



Crosslinked DADMAC polymers as cationic super absorbents

Sinan Korpe^a, Barış Erdoğan^b, Goknur Bayram^b, Serkan Ozgen^a, Yusuf Uludag^b, Niyazi Bicak^{c,*}

^a Middle East Technical University, Aerospace Engineering Dept., Ankara, Turkey

^b Middle East Technical University, Chemical Engineering Dept., Ankara, Turkey

^c Istanbul Technical University, Chemistry Dept., Maslak 34469, Istanbul, Turkey

ARTICLE INFO

Article history:

Received 27 February 2009

Received in revised form 31 March 2009

Accepted 10 April 2009

Available online 21 April 2009

Keywords:

Cationic hydrogel

Super absorbent

Crosslinking

Polyelectrolyte

Poly(DADMAC)

ABSTRACT

Loosely crosslinked cationic polyelectrolytes (polyquats) with super-water-sorption abilities are presented, for the first time. Hydrogels obtained by radically initiated copolymerization of *N,N*-diallyl, *N,N*-dimethyl ammonium chloride (DADMAC) with *N*-vinyl 2-pyrrolidone (NVP) in presence of *N,N,N',N'*-tetraallyl piperazinium dichloride (TAP) as crosslinker showed reasonably high equilibrium swelling ratios, as high as those for poly(acrylic acid)-based super absorbents.

The highest swelling ratios (up to 360) were attained by fully cationic hydrogels derived from DADMAC and 0.5% TAP. The hydrogels with 0.5–5% crosslinkers exhibited rapid expansion in neutral water, so that the equilibrium swelling values were attained within 2–3 min. The crosslinking densities of the gels were estimated by Flory-type swelling model using “phantom network elasticity” for the elastic contribution. This estimation revealed low crosslinking efficiencies of TAP (0.24–0.35) due to its double cationic charge.

In the study “the salt effect” and effects of the comonomer ratios and crosslinker contents on the swellings were also investigated.

© 2009 Elsevier Ltd. All rights reserved.

1. Introduction

Super absorbent hydrogels are crosslinked polymers exhibiting unusually high water uptake abilities [1]. These materials have found extensive use mostly in manufacturing of baby diapers [2] and sanitary napkins [3]. These have been used also in agriculture to retain moisture in the soil [4] and in construction to protect buildings from water drainage [5]. Humidity control in food packaging [6] and pressure sensitive switching in electronics [7] are other applications of super absorbents. Commercial super absorbent hydrogels are almost confined to crosslinked poly(acrylic acid). Swelling of this polymer depends on pH of the solution and ionization degrees of the carboxyl group involved [8]. In the literature, there appear numerous reports dealing with preparation and application of the super absorbent polymers. Crosslinked polymers of 2-acrylamido-2-methylpropanesulfonic acid have been demonstrated to show very high water imbibitions capacities [9]. Since the sulfonic acid group in this polymer is completely ionized, swelling of their hydrogels is not pH-dependent.

The use of *N*-isopropylacrylamide as comonomer has been demonstrated to impart temperature sensitivity into the super absorbent polymers [10].

Rathna and Damodaran described synthesis of protein-based super absorbent using glutaraldehyde as post-crosslinking agent

[11]. In principle, weakly crosslinked gels of water-soluble polymers with nonionic or ionic groups can be considered as potential super absorbents. However, fast response in swelling seems to be main criteria in application viewpoint.

Many cationic hydrogels and their water sorption characteristics have also been reported by our group [12] and others [13]. Zhai et al. reported radiation crosslinking of DADMAC-dimethylamino ethyl methacrylate copolymers yielding hydrogels for drug delivery [14]. Ha and Ren described preparation of kappa-carrageenan-DADMAC interpenetrating network hydrogels by UV irradiation [15]. Polymerization of vinyl monomers possessing quaternary ammonium groups, such as DADMAC [16] and methacrylamidopropyl trimethyl ammonium chloride (MAPTAC) [17] have found considerable interest in this respect.

Although, water sorption behavior of the crosslinked quaternary ammonium polymers (polyquats) is well known, to our best, there is yet no report dealing with super absorbency of the hydrogels with cationic charges.

Theoretical models on the gel swelling assume equilibrium between elastic, osmotic and polymer–solvent interaction forces [18]. In the case for charged hydrogels the later is negligible comparing with the osmotic forces. Since contribution of osmotic forces to the swelling depends on ionization degrees of the charged groups, logically fully ionized nature of the quaternary ammonium groups is expected to give poly(DADMAC) hydrogels with super-water-sorption abilities, if sufficient elasticity is imparted.

* Corresponding author.

E-mail address: bicak@itu.edu.tr (N. Bicak).

Herein we describe synthesis of super absorbent DADMAC–NVP copolymer gels, using *N,N,N',N'*-tetraallyl piperazinium dichloride as crosslinker.

2. Experimental

2.1. Materials

All the chemicals used were analytical grade products; 2,2'-azo bis-(2-methyl propionamidine) dihydrochloride (Alrich), *N,N*-dimethyl, *N,N*-diallyl ammonium chloride (DADMAC) (65% aqueous solution) (Alrich) were used as purchased.

N-vinyl pyrrolidone (NVP) (Alrich) was purified according to the procedure described in the literature [19] before use. *N,N'*-diallyl piperazine was prepared by reaction of piperazine with allyl chloride, as reported before [12].

2.2. Preparation of *N,N,N',N'*-tetraallyl piperazinium dichloride (TAP)

This was prepared by quaternization of *N,N'*-diallyl piperazine with allyl chloride as follows: To a 250 mL volume of flat bottom flask, 33.2 g (0.2 mol) *N,N'*-diallyl piperazine and 36.7 g (0.48 mol) allyl chloride were added and the mixture was left to stand for over 2 months at room temperature. The white solid was leached in 50 mL of diethyl ether and quickly filtered. The residue was washed with acetone (25 mL) and ether (25 mL). Since the product is very hygroscopic, it was stored in closed bottle without further drying. The crude yield was 52.2 g (81.2%). The yields within shorter contact times were always low (i.e. 21.3% for one week). It was observed that, the quaternization reaction can be hastened by heating at 80 °C in the presence of 50 mg KI. However, the product obtained was dark grey. For this reason two months of reaction time was chosen to obtain white product.

¹H-NMR spectrum, δ (ppm) in D₂O: 6.1 (4H, m, C=CH), 5.9 (8H, t, C=CH₂), 4.4 (8H, d, allylic protons), 4.03 (8H, s, piperazine ring protons).

2.3. Crosslinking copolymerization of DADMAC with NVP

The crosslinking copolymerizations were carried out in highly concentrated aqueous solutions of the monomer mixture (40%). In a typical procedure, a mixture of 9.94 g (0.04 mol) commercial *N,N*-diallyl, *N,N*-dimethyl ammonium chloride solution (65%), 1.07 g (9.5×10^{-3} mol) 1-vinyl 2-pyrrolidone, 0.16 g (5×10^{-4} mol) TAP and 0.14 g (5×10^{-4} mol) 2,2'-azo bis-(2-methyl propionamidine) dihydrochloride was placed in a 100 mL volume of three-necked flask equipped with a reflux condenser and a nitrogen inlet. The mixture was purged with nitrogen for 2 min.

Then 8.26 mL distilled water was added so that final total monomer concentration was to be 40% by weight. The flask was placed in a thermo-stated oil bath and the reaction was conducted at 65 °C under continuous stirring.

Generally, gelation took place within 15–75 min depending on the crosslinker content. The gels formed were left to stand for 24 h at this temperature, in order to reach the maximum degree of crosslinking. The resulting transparent gels were broken up and washed with water three times (3×400 mL) in a cotton purse. The gel samples were then transferred onto glass plates and dried at 75 °C under vacuum for 24 h.

Using this procedure, a series of gel samples with varying comonomer ratios and crosslinker contents was prepared.

In the first series mol fraction of the crosslinker (TAP) was kept constant at 1% and molar ratio of DADMAC component was changed to be 0, 0.3, 0.5, 0.7 and 0.995. In the second series, equimolar

DADMAC–NVP mixtures were polymerized in the presence various amounts of TAP (in 0.5%, 1%, 2%, 5% molar ratios). In the third series, poly(DADMAC) gel with 0.5% and 1% mol crosslinker was prepared.

FT-IR spectra of the products with NVP (which were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer) show typical C=O stretching vibration band of this segment. The quaternary group vibration of DADMAC segment appears around 2300 cm⁻¹.

2.4. Swelling measurements

Swelling of the gel samples were followed gravimetrically at room temperature. A weighed amount of dry gel sample (usually 0.1 g) was taken in a pouch and soaked into distilled water in a beaker. The pouch was removed at specific time intervals and left to suspend for a while (usually 30 min) for drainage excess of water. The bag was dried by a soft paper and weighed. Net weight of the swollen gel was assigned by subtracting wet weight of the bag. Wet weight of the bag was determined separately by the same way. Swelling ratio of the gel, q was defined as; water uptake per gram of dry polymer.

$$q = \frac{Q_s - Q_{dry}}{Q_{dry}} \quad (1)$$

where Q_s and Q_{dry} are weights of the swollen and dry gels, respectively. The equilibrium swelling values were determined based on weights of the samples after contacting with water for 16 h. Average of three measurements were used to assign the swelling ratios.

The effect of salt or acid on the water uptake capacity was studied similarly, except the gel samples were allowed to swell in NaCl and HCl solutions in appropriate concentrations (0.017–6.85 M).

The same procedure was followed in the kinetic experiments. To make precise assignments measurements were performed as soon as possible, in which final weights of swollen gels were determined after rapid suction.

3. Results and discussion

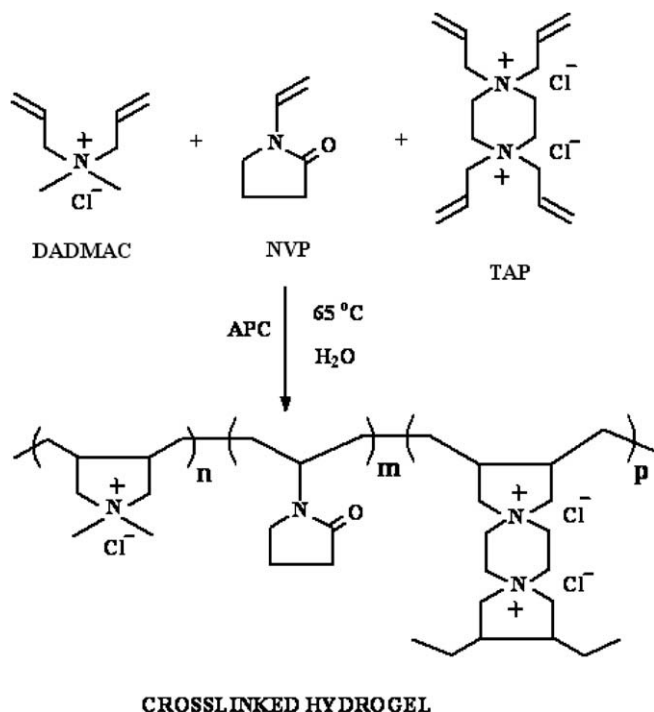
Topchiev et al. [20] reported that, copolymerization of DADMAC with *N*-vinyl pyrrolidone proceeds alternating fashion.

By adding bifunctional comonomer, TAP to the copolymerization mixtures, in this work we have prepared a series crosslinked gels with various comonomer ratios, by radical polymerization using 2,2'-azo bis-(2-methyl propionamidine) dihydrochloride (ABP) as initiator. An interesting aspect of DADMAC polymerization is that, this monomer can be polymerized only in highly concentrated solutions, due to strong Coulombic repulsion between the quaternary ammonium groups, as evident from Butler's pioneering work on the cyclopolymerization of this monomer [21]. Due to this reason, the terpolymerization reactions were performed at high monomer concentrations (40% w/w) at 65 °C.

Herein TAP was chosen as crosslinker due to its structural similarity with DADMAC and non-hydrolysability in acid and base solutions. Well-known water-soluble crosslinker, methylene bisacrylamide was not preferred owing to its relatively easy hydrolysis to give toxic formaldehyde especially in acid conditions [22].

The reactions, in these conditions resulted in gelation within 15–75 min, depending on concentration of the crosslinker, TAP (Scheme 1). This procedure yields hard and transparent gels in high yields (>92%). FT-IR spectra of the copolymer gels exhibit individual characteristic bands of NVP and DADMAC segments at 1660 and 2300 cm⁻¹, respectively, indicating involvement of the two components.

Since polymerization or copolymerization of diallyl ammonium monomers takes place mostly via five-membered ring formation,



Scheme 1. Crosslinking terpolymerization of DADMAC with NVP and TAP.

the gels obtained in this work must contain pyrrolidinium units in the main chain, as depicted in Scheme 1.

3.1. Swelling characteristics of the gels

Swellings of dry gel samples were assigned by weight gains in the swollen state. Fig. 1 shows that the swelling ratio of the gel sample with 1% mole of TAP increases monotonically by increasing DADMAC content. In the case of the gel constituting with DADMAC and TAP (1% mole), the equilibrium volume swelling ratio rises up to 150, whereas this ratio is around 21 for the case of crosslinked PNVP gel. This reveals that, incorporation of NVP segments into gel structure does not bring any enhancement in the swelling ratios. Moreover, brittleness of the resulting gels implied that, this component does not provide elastic contribution to accommodate more water in the crosslinked polymer matrix.

Fig. 2 shows the equilibrium swellings as a function of crosslinker ratio of the gel with 1/1 DADMAC/NVP molar ratio.

It was shown that, increasing TAP content of 1/1 DADMAC/NVP gel from 0.5% to 5% decreases its swelling ratio from 205.3 to 27

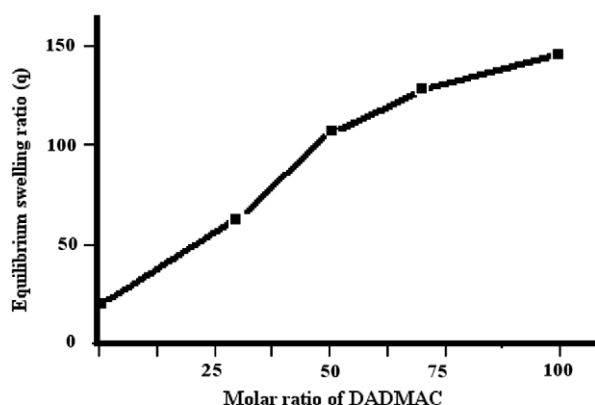


Fig. 1. Effect of DADMAC content on volume swelling ratio of the gels with 1% (mol/mol) crosslinker.

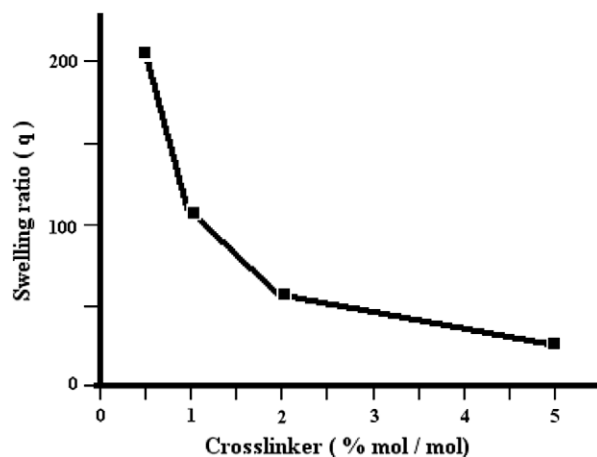


Fig. 2. Effect of TAP (0.5–5%) content on swelling ratio of 1/1 DADMAC/NVP gel.

(Fig. 2). This implied that the actual density of the crosslinking is somewhat lower than predicted from the stoichiometry of TAP (0.5×10^{-2} – 5×10^{-2} mol/mol).

To inspect the efficiency of TAP, crosslink densities were estimated by Flory-type gel swelling model using ideal Donnan equilibrium.

Various swelling models have been developed for correlation of crosslink densities with swelling ratios. In the Flory-type swelling model, the swelling pressure of a gel is assumed to be sum of three contributions [23].

$$\pi_{\text{sw}} = \pi_{\text{mix}} + \pi_{\text{elas}} + \pi_{\text{ion}} = 0 \quad (2)$$

where π_{mix} represents contribution of polymer–solvent interaction, π_{elas} is elastic contribution and π_{ion} represents osmotic pressure of the mobile ions in the gel phase. Flory–Rehner theory is applicable to swelling of neutral polymer gels successfully [24]. In this theory, π_{mix} is considered to be identical with that of uncrosslinked polymer at the same concentration in the same solvent [25]. This contribution is given by Flory–Huggins theory [26] as follows:

$$\pi_{\text{mix}} = -\frac{RT}{V_1} [\ln(1 - \phi_2) + \phi_2 + \chi \phi_2^2] \quad (3)$$

where R is gas constant, T is temperature, V_1 is molar volume of the solvent, ϕ_2 is volume fraction of the crosslinked polymer in swollen state and χ is polymer–solvent interaction parameter (Flory parameter). For highly swellable polyelectrolyte gels, this term is negligible comparing with π_{ion} term.

Two network models; “affine network model” and “phantom network model” have been developed for the elastic contribution in the gel swelling. These models describe extreme limits of the fluctuations of chain segments between the crosslink points. In affine network model, the elastic contribution is given [26] by:

$$\pi_{\text{elas}} (\text{affine}) = -2C_c RT \left[\left(\frac{\phi_2}{\phi_{20}} \right)^{1/3} - \frac{1}{2} \left(\frac{\phi_2}{\phi_{20}} \right) \right] \quad (4)$$

where C_c is crosslinker concentration at reference state, ϕ_{20} is volume fraction of dry gel at reference state. In this model, chain fluctuation between the crosslinks is completely suppressed, whereas in the phantom network model, the crosslink points fluctuate freely and neighboring segments are flexible. In the phantom network model, the elastic contribution is given [27] by:

$$\pi_{\text{elas}} (\text{phantom}) = -C_c NRT \left(\frac{\phi_2}{\phi_{20}} \right)^{1/3} \quad (5)$$

where N is efficiency of the crosslinker.

Of course, real elastic behavior of a gel is in between these limits and must be described by combination of these two network models, as reported by Praustnitz and co-workers [28]. In the case of loosely crosslinked polyelectrolyte gels, the elastic behavior approaches to that of phantom network model. Therefore, in the present work, phantom network elasticity was chosen for description of the elastic contribution.

By neglecting small contribution of π_{mix} , the osmotic pressure of mobile chloride ions, π_{ion} was simply balanced with π_{elas} (phantom).

Osmotic pressure of mobile ions (Cl^- and OH^-) in the gel phase is given [28] by:

$$\pi_{\text{ion}} = RT \sum (C_{\text{gel}} \gamma_{\text{gel}} - C_{\text{w}} \gamma_{\text{w}}) \quad (6)$$

where C_{gel} is concentration of mobile chloride and OH ions in the gel phase. γ_{gel} and γ_{w} are the activity coefficients of the mobile ions in the gel and water phase, respectively. Concentration of the chloride ions in DADMAC–NVP (1:1) gel was estimated by Donnan equilibrium, in which the chloride ions are replaced with OH anions. The Donnan equilibrium of HCl in these conditions can be written as:

$$\text{H}^+(\text{gel}) \cdot \text{Cl}^-(\text{gel}) \gamma_{\text{gel}} = \text{H}^+(\text{aq}) \cdot \text{Cl}^-(\text{aq}) \cdot \gamma_{\text{aq}} \quad (7)$$

Taking H^+ concentration of neutral water is 10^{-7} M, depletion of the chloride ions in the gel phase, x can be correlated with the initial chloride ion concentration, C as follows:

$$\text{H}^+(\text{gel}) = \frac{K_{\text{w}}}{x} \quad \frac{K_{\text{w}}}{x} (C_0 - x) = 10^{-7} x \quad (8)$$

where K_{w} is protonation constant of pure water ($K_{\text{w}} = 10^{-14} \text{ mol}^2/\text{L}^2$ at 25°C). Since quaternary ammonium groups of DADMAC and TAP are fully ionized [28], total concentration of the quaternary groups were assumed equal to concentrations of the chloride ions (C_0) prior to equilibrium. C_0 was calculated from the relationship;

$$C_0 = \frac{[\text{DADMAC}] + 2[\text{NVP}]}{V_{\text{sw}}} \quad (9)$$

where V_{sw} is volume of the gel (mL per gram of dry polymer) in swollen state. The terms in brackets represent molar quantities of DADMAC and TAP per gram in dry polymer. Those C_0 values were employed in Eq. (7) for calculation of the amounts of chloride ions (x) escaping from the gel phase.

The activity coefficients of mobile ions (γ) in the gel phase were estimated by extended Debye–Huckel theory [29] as follows:

$$\log \gamma(\text{gel}) = - \frac{0.503(Z_i)^2 \sqrt{I(\text{gel})}}{1 + 0.329a^0 \sqrt{I(\text{gel})}} \quad (10)$$

where, a^0 denotes average radius of Cl and OH^- ions in terms of angstrom ($\sim 3 \text{ \AA}$), $I(\text{gel})$ is the ionic strengths in the gel phase and is defined as:

$$I(\text{gel}) = \frac{1}{2} \sum C_i (Z_i)^2 \quad (11)$$

where Z_i is the ionic charge. In this calculation, total concentration of univalent mobile ions was taken as C_0 , due to loss of chloride ions is being compensated by OH^- ions exchanged. The x values calculated from Donnan equilibria of DADMAC–NVP (1:1) gels are of order of 10^{-4} M, their activity coefficients, $\gamma(\text{aq})$ in the aqueous phase were taken unity.

In order to find efficiency of the crosslinker, N the Eqs. (4) and (5) were combined and rearranged to:

$$N = \frac{(C_0 - x) \gamma(\text{gel}) - x \left(\frac{\phi_{20}}{\phi_2} \right)^{1/3}}{C_c} \quad (12)$$

This equation yielded crosslinking efficiencies 0.25–0.35 for DADMAC–NVP (1:1) gels with 0.5–5% crosslinker (Table 1). This calculation was repeated based on swelling of the same gel ($\phi_2 = 92.6$) with 1% crosslinker in NaCl solution (0.017 M). Donnan equilibrium of NaCl, $(C_0 + x)x = (a - x)^2$, indicated presence of 3.63×10^{-3} M NaCl in the gel phase at the equilibrium. Similar calculation yielded a crosslinking efficiency of 0.283, which is almost equal to that obtained from swelling in distilled water.

These results indicate that, efficiency of TAP in the crosslinking is always lower than that predicted from stoichiometry of the polymerization. This can be ascribed to strong electrostatic repulsion between TAP molecules with two positive charges. Moreover, crosslinking efficiency of TAP is proportional to its concentration and reduces from 0.354 to 0.241, while molar ratio of TAP varies between 5% and 0.5%. This might be due to less polymerization tendency of TAP in dilute conditions.

The highest swelling ratio, 360 was observed for poly(DADMAC) gel with 0.5% TAP. Although there is no commonly approved lower limit for the super-absorbency, the highest swelling ratio, 360 attained in this work falls in 200–1000 range, which was reported for poly(acrylic acid)-based super absorbents [30]. Similar estimation of the crosslinking efficiency of this gel prepared using 0.5% (mole/mole) TAP revealed an efficiency of 0.255, which is almost one fourth of the feed composition. Therefore real crosslinking degree of this gel is $0.5\% \times 0.255 \approx 0.13$ which indicates existing of Kuhn segments (chains between two crosslink points) longer than predicted. In this work, we have also attempted to prepare gels with even lower crosslinker contents. Unfortunately we were not able to obtain any gel using TAP lower than 0.5% in the same polymerization conditions.

3.2. Swelling kinetics of the gels

All the gel samples showed unusually fast swellings in distilled water. Fig. 3 shows swelling ratio–time plots of the gel samples with different DADMAC and crosslinker contents. The curves A and B at the bottom represent swelling of the crosslinked (1%) hydrogels with 70% and 99.5% DADMAC, respectively. The upper curve (curve C) is for the poly(DADMAC) gel with 0.5% crosslinker. In all cases, the swelling curves exhibit sudden jumps within 2 min and level off beyond that.

Table 1

Swelling and crosslinking characteristics of 1/1 DADMAC–NVP gels with various crosslinker contents.

Crosslinker (%)	Q/Q_0^a	ϕ_2	C_0 (M)	C_c (M)	x (M)	$\gamma(\text{gel})$	N
5	26.9	30.4	0.147	0.144	1.2×10^{-4}	0.780	0.354
2	56.8	64.2	0.067	0.06	0.82×10^{-4}	0.834	0.323
1	107.3	121.2	0.0347	0.03036	0.51×10^{-4}	0.889	0.285
0.5	206.0	232.8	0.018	0.0153	0.43×10^{-4}	0.904	0.241
1 ^b	82	92.6	0.04547	0.03036	3.63×10^{-3}	0.85	0.283
0.5 ^c	360	410	0.0172	0.0114	4.14×10^{-5}	0.905	0.255

^a The swelling ratios were average of three measurements and given in ± 0.2 error limits.

^b In 0.017 M NaCl solution.

^c Poly(DADMAC) hydrogel without NVP.

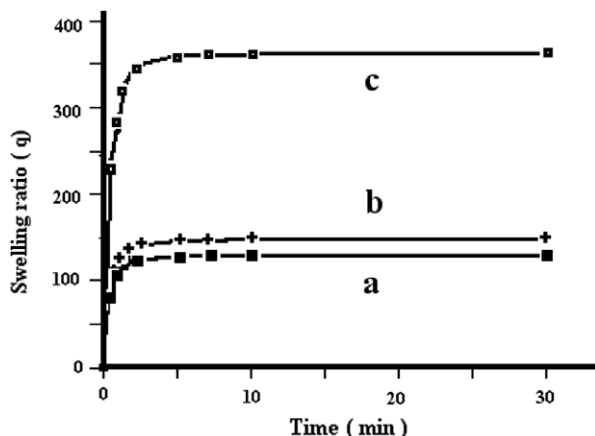


Fig. 3. Swelling ratio versus time plots for the gels with 70% DADMAC and 1% TAP (a), 99% DADMAC and 1% TAP (b) and 99.5% DADMAC and 0.5% TAP (c).

Swelling kinetics of polyelectrolyte gels is defined by the following differential equation [31]:

$$\frac{dQ}{dt} = k[Q_{\max} - Q] \quad (13)$$

where $Q(t)$ represents swelling ratio of gel (gram per gram of dry polymer) at time, t , $Q_{\max}$ denotes corresponding equilibrium ratio and k is the “swelling rate coefficient”.

Integration of this equation gives,

$$k = -\frac{1}{t} \ln \left[1 - \frac{Q(t)}{Q_{\max}} \right] \quad (14)$$

Using the kinetic values in Fig. 3, $\ln[1 - \frac{Q}{Q_{\max}}]$ was plotted against t for 0–2 min time interval (Fig. 4). From the slopes of the straight lines, the swelling rate coefficients were estimated to be $k = (2.7 \pm 0.3) \times 10^{-2}$, $(2.8 \pm 0.3) \times 10^{-2}$ and $(2.9 \pm 0.4) \times 10^{-2} \text{ s}^{-1}$ for the curves a, b and c respectively.

Obviously sharp rise of the curves is due to fast flow of water into the gel matrixes to compensate the osmotic pressure between inside and outside of the gel particles.

3.3. The salt effect

Swelling ratios were shown to be greatly reduced by NaCl in water. This reveals typical “salt effect” on poly(DADMAC) gels as

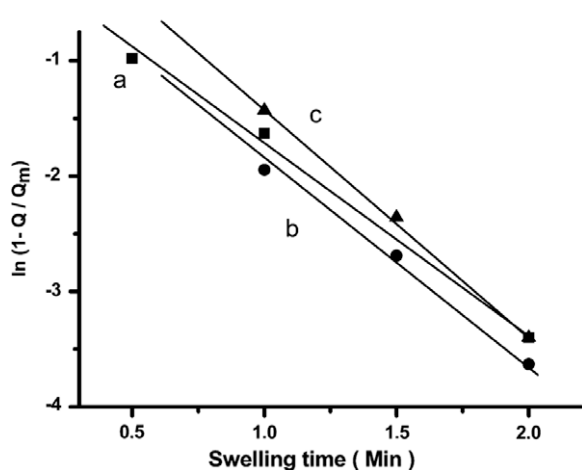


Fig. 4. Semi logarithmic plots of swelling kinetics within 0–2 min of time interval for the gels with 70% DADMAC and 1% TAP (a), 99% DADMAC and 1% TAP (b) and 99.5% DADMAC and 0.5% TAP (c).

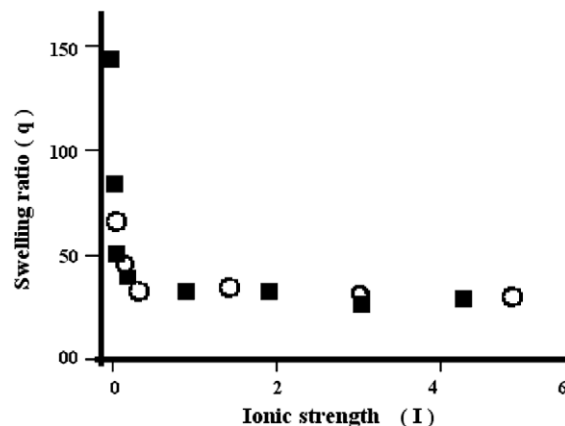


Fig. 5. Swelling ratio of poly(DADMAC) gel with 1% (mol/mol) TAPS in NaCl (○) and HCl (■) solutions, as a function of ionic strength.

reported by Khokhlov and his co-workers [32] on DADMAC-methylene bisacrylamide gels.

Fig. 5 shows that, swelling ratio of poly(DADMAC)–TAP (1%) gel reduces from 145 down to 30 in 0.2 M NaCl solution and further increase in concentration of brine does not change the swelling ratio.

Molar concentration of the quaternary ammonium group at this point is:

$$\frac{1/161.5}{30 \times 10^{-3}} = 0.206$$

This value fairly matches with the concentration of NaCl ($\sim 0.25 \text{ M}$) at the inflection point of the swelling curve. Sharp decrease of the swelling in presence of dilute NaCl is clear evidence for the salt effect on the cationic gels.

Similar shrinking effect was observed in the presence of HCl. Since quaternary ammonium groups of poly(DADMAC) are fully ionized in all pH ranges [33], acidity of the solution does not affect the swelling ratios as expected. Therefore, effect of HCl is due to its ions rather than its acidity. Indeed in the presence of HCl the swelling ratio–concentration curve exhibits almost the same trend as in the case for NaCl (Fig. 5). The same shrinking effect of NaCl was also observed in other gel samples constituting with NVP.

4. Conclusion

This study showed that, super absorbent hydrogels can also be prepared from cationically charged monomer, DADMAC using TAP as crosslinker. Copolymerizability of DADMAC with NVP allows preparing the copolymer gels in high yields. However, presence of NVP in the cationic hydro gels does not provide any advantage over DADMAC–TAP gels exhibiting better swelling abilities. The crosslinker, TAP, is superior to methylene bisacrylamide (BIS) as water soluble crosslinking agent, owing to susceptibility of the latter to hydrolysis yielding toxic formaldehyde. It is important to note that, high monomer concentration (40% or more) is essential to attain high polymerization yields. This makes it difficult to impart macroporosity into gels by using excess water as porogen, in the gel forming process.

Nevertheless, the procedure described in this work allows preparing cationic super absorbents in concentrated solutions. Having a swelling ratio of 360 in distilled water, the copolymer of DADMAC with TAP (0.5%) can be considered as super absorbent polymer. Considering with the antibacterial effect of linear quaternary ammonium polymers, this material is expected to show the same behavior. This is advantage of the cationic hydrogels over traditional poly(acrylic acid)-based super absorbents.

Although there remain many things to be studied, such as polymerization in more concentrated solutions, gel blocking and antibacterial effects, this cationic gel is promising material as super absorbent due to its fast swelling ability.

References

- [1] F.L. Buchholz, Keeping dry with super absorbent polymers, in: F.L. Buchholz, N.A. Peppas (Eds.), *Super Absorbent Polymers: Science and Technology*, ACS Symposium Series, 1994, pp. 38–43.
- [2] H. Omidian, S.A. Hashemi, P.G. Sammes, I.G. Meldrum, *Polymer* 39 (1998) 3459.
- [3] H. Hirose, M. Shibayama, *Macromolecules* 31 (1998) 5336.
- [4] A. Moriyoshi, I. Fukai, M. Takeguchi, *Nature* 344 (1990) 230.
- [5] K.S. Kazanskii, S.A. Dubrovskii, *Adv. Polym. Sci.* 104 (1992) 97.
- [6] T. Shimomura, T. Namba, in: F.L. Buchholz, N.A. Peppas (Eds.), *Superabsorbent Polymers, Science and Technology*, ACS Symposium Series 573, American Chemical Society, Washington, DC, 1994, pp. 112–115.
- [7] K. Sawahata, J.P. Gong, Y. Osada, *Macromol. Rapid Commun.* 16 (1995) 713.
- [8] J.E. Mark, B. Erman, *Rubberlike Elasticity, A Molecular Primer*, John Wiley and Sons Inc., New York, 1988.
- [9] F. Rosa, J. Bordado, M. Casquilho, *Polymer* 43 (2002) 63.
- [10] C. Zhang, A.J. Easteal, *J. Appl. Polym. Sci.* 94 (2004) 2083.
- [11] G.V.N. Rathna, D. Srinivasan, *J. Appl. Polym. Sci.* 81 (2001) 2190.
- [12] N. Bicak, B.F. Senkal, T. Sismanoglu, C. Ozeroglu, *J. Polym. Sci. Polym. Chem.: Part A* 38 (2000) 1006.
- [13] S.A. Ali, S.Z. Ahmed, E.Z. Hamad, *J. Appl. Polym. Sci.* 61 (1996) 1077.
- [14] Y.L. Zhang, L. Xu, M. Yi, M.L. Zhai, J.R. Wang, H.F. Ha, *Eur. Polym. J.* 42 (2006) 2959.
- [15] J. Ren, H.F. Ha, *Eur. Polym. J.* 37 (2001) 2413.
- [16] N. Liu, M. Yi, S.J. Chen, H.F. Ha, *Chin. J. Polym. Sci.* 20 (2002) 409.
- [17] J.P. Baker, L.H. Hong, H.W. Blanch, J.M. Praustnitz, *Macromolecules* 27 (1994) 1446.
- [18] J.P. Baker, L.H. Hong, H.W. Blanch, J.M. Praustnitz, *Polymer* 36 (1995) 1061.
- [19] C.H. Bamford, E. Schofield, D.J. Michael, *Polymer* 26 (1985) 945.
- [20] D.A. Topchiev, A.I. Martynenko, Y.E. Kabanova, V.D. Oppengeim, Y.E. Kirsh, T.M. Karaputadze, *Russ. Chem. Bull.* 39 (1990) 1788.
- [21] G.B. Butler, *J. Polym. Sci. Polym. Chem.: Part A* 38 (2000) 3451.
- [22] Y.L. Yin, R.K. Prudhomme, *ACS Symp. Ser.* 480 (1992) 91.
- [23] M. Ilavsky, *Polymer* 22 (1981) 687.
- [24] J. Ricka, T. Tanaka, *Macromolecules* 17 (1984) 2916.
- [25] G.B. McKenna, K.M. Flynn, Y. Chen, *Macromolecules* 22 (1989) 4507.
- [26] P.J. Flory, *Principles of Polymer Chemistry*, Cornell University, Ithaca, NY, 1953.
- [27] H.M. James, E. Guth, *J. Chem. Phys.* 15 (1947) 669.
- [28] H.H. Hooper, J.P. Baker, H.W. Blanch, J.M. Prausnitz, *Macromolecules* 23 (1990) 1096.
- [29] W. Stumm, J.J. Morgan, *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, third ed., John Wiley and Sons Inc., New York, 1996.
- [30] H. Omidian, S.A. Hashemi, P. Sammes, I.G. Meldrum, *Polymer* 39 (1998) 6697.
- [31] F.L. Buchholz, in: L. Brannon-Peppas, R. Harland (Eds.), *Absorbent Polymer Technology*, Elsevier Science Publishers, New York, 1990, pp. 233–247.
- [32] C.H. Jeon, E.E. Makhaeva, A. Khokhlov, *Macromol. Chem. Phys.* 199 (1998) 2665.
- [33] Z. Tong, X. Liu, *Macromolecules* 27 (1994) 844.