Radiation synthesis and characterization of poly($N,N$-dimethylaminoethyl methacrylate-co-$N$-vinyl 2-pyrrolidone) hydrogels

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Abstract

In this study, radiation synthesis and characterization of swelling behavior and network structure of poly($N,N$-dimethylaminoethyl methacrylate) (PDMAEMA), and poly($N,N$-dimethylaminoethyl methacrylate-co-$N$-vinyl 2-pyrrolidone) (P(DMAEMA-co-VP)), hydrogels were investigated. PDMAEMA and P(DMAEMA-co-VP) hydrogels in the rod forms were prepared by irradiating the ternary mixtures of DMAEMA/VP/cross-linking agent, ethyleneglycol dimethacrylate (EGDMA), by gamma rays at ambient temperature. In composition ranges where the three components were completely miscible, water was also added to the ternary mixture to provide the formation of homogeneous polymerization and gelation. The influence of irradiation dose, comonomer, VP, and cross-linking agent, EGDMA, content on the total percentage gelation and monomer conversion were investigated. The effect of pH and temperature on the swelling behavior of hydrogels have also been examined. Hydrogels showed typical pH response and temperature responses, such as low-pH and low temperature swelling and high-pH and high temperature deswelling. Polymer–solvent interaction parameter ($\chi$) and enthalpy and entropy changes appearing in the $\chi$ parameter for the P(DMAEMA-co-VP)–water system were determined by using Flory–Rehner theory of swelling equilibrium. The negative values for $\Delta H$ and $\Delta S$ indicate that prepared pure PDMAEMA and P(DMAEMA-co-VP) hydrogels have lower critical solution temperature (LCST) and Flory–Rehner theory of swelling equilibrium provides a satisfactory agreement to the experimental swelling data of the hydrogels.

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1. Introduction

Poly-electrolytes are polymers which contain relatively ionizable groups at levels ranging from a few mole percentage to 100% of the repeating units. Poly-electrolytes may be anionic, cationic or amphiphilic and may be synthetic or naturally occurring. The preparation of poly($N,N$-dimethylaminoethyl methacrylate) (PDMAEMA) and its copolymers has gained noticeable interest and a series of paper published by Siegel and Firestone in the late eighties [1–3]. They investigated the influence of comonomer $n$-alkyl ($n$-AMA) and methyl methacrylate (DMA) on the pH-dependent swelling properties and swelling kinetics. It

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was found that the extent of the transition from the collapsed hydrophobic state to the hydrophilic state changed depending on the comonomer composition and as the proportion of n-AMA to DMA is increased generally the extent of the transition is reduced and shifted to lower pH. It was also observed that increasing the length of the n-AMA side chain was also caused a reduction in the extent of the transition.

In recent years much more attention has been directed to PDMAEMA hydrogels that undergo controllable volume changes in response to small variation of pH and temperature changes in solution condition for use in a variety of novel application including controlled drug delivery [4,5] and gene transfer agent [6–8].

Traitel et al. [4] synthesized glucose-responsive insulin controlled release system based on the hydrogel, poly(2-hydroxy ethyl methacrylate-co-N,N-dimethylaminoethyl methacrylate), with entrapped glucose oxidase, catalase and insulin. It was found that pH sensitive poly(HEMA-co-DMAEMA) hydrogels can be used as glucose-responsive insulin release systems for the reducing blood glucose level.

Recently, Kim et al. [9] studied the PDMAEMA and polyethyl acrylamide microspheres. The release of hydrocortisone was studied in various pH and temperatures. It was found that the release of hydrocortisone in response to pulsatile pH changes and release rate increased drastically due to dissociation of polymer complex at acidic conditions. However, decrease of pH increased the LCST of polymer complex of microsphere led to the dissociation of aggregate polymer complex and released of hydrocortisone in stepwise manner. As a result of these studies, authors proposed that based on the pH/response sensitivity of hydrogen bond in the microsphere, pH/temperature response characteristics and enthalpy and entropy changes appearing in the $\chi$ parameter for the $\text{P(DMAEMA-co-VP)}$–water system were also determined.

2. Experimental

2.1. Chemicals

The two monomer used in this study, namely $N,N$-dimethylaminoethyl methacrylate (DMAEMA) and $N$-vinyl 2-pyrrolidone (VP) were obtained from Aldrich. The cross-linking agent EGDMA was obtained from BDH.

2.2. Preparation of hydrogels

Four components were used in the preparation of poly($N,N$-dimethylaminoethyl methacrylate-co-$N$-vinyl 2-pyrrolidone) $\text{P(DMAEMA-co-VP)}$ hydrogels, namely $N,N$-dimethylaminoethyl methacrylate, $N$-vinyl 2-pyrrolidone, cross-linking agent, ethylene glycol dimethacrylate and water. Various compositions were prepared where the four components showed complete miscibility. For the preparation of aqueous solutions, 2 ml of 100% DMAEMA, 90% DMAEMA and 10% VP, 70% DMAEMA and 30% VP (as volume ratio) containing mixtures were mixed 1 ml water and 0.1%, 0.5% and 1.0% by volume EGDMA were added into these solutions. The volume percentages of monomers in the initial mixtures are summarized in Table 1. In the notation used for the identification of samples, the numbers preceding the abbreviations denote the percentage composition by volume. Since the densities of the monomers are close to each other and the conversion is almost 100% we can assume that volume composition can be taken as the same as the weight composition. Thus, the prepared monomer solutions were placed in PVC straws of 3 mm diameter and irradiated up to 8.0 kGy in Gammacell-220 type $\gamma$-irradiator at a fixed dose rate of 0.16 kGy/h. Hydrogel obtained in long cylindrical shapes were cut into pieces of 2–3 mm and stored for later evaluations.
2.3. Composition of gels

Irradiated mixtures were dried in a vacuum oven at 315 K to constant weight and subjected to Soxhlet extraction with water as solvent. Uncross-linked polymer and/or residual monomer were removed with this extraction from the gel structure. Extracted gels were dried again in vacuum oven at 315 K to constant weight. The amount of uncross-linked DMAEMA was determined by titration of extract against HCl (0.02 mol/l) to phenolphthalein end point. Percentage gelation i.e., percentage conversion of monomers and cross-linking agent into insoluble networks, was based on the total weight of the cross-linking agent and monomers in the initial mixture.

2.4. Swelling studies

Dried hydrogels (2–3 mm thickness, 3 mm diameter) were left to swell in a solution of desired pH (2–9) ionic strength, I = 0.1 mol/l and temperature. Swollen gels were dried in vacuum oven at 315 K to constant weight. The amount of uncross-linked DMAEMA was determined by titration of extract against HCl (0.02 mol/l) to phenolphthalein end point. Percentage gelation i.e., percentage conversion of monomers and cross-linking agent into insoluble networks, was based on the total weight of the cross-linking agent and monomers in the initial mixture.

3. Result and discussion

3.1. PDMAEMA hydrogels

When pure N,N-dimethylaminoethyl methacrylate (DMAEMA) monomer was irradiated with gamma rays, polymerization and cross-linked reactions took place simultaneously. The total dose required for the onset of gelation was determined to be 40 kGy for this system. The hydrogels prepared above gelation dose showed low mechanical stability and ruptured upon swelling. This is most probably due to the presence of polymerized, but not cross-linked, DMAEMA chains entrapped in the gel structure. Their loss as sol fraction upon contact with water will naturally weaken the mechanical stability of gel. When DMAEMA irradiated at high doses i.e. 70 kGy, only 10% conversion from monomer to gel structure was observed.

3.2. P(DMAEMA/EGDMA) hydrogels

To decrease the gelation dose and increase the cross-link density at the same time, a difunctional cross-link agent, ethyleneglycol dimethacrylate (EGDMA) was added to monomer. The hydrogels obtained in the presence of 0–0.1% EGDMA behaved similarly to pure PDMAEMA gels. that is upon swelling the geometric shape of the gel was destroyed. This is probably due to insufficient formation of cross-links. The gels prepared with 0.1–1.0% EGDMA, however, were very stable and showed uniform swelling properties in water but disintegrated at low pH values. This behavior was attributed to inhomogeneous cross-link formation within the gel structure. When EGDMA added in 1.0–2.0%, the gels again ruptured when in contact with water, which is most probably due to increase of the inhomogeneous distribution of cross-link within the hydrogel. The internal pressure developed upon swelling of inhomogeneous network structure may be responsible for the poor mechanical properties of these gels. The effect of irradiation dose and the amount of EGDMA on % gelation of DMAEMA are given in Fig. 1(a). As can be shown from figure, the percentage gelation from monomer to insoluble network increases with increasing irradiation dose until 4.0 kGy. After that, gelation remains almost constant.

3.3. P(DMAEMA/VP/EGDMA) hydrogels

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to DMAEMA and EGDMA system. When pure N-vinyl 2-pyrrolidone monomer has been irradiated with gamma rays, polymerization and cross-link reactions take place simultaneously. The sensitizing effect of water for the gelation of N-vinyl 2-pyrrolidone (VP), acrylamide (AAm) and copolymers of AAm and VP were very well demonstrated in our previous studies [13–16]. So in this study the ternary mixtures of DMAEMA/VP/EGDMA were irradiated in the presence of water. The effect of irradiation dose on the percentage gelation of 90% DMAEMA and 10% VP, 70% DMAEMA and 30% VP and 0.1–1.0% EGDMA containing aqueous systems are given in Fig. 1 (b) and (c). When percentage gelation versus dose curves are compared with the DMAEMA/EGDMA system it can be seen that gelation is achieved at almost the same dose values. However, addition of VP and water promote both polymerization and cross-link reactions especially at low doses. Hydrogels obtained from ternary monomer mixtures were very homogeneous and had very high mechanical stability and were not disintegrated in aqueous solutions even at low pH values.

3.4. pH responsive characteristics of hydrogels

In order to follow the pH response of the PDMAEMA hydrogels, dry samples are allowed to swell to equilibrium in phosphate buffers of varying pH at fixed ionic strength (I = 0.1) and temperature (25 °C). Fig. 2 shows the changes in the equilibrium degree of swelling of PDMAEMA hydrogels containing various ratios of VP and EGDMA with changing pH values. Consistent with poly-electrolyte systems, swelling of these gels is strongly dependent on pH. A decrease in the pH from 8 to 2 caused a significant increase in the equilibrium volume swelling ratio of hydrogel. In all compositions maximum extent of swelling were reached at pH 2, this being due to complete protonization of amine groups of PDMAEMA at this pH value.

As can be seen from the figures, the value of the equilibrium volume swelling ratio of the hydrogel systems are strongly dependent on the concentration of the cross-linking agent in the network. Increase in the EGDMA content in the network reduced the swelling degree dramatically at all pH values especially when the concentration of EGDMA is relatively high. 0.25% and 2.0% EGDMA containing systems are given in Fig. 2 for comparison purpose.

The value of equilibrium volume swelling ratio depends on the concentration of ionizable groups in the network. Recently Şen et al. studied the cross-linked poly(N-vinyl 2 pyrrolidone-co-itaconic acid) poly-electrolyte hydrogels and the effect of pH on the equilibrium volume swelling ratio was investigated at various
pH values [17]. It was found that the addition of only minute amounts of itaconic acid comonomer (0.2 mol%) radically changed the swelling behavior of the hydrogel system. However, in this study, no significant changes on the equilibrium volume swelling ratio value was not observed with the variation of DMAEMA weight percent from 100 to 70 in the gel system as shown in Fig. 2. This can be attributed to unchanging of ionizable amine group/total amine group ratio by changing DMAEMA content in the gel system. It is quite well known that increase of weak acid or base concentration in the system decreases percentage of ionization groups from 100% (in extremely dilute solution) to below 5% when the solution is concentrated and remains almost constant after a certain concentration. The variation of hydrophilicity/hydrophobicity ratio with variation of composition may be another reason for this behavior, although decrease of ionizable groups with decreasing DMAEMA content increases hydrophilicity or swelling with VP content increases percentage swelling of hydrogel system. Consequently, almost the same equilibrium volume swelling ratio could be obtained for constant EGDMA, different DMAEMA/VP ratios.

3.5. Temperature-responsive characteristics of hydrogels

Fig. 3 represent the influence of temperature on the equilibrium volume swelling ratio of PDMAEMA and P(DMAEA-co-VP) hydrogels in water. As can be seen from figure, slightly cross-linked DMAEMA hydrogels exhibit sharp changes in water content as a function of temperature. The curve of the swelling ratio against the temperature becomes continuous volume transition for each hydrogel composition as the EGDMA content in the gel increased. Water content changes are due to volume collapse upon warming. It has been shown that a number of hydrogels demonstrate sharp or nearly continuous volume transition and associated phase transition from a low temperature, highly swollen gel network to a collapsed, high temperature phase near their critical points. For the poly PDMAEMA hydrogels, the hydrophilic group (amino $-$NH($\text{CH}_3)_2$) in the hydrogel structure forms an intermolecular hydrogen bond with the surrounding water at low temperatures (under the gel transition temperature, $\sim$30 °C) [18]. However, this behavior changes when the temperature is greater than the gel transition temperature. The hydrogen bond between the hydrophilic group and the surrounding water breaks, and the hydrogels become more hydrophobic, resulting in a collapsed state for the gel.

The phase transition is analogous though fundamental distinct from the lower critical solution phase transition (LCST). Cho et al. [19] have found that PDMAEMA has a LCST around 50 °C in water and with the formation of the gel network it exhibits transi-
tion temperature around 40 °C and shifts to the lower temperatures with the increasing cross-linking density. It is known that the LCST should decrease with the increasing hydrophobicity of the polymer. With the increase of cross-linker content in the gel network, the cross-linking density increases result in the decrease of swelling and the increase of hydrophobicity of the gel network.

The transition temperature of PDMAEMA and P(DMAEMA-co-VP) hydrogels were determined from the first derivative of the temperature versus $V/V_0$ curves in Fig. 3 and the results are given in Table 2. Table 2 indicates that the transition temperature is independent from the DMAEMA or VP content in the gel and also the cross-link density of the network structure. This behavior may be attributed to the higher degree of cross-linking of the hydrogel structure as a result of radiation induced and chemical cross-linking during preparation.

3.6. Molecular weight between cross-links

For the characterization of the network structure and determination of molecular weight between cross-links ($M_c$) of prepared hydrogels, the swelling properties at non-ionized state (pH 7) were first investigated. Swelling experiments were continued until a constant value of swelling was reached for each sample. This weight was used to calculate the volume fraction of polymer $V_{2m}$ and the equilibrium volume swelling ratio, $(V/V_0)$ (volume of swollen gel/volume of dry gel) by using Eq. (1). After swelling experiments the uniaxial compression was applied using the Universal Testing Instrument on the swollen gels at pH 7. Typical stress–strain curves of hydrogels are given in Fig. 4(a). Very similar stress–strain curves were obtained for P(DMAEMA-co-VP) hydrogels. As can be seen from the figure, the magnitude of strain percentage at maximum deformation decreased and stress increased with increasing EGDMA content. Shear modulus values of hydrogels were calculated by using elastic deformation theory and Eq. (2) [20]:

Table 2

<table>
<thead>
<tr>
<th>Gel name</th>
<th>Transition temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100DMAEMA0.1E</td>
<td>28.3</td>
</tr>
<tr>
<td>100DMAEMA0.5E</td>
<td>27.4</td>
</tr>
<tr>
<td>100DMAEMA1.0E</td>
<td>27.3</td>
</tr>
<tr>
<td>90DMAEMA10VPE0.1</td>
<td>27.9</td>
</tr>
<tr>
<td>90DMAEMA10VPE0.5</td>
<td>25.4</td>
</tr>
<tr>
<td>90DMAEMA10VPE1.0</td>
<td>26.8</td>
</tr>
<tr>
<td>70DMAEMA30VPE0.1</td>
<td>30.0</td>
</tr>
<tr>
<td>70DMAEMA30VPE0.5</td>
<td>26.7</td>
</tr>
<tr>
<td>70DMAEMA30VPE1.0</td>
<td>27.8</td>
</tr>
</tbody>
</table>
When the equation is applied to the initial stages of deformation, plots of $f$ vs. $\frac{k}{C_0}k_2$ yield straight lines, Fig 4 (b). Where, $k$ is deformation ratio and equal to $L/L_0$. $L_0$ and $L$ are the length of the undeformed and deformed hydrogels during compression, respectively. The $G$ value was calculated from the slope of lines and listed in Table 3. By using $G$ values and other relevant experimental parameters, $M_c$ values were calculated by using Eq. (3) and collected in Table 3:

$$G = \frac{\rho}{M_c} RT \nu_2^{3/2} \nu_2^{1/3}. \quad (3)$$

As can be seen from Table 3 the molecular weight between cross-link of PDMAEMA and P(DMAEMA-co-VP) hydrogels increases with increasing amount of EGDMA, ranging from 0.1% to 1.0% but not changes significantly with changing of VP content in the gel system.

### 3.7. Polymer–solvent interaction parameter

The polymer–solvent interaction parameter, $\chi$, is the one of the important factor effecting the swelling of gels. In poor solvents $\chi \geq 0.7$ and the equilibrium degree of swelling is not effected at all with variations in pH and temperature. In such solutions one can hardly expect any swelling [21,22]. For good solvents $\chi \leq 0.5$; however, because of increasing polymer–solvent interactions, equilibrium swelling is shifted to higher values at every pH.

For the determination of polymer–solvent interaction parameter of PDMAEMA and P(DMAEMA-co-VP)–water system at pH 7, the temperature sensitive swelling behavior of hydrogels was analyzed by using Flory–Rehner theory of swelling equilibrium. According to the Flory–Rehner theory, there are two contributions to the osmotic pressure $\pi$ of a non-ionic and unionized polyelectrolyte gel:

$$\pi = \pi_{\text{mix}} + \pi_{\text{el}}, \quad (4)$$

where, mixing ($\pi_{\text{mix}}$) and elastic-retractive ($\pi_{\text{el}}$) contribution are the osmotic pressure due to polymer–solvent mixing and due to deformation of network chains to a more elongated state respectively.

The first term in the right hand side of equation, for the mixing of polymer chains with the solvent can be given in terms of the Flory–Huggins relationship:

$$\pi_{\text{mix}} = -\frac{RT}{V_i} (\ln(1 - \nu_{2m}) + \nu_{2m} + \chi \nu_{2m}^2), \quad (5)$$

### Table 3

<table>
<thead>
<tr>
<th>Gel name</th>
<th>$\nu_{2m}$</th>
<th>$\nu_2$</th>
<th>$\rho$</th>
<th>$G$</th>
<th>$M_c$</th>
<th>$\chi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100D0.1E</td>
<td>0.2584</td>
<td>0.703</td>
<td>0.9244</td>
<td>42.05</td>
<td>31,570</td>
<td>0.595</td>
</tr>
<tr>
<td>100D0.5E</td>
<td>0.3124</td>
<td>0.718</td>
<td>0.9147</td>
<td>73.78</td>
<td>19,651</td>
<td>0.663</td>
</tr>
<tr>
<td>100D1.0E</td>
<td>0.5222</td>
<td>0.734</td>
<td>0.9103</td>
<td>111.4</td>
<td>15,848</td>
<td>0.677</td>
</tr>
<tr>
<td>90D10VPE0.1</td>
<td>0.1551</td>
<td>0.717</td>
<td>0.9023</td>
<td>17.94</td>
<td>64,700</td>
<td>0.544</td>
</tr>
<tr>
<td>90D10VPE0.5</td>
<td>0.2938</td>
<td>0.723</td>
<td>0.8987</td>
<td>68.84</td>
<td>21,084</td>
<td>0.578</td>
</tr>
<tr>
<td>90D10VPE1.0</td>
<td>0.3122</td>
<td>0.741</td>
<td>0.8942</td>
<td>111.7</td>
<td>11,495</td>
<td>0.686</td>
</tr>
<tr>
<td>70D30VPE0.1</td>
<td>0.1078</td>
<td>0.711</td>
<td>0.8928</td>
<td>15.25</td>
<td>67,880</td>
<td>0.536</td>
</tr>
<tr>
<td>70D30VPE0.5</td>
<td>0.1860</td>
<td>0.734</td>
<td>0.8888</td>
<td>61.70</td>
<td>20,626</td>
<td>0.585</td>
</tr>
<tr>
<td>70D30VPE1.0</td>
<td>0.2647</td>
<td>0.741</td>
<td>0.8731</td>
<td>99.39</td>
<td>14,755</td>
<td>0.746</td>
</tr>
</tbody>
</table>
where, \( V_1 \) is the molar volume of the solvent and \( v_{2m} \) is the polymer volume fraction and \( \chi \) is the Flory polymer–solvent interaction parameter. Polymer–solvent interaction parameter \( \chi \) is expressed as a series expansion in powers of the cross-linked polymer volume fraction \( v_{2m} \), i.e.,

\[
\chi = \chi_1 + \chi_2 v_{2m} + \chi_3 v_{2m}^2 + \cdots ,
\]  

(6)

where, the coefficients \( \chi_1, \chi_2, \) and \( \chi_3 \) are the functions of temperature and the molecular characteristics of the polymer–solvent system.

In the slightly swollen state, the constrained junction theory indicates that a real network exhibits properties closer to those of the Affine network model. Consequently Eq. (7) is more realistic representation for \( \pi_\text{el} \):

\[
\pi_\text{el} = -RT \frac{\rho}{\bar{M}_c} V_1 \left( (v_{2m})^{1/3} (v_2)^{2/3} - v_{2m}/2 \right). 
\]  

(7)

Using Eqs. (5) and (7) and putting \( \pi = 0 \), one obtains the following well-known equation:

\[
\ln \left( 1/v_{2m} \right) + v_{2m} + \frac{\rho}{\bar{M}_c} V_1 \left( (v_{2m})^{1/3} (v_2)^{2/3} - v_{2m}/2 \right) = 0. 
\]  

(8)

Here, \( v_2 \) is the polymer volume fraction in the relaxed state i.e. after cross-linking but before swelling, \( \rho \) is the density of polymer, \( V_1 \) is the molar volume of the swelling agent and \( \bar{M}_c \) is the average molecular weight between consecutive cross-links.

For large swelling ratio, we can neglect \( v_{2m} \) dependence of \( \chi \) defined by Eq. (6). In this case \( \chi \) reduces to \( \chi_1 \) and the following equation can be obtained for it:

\[
\chi_1 = \frac{\Delta G}{RT} = \frac{\Delta H - T \Delta S}{RT},
\]  

(9)

where, \( \Delta G, \Delta H \) and \( \Delta S \) are the changes in the free energy, enthalpy and entropy during the swelling of cross-linked polymer in a solvent respectively. By using experimentally determined equilibrium volume swelling ratios of the hydrogels in water Table 3 and \( \bar{M}_c \) values found from uniaxial compression experiments, and the other related parameters given in Table 3, \( \chi \) parameter at each temperature and polymer volume fraction were calculated by using Eq. (8).

The variation of \( \chi \) parameter for PDMAEMA and P(DMAEMA-co-VP) hydrogels with temperature and polymer volume fraction are given in Figs. 5 and 6 respectively. As can be seen from the Figure, at low temperatures or high swelling ratios, \( \chi \) parameter is almost independent from temperature changes. This indicates that the enthalpy and the entropy contribution to Flory interaction parameter are constant and \( \chi \) equals to \( \chi_1 \) in this swelling ratio and temperature [23]. The dashed lines

![Fig. 5. Variation of polymer–solvent interaction parameter \( \chi \) for PDMAEMA and P(DMAEMA-co-VP) hydrogels–water system as a function of inverse temperature. (a) 100DMAEMA, (b) 90DMAEMA10VP, (c) 70DMAEMA30VP hydrogels. EGDMA content of hydrogels are 0.1 (■), 0.5 (○), and 1.0 (▲) v/v %.](image)
in Fig. 5 are the linear regression lines obtained from the low temperature portion of the data points. $D_H$ and $D_S$ values appearing in the $v_1$ parameter were calculated from the slope and intercept of these lines. $D_H$ and $D_S$ values of all prepared hydrogels are given in Table 4. As can be seen from table, the signs of the both quantities are negative for all prepared hydrogels. The negative values for $D_H$ and $D_S$ indicate that PDMAEMA and P(DMAEMA-co-VP) hydrogels shows LCSTs in water. Almost constant $D_S$ value and increasing $D_H$ value with increasing EGDMA and VP content indicate that formation of polymer–solvent interactions are mainly controlled by enthalpy factor. However, with the comparison of the $D_H$ and $D_S$ values of PDMAEMA and P(DMAEMA-co-VP) hydrogels compared with $D_H$ and $D_S$ values of PNIPA and poly-(TBA-co-AAm) copolymers, it has been observed that the temperature dependence of the present hydrogels is weaker than that hydrogels. Calculated $D_G$ values for all hydrogel systems are also given in Table 4 ($T=25^\circ$C). Almost constant $D_G$ value indicates that temperature sensitivity of the PDMAEMA and

![Graph showing variation of polymer–solvent interaction parameter $\chi$ for PDMAEMA and P(DMAEMA-co-VP) hydrogels–water system as a function of polymer volume fraction.](image)

Table 4

<table>
<thead>
<tr>
<th>Gel name</th>
<th>$\Delta H$ (J/mol)</th>
<th>$\Delta S$ (J/mol K)</th>
<th>$\Delta G$ (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100DMAEMA0.1E</td>
<td>$-187 \pm 36$</td>
<td>$-49 \pm 0.1$</td>
<td>$1273 \pm 36.1$</td>
</tr>
<tr>
<td>100DMAEMA0.5E</td>
<td>$-307 \pm 43$</td>
<td>$-55 \pm 0.2$</td>
<td>$1332 \pm 43.2$</td>
</tr>
<tr>
<td>100DMAEMA1.0E</td>
<td>$-295 \pm 8$</td>
<td>$-56 \pm 0.1$</td>
<td>$1373 \pm 8.1$</td>
</tr>
<tr>
<td>90DMAEMA10VP0.1E</td>
<td>$-73 \pm 22$</td>
<td>$-4.5 \pm 0.1$</td>
<td>$1268 \pm 22.1$</td>
</tr>
<tr>
<td>90DMAEMA10VP0.5E</td>
<td>$-119 \pm 36$</td>
<td>$-4.8 \pm 0.1$</td>
<td>$1311 \pm 36.1$</td>
</tr>
<tr>
<td>90DMAEMA10VP1.0E</td>
<td>$-322 \pm 50$</td>
<td>$-5.7 \pm 0.2$</td>
<td>$1376 \pm 50.2$</td>
</tr>
<tr>
<td>70DMAEMA30VP0.1E</td>
<td>$-72 \pm 27$</td>
<td>$-4.7 \pm 0.1$</td>
<td>$1328 \pm 27.1$</td>
</tr>
<tr>
<td>70DMAEMA30VP0.5E</td>
<td>$-168 \pm 14$</td>
<td>$-4.9 \pm 0.1$</td>
<td>$1292 \pm 14.1$</td>
</tr>
<tr>
<td>70DMAEMA30VP1.0E</td>
<td>$-485 \pm 88$</td>
<td>$-6.2 \pm 0.3$</td>
<td>$1362 \pm 88.1$</td>
</tr>
</tbody>
</table>
P(DMAEMA-co-VP) hydrogels are independent from cross-link density and comonomer VP content in the hydrogel systems.

$\Delta H$ and $\Delta S$ concentration dependent parameters, by using non-linear regression analyses of the data, $\chi$, $v_{2m}$ and $T$ in Figs. 5 and 6 simultaneously for all prepared hydrogels represented in the following equation were obtained for the dependence of $\chi$ on $v_{2m}$ and temperature ($T$). The coefficients for each hydrogel system are given in Table 5:

$$\chi = \chi_1 + \left( a - \frac{b}{T} \right) v_{2m} + \left( c - \frac{d}{T} \right) v_{2m}^2.$$  \hspace{9cm} (10)

In order to control the Affine network theory and validity of $\chi$ parameters of hydrogels, the theoretical swelling ratios ($V/V_0$) were calculated by using Eqs. (8) and (10). The solid curves in Fig. 3 represent the theoretical swelling ratio of hydrogel as a function of the temperature. It is clearly seen that, after taking into account the sensitive dependence of the $\chi$ parameter on both temperature and polymer concentration, the prediction of the Flory–Rehner theory provides a satisfactory agreement to the experimental swelling data.

4. Conclusion

In this study, radiation synthesis of PDMAEMA and P(DMAEMA-co-VP) hydrogels have been investigated. Swelling studies show that pH and temperature are the basic parameters affecting the equilibrium volume swelling of hydrogels. Also, it is a notable fact that addition of 10% or 30% VP in PDMAEMA hydrogels does not change the swelling behavior and transition temperature of PDMAEMA and P(DMAEMA-co-VP) hydrogels. The experimental results clearly show that simple compression analyses at non-ionized state and Flory–Rehner theory can be used for the determination of polymer–solvent interaction parameter, enthalpy and entropy changes appearing in the $\chi$ parameter and the dependence of $\chi$ on the polymer volume fraction and temperature.

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