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Swelling behavior of amphiphilic gels based on hydrophobically modified dimethylaminoethyl methacrylate

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ABSTRACT

The amphiphilic gels based on hydrophobically modified dimethylaminoethyl methacrylate with different 1-bromoalkanes (1-$C_nH_{2n+1}Br$, $n = 2, 4, 6, 8, 12$) were synthesized by radiation-induced polymerization and crosslinking. The length of alkyl side chains had significant influence on the swelling behavior of the resulting gels. The swelling degree of the gels decreased with the increase of side chain length, and the gel hardly swelled when $n = 12$. The effect of temperature and ionic strength on the swelling behavior of the resulting gels revealed that (1) the gels with longer side chains ($n \geq 8$) had upper critical solution temperature, while other gels were not thermo-sensitive. (2) Antipolyelectrolyte effect was observed when immersing the gels ($n \geq 8$) in NaCl solutions in certain concentration range. The dramatic difference in swelling behavior was attributed to the different gel structures. The gels with short side chains ($n \leq 6$) had cellular structure of normal polyelectrolyte gels. The gels ($n \geq 8$) had an aggregation gel structure caused by the hydrophobic interaction among alkyl groups and the formation of ion-cluster between tetra-alkyl ammonium cation and Br^-, which had been analyzed with the aid of SEM, Br^--selective electrode and fluorescence molecular probe.

1. Introduction

Amphiphilic gels have been reported to have potential applications in drug delivery systems (DDS) [1], modern valves and actuators [2], tissue engineering [3], as well as membranes separation [4]. Generally, amphiphilic gels are synthesized by copolymerization and crosslinking of hydrophilic and hydrophobic monomers [5–8]. Swelling behavior of amphiphilic gels depends mightily on the chemical composition and the distribution of hydrophobic monomeric units along the macromolecular chains. For example, Philippova et al. [6] prepared a series of pH-responsive gels by copolymerization and crosslinking of acrylic acid and different *n*-alkyl acrylates ($n = 8, 12, 18$). It was found that the critical swelling transition pH shifted to alkaline pH with increasing hydrophobicity of the gel, due to the stabilization of the collapsed state of the gel by hydrophobic aggregation of *n*-alkyl side chains. Moreover, the presence of hydrophobic units in random sequence with ionic units provides the corresponding gels with the property of extensive swelling/deswelling upon a small change in the environmental conditions. Therefore, amphiphilic polymer gels containing both hydrophobic and hydrophilic units are possible to bear novel swelling behavior, such as "super salt-resistivity" and inversed thermo-sensitivity compared with their parent hydrogels [9].

Poly(dimethylaminoethyl methacrylate) (PDMAEMA) has temperature and pH-stimuli responsive properties and DMAEMA has been used as precursor for the synthesis of amphiphilic polymers [9–15]. Recently, we have synthesized a new-type amphiphilic monomer methacryloxyethyl dimethyloctane ammonium bromide (MODAB) by quaternization of DMAEMA with 1-bromooctane, and then prepared amphiphilic PMODAB gel by radiation-induced polymerization and crosslinking [9]. It was found that PMODAB gel possessed distinct swelling behaviors from those of their parent PDMAEMA gel, where hydrophobic interactions showed apparent correlation with swelling behavior of the gel. Studies have certified that amphiphilic polymers tended to form micelles and aggregations as the length of the hydrophobic side chain increased ($n \geq 8$) [16–18]. Moreover, the presence of ionic units in charged polyelectrolyte could arouse specific interactions between the ions/water molecules and the charged groups when immersing the gels in different aqueous media [13,19–21]. These interactions will lead to different stimuli-responsive swelling behaviors of polymer gels in certain circumstance, providing the possibility on the designation of novel functional materials.

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Therefore, the investigation on the swelling behavior of the amphiphilic gels upon ion, temperature, pH-stimuli attracts our long term efforts.

In this work, the amphiphilic gels based on hydrophobically modified dimethylaminoethyl methacrylate with different 1-bromoalkanes (1-$C_nH_{2n+1}Br$, $n = 2$, 4, 6, 8, 12) were synthesized by radiation technique. The influence of alkyl side chains on swelling kinetics, as well as the temperature, ion-stimuli swelling behavior of the gels was investigated with the aid of SEM, Br^--selective electrode and fluorescence molecular probe. It was expected that the results would provide novel ideas on the design of amphiphilic gels and elucidate the relationship between the gel structure and their special swelling behavior.

2. Experimental section

2.1. Materials

Dimethylaminoethyl methacrylate (DMAEMA, 99% purity), 1-bromoethane (BE, 98% purity), 1-bromobutane (BB, 98% purity), 1-bromohexane (BH, 99% purity), 1-bromooctane (BO, 99% purity) and 1-bromododecane (BD, 98% purity) were provided by Acros and used as supplied. Poly(ethyleneglycol dimethacrylate) (PEGDMA, $M_n = 875$) was purchased from Aldrich. Pyrene (98% purity) was provided by Acros and recrystallized before use. Other chemicals for this study were analytic reagents obtained from Beijing Chemicals Company and used as-received.

2.2. Synthesis and characterization of monomers

Amphiphilic electrolytes, methacryloxyethyl dimethylethane ammonium bromide (MEDAB), methacryloxyethyl dimethylbutane ammonium bromide (MBDAB), methacryloxyethyl dimethylhexane ammonium bromide (MHDAB), methacryloxyethyl dimethyloctane ammonium bromide (MODAB) and methacryloxyethyl dimethyldodecane ammonium bromide (MDDAB) were synthesized by quaternization of DMAEMA with BE, BB, BH, BO and BD, respectively, using the same method as that of MODAB reported in our previous work [9]. Their characterization was supplied in Supporting Information.

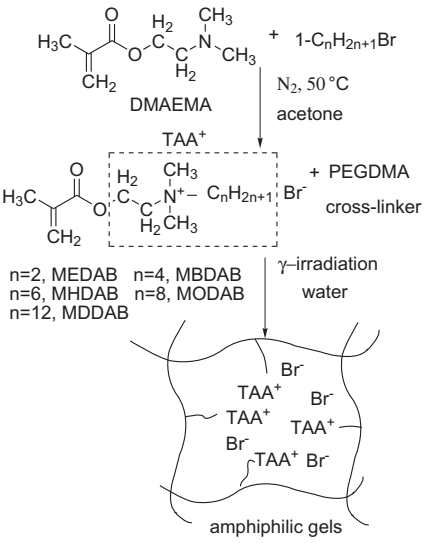
2.3. Synthesis of amphiphilic PMADAB gels

Synthesis route of amphiphilic poly(methacryloxyalkyl dimethylethane) ammonium bromide (PMADAB) gels is shown in Scheme 1. The concentrations of monomer and PEGDMA (cross-linker) are 1 mol L^{-1} and 1.2×10^{-4} mol L^{-1}, respectively. The monomer/PEGDMA aqueous solution was poured into glass tube with a diameter of 10 mm, and then bubbled with nitrogen for 15 min. Finally, the tube was sealed and irradiated to form the gels with desired absorbed dose at a dose rate of 20 Gy min^{-1} at room temperature. The resulting gels were cut into cylinders of ca. 5 mm length and dried in vacuum at 25 °C to constant weight.

2.4. Gel fraction

The sol part of the samples was extracted by deionized water (for gels ($n \leq 8$)) or acetone (for gel ($n = 12$)) and then dried in vacuum oven at 25 °C to constant weight. Gel fraction (G_f) of the gel was defined as

$$G_f(\%) = \frac{W_g}{W_0} \times 100 \quad (1)$$



Scheme 1. Synthesis route of amphiphilic gels.

where W_0, W_g were the weights of dried gel before and after removing sol, respectively.

2.5. Morphology

To maintain the network structure of amphiphilic gels, the swollen gels in different conditions were lyophilized. The cross-sectional morphology of amphiphilic gels in swollen state was then observed using Scanning Electron Microscope (SEM) (FEI Quanta 200F).

2.6. Swelling behavior

The gels synthesized at 5 kGy were used for swelling study, due to their good mechanical properties and high gel fractions. The dried gel was immersed in an excess amount of deionized water at 25 °C, and the swollen samples were weighed at various time intervals. The following equation was used to calculate S:

$$S = \frac{(W - W_0)}{W_0} \quad (2)$$

where W was the weight of swollen gel at desired time t, and W_0 was the weight of dried gel.

Temperature-dependent swelling was carried out in deionized water in a temperature range of 25–70 °C. The gel was swollen to equilibrium for a minimum period of 24 h. Ion-stimuli responsive swelling experiments were conducted in NaCl aqueous solutions with different concentrations (from 10^{-4} to 2 mol L^{-1}) at 25 °C. Each dried gel was immersed in the solution to reach swelling equilibrium, and then the swollen gel was removed from the media and weighed. The equilibrium degree of swelling (EDS) was also calculated according to Eq. (2), and here W was the weight of the gel at the equilibrium.

2.7. Br^--selective electrode potential measurement

The Br^--Selective Electrode Potential measurements were performed using a pH meter (Rex pHS-25), where a Br^- selective electrode (Rex pBr-1) and a reference electrode (Rex 232) were connected. All instruments were purchased from Shanghai Jingmi Scientific Instrument Co., Ltd. The Br^--selective electrode was activated in 10^{-3} mol L^{-1} KBr aqueous solution for 2 h before measurements. 0.1 mol L^{-1} KNO_3 was added into the sample

solutions to eliminate the influence of ionic strength on the potentials. Br^--selective potentials (E) of KBr aqueous solutions were measured in a range of 5×10^{-6} to 10^{-1} mol L^{-1}. All measurements were conducted at 27 ± 0.2 °C.

Dried gel with a certain weight was immersed into 100 mL deionized water or NaCl aqueous solution where the maximum EDS was reached in EDS–NaCl concentration curve. If the ion-clusters were formed between tetra-alkyl ammonium cation and Br^-, Br^- will not release in deionized water, however, will release in NaCl aqueous solution via ion-exchange. The amount of "free" Br^- released from the gel into the swelling medium was measured using a Br^--selective electrode, and then was calculated according to the calibration curve of E versus $\log(C_{KBr})$ ($R^2=0.9998$).

2.8. Fluorescence analysis

Fluorescence spectra were recorded with an F-4500 spectrofluorimeter using pyrene as probe. The quartz cell was connected to a thermostat via cycling water. Excitation and emission bandwidths were set at 10 nm and 2.5 nm, respectively. The excitation wavelength was 335 nm. The ratio of the intensities of the third (~386 nm) peak to the first (~375 nm) peak in the fluorescence spectrum of pyrene, i.e., I_3/I_1, was used to estimate the polarity of the pyrene microenvironment.

The gel samples for fluorescence measurements were prepared using the method prescribed by Philippova et al. [18]. To perform the fluorescence measurements, the gels were cut into suitable sizes to fit the quartz cell. In this study, the fluorescence emission spectra of pyrene embedded in PMODAB gel swollen at different temperatures and salt concentrations were measured. It should be noted that the gels were assured to attain swelling equilibrium in these different conditions before fluorescence measurements being conducted.

3. Results and discussion

3.1. Synthesis of amphiphilic PMADAB gels

Gel fractions of amphiphilic PMADAB gels and PDMAEMA gel as a function of absorbed dose are shown in Fig. 1. Similar to other gels, the formation of gels starts at a critical absorbed dose (gelation dose), and the gel fraction increases sharply with the increasing dose in a narrow range and then level off. It was found that amphiphilic gels were synthesized at lower dose and the gel fractions were much higher compared with that of their parent PDMAEMA gel. It has been reported that quaternary ammonium salt could be used as catalyst for the crosslinking of methacrylate monomers [22], therefore, the amphiphilic monomers containing quaternary ammonium group have high tendency to be crosslinked. Moreover, the presence of bromine (Br) in monomers is also favorable for the formation of gel [23].

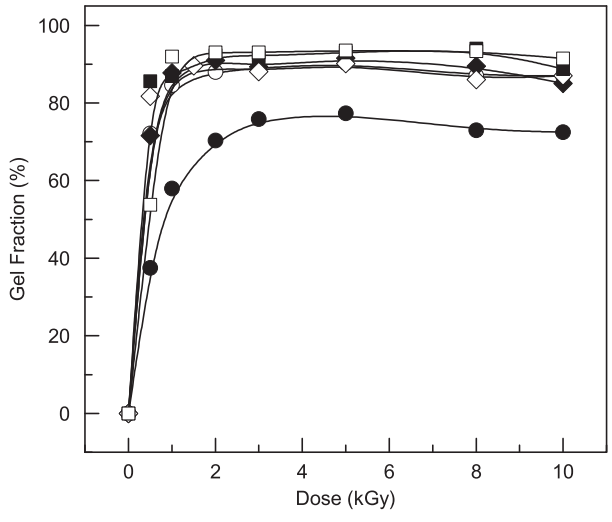


Fig. 1. Gel fraction of amphiphilic gels and PDMAEMA gel, ●-PDMAEMA gel; ○-PMEDAB gel; ◆-PMBDAB gel; ◇-PMHDAB gel; ■-PMODAB gel; □-PMDDAB gel.

3.2. Morphology of gels

With the observation of naked eye, the gels with shorter side chains ($n\le6$) and PDMAEMA gel are transparent and elastic, while the gels with longer side chains ($n\ge8$) are milk-white and opaque. Moreover, PMODAB gel is soft, while PMDDAB gel is fragile. In order to elucidate their difference on microstructure, the morphology of the gels in different swelling media was observed by SEM (Fig. 2). It was found that the amphiphilic gels with shorter side chains ($n\le6$) are similar to that of PDMAEMA gel (Fig. 2a), which has cellular structure of normal gels. Due to the similarity of the morphology of these gels ($n\le6$), we merely provide the image of PMBDAB gel ($n=4$) in Fig. 2b. However, PMODAB and PMDDAB gels are composed by aggregations, though the aggregations are of different appearance (Fig. 2c and d). The MADAB ($n\ge8$)/PEGDMA/H_2O solution was slightly opaque even before irradiation, which means that phase separation occurred in the solutions via monomer–solvent interaction. In our previous work, Xu et al. pointed out that the particulate aggregation of PMODAB gel is caused by the hydrophobic interactions between the octyl chains and ion-cluster formation between the tetra-alkyl ammonium cation and Br^- [9]. In this work, this hypothesis will be further proved by other experiments, i.e., the ion-cluster formation is studied by Br^--selective electrode, and the hydrophobic interaction is analyzed by fluorescence analysis.

3.3. Swelling behavior

Swelling isotherm of amphiphilic gels and PDMAEMA gel in deionized water at 25 °C is plotted in Fig. 3. It is clear that the length of alkyl side chains has obvious influence on the swelling behavior of the resulting gels. Schott [24] proposed second order kinetics model to describe the swelling procedure of hydrogels:

$$\frac{dS}{dt}=k_S(S_\infty-S)^2 \tag{3}$$

With initial condition $t=0$, $S=0$, it can be deduced as

$$\frac{t}{S}=A+Bt \tag{4}$$

where k_S is the rate constant of swelling, S_∞ is the maximum swelling degree theoretically. $A=1/k_SS_\infty^2=1/(dS/dt)_0$, which is the reciprocal of initial swelling rate (r_0). B is the reciprocal of S_∞. With the curve of $t/S\sim t$, S_∞ and k_S can be calculated. The results are presented in Table 1.

The value of S_∞ calculated by Eq. (4) ($S_{\infty,c}$) is similar to that obtained from experiments ($S_{\infty,e}$), showing that the model fit the swelling behavior of the amphiphilic gels, which was testified by correlation coefficients. The results manifested that amphiphilic gels with shorter alkyl chains possessed higher rate constant of swelling and EDS, indicating that these short-chain amphiphilic gels would become new-type absorbent materials. The difference in swelling rate and EDS of the resulting amphiphilic gels attributes mainly to the influence of different lengths of alkyl chains [3,25]. Generally, the EDS of the gel decreased after being hydrophobically modified, due to the increase of hydrophobicity [3]. For this reason,

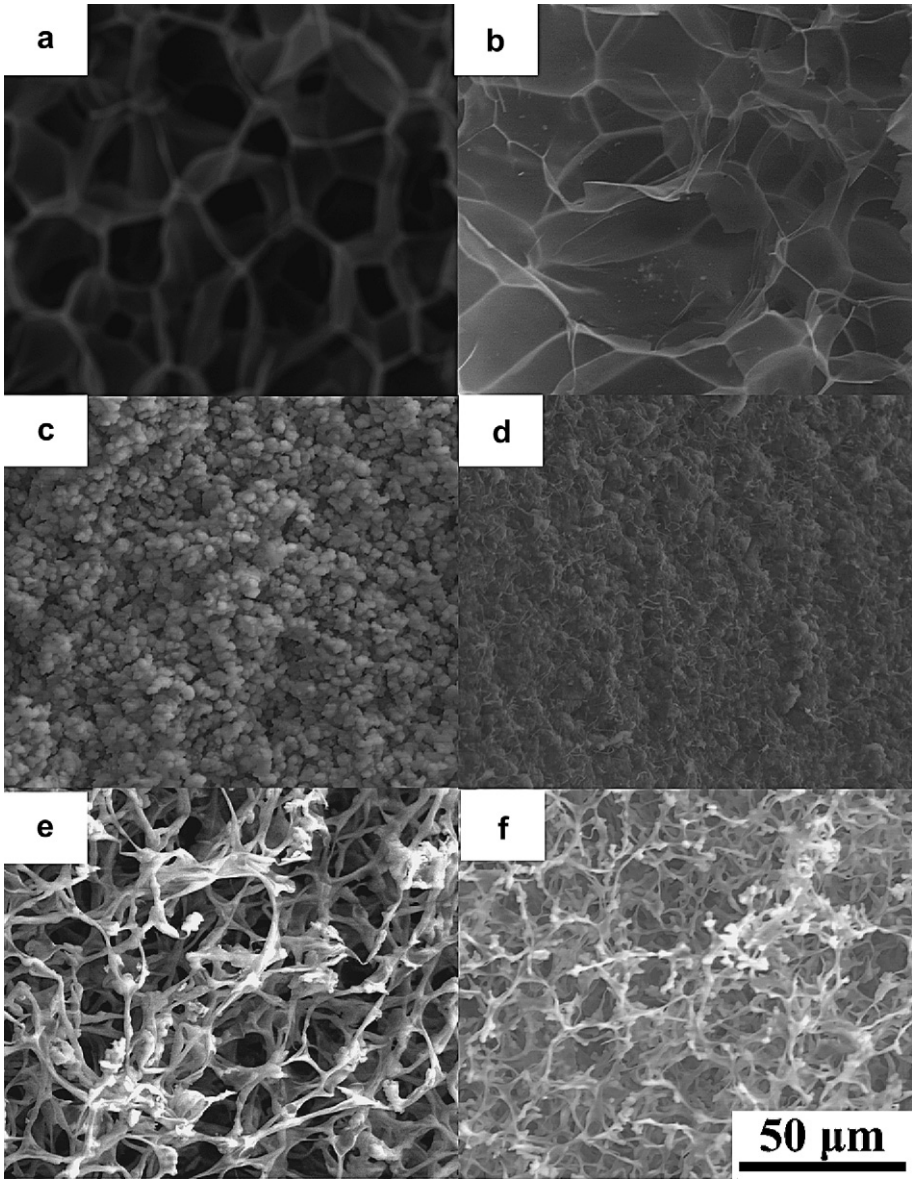


Fig. 2. SEM image of the swollen gels: (a) PDMAEMA gel swollen in water at 25 °C; (b) PMBDAB gel swollen in water at 25 °C; (c) PMODAB gel swollen in water at 25 °C; (d) PMDDAB gel swollen in water at 25 °C; (e) PMODAB gel swollen in water at 45 °C; (f) PMODAB gel swollen in NaCl solution with 5×10^{-3} mol L^{-1} at 25 °C.

the EDS of the resulting amphiphilic gels decrease with increasing alkyl chain length.

The following equation was usually used to describe the initial stages of swelling ($S/S_\infty \leq 0.6$) [10,26],

$$F = \frac{S}{S_{eq}} = kt^n \quad \text{or} \quad \ln F = \ln k + n \ln t \tag{5}$$

where 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 1. The values of diffusion exponent n indicate that the diffusion of water molecules into the gels can be regarded as non-Fickian diffusion. Due to the entanglement of alkyl chains in the amphiphilic gels, the relaxation rate of the polymer matrix is slower than the diffusing rate of water molecules in gels. Therefore, the relaxation of the polymer chain determines the swelling process so that the swelling of PMADAB gels behave as non-Fickian diffusion. Furthermore, n decreases with the increase of the length of alkyl side chains.

Fig. 3a also shows that the amphiphilic gels with shorter side chains ($n \leq 6$) have higher EDS than that of their parent PDMAEMA gel. The higher EDS is due to the characteristic of cationic polyelectrolytes of the resulting amphiphilic gels, while PDMAEMA gel is non-ionic in neutral solution. It is well established that swelling pressure of mobile counterions is mainly responsible for the swelling of polyelectrolyte gels [27,28]. The increasing charge density and osmotic pressure have positive effect on the EDS of polyelectrolyte gels. Another possible driving force of gel swelling could be the electrostatic repulsion force among the ionic groups [29], which favors an expanded conformation, leading to the diffusion of water molecules and other species into the interior of the gel. As a result, the EDS of the gel with shorter side chains ($n \leq 6$) are higher than their parent PDMAEMA gel.

However, the EDS of PMODAB and PMDDAB gels are only 1.9 and 0.17, respectively (Fig. 3b), PMDDAB gels hardly swells. This could be ascribed to the aggregation structure of PMODAB and PMDDAB gels, caused by strong hydrophobic associations and ion-cluster

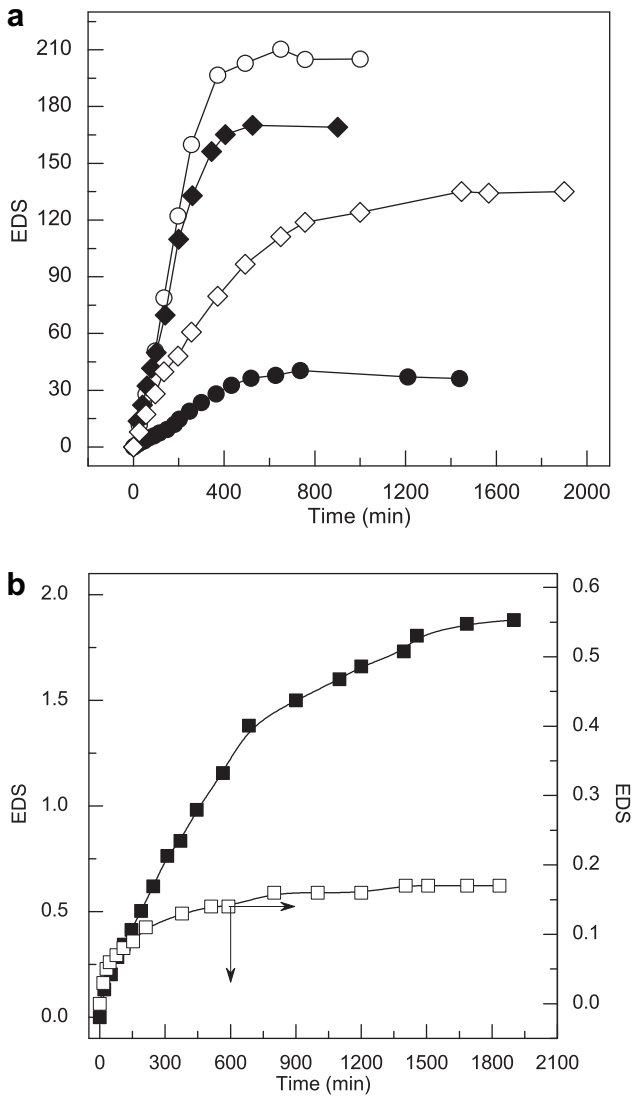


Fig. 3. Swelling kinetics of amphiphilic gels and PDMAEMA gel, (a)●-PDMAEMA gel; ○-PMEDAB gel; ◆-PMBDAB gel; ◇-PMHDAB gel; (b) ■-PMODAB gel; □-PMDDAB gel.

formation inside the gels. It is known that hydrophobic associations disfavor the swelling of gels. Besides, the formation of ion-cluster should lead to two main effects: the significant decrease of the osmotic pressure of mobile counterions in the gel and additional crosslinking point of the gel. And these two effects lead to a decrease of swelling degree of gel [30].

Table 1
Data of the swelling kinetics of amphiphilic gels.

	PMEDAB	PMBDAB	PMHDAB	PMODAB	PMDDAB
k_s (h^{-1})	8.9×10^{-2}	3.7×10^{-2}	6.0×10^{-2}	6.5×10^{-5}	1.3×10^{-5}
$S_{\infty,c}$	213.2	173.3	134.6	2.1	0.18
$S_{\infty,e}$	205.1	169.7	134.2	1.9	0.17
R_4	0.9980	0.9935	0.9944	0.9827	0.9989
k	1.3×10^{-3}	5.1×10^{-3}	3.9×10^{-2}	1.0×10^{-2}	5.3×10^{-3}
n	1.16	0.89	0.86	0.62	0.47
R_5	0.9997	0.9954	0.9960	0.9956	0.9904

$S_{\infty,c}$: The data were calculated according to Eq. (4).
$S_{\infty,e}$: The data were obtained by swelling experiments.
R_4: The correlation coefficient of Eq. (4).
R_5: The correlation coefficient of Eq. (5).

3.4. Temperature-stimuli responsive swelling

Fig. 4 demonstrates the temperature-stimuli swelling behavior of amphiphilic gels and PDMAEMA gel. It is found that alkyl side chains have prominent influence on the temperature-stimuli responsive of the resulting amphiphilic gels. Amphiphilic gels with shorter side chains ($n \leq 6$) are not thermo-sensitive (Fig. 4a), while PMODAB and PMDDAB gels have upper critical solution temperature (UCST) at 48 and 35 °C, respectively (Fig. 4b).

In the study of the LCST of water-soluble polymers, Taylor and Cerankowski proposed a general rule that the LCST should decrease with the increase of polymer hydrophobicity [31]. Recently, electrostatic repulsion was also found to play a significant role in the LCST of thermo-sensitive polymers by preventing the collapse and aggregation of the polymer chain [25,32]. For example, when poly(dimethylaminoethyl methacrylate-co-acrylamide) (poly(DMAEMA-co-AAm)) solution was acidified to pH 4, poly(DMAEMA-co-AAm) lost its thermo-sensitivity. Because N,N-dimethylaminoethyl groups of DMAEMA were fully ionized at pH 4 and the increased electrostatic repulsive force was developed between charged sites on DMAEMA, which interfered the hydrophobic interactions between

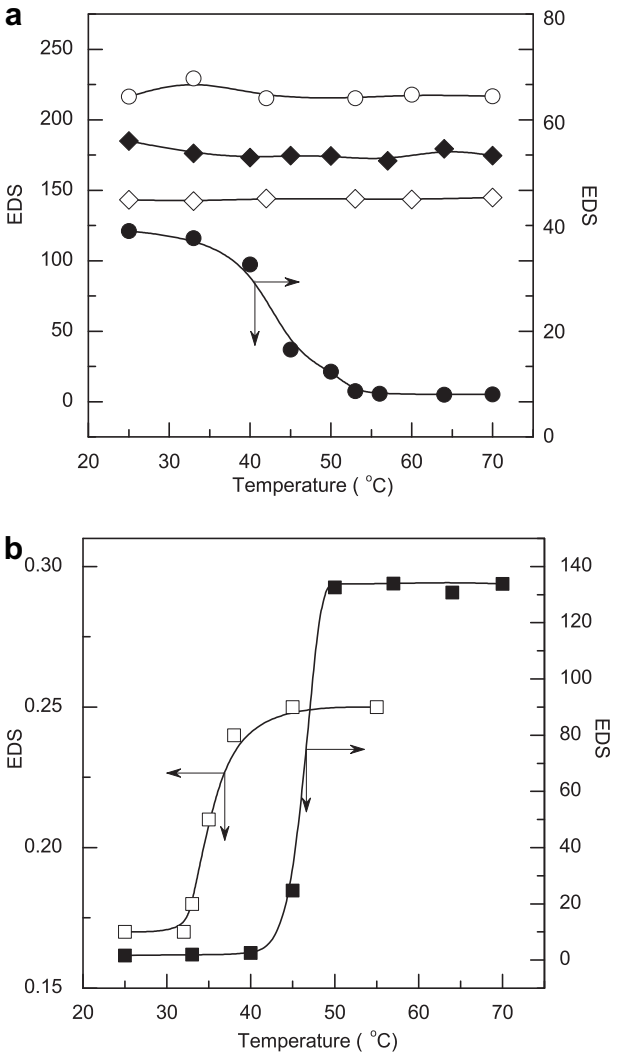


Fig. 4. Temperature-stimuli responsive swelling behavior of amphiphilic gels ($n = 2, 4, 6$) and PDMAEMA gel. (a) amphiphilic gels with shorter chains ($n = 2, 4, 6$) and PDMAEMA gel; (b) amphiphilic gels with longer chains ($n = 8, 12$). ●-PDMAEMA gel; ○-PMEDAB gel; ◆-PMBDAB gel; ◇-PMHDAB gel; ■-PMODAB gel; □-PMDDAB gel.

N,N-dimethylaminoethyl groups above LCST [32]. Similarly, amphiphilic gels with shorter side chains ($n \leq 6$) do not exhibit temperature sensitivity should be attributed to their molecular structure of cationic polyelectrolyte.

For the amphiphilic gels with longer chains ($n \geq 8$), the increment of gel volume can be ascribed to the phase transition from heterogeneous to homogeneous structure upon mixing of H (hydrophobic) and P (hydrophilic) portions at elevated temperature. Take PMODAB gel for example, it was observed that the long alkyl chains in PMODAB gel adopt an aggregate structure below the phase transition temperature (Fig. 2c), and became soft and flexible above UCST, i.e., aggregations were disrupted at higher temperature (Fig. 2e). The UCST of PMDDAB gel is lower than that of PMODAB gel, probably because the slight swelling of PMDDAB gel only occurred in the exterior of the network. Thus, lower energies are needed for the phase transition of PMDDAB gel compared with PMODAB gel. Investigations on this aspect are still underway in our laboratory.

3.5. Ion-stimuli responsive swelling

Ion-stimuli responsive swelling behavior (at 25 °C) of amphiphilic gels and PDMAEMA gel is shown in Fig. 5. Even though all resulting amphiphilic gels have similar strong cation-charged structure, their swelling behaviors are distinct. The amphiphilic gels with shorter hydrophobic alkyl chains ($n \leq 6$) behave similar with normal polyelectrolyte gels. For instance, their EDS decreased quickly with increasing NaCl concentration (Fig. 5a), due to the decrease of osmotic pressure, breakage of hydrogen bond as well as the screen of electrostatic repulsion force in the presence of electrolyte [27,28].

However, the amphiphilic gels with longer hydrophobic alkyl chains ($n \geq 8$) exhibit antipolyelectrolyte effect in NaCl solution with lower concentrations at 25 °C. PMODAB and PMDDAB gels show a maximum EDS in 5×10^{-3} mol L^{-1} and 2×10^{-3} mol L^{-1} NaCl aqueous solutions, respectively (Fig. 5b). The antipolyelectrolyte effect is correlated to the ion-cluster formation in the network. It is known that ion pairs are possibly formed inside the gel in strong polyelectrolyte gels and result in ion-cluster formation [13,33,34]. According to Desnoyers' hydration shell overlapping model, ions of similar hydration energy are apt to form a stable ion pair [35]. Large anions (like ClO_4^-) with low hydration energies can interact very strongly with the quaternary ammonium pendant groups through ion pair interactions [34]. Because Br^- (hydration energy is -321 kJ mol^{-1}) has inherent affinity to ammonium cations due to their similar hydration energies (for example, -292 kJ mol^{-1} for NH_4^+) [35], stable ion pairs are likely to formed between tetra-ammonium cation and Br^-. X-ray absorption fine structure (XAFS) spectra of Br^- in quaternary ammonium salt electrolyte have shown the coexistence of hydrated Br^- and that forms of ion pairs with the tetra-ammonium cations [36]. It was also confirmed that ion pairs are more easily to form in less polar systems [37]. The assertion on the formation of ionic pairs in amphiphilic gels, especially PMODAB and PMDDAB gels, could be verified using the Br^--selective electrode analysis. As we can see in Table 2, the "free" Br^- inside the gels decreased with the increasing of the hydrophobicity of the gels, because the local polarity of the polymer inside the gels became lower. The "free" Br^- in PMBDAB gel is about 31% of the total Br^- in the network, while, only 2.4% and 0.4% Br^- are "free" in PMODAB and PMDDAB gels. Therefore, PMBDAB gel can be deemed as polyelectrolyte and exhibits polyelectrolyte effect in NaCl aqueous solution. PMODAB and PMDDAB gels are in a different situation. Take PMODAB for example, 97.6% Br^- inside the network formed ion pairs with tetra-ammonium cations. As a result, swelling pressure of free counterions in PMODAB gel was very low, leading to a very small EDS. When PMODAB gel was immersed in 5×10^{-3} mol L^{-1} NaCl solution, 44.4% Br^- inside the gel became "free". The increment of "free" Br^- concentration might be ascribed to the dissociation of ion pairs by Cl^- (hydration energy is -347 kJ mol^{-1}) [35], which disfavored ion-cluster formation with ammonium cations. The increasing number of free ionic groups in PMODAB gels led to an increment of swelling degree due to the additional osmotic pressure provided by the released counterions inside the gel [13]. The increase of EDS could

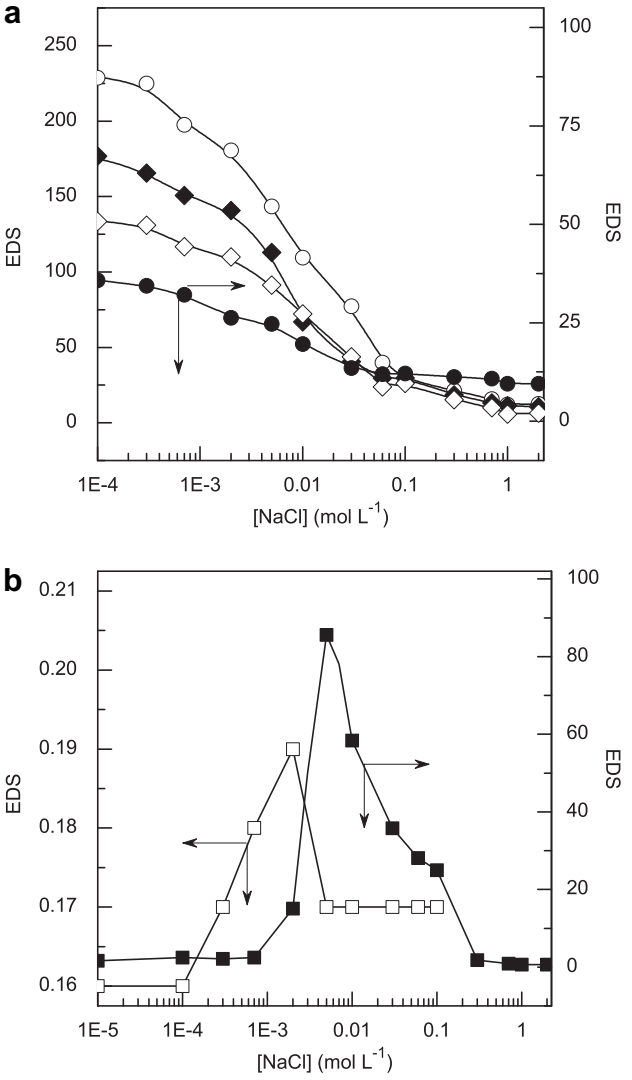


Fig. 5. Ion-stimuli responsive swelling behavior of amphiphilic gels and PDMAEMA gel. (a) Polyelectrolyte effect of amphiphilic gels ($n = 2, 4, 6$) and PDMAEMA gel at 25 °C; (b) antipolyelectrolyte effect of amphiphilic gels ($n = 8, 12$) at 25 °C. ●-PDMAEMA gel; ○-PMEDAB gel; ◆-PMBDAB gel; ◇-PMHDAB gel; ■-PMODAB gel; □-PMDDAB gel.

Table 2
The change of "free" Br^- percentages inside amphiphilic gels with the adding of NaCl.

Gel	["free" Br^-]/[total Br^-] (%)		
	H_2O	2×10^{-3} M NaCl solution	5×10^{-3} M NaCl solution
PMBDAB	30.1	37.9	43.1
PMODAB	2.4		44.4
PMDDAB	0.4	7.5	

["free" Br^-]: the concentration of Br^- ions which do not form ion pairs with tetra-ammonium cations.
[total Br^-]: the concentration of Br^- ions consist of free Br^- and that form ion pairs with tetra-ammonium cations.
"M" is abbreviated for mol L^{-1}.

Table 3
The intensity ratio I_3/I_1 of pyrene embedded in PMODAB gel at different temperatures and NaCl concentrations.

	Temperatures (°C)			[NaCl] solution (mol L^{-1})			
	25	48	60	5×10^{-4}	5×10^{-3}	0.05	0.5
I_3/I_1	0.74	0.69	0.69	0.72	0.69	0.73	0.74

also be ascribed to the enhanced hydrophilicity during the ion pair dissociation [34]. Xu et al. found that EDS of PMODAB gels in NaBr solution were lower than that in deionized water and decreased with increasing NaBr concentration [9]. In this work, it was observed that the aggregation structure of PMODAB gel was disrupted in NaCl solution with 5×10^{-3} mol L^{-1} (Fig. 2f).

The disassociation of ion pairs is less significant in PMDDAB than in PMODAB gel, because ion-exchange between Cl^- and Br^- mainly occurred in the exterior of the PMDDAB network. That explains well why the maximum EDS of PMDDAB gel was observed in NaCl solution with a lower concentration, compared with PMODAB gel.

3.6. Fluorescence measurements

PMODAB gel was selected for further fluorescence analysis. Table 3 shows the change of I_3/I_1 of pyrene embedded in PMODAB gel with the change of temperature and concentration of NaCl solutions. It can be observed that I_3/I_1 decreased from 0.74 (below UCST) to 0.69 (above UCST), which indicated that pyrene has been shifted from a relatively hydrophobic microenvironment to a more hydrophilic one, due to the breakdown of particulate aggregations at higher temperature (Fig. 2c).

The I_3/I_1 first decreased from 0.74 to 0.69 and then increased to 0.74 as the NaCl concentration increased from 0 to 0.5 mol L^{-1}, and the transition occurred at a concentration of 5×10^{-3} mol L^{-1}. The decrease of I_3/I_1 in the low NaCl concentration region (0–5×10^{-3} mol L^{-1}) suggested the increase of hydrophilicity around pyrene, which confirmed that the hydrophobic microdomains and ion pairs could be destructed by adding NaCl (Fig. 2d). When the NaCl concentration was higher than 5×10^{-3} mol L^{-1}, the gels began to deswell and the octyl chains could be more densely packed inside the microdomains which provided more hydrophobic sites for solubilized pyrene molecules, leading to the increment of I_3/I_1. These results correspond well with the swelling behavior, further supporting the antipolyelectrolyte swelling mechanism of PMODAB gel as we proposed.

4. Conclusions

Amphiphilic electrolytes, methacryloxyethyl dimethylalkyl ammonium bromides (MADAB) with different alkyl chains, were synthesized by quaternization of DMAEMA with 1-bromoalkanes (1-$C_nH_{2n+1}Br$, $n = 2, 4, 6, 8, 12$). Then the amphiphilic PMADAB gels were prepared successfully by radiation-induced polymerization and crosslinking, using PEGDMA as cross-linker. Study of swelling kinetics indicated that the length of alkyl side chains had significant influence on swelling behavior of the resulting gels. The EDS of the amphiphilic gels decreased as the length of side chains increased, and the gel hardly swollen in water when $n = 12$. The effect of temperature and salt concentration on the swelling behavior of the gels has been further investigated and found that (1) PMADAB gels with longer side chains ($n \geq 8$) had UCST, while other gels were not thermo-sensitive. (2) Antipolyelectrolyte effect was observed when immersing the gels ($n \geq 8$) in NaCl solutions at certain concentration range. The significant difference in swelling behavior between PMADAB gels with shorter side chains ($n \leq 6$) and that with longer side chains ($n \geq 8$) lies in their different gel structures. PMADAB gels ($n \leq 6$) have cellular gel structure, while PMADAB gels ($n \geq 8$) have an aggregation gel structure. With the aid of SEM, Br^--selective electrode and fluorescence molecular probe, it was suggested that the special swelling behavior of PMADAB gels ($n \geq 8$) was attributed to the aggregation gel structure caused by the hydrophobic interaction among alkyl groups and the formation of ion-clusters between tetra-alkyl ammonium cation and Br^-.

Appendix. Supplementary data

The supplementary data associated with this article can be found in the on-line version at doi:10.1016/j.polymer.2009.08.018.

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