# Determination of Average Molecular Weight Between Crosslinks and Polymer–Solvent Interaction Parameters of Poly(acrylamide-*g*-ethylene diamine tetraacetic acid) Polyelectrolyte Hydrogels

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**ABSTRACT:** Hydrogels containing tetraprotic acid moieties sensitive to pH changes of the swelling medium were prepared from the ternary systems acrylamide/ethylene diamine tetraacetic acid/water by irradiation with $\gamma$-rays at ambient temperature. Gel compositions of poly(acrylamide-*g*-ethylene diamine tetraacetic acid) [P(AAm-*g*-EDTA)] hydrogels were determined by using a differential pulse polarography technique. Equilibrium swelling behavior of these hydrogels was studied using an equation, based on the Flory–Huggins thermodynamic theory, the phantom network theory of James–Guth, and the approaches of Brannon-Peppas and Peppas, which was modified by the authors for determination of $\overline{M}_c$ and $\chi$ parameters. The equation modified by the authors for the determination of $\overline{M}_c$ and $\chi$ parameters were observed to describe very well the swelling behavior of the charged polymeric network. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 2168–2175, 2004

**Key words:** hydrogels; crosslinking; swelling; radiation; networks

## INTRODUCTION

Hydrogels are hydrophilic polymeric networks that absorb enough water to cause macroscopic changes in the sample dimension. The most important property of the hydrogels is its swelling degree because of its practical applications, such as in switches, drug delivery systems, recyclable adsorbents, sensors, and separation systems.[1–6] The swelling and mechanical properties of hydrogels can be controlled by the modification of the polymer backbone structure or the crosslinked density. Many research groups have presented theoretical models for network structure properties of hydrogels.[7–13]

The molecular weight between crosslinks ($\overline{M}_c$) for highly swollen networks is one of the basic parameters that describes the structure of electrolyte and nonelectrolyte-type hydrogel networks. This describes the average molecular weight of polymer chains between two consecutive junctions. These junctions may be chemical crosslinks, physical entanglements, crystalline regions, or even polymer complexes.[8] Several theories have been proposed to calculate the molecular weight between crosslinks in polymeric networks. The earliest theory to describe the equilibrium swelling characteristics of networks was developed by Flory and Rehner[9,10] for a crosslinked polymer system where the polymer chains are reacted in the solid state, and the macromolecular chains exhibit a Gaussian distribution. This theory describes the molecular weight between crosslinks for only nonionic polymer networks, as expressed in the following equation[11]:

$$\bar{M}_c = -\frac{(1 - 2/\phi)V_1 \nu_{2r}^{2/3} \nu_{2m}^{1/3}}{\bar{v}[\ln(1 - \nu_{2m}) + \nu_{2m} + \chi \nu_{2m}^2]} \tag{1}$$

where $\overline{M}_c$ is the average molecular weight between crosslinks, $\bar{v}$ is the specific volume of the polymer, $V_1$ is the molar volume of the swelling agent, $\nu_{2m}$ is the polymer volume fraction in the equilibrium-swollen system, $\nu_{2r}$ is the polymer volume fraction in the relaxed state (i.e., after crosslinking but before swelling), $\chi$ is the Flory polymer–solvent interaction parameter, and $\phi$ is the number of branches originating from a crosslinking site.

Thermodynamically, the swelling behavior of nonionic gel is governed by both the chemical potential of mixing and the chemical potential of elasticity. Elastic and mixing contributions to the chemical potential of nonionic gel is additive. In a nonionic gel and water system, water diffuses into the network by forces given by the difference of the chemical potential of water between the network inside and outside. Finally, the swelling gels reach the equilibrium state at a higher concentration of water in the gel phase. The stability is caused by contributions of elastic forces to

the chemical potential of solvent (water), which prevent the polymer network from becoming completely dissolved. If the polymer chains making up the network contain ionizable groups, the forces influencing swelling may be greatly increased because of localization of charges within the hydrogel.[13,14] Ionic polymer networks in aqueous salt solutions yield a far more complicated situation than that of neutral polymers. The equilibrium swelling ratios attained are often an order of magnitude larger than those of neutral networks, given that intermolecular interactions such as coulombic, hydrogen-bonding, and polar forces are present. Brannon-Peppas and Peppas derived an equation to describe this ionic contribution term for both anionic and cationic hydrogels.[12,15] The expression for a monoprotic acid containing anionic homopolymeric network is given in eq. (2), and theoretical swelling predictions based on this and other similar equations are well described by Brannon-Peppas and Peppas.[12]

$$\frac{V_1}{4I}\left(\frac{K_a}{10^{-\mathrm{pH}}+K_a}\right)^2\left(\frac{v_{2m}}{\bar{v}}\right)^2 = [\ln(1-v_{2m})+v_{2m}+\chi v_{2m}^2]$$

$$+\left(\frac{V_1}{\bar{v}\bar{M}_c}\right)\left(1-\frac{2\bar{M}_c}{\bar{M}_n}\right)v_{2r}\left[\left(\frac{v_{2m}}{v_{2r}}\right)^{1/3}-\left(\frac{v_{2m}}{v_{2r}}\right)\right] \quad (2)$$

where $K_a$ is the dissociation constant of polyacid, $I$ is the ionic strength of the swelling medium, and $\bar{M}_n$ is the number-average molecular weight of starting polymer.

By combining the approaches of James and Guth,[16] considering a phantom model for network structure, and that of Brannon-Peppas and Peppas[13] we obtained a modified expression from which the $\bar{M}_c$ and $\chi$ could be determined simultaneously for a copolymeric hydrogel with tetraprotic acid segments. In this expression the mixing, elastic-retroactive, and ionic contributions to chemical potential of a tetraprotic acid containing hydrogel in the equilibrium-swollen state were incorporated into the phantom model of network structure. In the highly swollen state, the constrained junction theory indicates that a real network exhibits properties closer to those of the phantom network model.[11] The equation derived was used to determine simultaneously $\bar{M}_c$ and $\chi$ parameters for poly(acrylamide-*g*-ethylene diamine tetraacetic acid) [P(AAm-*g*-EDTA)] hydrogels prepared from acrylamide and ethylene diamine tetraacetic acid by using a radiation-induced polymerization technique.

## EXPERIMENTAL

### Apparatus

A PAR model 174A polarographic analyzer system, equipped with a PAR mercury drop timer (Princeton Applied Research Co., Princeton, NJ), was used. A Kalousek electrolytic cell with reference saturated electrode (SCE), separated by liquid junction, was used in a three-electrode configuration. The counter electrode was platinum wire. The natural drop time of the mercury electrode was in the range 2–3 s (2.37 mg s$^{-1}$). The differential pulse (DP) polarograms were recorded with a Linseis LY 1600 X-Y recorder (Bremen, Germany). DP polarograms were recorded under the conditions of a drop life of 1 s, a scan rate of 5–10 mV s$^{-1}$, and a pulse amplitude of 50 mV.

### Chemicals

Acrylamide (AAm) was supplied from Merck (Darmstadt, Germany). A stock solution (0.1$M$) of ethylene diamine tetraacetic acid (EDTA) Na$_2$H$_2$Y·2H$_2$O ($M$ = 372.25 g mol$^{-1}$) was prepared by dissolving 37.225 g of EDTA, diluted to 1.0 L. Glacial CH$_3$COOH, H$_3$PO$_4$ (85%), H$_3$BO$_3$ and standardized NaOH were used to prepare Britton–Robinson (B-R) buffers (purchased from Merck, Darmstadt, Germany). B-R buffer solution was prepared in such a way that 2.3 mL glacial acetic acid, 2.7 mL phosphoric acid, and 2.4720 g boric acid were dissolved by dilution in triple-distilled water to 1.0 L; 50 mL portions of this solution were taken and the pH was adjusted between 2.0 and 9.0 by addition of appropriate amounts of 2.0$M$ NaOH.

### Preparation of hydrogels

Three components were used in the preparation of P(AAm-*g*-EDTA) hydrogels: AAm, EDTA, and distilled water. AAm monomer (2.5 g) was added to each solution (3.0, 6.0, 9.0, and 12.0 mL 0.1$M$ EDTA) and finally diluted to 15 mL. Monomer solutions thus prepared were in different compositions (respective AAm/EDTA mol ratios: 98.28/1.72; 96.79/3.21; 95.45/4.55; 94.45/5.55). These solutions were placed in PVC straws (4 mm diameter) and irradiated to 11.2 kGy in air at ambient temperature in a PX-γ-30 Isslodovateji γ-irradiator at a fixed dose rate of 2.8 kGy/h.

### Composition of hydrogels

The hydrogels, obtained in long cylindrical shapes, were cut into pieces of 3–4 mm and dried in a vacuum oven at 315 K for 42 h to a constant weight and subjected to Soxhlet extraction for about 10 days with water as solvent. The unreacted EDTA was removed with this extraction from the gel structure. Extracted gels were dried again in a vacuum oven at 315 K to constant weight and stored for later evaluations. The amount of unreacted EDTA in the extract was determined by a differential pulse polarography (DDP) technique. Although many organic or inorganic species that contain electroactive groups can be directly
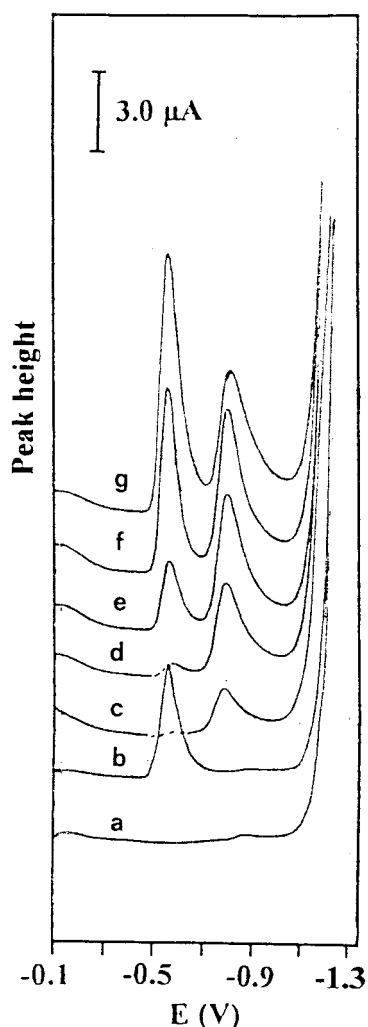
**Figure 1** Determination of the gel composition of P(AAm-*g*-EDTA) by the DPP technique: (a) 10 mL B-R buffer, pH = 3.0; (b) a + 50 $\mu$L 1.0 × 10$^{-2}$ *M* Cd$^{+2}$; (c) b + 1 mL extract solution of gel 1; (d) c + 50 $\mu$L 1.0 × 10$^{-2}$ *M* Cd$^{+2}$; (e) d + 50 $\mu$L 1.0 × 10$^{-2}$ *M* Cd$^{+2}$; (f) e + 50 $\mu$L 1.0 × 10$^{-2}$ *M* Cd$^{+2}$; (g) f + 50 $\mu$L 1.0 × 10$^{-2}$ *M* Cd$^{+2}$. Drop time 1.0 s, scan rate 5.0 mV s$^{-1}$, pulse amplitude 50 mV.

determined by the DPP technique,[17] electroinactive groups could also be determined by using an indirect method. In this work, P(AAm-*g*-EDTA) copolymeric gel that contains an electroinactive group (EDTA) was detected by means of Cd–EDTA complex. For this purpose, the polarogram of 5.0 × 10$^{-5}$ *M* Cd$^{+2}$ was recorded in pH = 3 (B-R buffer) solution through the scanning of the potential from −100 to about −1200 mV. During our polarographic studies, by addition of the 1.0 mL unreacted EDTA solution, the cadmium peak at about −600 mV decreased, whereas a new peak appeared at −800 mV attributed to the Cd–EDTA complex (Fig. 1). The amount of unreacted EDTA was determined from the peaks of −600 and −800 mV by continuous standard addition of Cd$^{2+}$ solution. Addition of 50 $\mu$L 1 × 10$^{-2}$ *M* Cd$^{2+}$ was

continued until the peak height of Cd–EDTA peak was constant. This point shows the detection of whole unreacted EDTA. Molar percentages of EDTA in P(AAm-*g*-EDTA)-1, P(AAm-*g*-EDTA)-2, P(AAm-*g*-EDTA)-3, and P(AAm-*g*-EDTA)-4 hydrogels were 1.57, 2.97, 4.21, and 5.23, respectively. The weight swelling ratio of hydrogels after preparation $q_F$ was calculated as

$$q_F = \frac{\text{mass hydrogel after preparation}}{\text{mass dry hydrogel}} \quad (3)$$

The volume fraction of polymer network after preparation $\nu_{2r}$ was calculated from $q_F$ values as

$$\nu_{2r} = \left[ 1 + \frac{(q_F - 1)\rho_{\text{polymer}}}{\rho_{\text{solvent}}} \right]^{-1} \quad (4)$$

where $\rho_{\text{polymer}}$ and $\rho_{\text{solvent}}$ are densities of polymer and solvent, respectively. The values $\rho_{\text{polymer}}$ and $\rho_{\text{solvent}}$ used were 1.35 and 1 g/mL, respectively. The density of hydrogels was determined with a pycnometer using benzene as a nonsolvent. The experimental values of $\nu_{2r}$ were between 0.114 and 0.127, depending on EDTA content in the hydrogel.

### Determination of equilibrium degree of swelling

For the swelling measurements, the hydrogels were synthesized, dried, and subjected to Soxhlet extraction in water to extract EDTA, after which they were dried again and immersed in a solution of desired pH (2–9), ionic strength $I$ (1 × 10$^{-4}$ mol cm$^{-3}$), and temperature (25°C). The hydrogels were weighed at different times until the hydrated weight remained constant. Swollen gels removed from water at regular intervals were surface-dried with filter paper and weighed, then placed in the same bath and left until equilibrium was reached. When the hydrogel stopped swelling, the surface was dried with filter paper after which the weight was measured again. The equilibrium was reached after an immersion time of about 7 days. The weight swelling ratios of hydrogels $q_w$ were calculated using the following equation:

$$q_w = \frac{\text{mass hydrogel in solution}}{\text{mass dry hydrogel}} \quad (5)$$

The volume fraction of the polymer network $\nu_{2m}$ was calculated as

$$\nu_{2m} = \left[ 1 + \frac{(q_w - 1)\rho_{\text{polymer}}}{\rho_{\text{solvent}}} \right]^{-1} \quad (6)$$

Each swelling ratio reported in this article is an average of at least three separate measurements. The equilibrium degree of hydrogels $q_v$ was calculated as

$$q_v = 1/\nu_{2m} \quad (7)$$

## THEORY OF SWELLING EQUILIBRIUM

The chemical potential of solvent in the network $\Delta\mu_1$ may be written as the sum of three terms, mixing (mix), elastic (el), and ionic (ion) contribution, as follows:

$$\Delta\mu_1 = \Delta\mu_{mix} + \Delta\mu_{el} + \Delta\mu_{ion} \quad (8)$$

The mixing term is satisfactorily represented by a Flory–Huggins-type expression of the form

$$\Delta\mu_{mix} = RT[\ln(1 - \nu_{2m}) + \nu_{2m} + \chi\nu_{2m}^2] \quad (9)$$

The elastic contribution to $\Delta\mu$ is defined by the James–Guth phantom network theory[16]:

$$\Delta\mu_{el} = RT\left[\frac{(1 - 2/\phi)V_1\rho\nu_{2r}^{2/3}\nu_{2m}^{1/3}}{\bar{M}_c}\right] \quad (10)$$

The ionic contribution to $\Delta\mu$ is obtained by Brannon-Peppas and Peppas[12] for the external electrolyte concentration.

$$\Delta\mu_{ion} = -V_1RT\left(\frac{i^2c_2^2}{4I}\right) \quad (11)$$

In the above equation, $i$ is the degree of ionization; $I$ is the ionic strength of the swelling medium; and $c_2$ is the concentration of ionizable polymer (mol cm$^{-3}$), which may be written in terms of polymer structural parameters for copolymeric hydrogels as

$$c_2 = \frac{f_c}{\bar{V}_r}\nu_{2m} \quad (12)$$

where $f_c$ is the mole fraction of the ionic unit in the gel system and $\bar{V}_r$ is the average molar volume of polymer repeat units[18]:

$$\bar{V}_r = 52.6 + 329.7f_c \quad (13)$$

By combining eqs. (11) and (12) we obtain

$$\Delta\mu_{ion} = -V_1RT\left(\frac{i^2\nu_{2m}^2f_c^2}{4I\bar{V}_r^2}\right) \quad (14)$$

The degree of ionization $i$ can be expressed in terms of other analytical variables of the polymer–solvent system. For gels with tetraprotic acid moieties there are four equilibria:

$$K_{a1} = \frac{[H^+][H_3A^-]}{[H_4A]} \quad (15)$$

$$K_{a2} = \frac{[H^+][H_2A^{-2}]}{[H_3A^-]} \quad (16)$$

$$K_{a3} = \frac{[H^+][HA^{-3}]}{[H_2A^{-2}]} \quad (17)$$

$$K_{a4} = \frac{[H^+][A^{-4}]}{[HA^{-3}]} \quad (18)$$

where $[H_4A]$ is the concentration of polymer chains; $[H_3A^-]$, $[H_2A^{-2}]$, $[HA^{-3}]$, and $[A^{-4}]$ are the concentration of dissociated polymer chains; and $[H^+]$ is the concentration of hydrogen ions. The ionization $i$ is defined as

$$i = (4 - \bar{n})/4 = (4\alpha_0 + 3\alpha_1 + 2\alpha_2 + \alpha_3)/4 \quad (19)$$

where $\bar{n}$ represents the average number of protons bound to carboxyl groups in the tetraprotic acid and $\alpha_0$, $\alpha_1$, $\alpha_2$, $\alpha_3$, and $\alpha_4$ are the ratios of the concentration of species $[A^{-4}]$, $[HA^{-3}]$, $[H_2A^{-2}]$, $[H_3A^-]$, and $[H_4A]$ to the analytical concentration ($C$) of tetraprotic acid, respectively. The $\alpha$ values can be defined by the following equations in terms of the dissociation constants $K_{a1}$, $K_{a2}$, $K_{a3}$, and $K_{a4}$ of the ionizable polymer[19]:

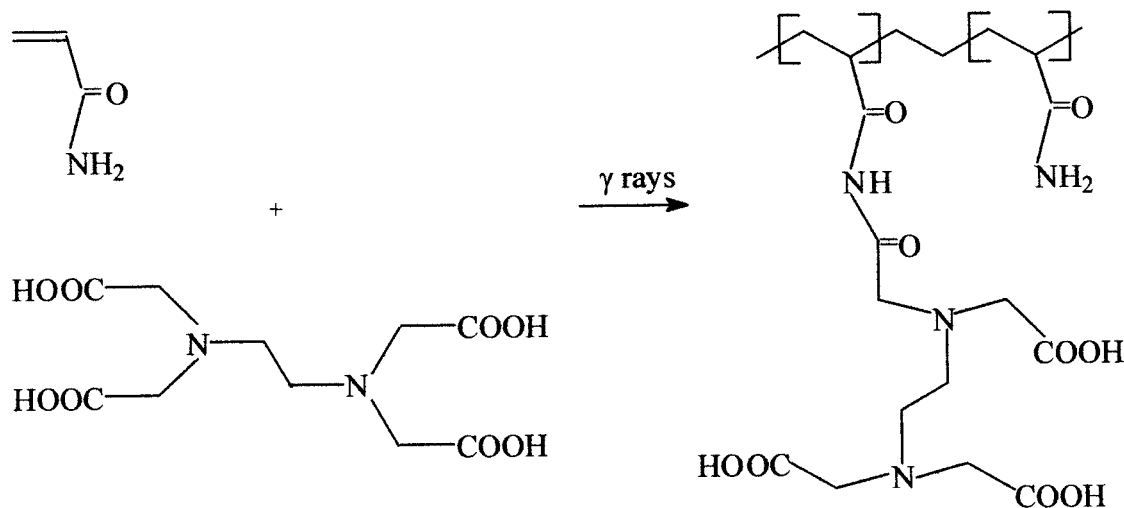$$\alpha_0 = \frac{[A^{-4}]}{C} = \alpha_4\left(\frac{K_{a1}K_{a2}K_{a3}K_{a4}}{[H^+]^4}\right) \quad (20)$$

$$\alpha_1 = \frac{[HA^{-3}]}{C} = \alpha_4\left(\frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3}\right) \quad (21)$$

$$\alpha_2 = \frac{[H_2A^{-2}]}{C} = \alpha_4\left(\frac{K_{a1}K_{a2}}{[H^+]^2}\right) \quad (22)$$

$$\alpha_3 = \frac{[H_3A^-]}{C} = \alpha_4\left(\frac{K_{a1}}{[H^+]}\right) \quad (23)$$

$$\alpha_4 = \frac{[H_4A]}{C}$$

$$= \left(1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} + \frac{K_{a1}K_{a2}K_{a3}K_{a4}}{[H^+]^4}\right)^{-1} \quad (24)$$

By combining eqs. (20)–(24) into eq. (19) and substituting in eq. (14), the following equation may be obtained for $\Delta\mu_{ion}$:

**Scheme 1**

$$\Delta\mu_{ion}$$

$$= -\left[\frac{\left[\begin{array}{c}4K_{a1}K_{a2}K_{a3}K_{a4} + 3(10^{-pH})K_{a1}K_{a2}K_{a3} \\ + 2(10^{-pH})^2 K_{a1}K_{a2} + (10^{-pH})^3 K_{a1}\end{array}\right]}{4\left[\begin{array}{c}(10^{-pH})^4 + (10^{-pH})^3 K_{a1} + (10^{-pH})^2 K_{a1}K_{a2} \\ + (10^{-pH})K_{a1}K_{a2}K_{a3} + K_{a1}K_{a2}K_{a3}K_{a4}\end{array}\right]}\right]^2$$
$$\times \frac{V_1 RT \nu_{2m}^2 f_c^2}{4I\bar{V}_r^2} \quad (25)$$

When the network is swollen to equilibrium with pure solvent, activity of the solvent in the network equals that of the surrounding pure solvent (i.e., unity). Consequently, the chemical potential of solvent in the network equates to zero. From eqs. (7)–(25), the thermodynamic equilibrium condition may be written as

$$RT[\ln(1 - \nu_{2m}) + \nu_{2m} + \chi\nu_{2m}^2]$$
$$+ RT\left[\frac{(1 - 2/\phi)V_1\rho\nu_{2r}^{2/3}\nu_{2m}^{1/3}}{\bar{M}_c}\right]$$
$$- \left[\frac{\left[\begin{array}{c}4K_{a1}K_{a2}K_{a3}K_{a4} + 3(10^{-pH})K_{a1}K_{a2}K_{a3} \\ + 2(10^{-pH})^2 K_{a1}K_{a2} + (10^{-pH})^3 K_{a1}\end{array}\right]}{4\left[\begin{array}{c}(10^{-pH})^4 + (10^{-pH})^3 K_{a1} + (10^{-pH})^2 K_{a1}K_{a2} \\ + (10^{-pH})K_{a1}K_{a2}K_{a3} + K_{a1}K_{a2}K_{a3}K_{a4}\end{array}\right]}\right]^2$$
$$\times \frac{V_1 RT \nu_{2m}^2 f_c^2}{4I\bar{V}_r^2} = 0 \quad (26)$$

The complete equilibrium expression, which accounts for the mixing, elastic-retractive, and ionic contributions to the chemical potential of tetraprotic polymeric networks, is shown in the following equation:

$$\left[\frac{\left[\begin{array}{c}4K_{a1}K_{a2}K_{a3}K_{a4} + 3(10^{-pH})K_{a1}K_{a2}K_{a3} \\ + 2(10^{-pH})^2 K_{a1}K_{a2} + (10^{-pH})^3 K_{a1}\end{array}\right]}{4\left[\begin{array}{c}(10^{-pH})^4 + (10^{-pH})^3 K_{a1} + (10^{-pH})^2 K_{a1}K_{a2} \\ + (10^{-pH})K_{a1}K_{a2}K_{a3} + K_{a1}K_{a2}K_{a3}K_{a4}\end{array}\right]}\right]^2$$
$$\times \frac{V_1 f_c^2}{4I\bar{V}_r^2} - \nu_{2m}^{-2}\ln(1 - \nu_{2m}) - \nu_{2m}^{-1}$$
$$= \chi + \frac{(1 - 2/\phi)V_1\rho\nu_{2r}^{2/3}\nu_{2m}^{-5/3}}{\bar{M}_c} \quad (27)$$

## RESULTS AND DISCUSSION

### Synthesis of hydrogels

When an aqueous solution of the AAm monomer is irradiated with γ-rays in the presence of EDTA, free radicals are generated not only by reaction with the monomer, but even more efficiently with the solvent water and grafting agent EDTA. The radiolysis products of water, especially hydroxyl free radicals, are very effective in attacking the monomer and already formed polymer chain. The reaction of these radicals with the monomers and EDTA leads to the formation of random graft P(AAm-*g*-EDTA) copolymers during the radiation-induced polymerization of AAm. When the radiation dose has been increased beyond a certain value, polymer chains crosslink and gel is then obtained. γ-ray–induced graft copolymerization of AAm and EDTA is a free-radical process, and can be designated as shown in **Scheme 1**:

The mole percentages of the AAm monomer and the grafting agent EDTA in the initial mixtures, the corresponding composition of AAm and EDTA in the polymers, and the percentage gelation are summarized in Table I.

**TABLE I**
**Mole Percentage of EDTA in Feed and in Gel Systems,**
**and Percentage Gelation**

| | Mol % EDTA | | |
|---|---|---|---|
| Gel name | In feed | In gel | % Gelation |
| P(AAm-*g*-EDTA)-1 | 1.72 | 1.57 | 89.4 |
| P(AAm-*g*-EDTA)-2 | 3.21 | 2.97 | 91.5 |
| P(AAm-*g*-EDTA)-3 | 4.55 | 4.21 | 91.8 |
| P(AAm-*g*-EDTA)-4 | 5.55 | 5.23 | 93.6 |

## Determination of $\overline{M}_c$ and $\chi$ values of hydrogels

The hydrogel equilibrium swelling ratio is an important parameter that describes the amount of solvent within the hydrogel at equilibrium. It is a function of network structure, crosslinking ratio, hydrophilicity, and degree of ionization of functional groups. Hydrogels may contain functional groups that interact with the external environment (temperature, ionic strength, and pH of swelling agent). Their response to environment conditions may increase or decrease the volume of the hydrogel.[20]
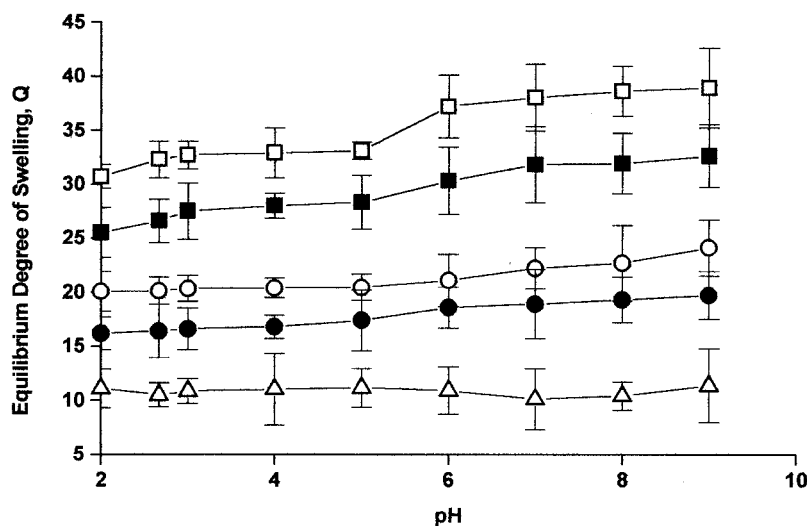
The equilibrium swelling behaviors of P(AAm-*g*-EDTA) hydrogels were investigated as a function of pH at fixed ionic strength ($I = 1 \times 10^{-4}$ mol cm$^{-3}$) and temperature ($T$ = 25°C). The equilibrium swelling studies were performed on three samples of each hydrogel at different pH values. Figure 2 shows the swelling behavior of P(AAm-*g*-EDTA) hydrogels containing various mole ratios of EDTA at various pH media. The equilibrium degrees of swelling of nonionic PAAm hydrogels at different pH values are also included in Figure 2 for comparison. As may be seen from this figure, there is no effect of pH on the equi-

librium degree of swelling of pure PAAm hydrogels. However, the equilibrium degree of swelling of the P(AAm-*g*-EDTA) hydrogels significantly increased depending on pH of the solution by incorporation of EDTA into the PAAm chain. Charged groups attached to the polymeric network structure played an essential role in swelling properties. Previous studies have shown that the swelling behavior of charged hydrogels is a function of the ionic composition of swelling agent.[21] The effect of pH on the collapse of poly(acrylamide-*co*-acrylic acid) copolymer was reported by Ricka and Tanaka.[22]

The change in equilibrium degree of swelling with pH was also evaluated for the determination of average molecular weight between crosslinks and the polymer–solvent interaction parameter. If the swelling data of a gel are used to plot the left-hand side of eq. (27), which is derived for prediction and understanding of swelling behavior of a hydrogel containing tetraprotic acid (*A*) against the coefficient of $1/\overline{M}_c$ on the right-hand side (*B*), a linear relation may be obtained with $\chi$ and $\overline{M}_c$ values as the intercept and inverse slope, respectively, as expressed by the following equation:

$$A = \chi + |B/\bar{M}_c| \qquad (28)$$

When the pH increases, the magnitude of $i^2 V_1 X^2 / 4 I v_e^2$ of eq. (27) does change slightly. On the other hand, pH changes significantly affect the last part of eq. (27) $[v_{2m}^{-2}\ln(1 - v_{2m}) - v_{2m}^{-1}]$. Because the equilibrium degree of swelling depends on pH, the contribution of this part of the equation affects the whole equation, resulting in a decrement of *A* [in eq. (28)]. To use this



**Figure 2** Effect of pH on the equilibrium degree of swelling values of P(AAm-*g*-EDTA) hydrogels: (△) PAAm; (●) P(AAm-*g*-EDTA)-1; (○) P(AAm-*g*-EDTA)-2; (■) P(AAm-*g*-EDTA)-3; (□) P(AAm-*g*-EDTA)-4.
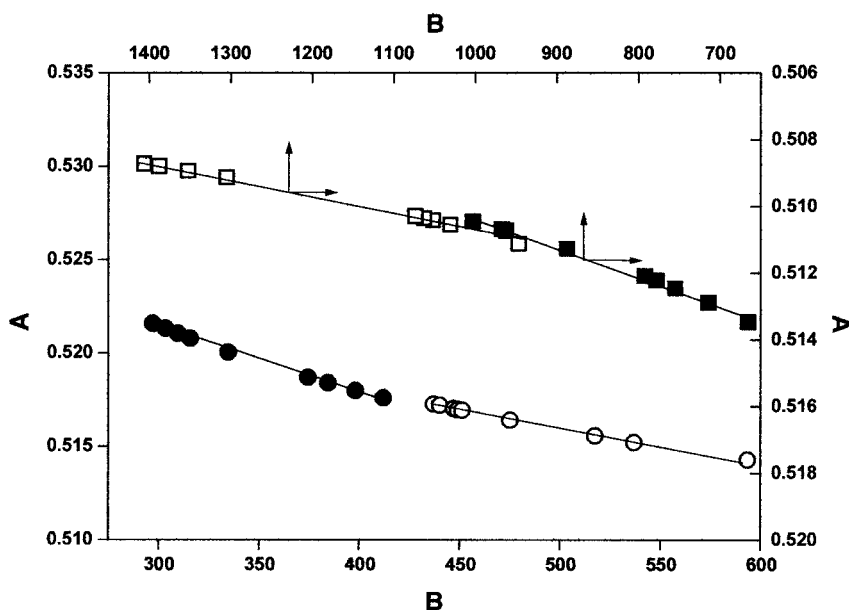
**Figure 3** Determination of $\chi$ and $\overline{M}_c$ values of P(AAm-*g*-EDTA) hydrogels from swelling data: (●) P(AAm-*g*-EDTA)-1 ($r^2$ = 0.998); (○) P(AAm-*g*-EDTA)-2 ($r^2$ = 0.998); (■) P(AAm-*g*-EDTA)-3 ($r^2$ = 0.996); (□) P(AAm-*g*-EDTA)-4 ($r^2$ = 0.997).

equation on a wide scale, the term $B/\overline{M}_c$ must be taken as an absolute value. This approach is consistent with the fact that $\overline{M}_c$ obviously cannot take a negative value.

The relevant experimental parameters to be used with eq. (27) are as follows: ionic strength, $I = 1 \times 10^{-4}$ mol cm$^{-3}$; molar volume of the solvent, $V_1 = 18$ cm$^3$ mol$^{-1}$; the number branches originating from a crosslinking site, $\phi = 4$; and p$K_{a1}$ = 1.99, p$K_{a2}$ = 2.67, p$K_{a3}$ = 6.16, and p$K_{a4}$ = 10.26 for EDTA-containing hydrogels. In the preparation of hydrogels, no crosslinking agents were used in this work. Crosslinking agents were obtained by high-energy radiation. It was previously determined and has been known for some time that the radiation-induced crosslinks product has a functionality $\phi \geq 3$.[23] In any case there are four branches originating from a crosslinking site. By using the experimentally measured polymer volume fraction $v_{2m}$ of the gels in their equilibrium-swollen state and the above-mentioned data, it is possible to establish the corresponding linear relationships as shown in Figure 3. The respective $\overline{M}_c$ and $\chi$ values were determined by linear

regression analysis of the lines presented in Figure 3, which are listed in Table II. A decrease in the $\chi$ parameter is shown as the EDTA percentage increases, confirming the sufficiency of water concentration with respect to the EDTA. The $\chi$ parameter of crosslinked pure PAAm has been reported to be 0.494.[24] The $\chi$ values at pH interval 2–9 given in Table II are in very good accordance with this reported value of interaction parameter. A value of 0.515 ± 0.001 was obtained for P(AAm-*g*-EDTA)-4 with an EDTA content of 5.23 mol %. A comparison of $\overline{M}_c$ values listed in Table II and equilibrium swelling values shown in Figure 2 shows that gels containing higher EDTA moieties swell more at and above pH 9. The $\overline{M}_c$ values show an increase with increasing EDTA content in the gels. The former effect indicates that EDTA does not act as a crosslinking agent. A similar behavior was observed during the swelling studies reported on poly(*N*-vinyl-2-pyrrolidone/itaconic acid) hydrogel systems.[25]

**TABLE II**
**$\chi$ and $\overline{M}_c$ Values of P(AAm-*g*-EDTA) Hydrogels**

| Gel name | $\chi$ | $\overline{M}_c$ |
|---|---|---|
| P(AAm-*g*-EDTA)-1 | 0.532 ± 0.001 | 28,700 ± 600 |
| P(AAm-*g*-EDTA)-2 | 0.526 ± 0.001 | 51,600 ± 1300 |
| P(AAm-*g*-EDTA)-3 | 0.519 ± 0.001 | 115,000 ± 3900 |
| P(AAm-*g*-EDTA)-4 | 0.515 ± 0.001 | 198,000 ± 5200 |

## References

1. Scranton, A. B.; Rangarajan, B.; Klier, J. Adv Polym Sci 1995, 122, 1.
2. Huang, X.; Li, Y.; Xiao, J.; Yan, C. J Appl Polym Sci 1995, 55, 1179.
3. Putnam, P.; Kopecek, J. Adv Polym Sci 1995, 122, 55.
4. Güven, O.; Şen, M. Angew Makromol Chem 1995, 5, 207.
5. Karadağ, E.; Saraydın, D.; Güven, O. Sep Sci Technol 1995, 30, 3747.

6. Saraydın, D.; Karadağ, E.; Güven, O. Sep Sci Technol 1995, 30, 3291.

7. Gudeman, L. F.; Peppas, N. A. J Appl Polym Sci 1995, 55, 919.

8. Peppas, N. A. J Bioact Compat Polym 1991, 6, 241.

9. Flory, P. J.; Rehner, J. J Chem Phys 1943, 11, 512.

10. Flory, P. J.; Rehner, J. J Chem Phys 1943, 11, 521.

11. Mark, J. E.; Erman, B., Eds. Rubberlike Elasticity: A Molecular Primer; Wiley: New York, 1988.

12. Brannon-Peppas, L.; Peppas, N. A. Chem Eng Sci 1991, 46, 715(1991).

13. Flory, J. Principles of Polymer Chemistry; Cornell University: Ithaca, NY, 1953.

14. Hooper, H. H.; Baker, J. P.; Blanch, H. W.; Prausnitz, J. M. Macromolecules 1990, 23, 1096.

15. Bell, C. C.; Peppas, N. A. Adv Polym Sci 1995, 122, 125.

16. James, H. M.; Guth, E. J Chem Phys 1943, 11, 455.

17. İnam, R.; Somer, G. Talanta 1999, 50, 609.

18. Durmaz, S.; Okay, O. Polymer 2000, 44, 3693.

19. Butler, N. J., Ed. Ionic Equilibrium: A Mathematical Approach; Addison-Wesley: Reading, MA, 1964.

20. Khare, A.; Peppas, N. A. Biomaterials 1995, 16, 559.

21. Çaykara, T.; İnam, R.; Özyurek, C. J Polym Sci Part A: Polym Chem 2001, 39, 277.

22. Ricka, S.; Tanaka, T. Macromolecules 1984, 17, 2916.

23. Wilson, J. E. Radiation Chemistry of Monomers, Polymers and Plastics; Marcel Dekker: New York, 1974.

24. Rosiak, J.; Burczak, K.; Zolozynzka, T.; Pekala, W. Radiat Phys Chem 1983, 22, 917.

25. Şen, M.; Yakar, A.; Güven, O. Polymer 1999, 44, 2969.