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ORIGINAL PAPER

pH-responsive swelling behavior, elasticity and molecular characteristics of poly(*N*,*N*-dimethylaminoethyl methacrylate) gels at various initial monomer concentrations

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Abstract The equilibrium swelling degree and the modulus of elasticity of pH-responsive poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA) gels prepared at various initial monomer concentrations were investigated both in buffer solutions and in aqueous salt solutions. As pH of the solution is increased, PDMAEMA gels first remain in the swollen state up to pH 7.7, then exhibit pH-sensitive phase transitions at 8.0 in which PDMAEMA gels attain a collapsed state. The swelling kinetic measurements of PDMAEMA gels showed that pH sensitivity of PDMAEMA is quite stable and the swelling process is reproducible in accordance with pH changing. The swelling behavior of PDMAEMA gels was analyzed by Flory-Rehner theory and the results were combined by the results of compression measurements to calculate the molecular characteristics of gels. The resulting pH-responsive PDMAEMA gels were elastic and displayed good swelling behavior both in buffer solutions and in aqueous salt solutions, therefore, they can be used as a kind of carrying material in drug delivery systems.

Keywords Poly(*N*,*N*-dimethylaminoethyl methacrylate) · Gels · Initial monomer concentration · Swelling · Elasticity · pH sensitive phase transition

Introduction

pH-responsive gels provide a variety of applications ranging from material science to biomedical engineering. In recent years, the interest in these gels has exponentially increasing because of their biocompatibility and promising potential use in bio-related applications [1]. Among them, poly(*N*,*N*-dimethylaminoethyl methacrylate) (PDMAEMA)-based gels have received considerable attention for use as

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drug delivery devices [2, 3], support carriers [4, 5] and gene transfer agents [6–8]. PDMAEMA is a well-known cationic polyelectrolyte and exhibits both temperature- and pH-responsive swelling behavior. Since *N*,*N*-dimethylaminoethyl methacrylate (DMAEMA) has a structure similar to *N*-isopropylacrylamide (NIPA), PDMAEMA shows a temperature sensitivity similar to poly(*N*-isopropylacrylamide) (PNIPA) [9–12]. Thus, PDMAEMA hydrogels also show controllable volume changes in response to small variation of temperature in the solution condition. The phase transition temperature of PDMAEMA hydrogels in aqueous solutions falls in the wide range of 38–50 °C [10, 13].

Owing to bearing weak acidic or basic groups that ionize in a given pH range of the swelling medium, investigations of the swelling behavior of pH-responsive gels has gained noticeable interests. Since PDMAEMA is a pH-responsive polybase and it has amine groups in its side chain, in recent years much more attention has been directed to pH-dependent swelling of PDMAEMA hydrogels. The tertiary amine groups on DMAEMA are weakly basic and gain protons under acidic condition and release them under basic condition. In the structure of DMAEMA, the presence of hydrophobic basic group together with hydrophilic group makes it a special hydrogel which exhibits a combined pH- and temperature sensitivity. The variations in the pH of the swelling medium cause changes in the network ionization and also in the interactions between polymer chains or between polymer chains-solvent at the molecular level. As reported previously, PDMAEMA has a pK_a of about 8.44 in pure water and Feil et al. [14, 15] showed that pH-responsive hydrogels may exhibit phase transition very close to the pK_a of the corresponding linear polyelectrolyte.

Cho et al. [16] synthesized PDMAEMA hydrogels in the presence of BAAm as a crosslinker and *N*,*N*-azobis(isobutyronitrile) as an initiator and investigated the temperature-dependent equilibrium swelling behavior of hydrogels as a function of BAAm content. It was found that increasing BAAm content in the gel network also increases the crosslinking density resulting in the decrease of the swelling and in the increase of hydrophobicity of the gel network. They also reported that the transition temperature between the shrunken and the swollen state of PDMAEMA hydrogels was observed around 40 °C and it was shifted to the lower temperature values by the increase of BAAm content.

Patrickios and co-workers [17] also studied the swelling ability of the crosslinked star copolymer networks synthesized using group transfer polymerization. They prepared both amphiphilic conetworks based on the hydrophobic monomer benzyl methacrylate—the ionizable hydrophilic DMAEMA and ampholytic conetworks based on the negatively ionizable methacrylic acid—the positively ionizable DMAEMA. The swelling degree of all the conetworks were measured as a function of pH or in a mixture of solvents and the effect of the chemical structure, the charged density, and the architecture of the networks on their swelling were investigated. The swelling degree was found to be influenced more by the charge density of the conetwork than by the compatibility with the solvent, and more by the solvent compatibility than by the architecture of the conetwork.

The type of the crosslinker used in the gel preparation significantly affects the swelling behavior and the mechanical properties of the resulting gels. In the case of PDMAEMA and poly(2-dimethylaminoethyl methacrylate-co-butyl methacrylate)

P(DMAEMA-co-BMA) hydrogels synthesized by the presence of ethylene glycol dimethacrylate (EGDMA) as a crosslinking agent, it was found that the equilibrium degree of swelling of PDMAEMA and P(DMAEMA-co-BMA) hydrogels with changing pH values at different temperatures strongly depends on the concentration of the crosslinking agent in the network structure. An increase in the EGDMA content in the network reduced the swelling degree dramatically at all pH values. It was also observed that the water content of the P(DMAEMA-co-BMA) hydrogels is strongly dependent on both pH and temperature [18]. Moreover, the polymer conetworks based on end-linked homopolymers and amphiphilic gradient copolymers were synthesized by the atom transfer radical polymerization of DMAEMA as hydrophilic monomer, methyl methacrylate as hydrophobic monomer and EGDMA as hydrophobic crosslinker. It was found that the degrees of swelling of all the conetworks in tetrahydrofuran were higher than those measured in pure water, whereas the aqueous swelling increased by lowering the pH and increasing the DMAEMA content of the conetworks [19].

It is well-known that the gel structure and thus, the molecular characteristics of gels, the swelling capacity, the mechanical properties, the effective crosslink density, and the clarity strongly depend on the initial monomer concentration which is usually given in terms of the polymer network concentration just after the gel preparation, v_2^0 [20–27]. Decreasing polymer network concentration v_2^0, i.e., increasing the amount of water at polymerization increases the disentanglement of the polymer chains and by this way, the network formed in a dilute solution can swell highly in a good solvent. Moreover, the probability of the cyclization and the multiple crosslinking reactions during crosslinking increases with decreasing polymer concentration v_2^0 and thus, a large amount of the crosslinker is wasted in ineffective crosslinks. Therefore, the resulting network structure becomes increasingly loose as the volume fraction of the crosslinked polymer after the gel preparation increases [28, 29]. The swelling degree of poly(acrylamide) (PAAm) gels prepared at various v_2^0 but at a fixed crosslinker ratio was investigated by Baker et al. [30] and it was found that the degree of swelling of PAAm gels decreases while the elastic modulus increases with increasing v_2^0. On the other hand, Shibayama et al. [31] showed that the linear swelling ratio of PNIPA hydrogels is independent on the initial monomer concentration. It was observed that the number of chain entanglements acting as additional crosslink points increases with increasing initial monomer concentration. Furthermore, a direct correlation between the equilibrium swelling of poly(*N*,*N*-dimethylacrylamide) (PDMAAm) gels and the initial monomer concentration was developed by Bromberg et al. [32]. More recent study for the equilibrium swelling degree and the modulus of elasticity of PDMAAm hydrogels investigated over the entire range of the initial monomer concentration was published by Okay and co-workers [33, 34] and it was found that the linear swelling ratio of swollen PDMAAm increases linearly with increasing monomer concentration in the range of $v_2^0 = 0.1$–1.0. These authors have been mentioned that the gel properties and the resulting network structures are highly dependent on the gel preparation conditions, but no report was given on the effect of the polymer network

concentration for PDMAEMA gels prepared in the presence of BAAm as a crosslinker.

In this study, a series of PDMAEMA gels was prepared at various initial monomer concentrations but at a fixed crosslinker ratio. Owing to the fact that DMAEMA is a liquid at room temperature and miscible with water, PDMAEMA gels could be prepared in aqueous solutions at monomer concentrations from a few percent up to bulk conditions and by this way, it is possible to investigate the swelling behavior and the mechanical properties over the whole range of the gel preparation concentration, which have not been reported before for PDMAEMA gels prepared in the presence of BAAm. The role of pH on the swelling behavior and pH-dependent phase transition as well as the swelling kinetics of PDMAEMA gels were investigated in buffer solutions. The dependence of the mechanical properties of PDMAEMA gels on the initial monomer concentration was also analyzed by the elasticity tests. As will be seen below, the combined results obtained from the swelling and the mechanical measurements were used to calculate the characteristic network parameters of PDMAEM gels prepared at various initial monomer concentrations.

Experimental

Materials

N,*N*-dimethylaminoethyl methacrylate (DMAEMA, Fluka) as main monomer, *N*,*N*′-methylenebis(acrylamide) (BAAm, Merck) as crosslinking agent, ammonium persulfate (APS, Merck), and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED, Merck) as redox-initiator system were used as received. Hydrochloric acid (Merck), potassium dihydrogen phosphate (Riedel–de Haen), potassium phosphate (J. T. Baker), disodium hydrogen phosphate (Merck), and sodium chloride (Merck) were used for the preparation of buffer solutions. All of the reagents and the solvents were of the highest available purity and were used as received. Distilled water was used for the preparation of gels as well as for the swelling experiments.

Preparation of PDMAEMA gels

pH-responsive PDMAEMA gels were prepared by free-radical crosslinking polymerization of DMAEMA and BAAm in aqueous solution in the presence of 3.51 mM APS as an initiator and 24.9 mM TEMED as an accelerator. The stock solutions of APS and TEMED were prepared by dissolving 0.080 g APS and 0.375 mL TEMED separately in 10 mL of water. The initial molar concentration of the monomers (BAAm + DMAEMA) was denoted by C_o. Since the gels prepared at C_o less than 0.85 M was too weak to withstand the swelling and the mechanical measurements, C_o was varied between 0.85 and 7.55 M. The crosslinker ratio X (mole ratio of the crosslinker BAAm to the monomer DMAEMA) was fixed at 1/80. The feed compositions and the parameters for the preparation of PDMAEMA gels are shown in Table 1. To illustrate the synthetic procedure in the polypropylene

Table 1 Feed compositions and parameters for the preparation of PDMAEMA gels

C_o, M	$v^0_{2,\,theo}$	$v^0_{2,\,exp}$
0.85	0.075	0.093
1.00	0.085	0.107
1.15	0.095	0.124
2.25	0.175	0.207
3.35	0.218	0.256
4.50	0.375	0.424
5.65	0.469	0.543
6.75	0.562	0.588
7.55	0.628	0.567

3.51 mM APS and 24.9 mM TEMED were used in the feed. The crosslinker ratio X (mole ratio of the crosslinker BAAm to the monomer DMAEMA) was fixed at 1/80

syringes, the details for the preparation of a PDMAEMA gel at $C_o = 1.15$ M can be given as follows:

DMAEMA (1.195 mL), BAAm (13.50 mg), and TEMED stock solution (1.0 mL) were mixed in a 10 mL graduated flask. When the homogenous mixture was obtained, the nitrogen was bubbled through this mixture for 20 min to remove the dissolved oxygen from the system. The initiator APS stock solution (1.0 mL) was added to the mixture and then, the reaction solution was completed to 10 mL with distilled water. After shaking the flask, the solution was transferred to the cylindrical polypropylene syringes with the inner diameters of 5.00 mm and lengths of 15 cm. Then, the syringes were sealed and the polymerization reaction was carried out at -18 °C for 1 day. It was examined that at room temperature, it is not possible to prepare PDMAEMA gels over the whole range of the monomer concentration, since the gels prepared at room temperature are too weak and do not have the cylindrical form which is needed for the measurements. The preparation of PDMAEMA gels over the whole range of the monomer concentration was achieved when the polymerization reactions were carried out at subzero temperature. Upon completion of the polymerization reaction, the gel samples were carefully removed from the syringes without destroying their cylindrical shapes. The resulting gels were cut into samples of about 10 mm in length and then the gel samples were immersed in an excess of distilled water for 2 weeks, the water was changed every day in order to remove the residual unreacted monomers and the sol fraction of the polymer. Then, the gel samples were dried according to the following procedure: the swollen gel samples were successively washed with solutions whose compositions were changed gradually from water to pure acetone. This solvent exchange process facilitates the final drying of the gel samples. The collapsed gel samples after the treatment with acetone were dried in vacuum oven at room temperature to the constant weight and then stored in a vacuum desicator.

The initial monomer concentration can be given in terms of the polymer network concentration. The volume fraction of the crosslinked polymer network after the gel preparation was denoted by v^0_2, the degree of dilution of the gel network after their preparation. In order to determine v^0_2 values of PDMAEMA gels, the gel samples

after preparation were first swollen in water and then dried to constant mass as described above. The experimental values of v_2^0 of PDMAEMA gels were calculated as:

$$v_2^0 = \left[1 + \frac{(q_F - 1)\rho}{d_1}\right]^{-1} \quad (1)$$

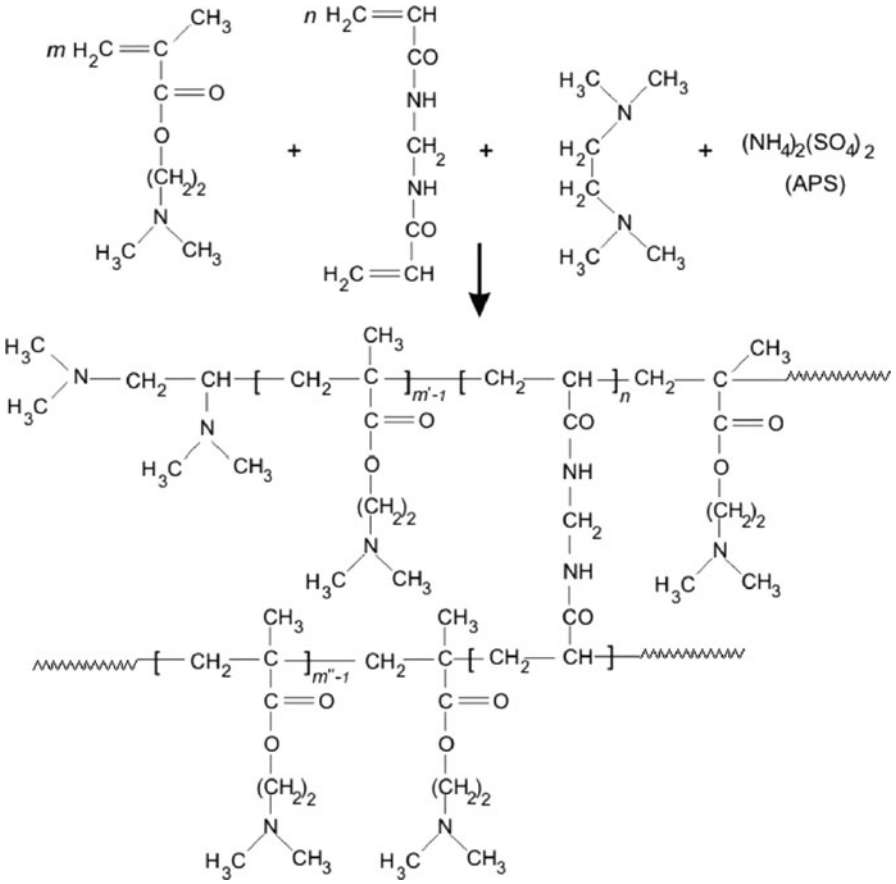
where q_F is the dilution degree after the gel preparation (mass of gel after preparation/mass of dried gel), ρ and d_1 are the densities of PDMAEMA polymer and water, respectively. The values ρ and d_1 used in this study were 1.20 and 1.00 g/mL, respectively. By assuming that the monomer conversion is complete after the crosslinking, it is possible to calculate the theoretical value of v_2^0 from the initial molar concentration of the monomers C_o, by using the equation, $v_2^0 = 10^{-3}\, C_o\, \overline{V}_r$, where $\overline{V}_r$ is the molar volume of PDMAEMA repeat units (in mL/mol). The theoretical values of v_2^0 and the experimentally determined v_2^0 values calculated from Eq. 1 are also shown in Table 1. As it is seen that the experimental v_2^0 values are close to the theoretical ones which would indicate that under the reaction conditions, both the monomer conversions and the gel fractions are complete. In addition, the slight variation in the values indicates the presence of the residual water in the dried polymers. In the literature, it was shown that the gel structures always contain about 10–20 wt% water, even after several months drying under vacuum [35]. Thus, the theoretical v_2^0 values were used for the further calculations.

In the free-radical crosslinking polymerization of DMAEMA and BAAm using APS-TEMED as a redox-initiator system, the first step occurs between APS and TEMED in which the TEMED molecule is left with an unpaired valance electron [36, 37]. The formation of PDMAEMA gels by free-radical crosslinking polymerization of DMAEMA and BAAm monomers was schematically illustrated in Scheme 1.

Characterization of PDMAEMA gels

Equilibrium swelling measurements

The equilibrium swelling measurements of PDMAEMA gels were carried out in distilled water, in buffer solutions as well as in aqueous NaCl solutions. pH-dependent swelling studies of PDMAEMA gels were performed in buffer solutions ranging pH from 2.1 to 11.2 at room temperature. The buffer solutions were prepared immediately prior to use, via standard procedures. For the swelling studies, the gel samples taken from the same gel were immersed in an excess of the solutions for at least 2 weeks to reach the equilibrium swelling at room temperature. Then, by using the volumetric and gravimetric techniques, the equilibrium swelling of PDMAEMA gels was tested both by measuring the diameters and by weighing the gel samples. The weight swelling ratio of PDMAEMA gels, q_w, was calculated as:



Scheme 1 Formation of PDMAEMA gels by free-radical crosslinking polymerization of DMAEMA and BAAm in the presence of APS–TEMED

$$q_w = \frac{m_{\text{swollen}}}{m_{\text{dry}}} \tag{2}$$

where m_{swollen} and m_{dry} are the weights of the gel sample just after equilibrium swelling and after drying, respectively. The diameter of PDMAEMA gel samples both after equilibrium swelling and after preparation was measured by a calibrated digital compass (Mitutoyo Digimatic Caliper, Series 500, resolution: 0.01 mm). Four measurements were carried out on each gel sample to achieve good precision and the volume of the equilibrium swollen gels, V_{eq}, that is the ratio of the volume of equilibrium swollen gel to volume of the gel just after preparation was calculated as:

$$V_{\text{eq}} = \left(\frac{R_{\text{swollen}}}{R_{\text{prep}}}\right)^3 \tag{3}$$

where $R_{swollen}$ and R_{prep} are the diameters of PDMAEMA gel samples after equilibrium swelling and after preparation, respectively. The equilibrium volume swelling ratio of gels q_v and the volume fraction of the crosslinked polymer in the equilibrium swollen gel $v_{2,eq}$ were calculated from the polymer network concentration after the gel preparation v_2^0 as:

$$q_v = \frac{1}{v_{2,eq}} = \frac{V_{eq}}{v_2^0} \tag{4}$$

The swelling behavior of PDMAEMA gels were also performed in aqueous NaCl solutions at room temperature. The diameter of PDMAEMA gel samples after equilibrium swelling in water was first measured and then transferred to the vials containing the least concentrated aqueous NaCl solution. The concentration of NaCl solutions ranged from 10^{-5} to 1.0 M. The gel samples were allowed to swell in the solution at least for 2 weeks, during which aqueous NaCl was refreshed to keep the concentration as constant. When the swelling equilibrium was established, the diameter of the gel samples were measured again and then transferred into the next dilute NaCl solution. The sample diameters were monitored until the changes were within 1% of the previous measurement. Each swelling data reported in this study is an average of at least four separate measurements.

Compressive mechanical testing

In order to characterize the network structure of PDMAEMA gels, the uniaxial compression tests were performed using a home-made compression measurement apparatus of ITU (Istanbul Technical University). For the compression tests performed on PDMAEMA gels, the details can be given as follows: a cylindrical PDMAEMA gel sample of 7 mm in diameter and 10 mm in length was placed on the digital electronic balance. A load was transmitted vertically to the gel through a rod fitted with a PTFE (Teflon) end-plate. The force acting on the gel F was calculated from the data reading of the balance m as $F = mg$, where g is gravitational acceleration ($g = 9.8030$ m s^{-2}) and the resulting deformation, $\Delta l = l_o - l$ where $l_o$and l are the initial undeformed and deformed lengths, respectively, was measured using a digital comparator (IDC type Digimatic Indicator 543-262, Mitutoyo) which was sensitive to the displacements of 10^{-3} mm. The deformation was studied applying a force up to about 20% compression. The force and the resulting deformation were recorded after 15 s of relaxation. The elastic modulus at equilibrium G was calculated according to the following equation:

$$f = F/A = G\left(\alpha - \alpha^{-2}\right) \tag{5}$$

where f is the compressive stress applied that is the force F acting per unit cross-sectional area A of the gel sample and α is the deformation ratio (deformed length/initial length) calculated as $\alpha = 1 - \Delta l/l_o$. The elastic modulus of the PDMAEMA gels at swollen equilibrium was determined using a computer program from the slope of a linear plot of f versus $(\alpha - \alpha^{-2})$. Each elastic modulus data reported in this study is an average of at least four separate measurements.

According to the theory of rubber elasticity, for a network of Gaussian chains, the elastic modulus of swollen gels, G, is related to the effective crosslink density v_e by the following equation [38, 39]:

$$G = Av_eRT\left(v_2^0\right)^{2/3}v_{2,eq}^{1/3} \tag{6}$$

where $v_{2,eq}$ is the volume fraction of the crosslinked polymer in the equilibrium swollen gel, the front factor A equals to 1 for an affine network and $1 - 2/\phi$ for a phantom network, where ϕ is the functionality of the crosslinks, R and T are in their usual meanings. Since $v_2 = v_2^0$ for the gels just after preparation, the elastic modulus G_0 after preparation becomes:

$$G_0 = A\ v_e\ RT\ v_2^0 \tag{7}$$

For a network of Gaussian chains, the reduced modulus G_r is defined as the ratio of the elastic modulus of the equilibrium swollen gel to that of the same gel after its preparation and it is related with v_2^0, $v_{2,eq}$ and the volume of the equilibrium swollen gels V_{eq}as follows:

$$G_r = \frac{G}{G_0} = \left(\frac{v_{2,eq}}{v_2^0}\right)^{1/3} = V_{eq}^{-\frac{1}{3}} \tag{8}$$

The effective crosslink density, v_e, which is defined as the concentration of the elastically active chains can be calculated from the elastic modulus of gels and it is related to the number of segments between consecutive crosslinks N and the average molecular weight of network chains $\overline{M}_c$, by the following equation:

$$v_e = \frac{\rho}{\overline{M}_c} = \frac{1}{NV_1} \tag{9}$$

where, ρ is the polymer density, V_1 is the molar volume of segment, which is generally taken as the molar volume of water (18 mL/mol). Since the gels prepared in this study were highly swollen, the phantom network model ($\phi = 4$) was used for the calculations of the molecular characteristics of PDMAEMA gels. The typical stress–strain dependencies of PDMAEMA gels prepared at various initial monomer concentrations are shown in Fig. 1.

Results and discussion

pH-responsive characteristics of PDMAEMA gels

pH-dependent swelling behavior of PDMAEMA gels were investigated in buffer solutions of various pH's. Since, in the molecular structure of DMAEMA, there is an active amino group with stronger basicity, the protonation of the tertiary group could induce the swelling ratio to change with changing pH. In Fig. 2, the volume of the equilibrium swollen PDMAEMA gels prepared at various initial monomer concentrations is shown as a function of the pH.

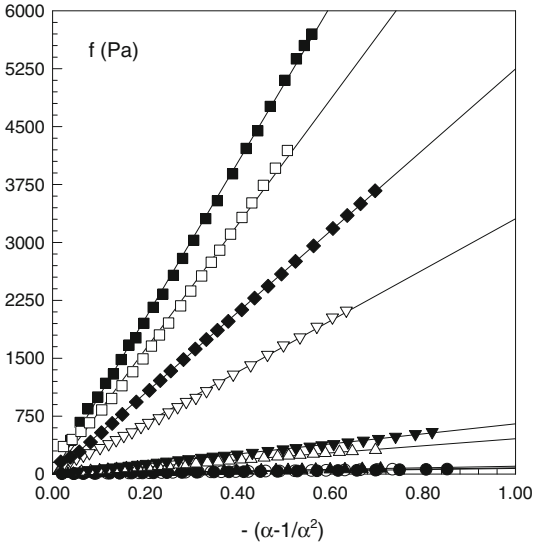


Fig. 1 Typical stress–strain data for PDMAEMA gels just after their equilibrium swelling in water. The initial molar concentration of the monomers C_o/M: 0.85 (*filled circle*), 1.00 (*open circle*), 1.15 (*filled triangle*), 2.25 (*open triangle*), 3.35 (*filled inverted triangle*), 4.50 (*open inverted triangle*), 5.65 (*filled square*), 6.75 (*open square*), 7.55 (*filled diamond*)

Figure 2 shows that PDMAEMA gels are in the swollen state at pH below 7.7 while they are in the collapsed state at or above pH 8.0. In a narrow range of pH between 7.7 and 8.0, PDMAEMA gels undergo a pH-sensitive phase transition during which about eightfold change in the gel volume was observed. This drastic change in the gel volume can also be seen in the photographs shown in Fig. 3 taken from a PDMAEMA gel sample prepared at $C_o = 6.75$ M at pH 7.7 (left) and 8.0 (right) by a digital camera (Sony, Cyber-shot, 8.1 Mega pixel). Sutani et al. [40] reported the dissociation constant pK_a of PDMAEMA as 8.44. It is seen clearly from Fig. 2 that the phase transition pH of PDMAEMA gels is very close to the pK_a

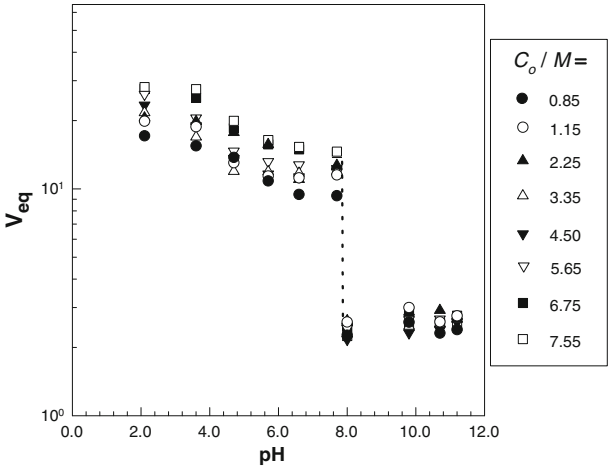


Fig. 2 The volume of the equilibrium swollen PDMAEMA gels V_{eq} shown as a function of the pH value. The initial monomer concentrations C_o are already indicated in the figure

of the corresponding linear polyelectrolyte. An appropriate balance of the hydrophilicity and hydrophobicity in the molecular structure of the polymer network is believed to be the key component in the phase transition behavior of the resulting gels. Hence, the phase transition pH of PDMAEMA homopolymer was found approximately to be 9.0 by Han et al. [15, 23] and also decreased upon copolymerization with the hydrophobic comonomers such as hydroxypropyl methacrylate.

In Fig. 4, the equilibrium volume swelling ratio q_v and the weight swelling ratio of PDMAEMA gels q_w in pH 2.1 and 8.0 buffer solutions are shown as a function of the initial monomer concentration. The curves are the best fit to the experimental data. It was found that the equilibrium swelling values of PDMAEMA gels at pH 2.1 are much higher than those at pH 8.0 over all range of C_o. Since PDMAEMA is a pH-responsive cationic polyelectrolyte containing tertiary amino groups, it was observed that the water content of the PDMAEMA gels is strongly dependent on pH. The tertiary amine groups on DMAEMA are weakly basic and thus, at room temperature, as the pH is lowered to the acidic region, the tertiary amine side chains of the polymer become protonated, increasing the charge density of the network and causing the PDMAEMA gel to swell. The concomitant increase in the mobile counterion content of the network sharply increases the internal osmotic pressure which in turn induces the observed transition [11, 38].

The swelling kinetics of gels depend on the several parameters which include the presence of hydrophilic groups, the crosslink density, the elasticity of the polymer network structure and the properties of the swelling medium. In order to explain the swelling kinetics of PDMAEMA gels, two representative pH values were chosen. Figure 5 shows the response rates of PDMAEMA gels by repeatedly changing the pH in the medium from 2.1 to 8.0. Here, the normalized gel volume V_{rel} (volume of the gel at time *t*/equilibrium swollen volume in pH 2.1 solution) is plotted against the time of the deswelling in pH 8.0 solution and the reswelling in pH 2.1 solution. As it is seen that PDMAEMA gels attain their equilibrium collapsed states within 100 min and its reswelling in pH 2.1 solution to attain the equilibrium swollen state requires about 7 h. The swelling kinetics measurements of PDMAEMA gels also showed that the pH sensitivity of PDMAEMA is quite stable and the swelling process is reproducible in accordance with pH changing.

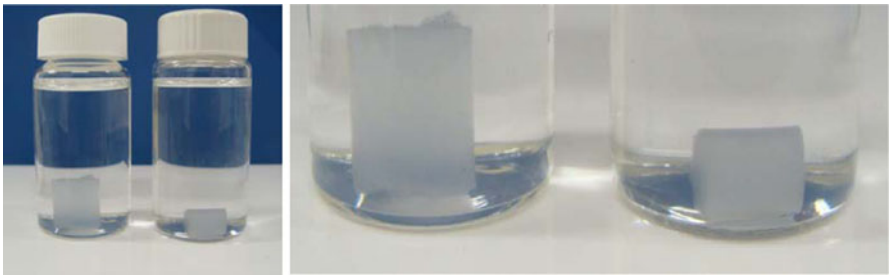


Fig. 3 Photographs of a PDMAEMA gel prepared at $C_o = 6.75$ M. pH 7.7 (*left*) and 8.0 (*right*)

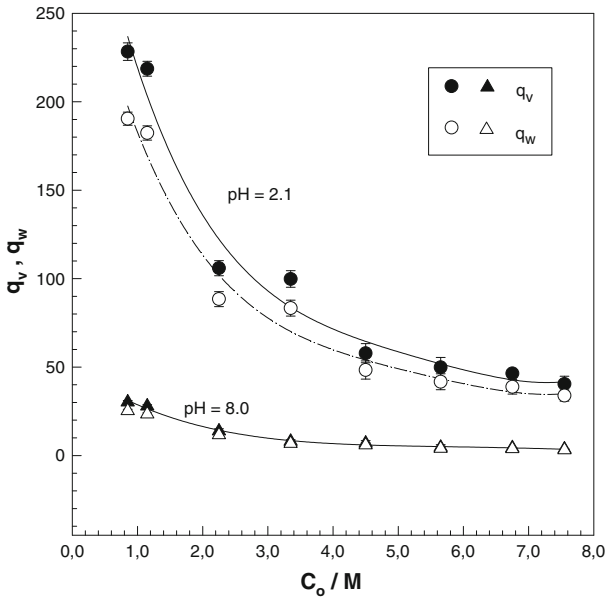


Fig. 4 The volume swelling ratio q_v and the weight swelling ratio of PDMAEMA gels q_w shown as a function of the initial monomer concentration, C_o at pH 2.1 (*filled and open circle*) and pH 8.0 (*filled and open triangle*). The curves are the best fit to the experimental data

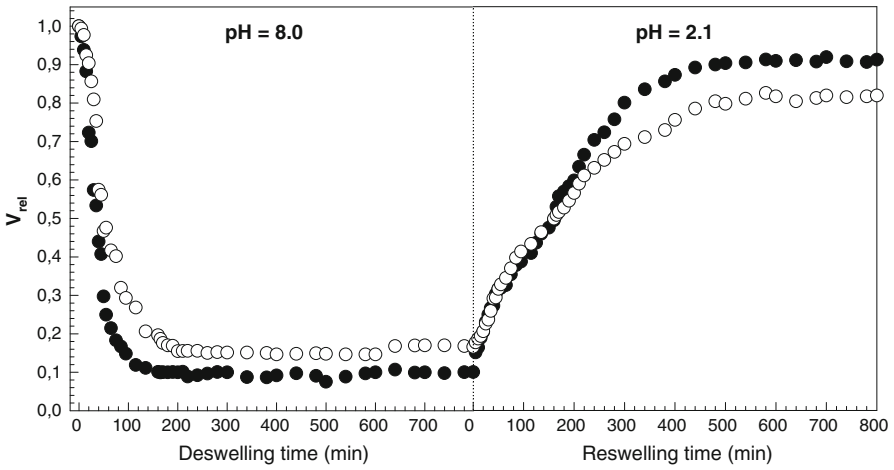


Fig. 5 The normalized volume of PDMAEMA gels V_{rel} shown as a function of the time of deswelling in pH 8.0 solution and reswelling in pH 2.1 solution. The initial monomer concentration is C_o/M = 4.50 (*open circle*) and 7.55 (*filled circle*)

Swelling of PDMAEMA gels in aqueous NaCl solutions

In Fig. 6, the volume of the equilibrium swollen PDMAEMA gels V_{eq} is shown as a function of the NaCl concentration in the external solution. The initial monomer

concentration of gels C_o is already indicated in the figure. The swelling measurements in aqueous NaCl solutions showed that PDMAEMA gels also exhibit salt sensitive swelling behavior over the entire range of the initial monomer concentrations. As shown in the Fig. 6, the swelling ratio of PDMAEMA gels decreases with increasing salt concentration in the external solution. The decrease in V_{eq} is first rapid up to 10^{-2} M NaCl concentration, this is mainly due to a decrease in the concentration difference of the counter ions inside and outside of the gel. As the NaCl concentration further increases, the decrease in V_{eq} slows down and between 10^{-1} and 10^{0} M NaCl, V_{eq} values slightly decrease with increasing salt concentration. During the swelling of PDMAEMA gels in concentrated NaCl solutions, the mobile counterion concentration (Na^+) in the external solution is higher than that of in the gel phase, which results in an osmotic pressure that water molecules inside the gel flow from the gel to the solution phase so that the PDMAEMA gel deswells as observed in the figure.

Molecular characteristics of network structure of PDMAEMA gels

In addition to the swelling measurements, the analysis of the deformation of the polymer network resulting from the compressive mechanical testing is one of the important way to characterize the network structure. Thus, the elasticity of polymer networks has been the subject of the numerous experimental studies to make a relation between the elastic modulus and the molecular structure. The influence of

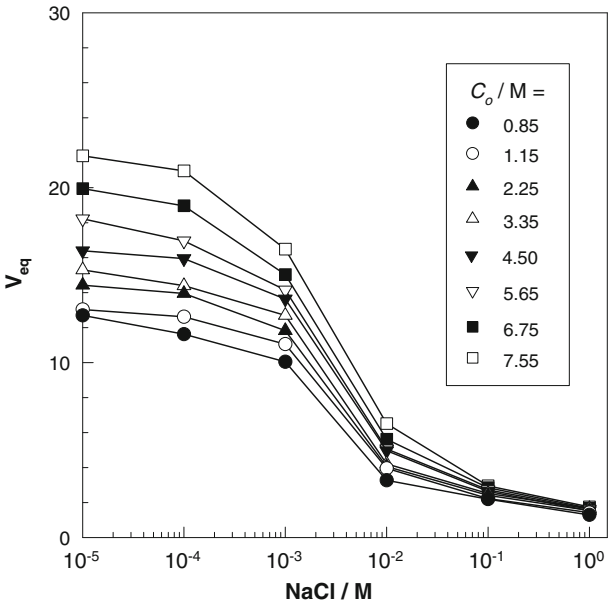


Fig. 6 The volume of the equilibrium swollen PDMAEMA gels V_{eq} shown as a function of the NaCl concentration in the external solution. The *solid curves* only show the trend of the data. The initial monomer concentration of gels C_o are already indicated in the figure

the network structure on the elastic behavior is reflected principally through the macroscopic elastic modulus. In Fig. 7a, the elastic modulus of PDMAEMA gels after equilibrium swelling in water G is shown as a function of C_o. Figure 7b shows the swelling ratio of PDMAEMA gels after equilibrium swelling in water in terms of the volume fraction of the crosslinked polymer in the equilibrium swollen gel $v_{2,eq}$ plotted as a function of C_o. By using the G, $v_{2,eq}$ and v_2^0 values of PDMAEMA gels together with Eq. 6, one may calculate the effective crosslink densities v_e of PDMAEMA gels. The results for the phantom network model ($\phi = 4$) are shown in Fig. 7b as solid symbols plotted against C_o. The curves in Fig. 7b only show the trend of the experimental data.

As seen from Fig. 7a, the elastic modulus of PDMAEMA gels after equilibrium swelling in water G first increases with increasing C_o up to 5.65 and then slightly decreases with further increasing C_o. During the swelling process, the network chains are forced to attain more elongated and less probable configurations. The absorption of water by the gel causes the network to expand and its chains to stretch. As a result, the chains making up the network is assumed in a stretched conformation as the polymer network swells. Hence, like pulling a spring from both ends, a decrease in the chain configurational entropy is produced by the swelling process. Since the network chains in these swollen gels are in the expanded configuration with respect to dry state, the increase of the elastic modulus is connected with the high stretching of the network chains. However, for $C_o > 5.65$, the elastic modulus slightly decreases as the polymer network concentration increased. In this region, the swelling of PDMAEMA gels in terms of $v_{2,eq}$ also decreases with increasing C_o as seen from Fig. 7b.

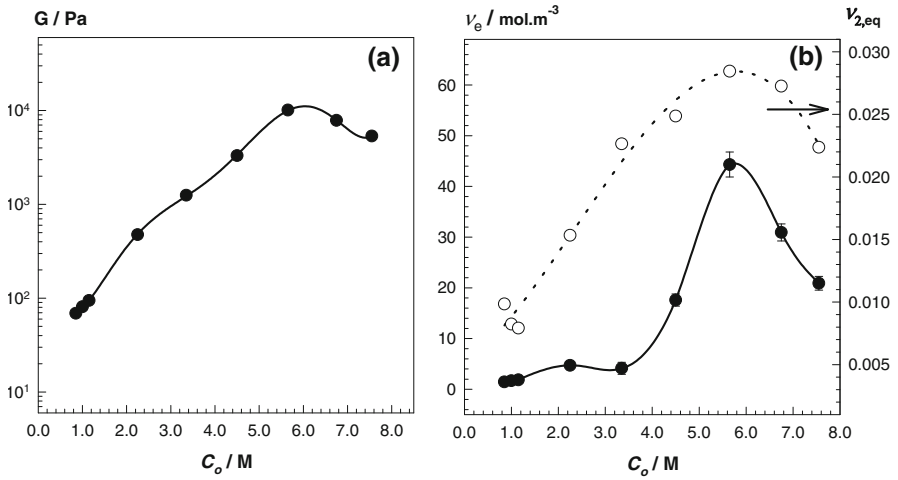


Fig. 7 **a** Elastic modulus of PDMAEMA gels after equilibrium swelling in water G shown as a function of C_o. **b** Effective crosslink density v_e of gels shown as a function of C_o by *solid symbols*. The volume fraction of the crosslinked polymer in the equilibrium swollen gel $v_{2,eq}$ is also shown by *open symbols*. The *curves* show the trend of the data

As shown in Fig. 7b that both $v_{2,eq}$ and v_e increase with increasing C_o up to 5.65. Since the polymer network concentration of gels v_2^0 is inversely proportional to the volume swelling ratio of gels q_v (Eq. 4), it can be concluded that increasing the gel preparation concentration results in increased $v_{2,eq}$. Owing to the fact that increasing polymer network concentration during the gel formation decreases the probability of the cyclization and the multiple crosslinking reactions, increasing C_o results in increased effective crosslink densities. Another point shown in Fig. 7b is that, for $C_o > 5.65$, both the volume fraction of the crosslinked polymer in the equilibrium swollen gel and the effective crosslink density decrease with increasing C_o. Since the polymer concentration is relatively high in this regime, the pendant vinyl groups during the gel formation tend to have lower relative reactivities because of the steric hindrance. Previous studies also showed that at high monomer concentrations, the receptibility of the pendant vinyl groups by the other polymer molecules is strongly reduced [25, 28]. As the average reactivity of pendant vinyls for intermolecular reactions compared to the monomeric vinyls decreases, it was found that a fraction of pendant vinyl groups remains unreacted in the final gel. This leads to the observed decrease in the crosslink density of PDMAEMA gels on rising C_o. It can be concluded that the PDMAEMA gel crosslink density becomes maximum at $C_o = 5.65$ and then decreases due to the cyclization and the steric effects going downward from the maximum point to the lower or higher polymer concentrations, respectively.

During the compressive mechanical testing, the photographs of PDMAEMA gels prepared at $C_o = 7.55$ M are shown in Fig. 8. The images in the figure demonstrate how the PDMAEMA gel remains mechanically stable up to larger compression. Since the PDMAEMA gels exhibit a high modulus of elasticity (Table 2), they were tough and it was found that they can be compressed up to about 80% strain without any crack development. As the PDMAEMA gel is compressed under the piston, the gel releases its water and after the release of the load, the gel sample immediately recovers its original shape as seen from the images.

For a network of Gaussian chains, the reduced modulus G_r of gels should decrease continuously with the gel swelling due to the decrease of the concentration of the elastically effective network chains. For this reason, the reduced modulus G_r of PDMAEMA gels at a given degree of swelling was calculated using the Eq. 8 and the results were plotted against the equilibrium gel volume V_{eq} in Fig. 9a. The reduced modulus monotonically decreases as the gel swells beyond its swelling degree after preparation. According to Eq. 8, the double-logaritmic G_r versus V_{eq} plot should exhibit a slope of $-1/3$ for Gaussian chains. The solid curve is the best fit to the experimental data, which gives an exponent -0.35 ± 0.06, close to the theoretical value of $-1/3$. It is seen that Fig. 9a shows good relation with the theory. Thus, it can be concluded that PDMAEMA gels swollen to equilibrium in water behave as Gaussian. Since the swelling of gels is strongly affected by the polymer–solvent interaction parameter, χ, the swelling behavior of PDMAEMA gels was also analyzed by using Flory-Rehner theory of swelling equilibrium [38]. For the calculation of the interaction parameter χ between the PDMAEMA network and water, the following expression of Flory-Rehner equation for phantom chains was used:

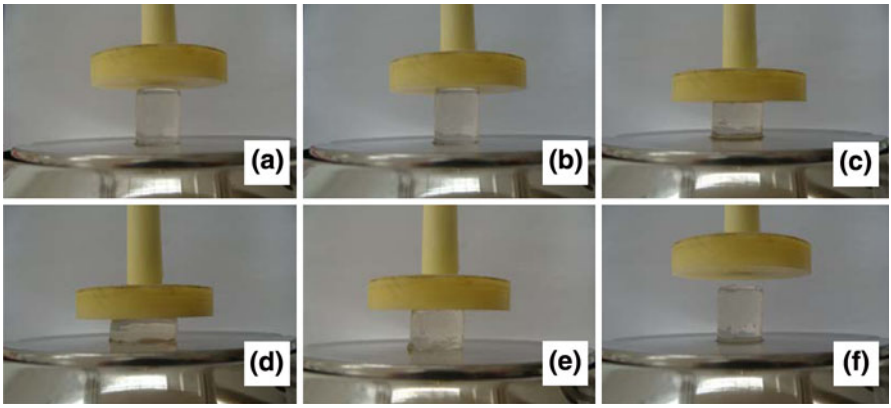


Fig. 8 Photographs of PDMAEMA gels prepared at $C_o = 7.55$ during the uniaxial compression tests. Strain % in the measurements: **a** 0%, **b** 5%, **c** 30%, **d** 80%, **e** 25%, and **f** 0%

Table 2 Molecular characteristics of PDMAEMA gels

C_o, M	G/Pa	$\overline{M}_c$/kg mol^{-1}	N_{phan}	χ
0.85	69 (3)	820.7 (15.4)	37996	0.4981
1.00	81 (1)	710.3 (6.8)	32884	0.4941
1.15	95 (7)	647.6 (5.2)	29984	0.4917
2.25	475 (17)	254.7 (3.4)	13793	0.4905
3.35	622 (25)	290.4 (2.6)	13445	0.4989
4.50	3308 (12)	68.2 (1.4)	3158	0.4696
5.65	10116 (222)	27.1 (1.3)	1254	0.4189
6.75	7852 (409)	38.8 (1.5)	1796	0.4325
7.55	5352 (306)	57.4 (1.2)	2657	0.4299

C_o the initial molar concentration of the monomers, G the elastic modulus of gels after equilibrium swelling in water, $\overline{M}_c$ the average molecular weight between consecutive crosslinks, N the average number of segments between two successive crosslinks, χ the interaction parameter between the PDMAEMA network and water. The *numbers* in parenthesis are the standard deviations of the separate measurements

$$\chi = -\frac{\ln\left(1 - v_{2,eq}\right) + v_{2,eq} + 0.5\left(\rho/\overline{M}_c\right)V_1\left(v_{2,eq}\right)^{1/3}\left(v_2^0\right)^{2/3}}{\left(v_{2,eq}\right)^2} \tag{12}$$

By using the experimentally determined equilibrium swelling ratios and the $\overline{M}_c$ values of PDMAEMA gels, the interaction parameter χ of the PDMAEMA–water system was obtained as $\chi = 0.475 \pm 0.028$ in the range of $v_{2,eq}$ between 0.0098 and 0.0224. It was found that the χ parameter of PDMAEMA–water system which describes the total interaction between the PDMAEMA network and water is nearly independent on v_2 in the range of interest. The elastic modulus of gels after equilibrium swelling in water G, $\overline{M}_c$ values of gels found from the uniaxial

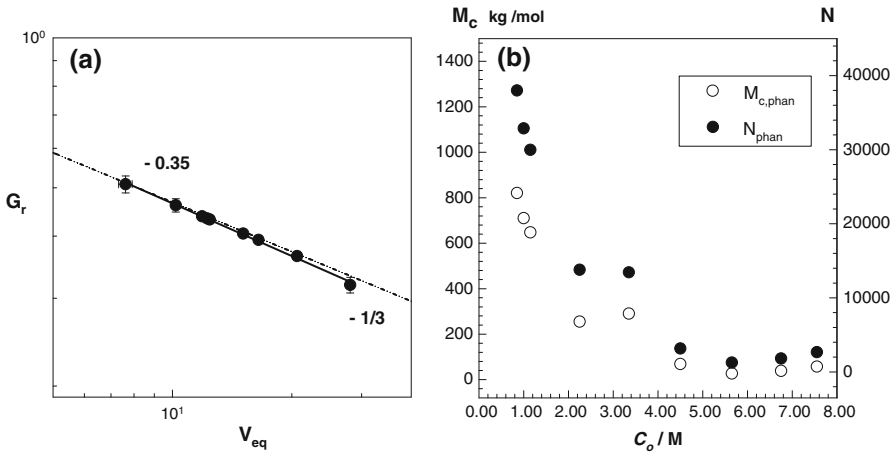


Fig. 9 **a** Reduced modulus G_r shown as a function of the volume of equilibrium swollen gel V_{eq}. The *solid curve* is the best fit to the experimental data. The *dotted curve* represents the prediction of Eq. 8. The corresponding slopes are already shown. **b** Network chain length N (*filled symbols*) and the average molecular weight between consecutive crosslinks $\overline{M}_c$ of PDMAEMA gels (*open symbols*) with $X = 1/80$ shown as a function of C_o

compression experiments, χ parameter at each initial monomer concentration and the other related parameters are already given in Table 2.

For PDMAEMA gels, from uniaxial compression measurements, the network chain length N was calculated by using Eq. 9. In Fig. 9b, the filled symbols show the network chain length N of PDMAEMA gels plotted as a function of C_o and the average molecular weight between consecutive crosslinks $\overline{M}_c$ of PDMAEMA gels is also shown by the open symbols. It is seen that both N and $\overline{M}_c$ decreases first rapidly up to about $C_o = 5.6$ M, but then, they increases only slightly with C_o. The slight variation of N in this high concentration regime is due to the reducing reactivity of the pendant vinyl groups during crosslinking as well as due to the increasing extent of the chain entanglements. Previous works showed that PDMAAm hydrogels also exhibit similar behavior in the range of v_2^0 below 0.30 [33, 34]. Thus, it can be concluded that the effective crosslink density of PDMAEMA gels is very sensitive to the initial monomer concentration if C_o is below 5.6 M. This behavior can be explained with decreasing probability of the cyclization as the monomer concentration during polymerization is increased.

Conclusions

In this study, pH-responsive PDMAEMA gels were obtained by free radical crosslinking polymerization of DMAEMA with BAAm using APS-TEMED as a redox-initiator system. The effect of the initial monomer concentration on the polymerization of DMAEMA, the equilibrium swelling behavior and the mechanical properties of resulting PDMAEMA gels were investigated. pH-dependent

swelling measurements in buffer solutions ranging from pH 2.1 to 11.2 showed that PDMAEMA gels are pH-responsive and exhibit pH-sensitive phase transition at pH 8.0. As pH is lower than 8.0, the tertiary amine group becomes protonated and thus, the charge density of the network increases and PDMAEMA gels remains in the swollen state. When pH is higher than 8.0, the gels tend to be compact. It was also observed that the phase transition pH of PDMAEMA gels is very close to the pK_a of the corresponding linear PDMAEMA polyelectrolyte. The swelling kinetic measurements of PDMAEMA gels performed by repeatedly changing the pH values from 2.1 to 8.0 showed that the pH sensitivity of PDMAEMA is quite stable and the swelling process is reproducible in accordance with pH changing. From the equilibrium swelling studies of gels in aqueous NaCl solutions, it was found that PDMAEMA gels also exhibit strong salt sensitive swelling behavior over the entire range of the initial monomer concentrations. The elasticity of PDMAEMA gels studied by the uniaxial compression measurements showed that the elastic modulus of PDMAEMA gels in equilibrium swollen increases with increasing initial monomer concentration. The elasticity data was also used to characterize the molecular characteristics of PDMAEMA gels. Both the effective crosslink density v_e and $v_{2,eq}$ of gels first increase with increasing C_o due to the decreasing extent of the cyclization and the multiple crosslinking reactions and then, decrease with further increasing C_o due to the increasing extent of the chain entanglements in this high concentration regime.

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