

Overshooting Effect of Poly(Dimethylaminoethyl Methacrylate) Hydrogels

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ABSTRACT: An overshooting effect was observed during the swelling procedure of poly(dimethylaminoethyl methacrylate) (PDMAEMA) gel for the first time. The effects of the temperature, ionic strength, and pH on the overshooting effect of the PDMAEMA gel were investigated. We found that the overshooting effect of the gel could not be eliminated by changing the temperature; however, the overshooting effect was indiscernible in high-concentration NaCl solutions (>0.2 mol/L) and basic (pH 11.9) and acidic solutions (pH = 2.1). The overshooting effect of the PDMAEMA gel was attributed to the dynamic conformational changes of the side chains of

dimethylaminoethyl methacrylate (DMAEMA) units during the swelling of the gels. In the presence of NaCl or NaOH, the stretching of the macromolecular chains of the gels was disrupted. While in acidic solution, the protonation of tertiary amino groups in the DMAEMA units made the side chains of the DMAEMA units change from the cyclic conformation to the stretched one; this was analyzed with the aid of Fourier transform infrared spectroscopy. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2027–2033, 2011

Key words: hydrogels; kinetics (polym.); swelling

INTRODUCTION

Stimuli-responsive hydrogels, which will change their structure and physical properties in response to external stimuli, are very attractive materials for applications in biomaterial science and technology, such as controlled drug-delivery systems.^{1,2} An important parameter to consider in designing these systems is the swelling kinetics of the hydrogels. After reviewing the current literature, we found the swelling curves of hydrogels presenting a curvature, which is known as an overshooting effect, in some articles.^{3–11} When a gel exhibits an overshooting effect during the swelling process, it will first swell to a maximum swelling ratio (SR) and then gradually deswell before it reaches swelling equilibrium.

Since the first report of an overshooting effect in the 1980s, much attention has been paid to the qualitative explanation of this phenomenon. Peppas and coworkers^{3–5} assumed that the phenomenon was related to the relaxation of the macromolecular chain in polystyrene gels; that is, the solvent diffuses into the gel network before chain relaxation (diffusion is faster than relaxation), and SR reaches a maximum.

However, when the chains do finally relax, the solvent is forced out of the network, and the swelling equilibrium is eventually achieved. Lee and Chen¹² described the overshooting effect of copolymeric gels prepared from 2-hydroxyethyl methacrylate and 3-dimethyl(methacryloyloxyethyl) ammonium propane sulfonate. They also assumed that the phenomenon was associated with molecular relaxation in the gels. Some groups^{7,8,10} have held the opinion that the deswelling was caused by physical crosslinking within the gel systems. Valencia and Pierola⁷ attributed the overshooting effect of poly(*N*-vinylimidazole-*co*-sodium styrenesulfonate) gels to the formation of ionic pairs. During the swelling process of the gel, ionic pairs formed between sulfonate groups and neighboring protonated imidazole moieties with the relaxation of the macromolecular chains. The ionic pairs behaved as crosslinking points that decreased SR. Diez-Pena et al.⁸ and Yin et al.¹⁰ observed a remarkable overshooting effect of poly(*N*-isopropylacrylamide-*co*-methacrylic acid) hydrogels and poly(sodium alginate-*g*-acrylic acid) hydrogels in acidic medium, respectively. Both explained the phenomenon on the basis of a cooperative physical crosslinking process caused by hydrogen-bond formation between the carboxyl groups of the hydrogels in a hydrophobic environment. The appearance of intermolecular forces changed the degree of crosslinking and led to the decrease in SR of the gel.

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From the previously discussed references, we found no universal explanation for the overshooting effect of the gels because it was observed in totally different gel systems and depended on a large number of factors, such as geometry of the sample,⁴ temperature,¹² pH of the swelling medium,^{8,10} crosslinking degree,³ and ionic strength of the medium.¹³ So the overshooting effect of gels needed be investigated further.

Poly(dimethylaminoethyl methacrylate) (PDMAEMA) is an important stimuli-sensitive polymer because of its thermal and pH stimuli-responsive phase-transition behavior.¹⁴ Plenty of research studies have been concerned with the synthesis and characterization of PDMAEMA-based gels and their applications as controlled release systems and water treatment.^{15–17} In our previous study, PDMAEMA-based hydrogels were synthesized by γ or UV radiation.^{18–25} The PDMAEMA hydrogel was found to have a lower critical swelling temperature from 40 to 50°C, depending on the synthesis conditions. The pH stimuli response occurred at a critical pH value of about 3; that is, the hydrogel deswelled significantly at pH 3. Furthermore, the PDMAEMA hydrogel exhibited a polyelectrolyte effect in NaCl aqueous solutions.

In our recent study on the specific swelling of hydrophobically modified PDMAEMA gels, an overshooting phenomenon of the PDMAEMA gels was also observed.²⁵ In this study, the mechanism of the overshooting effect of the PDMAEMA gels was investigated. We expected that the results would be useful for their applications in drug-delivery systems, water treatment, and so on.

EXPERIMENTAL

Materials

Dimethylaminoethyl methacrylate (DMAEMA; 99% purity) was provided by Acros (Geel – Belgium) and was used as supplied. Poly(ethylene glycol dimethacrylate) (PEGDMA; number-average molecular weight = 875) was purchased from Aldrich (St. Louis, MO). Other chemicals were analytic reagents obtained from Beijing Chemicals Co. and were used as received.

Synthesis of the PDMAEMA gels

The PDMAEMA gels were synthesized by radiation-induced crosslinking with the same method reported in our previous study.²⁵ The concentrations of the monomer and PEGDMA (crosslinker) were 1 and 1.2×10^{-4} mol/L, respectively. The DMAEMA/PEGDMA aqueous solution was poured into the glass tube with a diameter of 10 mm and then bubbled with nitrogen for 15 min. Finally, the tube

was sealed and irradiated at 5 kGy to form gels at a dose rate of 20 Gy/min at room temperature. The resulting gels were cut into cylinders of about 5 mm in length and dried *in vacuo* at 25°C to a constant weight.

Characterizations of the PDMAEMA hydrogels

Swelling experiments

The dried gels were immersed in different media until swelling equilibrium was reached. The swollen gels were withdrawn at regular time intervals from the media, weighed after the removal of excess surface water with filter paper, and placed again in the same solution. SR was obtained with the following equation:

$$SR = \frac{(W - W_0)}{W_0} \quad (1)$$

where W is the weight of the swollen gel at the desired time and W_0 is the weight of the dried gel.

The temperature-dependent swelling kinetics were studied in deionized water in the temperature range 25–60°C. Ion-stimuli responsive swelling experiments were conducted in an NaCl aqueous solution with different concentrations ranging from 10^{-4} to 1 mol/L. The pH-dependent swelling kinetics were conducted in an acid solution (pH 2.1) and a basic solution (pH 11.9). To diminish the influence of ion species and ionic strength on the swelling behavior of the PDMAEMA hydrogel, solutions with various pH values were prepared from HCl + NaCl for low pH and NaOH + NaCl for high pH with a fixed total ion concentration of 0.01 mol/L.

Scanning electron microscopy (SEM) analysis

To maintain the network structure of the PDMAEMA hydrogels, the swollen gels were lyophilized. The cross-sectional morphology of the gels in the swollen state was then observed with SEM (FEI Quanta 200F).

Fourier transform infrared (FTIR) spectroscopy analysis

The FTIR measurement was performed on a Nicolet iN10 MX (ANALYZE Inc., Chandler, AZ, United States) with a Nicolet NicPlan IR microscope attachment (resolution = 4 cm^{-1} , scans = 64 time) and an MCT/A detector over the range $4000\text{--}650 \text{ cm}^{-1}$. If an overshooting effect was observed in the swelling medium, the swollen gels at different swelling processes were used for the experiments; otherwise, the gels swollen to equilibrium were used.

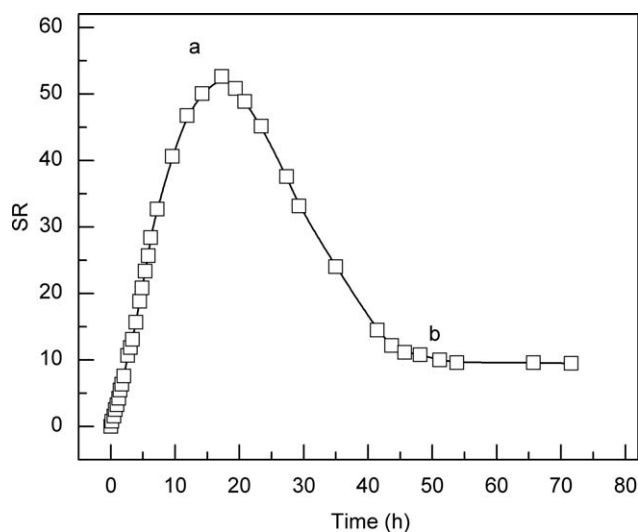


Figure 1 Dynamic swelling curve (SR vs time) of the PDMAEMA hydrogels in water at 25°C.

RESULTS AND DISCUSSION

Overshooting effect of the PDMAEMA hydrogels

The dynamic swelling curve of the PDMAEMA hydrogels in water (25°C) is shown in Figure 1. SR of the hydrogels increased rapidly at the initial swelling stage, then slowed down gradually, and finally reached equilibrium. This phenomenon is called an *overshooting effect* of the PDMAEMA hydrogels. From our observation, the PDMAEMA hydrogels were transparent before the maximum SR was reached, and the hydrogels became opaque after the overshooting. The opacity of the gels was found to be dependent on the aggregation of macromolecular chains in the gels.^{8,26} The SEM image in Figure 2 shows the internal morphologies of the PDMAEMA hydrogels at different swelling states. The pore of the gel network at the maximum SR [Fig. 2(a)] was approximately four times larger than that corre-

sponding to the equilibrium SR [Fig. 2(b,c)]; this showed that the aggregation of the macromolecular chains occurred in the deswollen PDMAEMA gels.

van de Wetering et al.²⁷ studied the hydrolytic stability of PDMAEMA and proposed that the side chains of the DMAEMA units in the polymer adopted a cyclic conformation (see Scheme 1) instead of a stretched one, which made the amino group less accessible for protonation and the ester group less susceptible to nucleophilic attack of hydroxyl ions. Obviously, the cyclic conformation is a thermodynamically stable status. On the basis of these considerations, we propose that there exist two conformations of the side chains of DMAEMA units during the swelling process of the PDMAEMA hydrogel: the cyclic conformation (preferential) and the stretched conformation. As described in Scheme 1, the side chains of the DMAEMA units in the dried gel adopted the cyclic conformation; when the gel was immersed in water, the hydrogen-bond interaction between the tertiary amino group and water overwhelmed the conjugation interaction between the amino group and carboxyl, the side chains of the DMAEMA units changed into the stretched conformation, and SR of the gel increased. However, the molecular chains eventually returned to the cyclic conformation, which was the thermodynamically stable conformation. The formation of the cyclic conformation of the side chains of the DMAEMA units may be considered as a kind of aggregation [Fig. 2(b)], which diminished the swelling capacity and, therefore, led to water expulsion.

Influence of the temperature on the overshooting effect of the PDMAEMA hydrogels

The influence of temperature on the overshooting effect of the PDMAEMA hydrogels is shown in Figure 3. When the temperature was lower than

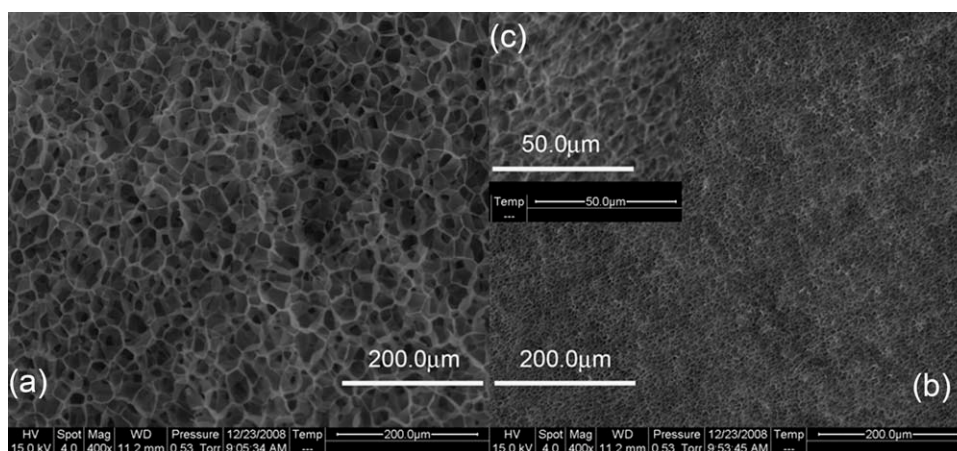
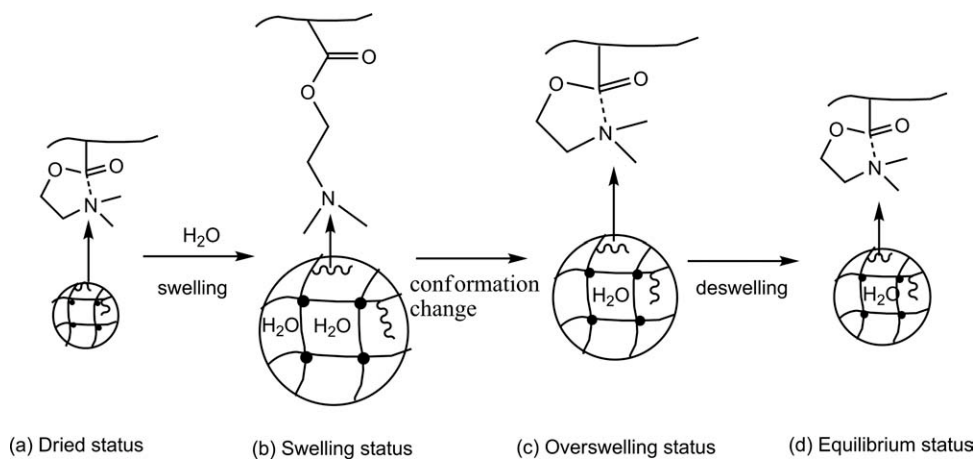


Figure 2 SEM image showing the morphology of the PDMAEMA hydrogels at different swelling states: (a,b) different swelling states when the SR reached maximum and equilibrium, respectively and (c) partial enlarged detail of part b.



Scheme 1 Scheme of the structure of the PDMAEMA gel at different swelling stages.

35°C, the maximum SR and swelling equilibrium time of the PDMAEMA hydrogels did not change much; however, when the temperature increased from 35 to 45°C, the maximum SR and swelling equilibrium time of the gel decreased from 52 to 33 h and 55 to 45 h, respectively; when the temperature was higher than 45°C, the swelling curves of the PDMAEMA hydrogels did not change much. The result was reasonable because the PDMAEMA hydrogels had a lower critical swelling temperature around 48°C.²⁵ Furthermore, this result was similar to that observed by Shieh and Peppas²⁸ in poly(2-hydroxyethyl methacrylate-*co*-multiethylene glycol dimethacrylate) gels and Lee and Chen¹² in poly[2-hydroxyethyl methacrylate-*co*-3-dimethyl-(methacryloyloxyethyl)] gels.¹² The entropy of the polymeric chain increased, and the relaxation motion of the polymeric chain accelerated with a rise in temperature. Thus, the swelling time of the gel to reach equilibrium decreased as the temperature increased.

Influence of the ionic strength on the overshooting effect of the PDMAEMA hydrogels

Figure 4 shows the influence of the NaCl concentration on the overshooting effect of the PDMAEMA hydrogels. The maximum SR of the PDMAEMA hydrogels decreased reasonably with increasing NaCl concentration because of the polyelectrolyte effect, as we reported earlier.²⁵ The overshooting effect of the PDMAEMA hydrogels gradually weakened with the addition of NaCl and was finally indiscernible when the NaCl concentration was greater than 0.2 mol/L. It is known that the addition of salt to the swelling medium will decrease the chemical potential of water and make the solubility of the solvent decrease; this increases the free energy of mixing of the network chains with solvent.²⁹ As a result, the stretching of the macromolecular chains of DMAEMA units were weakened in salt solutions.

When the concentration of the NaCl solution reached a critical value, the side chains of the DMAEMA units mainly adopted the cyclic conformation, and the overshooting phenomenon was indiscernible.

Influence of pH on the overshooting effect of the PDMAEMA hydrogels

Figure 5 shows the influence of pH on the overshooting effect of the PDMAEMA hydrogels. We concluded from Figure 5 that the pH of the external media exerted a dramatic influence on the overshooting effect of the PDMAEMA hydrogels. On one hand, the overshooting effect of the gel was indiscernible in the solutions at pH 2.1 and 11.9; on the other hand, the equilibrium SR of the gel in acidic and basic solutions was much higher than that in water. As shown in Scheme 2, the free electron pair of the amino group conjugates with the carboxyl in the DMAEMA units when the gel was immersed in

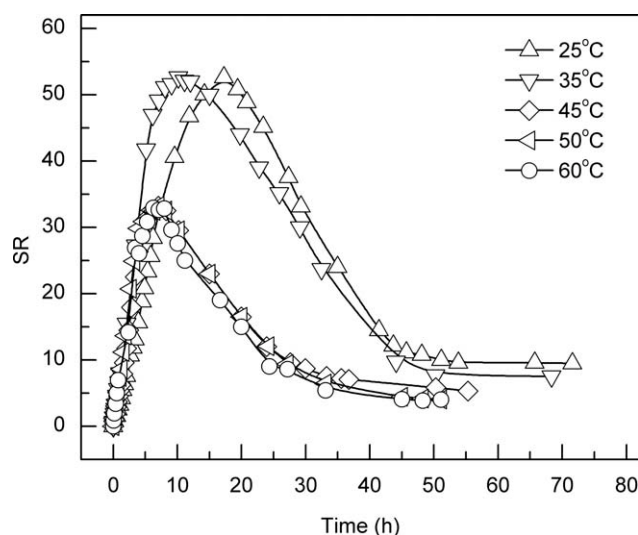


Figure 3 Dynamic swelling curves (SR vs time) of the PDMAEMA hydrogels in water at different temperatures.

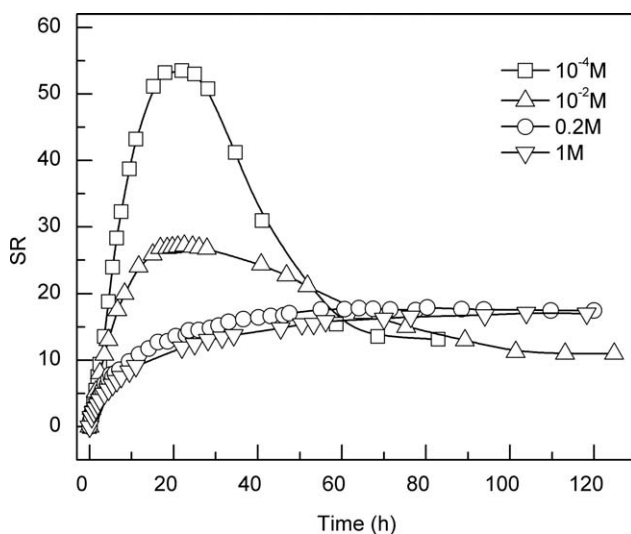


Figure 4 Dynamic swelling curves (SR vs time) of the PDMAEMA gels in NaCl solutions with different concentrations at 25°C.

water and led to a decrease in the swelling ability. However, this coordination was severely weakened in the acidic solution because the protonation of tertiary amino group dominated and the side chains of DMAEMA units in the gel mostly adopted the stretched conformation [Scheme 2(b)]. Moreover, when the tertiary amino group was protonated, the larger ionic osmotic pressure of the network led to a higher equilibrium SR of the gel. The indiscernibility of the overshooting effect of the PDMAEMA gels in the basic solution could be explained in a similar way as that in the NaCl solution. The higher equilibrium SR was probably due to the physical adsorption of OH^- of the hydrophobic chains in the PDMAEMA gels.³⁰

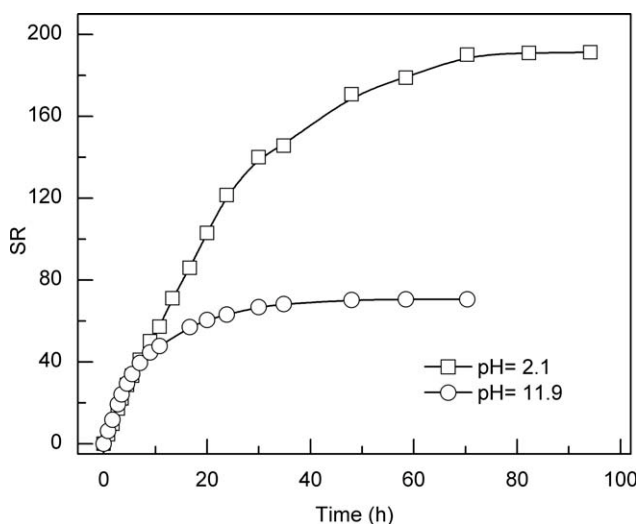
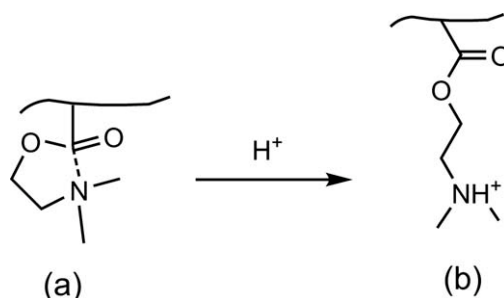


Figure 5 Dynamic swelling curves (SR vs time) of the PDMAEMA gels in different pH solutions at 25°C.



Scheme 2 Proposal mechanism for the conformational change of the side chains of DMAEMA units of the PDMAEMA gel in different media: (a) water and (b) acid solution.

FTIR analysis

To understand the mechanism of the overshooting effect of the PDMAEMA hydrogels, the effects of the swelling ratio, salt, and pH on the FTIR spectra of the PDMAEMA hydrogels were investigated. Figure 6 shows the FTIR spectra of the PDMAEMA hydrogels swollen in different media. Figure 6(a) shows the FTIR spectrum of the PDMAEMA gel swollen in water. The contribution of the characteristic peaks of Figure 6(a) can be described as follows: 3400 cm^{-1} ($\nu_{\text{H-O}}$ stretching H_2O), 2947 cm^{-1} ($\nu_{\text{C-H}}$ stretching CH_2 , CH_3), $2820\text{--}2760\text{ cm}^{-1}$ ($\nu_{\text{C-H}}$ stretching N-CH_2 , $\text{CH}_3\text{-N}$), and 1728 cm^{-1} ($\nu_{\text{C=O}}$ stretching C=O). The spectra of the gel

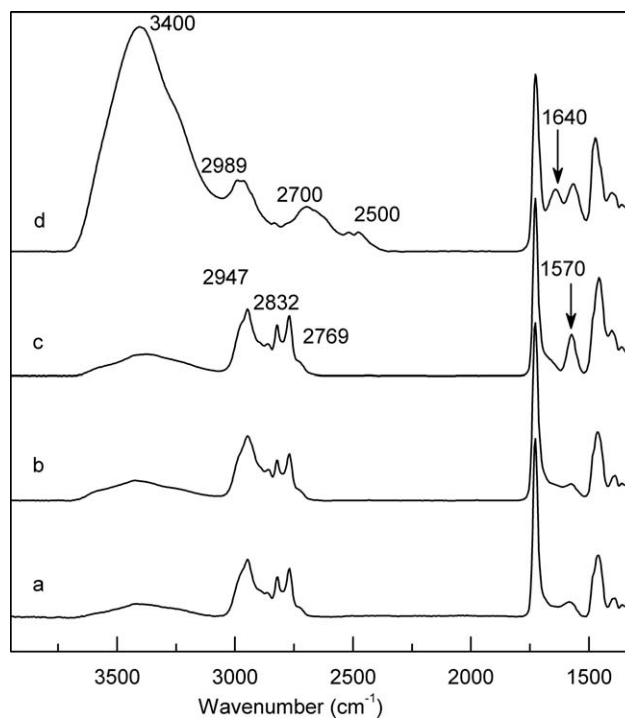


Figure 6 FTIR spectra of the PDMAEMA hydrogels swollen in different media: (a) water, (b) NaCl solution (0.01 mol/L), (c) basic solution (pH 11.9), and (d) acidic solution (pH 2.1).

swollen at different periods were recorded (not shown in the figure), and we found that the absorption intensity at 3400 cm^{-1} changed reasonably with SR of the gels. The band around 1570 cm^{-1} shown in Figure 6(a) was attributed to the vibration caused by the coordination of the free electron pair of the tertiary amino group with the carboxyl in DMAEMA units in the gels. According to the previous discussion, the dynamic conformational changes of the side chains, which occurred during the swelling of DMAEMA, should have influenced the band around 1570 cm^{-1} because of the hydrogen-bond interaction between the tertiary amino group and water. Unfortunately, this change was not observed; this implied that the conformational changes of the DMAEMA side chains in the swelling–deswelling process of the PDMAEMA gel might not have been strong enough to be recorded by FTIR. Figure 6(b,c) shows the FTIR spectra of the PDMAEMA gel swollen in NaCl solution (0.01 mol/L) and basic solution (pH 11.9), respectively. As shown in Figure 6(b,c), the band at 3400 cm^{-1} increased compared that shown in Figure 6(a) because of the increase in SR of the gels. In addition, the band at 1570 cm^{-1} in Figure 6(c) increased, and the possible reason was that the stretching of the macromolecular chains was severely disrupted with the addition of NaCl and NaOH and the cyclic conformation of the side chains of DMAEMA units was dominant. Figure 6(d) shows the FTIR spectrum of the PDMAEMA gel swollen in acidic solution (pH 2.1); this was markedly different with those shown in Figure 6(a–c) in that

1. A much higher intensity of the broad band at 3400 cm^{-1} was observed in the acidic solution, which showed that water interacted strongly with H^+ and formed water clusters.³¹
2. A marked blueshift of the band at 2947 cm^{-1} was observed when the swelling medium was changed from water to the acidic solution. Because CH_2 stretching modes are very sensitive to the conformational order of hydrocarbon chains^{32,33} (showing a shift to higher frequencies when the conformational disorder is increased), we assumed that protonation of the tertiary amino group introduced conformational changes to the side chains of the DMAEMA units in the network.
3. The bands at 2832 and 2769 cm^{-1} seemed to merged into bands around 2989 and 2700 cm^{-1} in acidic solution.
4. A new peak appeared at 1640 cm^{-1} , which was attributed to the N–H asymmetric deformation vibrations of NH^+ .

Thus, the results of the FTIR spectrum of PDMAEMA gel swollen in the acidic solution clearly shows that the protonation of the tertiary amino

group dominated in the acidic solution and that the side chains of DMAEMA units in the gel mostly adopted the stretched conformation [Scheme 2(b)].

CONCLUSIONS

PDMAEMA gels were prepared by radiation-induced crosslinking with PEGDMA as a crosslinker. The dynamic swelling experiment indicated that the swelling process of the PDMAEMA gels exhibited a remarkable overshooting effect in water; that is, the gels first swelled to a maximum SR, and this was followed by a gradual deswelling until the swelling equilibrium was reached. The overshooting effect of the PDMAEMA gels was a consequence of dynamic conformational changes of the side chains of the DMAEMA units in the gels during the period of gel swelling. The side chains of the DMAEMA units of the gels preferentially adopted a cyclic conformation and then changed into a stretched one with the swelling process of the gel; they finally returned to the cyclic conformation, which was thermodynamically stable. The formation of the cyclic conformation may be considered a kind of aggregation, which decreased the swelling capacity and, therefore, led to water expulsion.

The effects of the temperature, ionic strength, and pH of the external media on the overshooting effect of the PDMAEMA hydrogels were studied, and the results indicate that

1. The overshooting effect of the gel could not be eliminated by a change in the temperature. Furthermore, the maximum SR decreased, and the time to reach the equilibrium SR decreased with increasing temperature.
2. The overshooting effect existed in lower concentration NaCl solutions but was indiscernible in higher ones.
3. The overshooting effect was indiscernible in both acidic and basic solutions. The overshooting effect became indiscernible when the PDMAEMA gel was immersed in NaCl solutions with a high concentration and basic solutions because the stretching of the macromolecular chains was disrupted with the addition of NaCl and NaOH. While in acidic solution, the protonation of tertiary amino groups in the DMAEMA units made the side chains of the DMAEMA units change from the cyclic conformation to the stretched one. Thus, the overshooting effect of the PDMAEMA gel became indiscernible in acidic solution.

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