1184 (2000). doi:10.1038/81176
12. B. Vazquez, J.S. Roman, C. Peniche et al., Polymeric hydrophilic hydrogels with flexible hydrophobic chains. Control of the hydration and interactions with water molecules. Macromolecules **30**, 8440–8446 (1997). doi:10.1021/Ma970863l
13. H. Feil, Y.H. Bae, J. Feijen et al., Mutual influence of Ph and temperature on the swelling of ionizable and thermosensitive hydrogels. Macromolecules **25**, 5528–5530 (1992). doi:10.1021/Ma00046a063
14. J.W. Chen, J.R. Shen, Swelling behaviors of polyacrylate superabsorbent in the mixtures of water and hydrophilic solvents. J. Appl. Polym. Sci. **75**, 1331–1338 (2000). doi:10.1002/(SICI)1097-4628(20000314)75:11<1331:AID-APP2>3.0.CO;2-R
15. C.C. Li, M.L. Zhai, J. Peng et al., Swelling behaviour of amphiphilic poly(methacryloxyethyl dimethylalkane ammonium bromide) gels in alcohol/water solvent systems. J. Nucl. Sci. Technol. **25**, 020603 (2014). doi:10.13538/j.1001-8042/nst.25.020306
16. K. Iseda, M. Ohta, T. Ono et al., High swelling ability of polystyrene-based polyelectrolyte gels at low temperature. Soft Matter **7**, 5938–5940 (2011). doi:10.1039/C1sm05542a
17. T. Ono, T. Sugimoto, S. Shinkai et al., Lipophilic polyelectrolyte gels as super-absorbent polymers for nonpolar organic solvents. Nat. Mater. **6**, 429–433 (2007). doi:10.1038/Nmat1904
18. Y.S. Ye, S. Sharick, E.M. Davis et al., High hydroxide conductivity in polymerized ionic liquid block copolymers. ACS Macro Lett. **2**, 575–580 (2013). doi:10.1021/Mz400210a
19. J.H. Choi, Y.S. Ye, Y.A. Elabd et al., Network structure and strong microphase separation for high ion conductivity in polymerized ionic liquid block copolymers. Macromolecules **46**, 5290–5300 (2013). doi:10.1021/Ma400562a
20. T. Ishikawa, M. Kobayashi, A. Takahara, Macroscopic frictional properties of poly(1-(2-methacryloyloxy)ethy1-3-butyl imidazolium bis(trifluoromethanesulfonyl)-imide) brush surfaces in an ionic liquid. ACS Appl. Mater. Interfaces **2**, 1120–1128 (2010). doi:10.1021/Am9009082
21. H. Chen, Y.A. Elabd, Polymerized ionic liquids: solution properties and electrospinning. Macromolecules **42**, 3368–3373 (2009). doi:10.1021/Ma802347t
22. K. Vijayakrishna, S.K. Jewrajka, A. Ruiz et al., Synthesis by RAFT and ionic responsiveness of double hydrophilic block copolymers based on ionic liquid monomer units. Macromolecules **41**, 6299–6308 (2008). doi:10.1021/Ma800677h
23. A. Chapiro, Radiation chemistry of polymers. Radiat. Res. Suppl. **4**, 179–191 (1964). doi:10.2307/3583578
24. V.S. Ivanov, *Radiation Chemistry of Polymers* (CRC Press, Ohio, 1992), p. 5
25. E. Jabbari, S. Nozari, Swelling behavior of acrylic acid hydrogels prepared by gamma-radiation crosslinking of polyacrylic acid in aqueous solution. Eur. Polym. J. **36**, 2685–2692 (2000). doi:10.1016/S0014-3057(00)00044-6
26. N. Liu, M. Yi, M.L. Zhai et al., Radiation synthesis and characterization of polyDMAEMA hydrogel. Radiat. Phys. Chem. **61**, 69–73 (2001). doi:10.1016/S0969-806X(00)00373-X
27. G.A. Becht, M. Sofos, S. Seifert et al., Formation of a liquid-crystalline interpenetrating poly(ionic liquid) network hydrogel. Macromolecules **44**, 1421–1428 (2011). doi:10.1021/ma102146r
28. T.K. Carlisle, W.M. McDanel, M.G. Cowan et al., Vinyl-functionalized poly(imidazolium)s: a curable polymer platform for cross-linked ionic liquid gel synthesis. Chem. Mater. **26**, 1294–1296 (2014). doi:10.1021/Cm403885r
29. M. Isik, R. Gracia, L.C. Kollnus et al., Cholinium-based poly(ionic liquid)s: synthesis, characterization, and application as biocompatible ion gels and cellulose coatings. ACS Macro Lett. **2**, 975–979 (2013). doi:10.1021/Mz400451g
30. M.T. Rahman, Z. Barikbin, A.Z.M. Badruddoza et al., Monodisperse polymeric ionic liquid microgel beads with multiple chemically switchable functionalities. Langmuir **29**, 9535–9543 (2013). doi:10.1021/la401613w
31. Y. Xiong, J. Liu, Y. Wang et al., One-step synthesis of thermosensitive nanogels based on highly cross-linked poly(ionic liquid)s. Angew. Chem. Int. Edit. **51**, 9114–9118 (2012). doi:10.1002/anie.201202957
32. J. Bandomir, A. Schulz, S. Taguchi et al., Synthesis and characterization of polymerized ionic liquids: mechanical and thermal properties of a novel type of hydrogels. Macromol. Chem. Phys. **215**, 716–724 (2014). doi:10.1002/macp.201400009
33. C. Reichardt, Solvatochromic dyes as solvent polarity indicators. Chem. Rev. **94**, 2319–2358 (1994). doi:10.1021/Cr00032a005
34. S.G. Roy, U. Haldar, P. De, Remarkable swelling capability of amino acid based cross-linked polymer networks in organic and aqueous medium. ACS Appl. Mater. Interfaces **6**, 4233–4241 (2014). doi:10.1021/Am405932f
35. S.G. Starodoubtsev, A.R. Khokhlov, E.L. Sokolov et al., Evidence for polyelectrolyte ionomer behavior in the collapse of polycationic gels. Macromolecules **28**, 3930–3936 (1995). doi:10.1021/Ma00115a027
36. A.R. Khokhlov, E.Y. Kramarenko, Polyelectrolyte/ionomer behavior in polymer gel collapse. Macromol. Theory Simul. **3**, 45–59 (1994). doi:10.1002/mats.1994.040030104
37. H. Schott, Swelling kinetics of polymers. J. Macromol. Sci. Phys. **B31**, 1–9 (1992). doi:10.1080/00222349208215453
38. N.M. Franson, N.A. Peppas, Influence of copolymer composition on non-fickian water transport through glassy copolymers. J. Appl. Polym. Sci. **28**, 1299–1310 (1983). doi:10.1002/app.1983.070280404
39. V.T. Wyatt, The effects of solvent polarity and pKa on the absorption of solvents into poly(glutaric acid- glycerol) films. J. Appl. Polym. Sci. **131**, 40434 (2014). doi:10.1002/App.40434
40. J. Przybytek, P. Krieger, *High Purity Solvent Guide (2nd Edn) Burdick & Jackson Laboratories* (American Scientific Products, Muskegon, MI, 1984), p. 128
41. L. Snyder, Classification of the solvent properties of common liquids. J. Chromatogr. A **92**, 223–230 (1974). doi:10.1016/S0021-9673(00)85732-5
42. J. Bibette, F. Leal-Calderon, V. Schmitt et al., *Emulsion Science: basic principles. An overview* (Springer, Berlin, 2003), pp. 1–138
43. D.J. Mcclements, S.R. Dungan, Factors that affect the rate of oil exchange between oil-in-water emulsion droplets stabilized by a nonionic surfactant—droplet size, surfactant concentration, and ionic-strength. J. Phys. Chem. **97**, 7304–7308 (1993). doi:10.1021/J100130a030
44. C. Goubault, K. Pays, D. Olea et al., Shear rupturing of complex fluids: application to the preparation of quasi-monodisperse water-in-oil-in-water double emulsions. Langmuir **17**, 5184–5188 (2001). doi:10.1021/La010407x

45. C.C. Lin, A.T. Metters, Hydrogels in controlled release formulations: network design and mathematical modeling. Adv. Drug Deliv. Rev. **58**, 1379–1408 (2006). doi:10.1016/j.addr.2006.09.004
46. E.S. Dragan, M. Cazacu, A. Nistor, Ionic organic/inorganic materials. III. Stimuli responsive hybrid hydrogels based on oligo(N, N-dimethylaminoethylmethacrylate) and chloroalkyl-functionalized siloxanes. J. Polym. Sci. A Polym. Chem. **47**, 6801–6813 (2009). doi:10.1002/Pola.23720
47. J.W. Paquette, K.J. Kim, D. Kim, Low temperature characteristics of ionic polymer-metal composite actuators. Sens. Actuators A Phys. **118**, 135–143 (2005). doi:10.1016/j.sna.2004.08.006