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Temperature-, pH-, and Ion-Stimulus-Responsive Swelling Behaviors of Poly(dimethylaminoethyl methacrylate) Gel Containing Cholic Acid

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ABSTRACT: Poly(dimethylaminoethyl methacrylate) hydrogels containing cholic acid (PDMAEMA–CA) were synthesized by radiation crosslinking. The introduction of 10 and 20 mol% cholic acid (CA) into the poly(dimethylaminoethyl methacrylate) (PDMAEMA) hydrogel decreased the maximum swelling ratio (SR) of the gel from 40 to 6 and 5, respectively. The incorporation of CA with dimethylaminoethyl methacrylate led to a decrease in the lower critical swelling temperature of the gel from 44 to 42°C but did not exert big influence on the ion-stimulus-responsive properties of the gel. However, the pH sensitivity of the PDMAEMA–CA gel was quite different from that of PDMAEMA gel. The SR of PDMAEMA gel decreased at pH 2.5, whereas the SRs of the PDMAEMA–CA gels showed a convex-upward function of pH; that is, SR of the PDMAEMA–10% CA gel first increased (pH 1.2–3.2) and then decreased (pH 3.2–11.9) with increasing pH. The pH-stimulus-responsive swelling behavior of the PDMAEMA–20% CA gel was similar to that of the PDMAEMA–10% CA gel except for the unique swelling behavior exhibited in the lower pH region. The unique decrease in SR in strong acidic solutions was attributed to aggregations driven by the hydrophobic interactions between CA molecules. Phase separation of the gel in strongly acidic solutions was observed; that is, the margin of the swollen gel was transparent and elastic (cellular structure), whereas the core of it was opaque (aggregated structure) as recorded by scanning electron microscopy. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 39998.

KEYWORDS: crosslinking; gels; polyamides; stimuli-sensitive polymers; swelling

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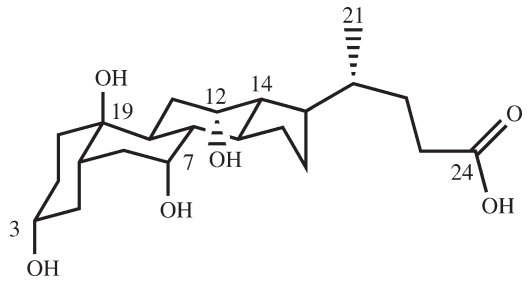
INTRODUCTION

Hydrogels that are sensitive to environmental stimuli, with unique and desirable sensitivities to temperature, pH, magnetic fields, light, and so on, have been studied extensively.[1] During the last decade, thermosensitive and pH-sensitive hydrogels have attracted great interest and have played an important role in controlled drug-delivery systems because temperature and pH are important triggering signals for phase transitions in hydrogels, and they are important environmental factors in drug-delivery systems and other biomedical systems.[2–4]

Poly(dimethylaminoethyl methacrylate) (PDMAEMA) is an important stimuli-sensitive polymer because of its temperature- and pH-stimulus-responsive phase-transition behaviors. Plenty of research studies concerned with the synthesis and characterization of PDMAEMA-based gels and their applications in controlled release systems and heavy-metal-ion adsorption have been done in our group and other colleague groups.[5–10] In our previous study, PDMAEMA hydrogels were prepared by γ-ray radiation crosslinking. We found that the PDMAEMA hydrogels exhibited an overshooting effect during swelling; that is, the swelling ratio (SR) of the hydrogels increased rapidly in the initial swelling stage, then slowed down gradually, and finally reached equilibrium.[10] The overshooting effect of the PDMAEMA gel was attributed to cyclic conformation (see Figure 2) of the side chains of the dimethylaminoethyl methacrylate (DMAEMA) units during the swelling of the gels.[10,11]

The elimination of its overshooting effect has practical meaning. Because of its complicated situation, the overshooting effect of the PDMAEMA hydrogel may limit its applications in separation and the biomedical field. It was found that the protonation of the amino groups of DMAEMA block the cyclic conformation and thus eliminate the overshooting effect of the PDMAEMA hydrogel.[10] It is believed that the introduction of

Additional Supporting Information may be found in the online version of this article.

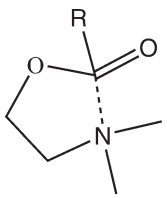


Scheme 1. Structure of CA.

some groups, such as OH, that are prone to forming hydrogen bonds will hinder the overshooting effect of the gel.

In this study, cholic acid (CA) was incorporated into PDMAEMA. As one of the major primary bile acids, CAs are natural compounds biosynthesized in the liver, and they help in the solubilization of fats in the diet.[12] CA is water-soluble and possesses reactive groups on its skeleton: three hydroxyl groups and a carboxylic acid group (Scheme 1). These properties may provide more chances for them to be derived into hydrogelators, a necessity for the creation of biocompatible gel materials that may find uses in the biomedical and pharmaceutical fields. CA has attracted great interest during the past few years, mainly because of its superior biocompatibility, unique amphiphilic structure, chirality, and in particular, its ability to aggregate in various solvents or mediums. It is these properties that make CA and steroids ideal building blocks for the creation of novel supramolecular structures. They have been used in the creation of novel, low-molecular-mass gelators, which are key components in the formation of supramolecular gels.[13–15] Thus, CA was incorporated into the PDMAEMA gel to obtain poly(dimethylaminoethyl methacrylate) blended hydrogels containing cholic acid (PDMAEMA–CA). We hoped that the overshooting effect of the blend gel would be eliminated without a loss of thermosensitivity or pH sensitivity.

As we expected, the introduction of 10 and 20 mol% CA into the PDMAEMA gel eliminated the overshooting effect of the gel. The incorporation of CA with DMAEMA did not exert a big influence on the temperature or ion-stimulus-responsive properties of the gel. Interestingly, the pH sensitivity of the PDMAEMA–CA gel was quite different from that of PDMAEMA gel. The unique pH sensitivity of the PDMAEMA–CA gel was related to the microstructure of the gel and was studied with scanning electron microscopy (SEM).



R: $C(CH_3)=CH_2$

Figure 1. Ring conformation of DMAEMA.

EXPERIMENTAL

Materials

DMAEMA (99% purity) and CA (99%) were provided by Acros and were used as supplied. Poly(ethylene glycol dimethacrylate) (PEGDMA; number-average molecular weight = 875), the crosslinker, was purchased from Aldrich. CA was supplied by Sigma-Aldrich-Fluka. Other chemicals for this study were analytic reagents obtained from Beijing Chemicals Co. and were used as received.

Synthesis of the Hydrogels

The PDMAEMA and PDMAEMA–CA gels were synthesized by radiation-induced crosslinking with the same method reported in our previous study.[10] All of the experiments were performed at a total monomer concentration of 1 mol/L (for the PDMAEMA–CA1 gel, $n_{DMAEMA}/n_{CA} = 9{:}1$; PDMAEMA–CA2 gel, $n_{DMAEMA}/n_{CA} = 8{:}2$, where n represents for the molarity of the monomer) with PEGDMA (0.35 mol %) as the crosslinker. The monomers, PEGDMA, and water solution were 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 gels with desired absorbed doses at a dose rate of 20 Gy/min at room temperature. The resulting gels were cut into cylinders about 5 mm in length and dried *in vacuo* at 25°C to a constant weight.

Fourier Transform Infrared (FTIR) Characterizations of the Monomers and Gels

The FTIR measurements of the CA, DMAEMA, PDMAEMA gel, and PDMAEMA gels were performed at a Nicolet Magna-IR 750 instrument with a Nicolet NicPlan IR microscope attachment (resolution = 4 cm/P, 64 scans) and an mercury cadmium tellurium/A (MCT/A) detector. The swollen gels that reached swelling equilibrium were used directly for the experiments. The spectra are illustrated in Figure 2. The three peaks observed in the CA spectra (3000–3500 cm^{-1}) were ascribed to the vibration caused by OH in different environments. The broad peak (3000–3600 cm^{-1}) observed in the three gels was caused by water in the gels. The three peaks observed in the CA spectra (3000–3500 cm^{-1}) were not observed in the gels because of overlapping with the broad peak of water. The peak at 1570 cm^{-1} observed in DMAEMA and the PDMAEMA hydrogel was attributed to the vibration caused by the coordination of the free electron pair of the tertiary amino group with the carboxyl in DMAEMA. The attributions of other characteristic peaks observed in the spectrum were as follows: 2900–3050 cm^{-1} [$\nu_{(C-H)}$ of saturated CH_2 and CH_3], 1730 cm^{-1} [$\nu_{(C=O)}$], 1635 cm^{-1} [$\nu_{(C=C)}$], 1470 cm^{-1} [$\delta_{as(CH3)}$], 1320 cm^{-1} [$\delta_{s(CH3)}$], 1290 cm^{-1} [$\nu_{as(C-O-C)}$], and 1160 cm^{-1} [$\nu_{s(C-O-C)}$].

Gel Fraction (G_f)

The sol parts of the samples were extracted with methanol and then dried in a vacuum oven at 25°C to constant weight. G_f was defined as follows:

$$G_f(\%) = W_g/W_0 \times 100 \quad (1)$$

where W_0 and W_g are the weights of the dried gel before and after sol removal, respectively.

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. We obtained the SR by weighing the initial and swollen samples at various time intervals. The following equation was used to calculate SR:

$$SR = (W - W_0)/W_0 \quad (2)$$

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

The classical gravimetric method was used to measure the SR, temperature, ionic strength, and pH sensitivity of the hydrogels. Swelling studies were performed in distilled water at different temperatures from 20 to 70°C; this covered the expected range of the lower critical swelling temperature (LCST) of the hydrogel samples. This was done in solutions of different ionic strengths ([NaCl] = 10^{-5} to 2.0 mol/L) and solutions of different pH values (from 0.9 to 12.0) at a fixed ionic strength. The addition of NaCl was done to maintain a constant ionic strength ($I = 0.1$ mol/L) of the acid/basic solutions. The hydrogels were immersed to reach a swollen equilibrium at each predetermined condition. Then, the hydrogel samples were taken out, and excess water on the sample surface of the wet hydrogel was removed with wet filter paper. Then, the samples were weighed until they reached a constant weight. Each sample was measured three times, and the average value of the three measurements was taken. The equilibrium degree of swelling (EDS) was also calculated according to eq. (2), where W was taken the weight of the gel at equilibrium.

Morphology

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

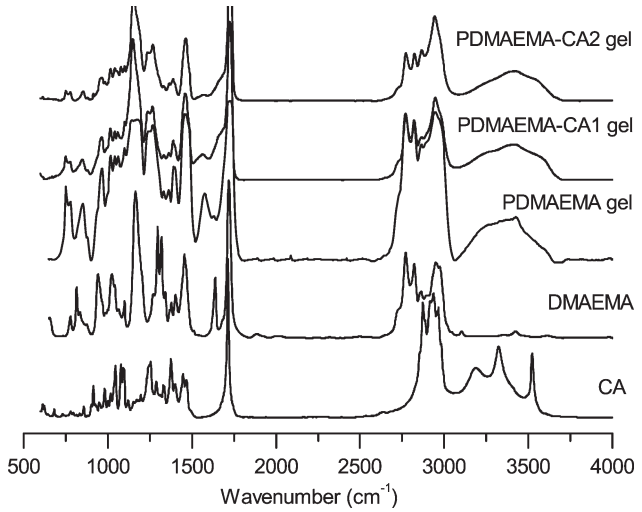


Figure 2. FTIR spectrum of CA, DMAEMA, PDMAEMA gel, PDMAEMA–CA1 gel, and PDMAEMA–CA2 gel.

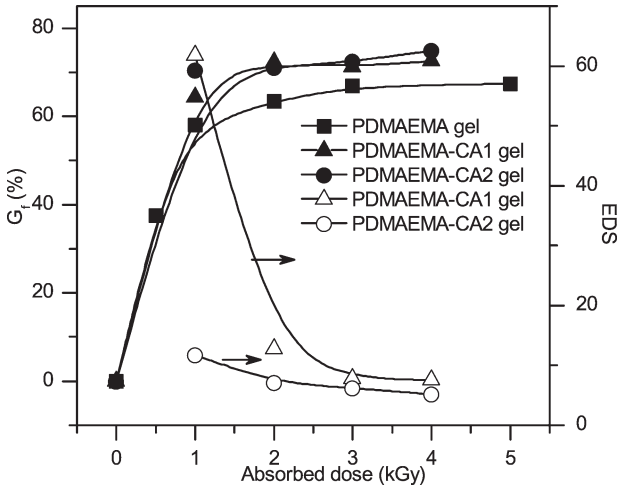


Figure 3. Influence of the absorbed dose on the G_f and EDS values of PDMAEMA–CA and PDMAEMA gels.

RESULTS AND DISCUSSION

Synthesis of the PDMAEMA–CA Gels

Figure 3 shows the influence of the absorbed dose on G_f and EDS of the gel. Similar to the pure PDMAEMA hydrogels,[9] the formation of the PDMAEMA–CA gels started at a critical absorbed dose, and G_f increased with the increasing dose in a narrow range and then leveled off. The maximum G_f values of the PDMAEMA–CA gels were almost the same, whereas the EDS of the gel (prepared with the absorbed dose) decreased with increasing CA amount. In our previous study, we found that the gel strength of the pure PDMAEMA hydrogel prepared at lower than 4 kGy was very low and showed weak mechanical properties.[9] It was hard to get an accurate SR of PDMAEMA gels prepared with less than 4kGy because the gel became fragile after it was swollen in water. After CA was incorporated into the PDMAEMA hydrogels, the gel strength improved greatly. The elasticity of the hydrogel increased with increasing dose and then decreased around 4 kGy. The gel became fragile above 4 kGy. On the other hand, EDS of PDMAEMA–CA gels decreased with increasing absorbed dose. Therefore, to obtain transparent and elastic PDMAEMA–CA and PDMAEMA hydrogels with higher gel strengths and desirable swelling capacities, one should not use a radiation dose higher than 4 kGy (4 kGy was applied in the following experiment).

It should be mentioned that we focused on the stimuli-responsive properties of the PDMAEMA–CA gels. The gelation ability of CA and the mechanical properties of the PDMAEMA–CA gels will be studied extensively in a future work.

Swelling Dynamics of the PDMAEMA–CA Gels

We concluded that the swelling dynamics of the PDMAEMA–CA gels were quite different from those of the PDMAEMA gels (Figure 4). The swelling curves of the PDMAEMA–CA gels were typical diagrams of the swelling process of hydrogels in water. The swelling of the PDMAEMA–CA gels was quick at the beginning and then became slower and slower until the gel reached its equilibrium SR. The dried gel could reach swelling equilibrium in 48 h. We found in our previous study[9] and in

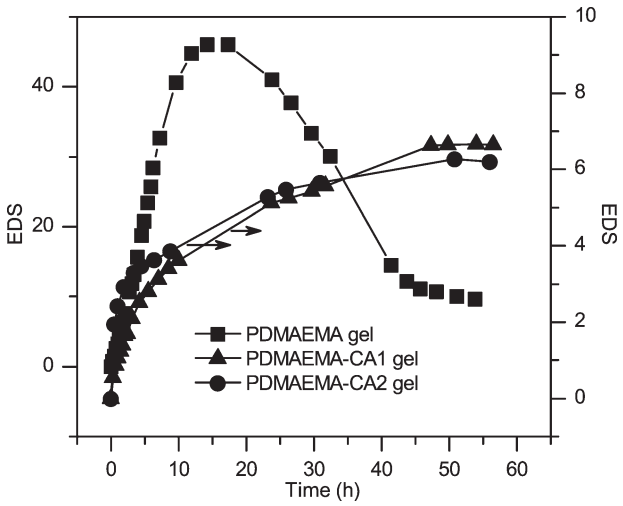


Figure 4. Dynamic swelling curves (SR vs time) of the PDMAEMA–CA and PDMAEMA gels in water at 25°C.

this study that the pure PDMAEMA gel exhibited an overshooting effect during swelling; that is, the SR of the hydrogel increased rapidly at the initial swelling stage, then slowed down gradually, and finally reached equilibrium. After we introduced CA into the PDMAEMA gel, the overshooting effect of the gel disappeared. According to the previous discussion,[10] the band around 1570 cm^{-1} observed in the PDMAEMA hydrogel (Figure 2) was attributed to the vibration caused by the coordination of the free electron pair of the tertiary amino group with the carboxyls in the DMAEMA units in the gels (Figure 1). As previously mentioned, the OH and COOH groups on CA tended to form hydrogen bonds with the amino groups of DMAEMA; this blocked the cyclic conformation. As shown in Figure 2, the absorption intensity at 1570 cm^{-1} decreased with increasing CA, and the band was hardly observed in the PDMAEMA–CA2 gel. We concluded that the introduction of enough OH and COOH groups into the PDMAEMA gel system hindered its overshooting effect.

Compared with that of the PDMAEMA gel (EDS ≈ 10), EDS of the PDMAEMA–CA gel (∼6) was smaller, not to mention that the maximum swelling ratio (SR_{max}) of the PDMAEMA gel was much higher (ca. 45). CA and its derivatives as gelators have been studied by many groups.[16–18] It has been found that the gelator molecules will form aggregates and promote the formation of physical gels. In the case of the PDMAEMA–CA gels, the aggregation was based on the hydrogen bonds between the amide groups in PDMAEMA and OH and COOH groups in CA, which blocked the cyclic conformation of DMAEMA and increased the crosslinking density of the PDMAEMA–CA gels; this led to a decrease in EDS of the gel. Another factor was the strong hydrophobicity of CA; even though CA is an amphiphilic molecule, the solubility of CA in water is quite limited. As a result, the introduction of CA into the PDMAEMA gel significantly decreased SR of the gel.

It should be noted that to simplify the system, the gels were allowed to swell for 48 h at each predetermined condition in the following swelling experiments.

Figure 5 shows the macroscopic and microscopic morphologies of the PDMAEMA–CA and PDMAEMA gels. With the observation of naked eye, the PDMAEMA–CA gels were less transparent than the PDMAEMA gel with SR_{max}. To elucidate the differences in their microstructures, the morphology of the gels was observed by SEM. The PDMAEMA gel at SR_{max} had a cellular structure with a pore size of about 20 μm [Figure 5(a)]. However, uniform pores were not observed in the PDMAEMA–CA1 [Figure 5(b)] and PDMAEMA–CA2 [Figure 5(c)] gels. It

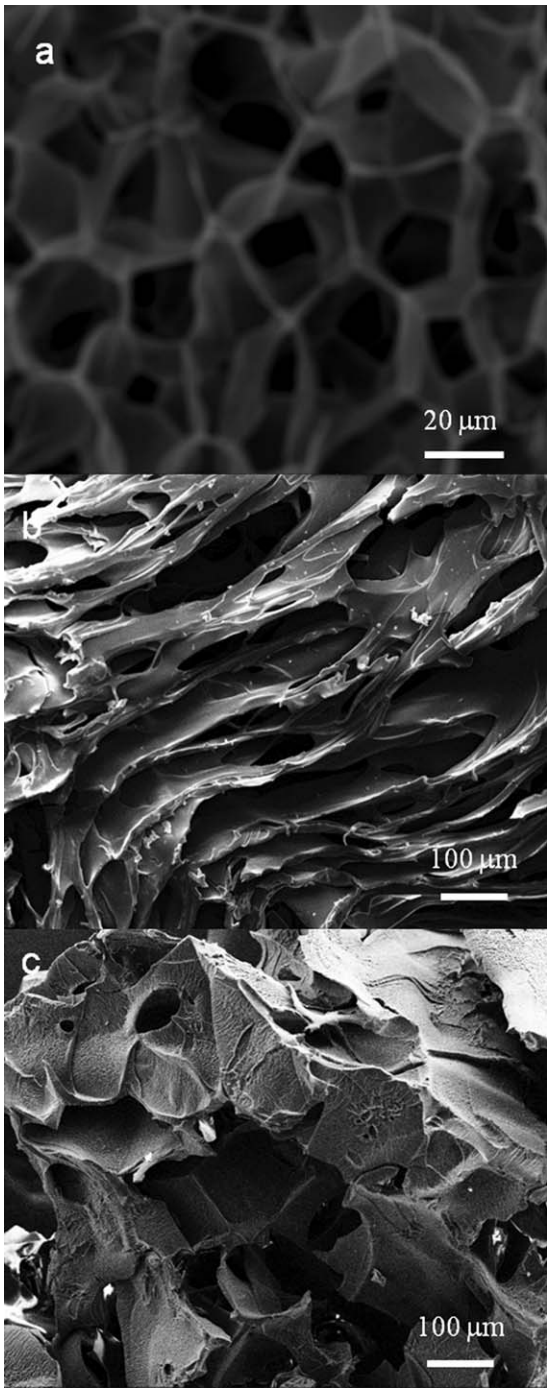


Figure 5. Microscopic morphologies (SEM) of the PDMAEMA–CA and PDMAEMA gels: (a) PDMAEMA gel at SR_{max}, (b) PDMAEMA–CA1 gel, and (c) PDMAEMA–CA2.

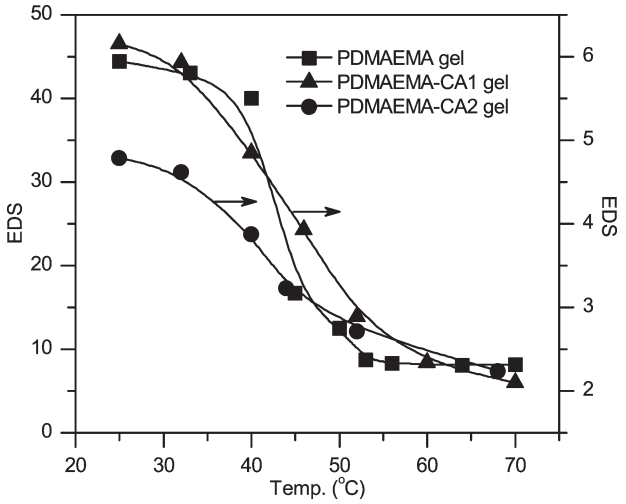


Figure 6. Temperature-stimulus-responsive swelling behavior of the PDMAEMA–CA and PDMAEMA gels.

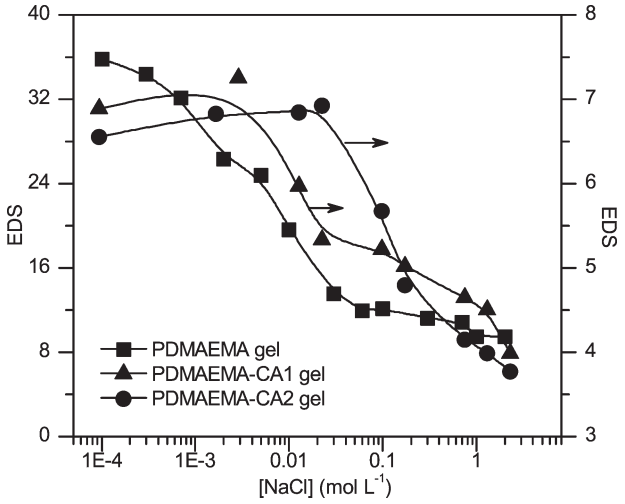


Figure 7. Ion-stimulus-responsive swelling behavior of the PDMAEMA–CA and PDMAEMA gels (25°C).

was probable that aggregation occurred in the PDMAEMA–CA gel systems and that this diminished the swelling capacity and, therefore, led to water expulsion.

Temperature-Stimulus-Responsive Swelling Behavior of the PDMAEMA–CA Gels. Figure 6 illustrates the effect of temperature on the EDS of the PDMAEMA–CA gels. The LCST was determined as the temperature where $SR = (SR_{max} - SR_{min})/2$ (SR_{max} and SR_{min} represent maximum swelling ratio and minimum swelling ratio, respectively). LCST of the PDMAEMA–CA1 gel was determined to be 45°C; this was very close to that of the pure PDMAEMA hydrogel (ca. 44°C). With increasing amount of CA, LCST of the PDMAEMA–CA gel decreased from 45°C (PDMAEMA–CA1) to 42°C (PDMAEMA–CA2) because of the hydrophobicity of CA. In a study of the LCSTs of polymers, Taylor and Cerankowski[19] proposed a general rule that the LCST should decrease with an increase in the polymer hydrophobicity and vice versa. As stated previously, CA is a facially amphiphilic biomolecule possessing a rigid steroid skeleton structure (hydrophobic part) and four hydrophilic groups (hydrophilic part; Scheme 1). The influence of the hydrophobic and hydrophilic parts on the LCST of the gel may counteract each other; thus, the introduction of amphiphilic CA into PDMAEMA hydrogels did not have a significant influence on the LCST of the PDMAEMA hydrogels.

Ion-Stimulus-Responsive Swelling Behavior of the PDMAEMA–CA Gels. The ion-stimulus-responsive swelling behavior (at 25°C) of the PDMAEMA–CA gels is shown in Figure 7. It was clear that incorporation of 10 and 20 mol% CA had no obvious effect on the ion-stimulus response of the PDMAEMA hydrogel. Similar to that of the pure PDMAEMA gel, EDS of the copolymer gel decreased quickly with increasing NaCl concentration because of the decrease in osmotic pressure, breakage of hydrogen bonds, and screening of electrostatic repulsion forces in the presence of electrolytes.

pH-Stimulus-Responsive Swelling Behavior of the PDMAEMA–CA Gels. Figure 8 shows the EDS values of the PDMAEMA–CA gels in solutions with different pHs. EDS of the gel decreased significantly with increasing ionic strength of the solution (Figure 7). For this reason, the ionic strength of the solutions was fixed at 0.1 mol/L to prevent the influence of ionic strength on the swelling of PDMAEMA–CA gel. In our previous work and this study, we found that pure PDMAEMA exhibited pH sensitivity at pH 2.5. Briefly, EDS of PDMAEMA was rather high in acidic buffer (pH 1.0–2.5) and decreased dramatically with the increase of pH; the curve leveled off when the pH was higher than 2.5. It was clear that the inclusion of CA in the PDMAEMA had a significant effect on the pH-stimulus response of the blend gel. The EDS values of the PDMAEMA–CA gels in strongly acidic solutions (pH 1.2–3.2 for the PDMAEMA–CA1 gel and pH 1.0–2.1 for the PDMAEMA–CA2 gel) increased with pH, reached a maximum (ca. pH 3.2 for the PDMAEMA–CA1 gel and pH 2.1 for the PDMAEMA–CA2 gel), and then decreased dramatically with further increases in pH. The curve leveled off when the pH was increased even further. The pH-stimulus-responsive swelling behavior of the PDMAEMA–CA2 gel was similar to that of the

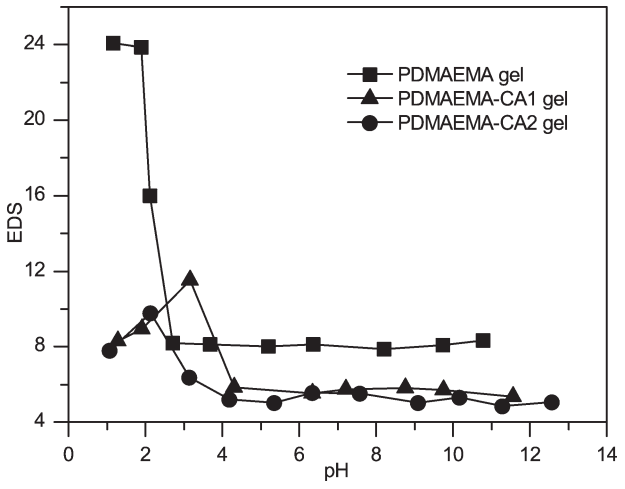


Figure 8. pH-stimulus-responsive swelling behavior of the PDMAEMA–CA and PDMAEMA gels (25°C).

PDMAEMA–CA1 gel except for the unique swelling behavior exhibited in the lower pH region. In the following discussion, the PDMAEMA–CA1 gel is used as an example.

PDMAEMA has typical cationic-component tertiary amine groups, which are ionized in the lower pH region and positively charged; as a result, PDMAEMA became more extended because of the increased osmotic pressure among the hydrogels. On the other hand, it was difficult for PDMAEMA to produce enough ionized amino groups in the higher pH condition, so the hydrogels took a contracted form. As described previously, aggregations driven by the hydrogen bonds between the amide groups in PDMAEMA and the OH and COOH groups in CA were dominant in the gel. As a result, the homogeneous cellular structure of the pure PDMAEMA gel (pore diameter $\approx$ 20 um)[10] was not observed in the PDMAEMA–CA gel swollen in distilled water [Figure 5(b)]. As mentioned previously, the OH and COOH groups on CA formed hydrogen bonds with the amide groups in DMAEMA in water. With the addition of HCl and amine groups, which were ionized and positively charged, the PDMAEMA–CA gel become more extended because of the increasing osmotic pressure among the hydrogels. Because of the protonation of amide groups, the hydrogen bonds between amide groups and OH and COOH groups weakened; this decreased the crosslinking density of the gel and thus increased EDS of the PDMAEMA–CA gel as well. It seemed that small amounts of HCl promoted the miscibility of different phases [Figure 9(c)]. We should mention that the small opaque part shown in Figure 8(c) was still there even after 2 months. The further addition of HCl led to phase separation. The hydrophobic interactions were strengthened, whereas the hydrogen bonding was weakened. In a strongly acidic solution, the hydrogen bonding between CA molecules, amide groups, and OH and COOH groups weakened, and the hydrophobic interactions between CA were strengthened. Because of its amphiphilicity, CA formed micelles with a hydrophobic part in the core and a hydrophilic part in the corona. Further aggregation led to phase separation in the PDMAEMA–CA gel. We observed that the margin of the gels swollen in a strongly acidic solution (pH 1.28) was transparent, whereas the core of the swollen gel was opaque with no elasticity [Figure 9(b)]. This was quite similar to the hydrophobically modified PDMAEMA gel we reported earlier.[9] The microcosmic morphology between the transparent part [Figure 10(a)] and the opaque part was quite different [Figure 10(b)]. The former [Figure 10(a)] had a cellular structure (pore diameter $\approx$ 20–30 um) similar to that of the pure PDMAEMA hydrogel, whereas the latter [Figure 10(b)] did not. Compared with that of the pure PDMAEMA hydrogel (ca. 6),[5] ionization of the OH and COOH groups made EDS of the PDMAEMA–CA gel ($\sim$5.5) did not decrease so much in basic solutions. The PDMAEMA–CA gel took a contracted but not aggregated form [Figure 10(d)].

As mentioned previously, the pH-stimulus-responsive swelling behavior of the PDMAEMA–CA2 gel was similar to that of the PDMAEMA–CA1 gel. The unique swelling behavior of the PDMAEMA–CA2 gel occurred in the lower pH region because more hydrogen bonds were involved in the PDMAEMA–CA2

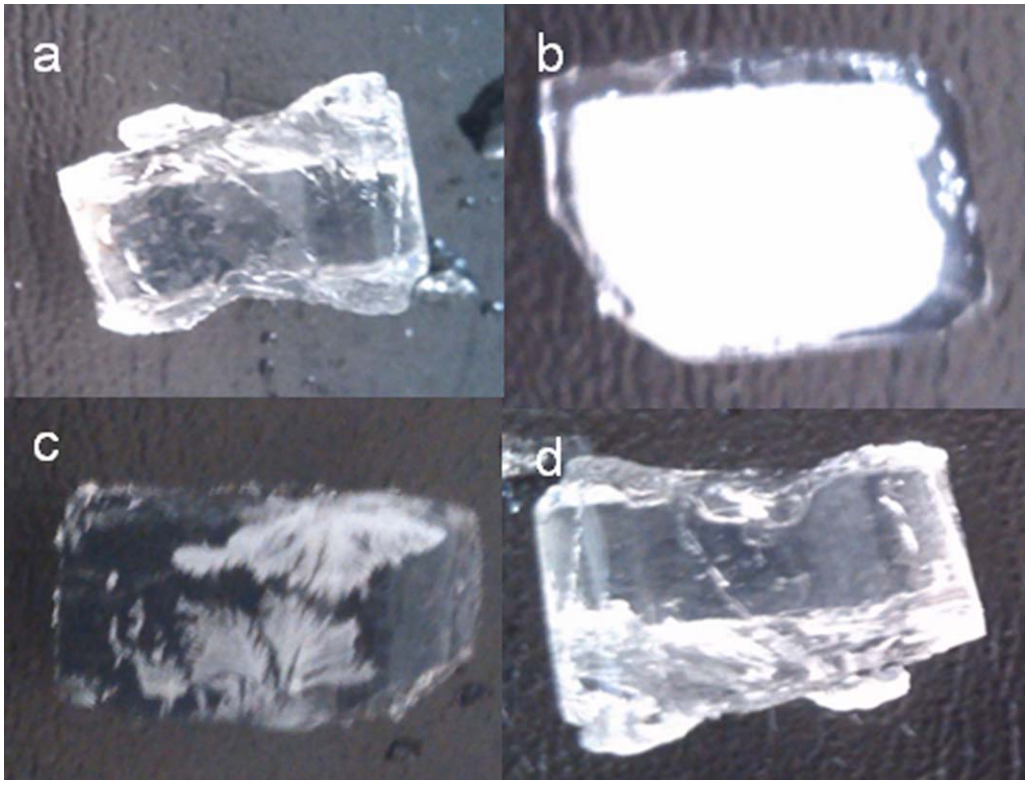


Figure 9. Macroscopic morphologies of the PDMAEMA–CA1 gels swollen in different media (the size of the photos does not represent the real size of the swollen gels.): (a) H_2O, (b) pH 1.28, (c) pH 3.16, and (d) pH 11.56.

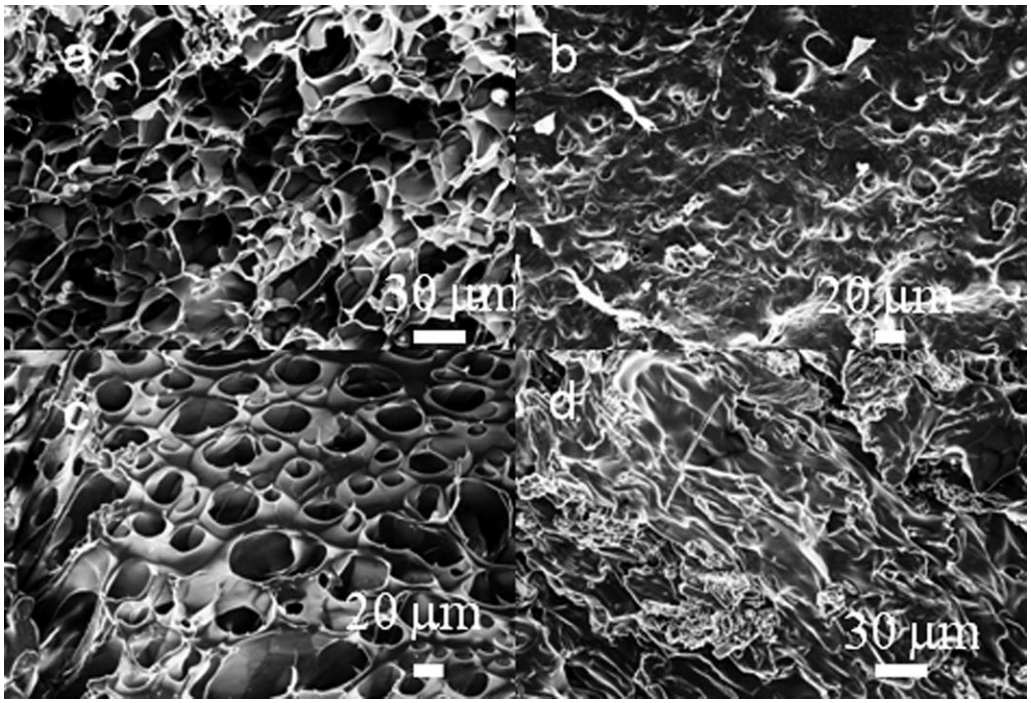


Figure 10. SEM images of the PDMAEMA–CA1 gels swollen in different media: (a) pH 1.28, margin of the swollen gel in Figure 8(b); (b) pH 1.28, core of the swollen gel in Figure 8(b); (c) pH 3.16; and (d) pH 11.56. The scale bars in parts a, b, c, and d represent 30, 20, 20, and 30 μm, respectively.

gel system and more H^+ would be needed to break the hydrogen bonds. As discussed previously, hydrophobic interactions were strengthened, whereas hydrogen bonding was weakened. Unlike the PDMAEMA–CA1 gel system, the PDMAEMA–CA2 gel swollen in pH 1.09 solution was totally opaque with no elasticity (see Figure S1b in the Supporting Information). Even though the snowflake structure in Figure 9(c) was not observed in Figure 10(c), a very trace amount of the snowflake structure was found floating in the swelling beaker.

CONCLUSIONS

Multistimuli-responsive PDMAEMA–CA gels were synthesized from DMAEMA and CA by γ radiation. The incorporation 10 and 20 mol% CA into the gel system significantly changed the swelling behavior of the PDAMEAM gels. Because of the hydrogen bonds between the amide groups in PDMAEMA and the OH and COOH groups in CA, the EDS value of PDMAEMA–CA was smaller than that of the PDMAEMA gel.

The temperature-, ionic-strength-, and pH-stimulus responses of the PDMAEMA–CA gel was investigated and compared with those of the PDMAEMA gel. The incorporation of CA with DMAEMA did not exert a big influence on the temperature- or ion-stimulus response of the gel. The LCSTs of the PDMAEMA–CA1 gel and PDMAEMA–CA2 gel were about 45 and 42°C; these were very close to that of the pure PDMAEMA hydrogel (44°C). The PDMAEMA–CA gels also exhibited a polyelectrolyte effect in an NaCl aqueous solution. Interestingly, the inclusion of CA in PDMAEMA had a significant effect on the pH-stimulus response of the gel. Unlike the steady EDS of the pure PDMAEMA gel in the strongly acid solution, the EDS of the PDMAEMA–CA1 gel increased with increasing pH (pH 1.2–3.2). This was attributed to the aggregation driven by hydrophobic attractions between the CA molecules. The phase separation and change in the microstructures of the gel with pH could be verified by SEM analysis. The pH-stimulus-responsive swelling behavior of the PDMAEMA–CA2 gel was similar to that of the PDMAEMA–CA1 gel except that its unique swelling behavior occurred in a lower pH region because more hydrogen bonds were involved in the PDMAEMA–CA2 gel system.

ACKNOWLEDGMENTS

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