DOI: 10.1002/masy.200750819

# Swelling of the Zwitterionic Copolymer Networks and Dehydration of their Hydrogels

*I. Kamenova,*[1] *M. Harrass,*[2] *B. Lehmann,*[2] *K. Friedrich,*[2] *I. Ivanov,*[1] *G. Georgiev**[1]

**Summary:** The polyelectrolyte and antipolyelectrolyte effects on the degree of swelling (Q) and dehydration activation energy ($E_a$) of homo- and copolymer single and double networks, consisting of monomer units with polyelectrolyte and antipolyelectrolyte association abilities are determined and compared. An original correlation between Q and $E_a$ is outlined and explained.

**Keywords:** activation energy; Hydrogels; kinetics; self-organization; thermogravimetric analysis

## Introduction

The comparison of the opposite directed polyelectrolyte and antipolyelectrolyte effects on the swelling behavior of the corresponding networks is of both scientific and applied interest.[1–4] In the work presented such comparison for single (SN) and double (DN) homo- and copolymer networks of 2-acrilamido-2-methylpropanesulfonic acid (AMPS), N-(3-sulfopropyl)-N-methacryloyl-N,N-dimethylamonium betaine (DMAPS) and acrylamide (AAm) is performed. From the literature available the swelling behavior of the polyzwitterionic (PZ) networks are poor investigated,[5–7] and for PZ DN the information obtained here is new. The application of the experimental and the theoretical approaches for the description of the solid-state destruction reactions[8–12] to treat the hydrogel dehydration kinetics allows to outline an original correlation between the equilibrium degree of swelling ($Q_{eq}$) and the activation dehydration energy ($E_a$). The explanation based on the stimulated change of the energy of interaction between monomer units and water molecules is proposed.

## Experimental Part

### Materials

AMPS (Merck, Germany), AAm (Merck, Germany) and (DMAPS) (Merck, Germany) as a monomers, was used as received, N,N′-Methylenebisacrylamide (MBAA) (Fluka, Switzerland), as a cross-linking agent, potassium persulfate (Fluka, Switzerland) as initiator, was used as received.

### Gel Preparation

Synthesis of SN hydrogel PAMPS gel, as the first network of DN gel, was obtained by radical polymerization using MBAA as a cross-linker and Potassium persulfate as an initiator. Monomer concentration was 1 mol/l, cross-linker was 4 mol% with respect to the monomer concentration, and initiator was 0.1 mol% with respect to the monomer concentration. Aqueous solution containing a monomer, cross-linker, and the initiator was bubbled with nitrogen for 30 min, and then was subsequently polymerized in the presence of at 70 °C for 7.5 h.

The DN hydrogel was synthesized by a sequential network form action technique (two-step method). The PAMPS gel (1st network) was immersed in an aqueous solution of 3M AAm or DMAPS, containing 0.1 mol% MBAA, and 0.1 mol% potassium persulfate for 1 day until reaching the equilibrium. The 2nd network(DMAPS or AAm) was subsequently polymerized in

---

[1] University of Sofia, Faculty of Chemistry, 1J. Bourchier Avenue, 1164-Sofia, Bulgaria
E-mail: georgs@chem.uni-sofia.bg
[2] Institute of Composite Materials, 58 Erwin-Schrödinger Avenue, 67663 Kaiserslautern, Germany

the presence of the PAMPS gel at 60 °C for 6 h. After polymerization, the DN gel was immersed in pure water for 1 week The water was changed 2 times every day to remove any unreacted materials. PDMAPS and PAAm SN gel was synthesized in the same procedure as that of DN gel without adding the PAMPS network.

### Equilibrium Swelling Ratio

Pieces of the polymer networks were weighed after drying. Then they were immersed into distilled water (150 ml) for 4 days in order to reach the equilibrium swelling state. After 4 days, the weight of the samples practically did not change further. The equilibrium swelling ratio was determined, by applying the following relationship:

$$Q_{eq} = (w_{SW} - w_d)100/w_d$$

Here, $w_{sw}$ and $w_d$ are the weight of the sample in the swollen and in the dry state, respectively.

When a sample containing water was measured, with an open aluminum pan.

### Thermogravimetric Analysis (TGA)

The TGA thermograms were carried out on a Mettler (TGA 50; Mettler-Toledo, Inc.) at a heating rates of 5, 10, 15 and 20 °C/min,under nitrogen (flow rate of 30 ml/min), over a temperature range from room temperature to 250 °C. When a samples (15 ± 3 mg) containing water ware measured, with an open aluminium crucibles. The primary TGA thermograms were used to determine the kinetic parameters such as activation energy of thermal evaporation of water.

### Isoconversional Method

Isoconversional methods are known to allow for model-independent estimation of the activation energy. To use the isoconversional methods, a series of experiments have to be conducted at different heating rates. The isoconversional method suggested by Friedman[13] uses a differential form of the rate equation, whereas the methods of Ozawa,[14] Flynn & Wall[15] use approximations of the integral, which lead to simple linear equations for evaluating the activation energy. The accurate values for rate, $(d\alpha/dt)_j$, are obtainable from $\alpha$ and T data. Friedman's differential method was used to calculate $E/R$ from the slope of a plot of ln $(d\alpha/dt)_{k,j}$ vs. $1/T_{k,j}$ where $T_{k,j}$ is the temperature at which fraction $\alpha_k$ was reached in an experiment at heating rate $\beta_j$ since

$$-\frac{E}{R} = \frac{d\ln\left(\frac{d\alpha}{dt}\right)_{k,j}}{d\left(\frac{1}{T_{k,j}}\right)} \qquad \alpha = \alpha_k \qquad (1)$$

Dependences for different conversions of dehydration $\alpha = 10\%$, 30%, 50%, 70% from slopes of the curves is calculate the activation energy of deswelling ($E_a$) for different conversions of dehydration ($\alpha$ %) for DN in aqueous solution in addition or without salt (0.5M NaCl).

## Results and Discussion

### SN and DN Equilibrium Degree of Swelling

From the results presented in the Table 1 it becomes clear that the inclusion of the

***Table 1.***
$Q_{eq}$ in a distilled water and in aqueous NaCl solutions of the homo- and copolymer SN and DN of DMAPS, AMPS and AAm at T = 25°C. The weight ratio between first and second networks forming DN is 20.

| No | Network | $m_{DMAPS}$ | $Q_{eq}$ | | |
|---|---|---|---|---|---|
| | | | $H_2O$ | 0.1 M NaCl | 0.5 M NaCl |
| 1 | SN (DMAPS) | 1.0 | 1.52 | 6.19 | 19.49 |
| 2 | SN (AMPS) | 0.0 | 86.72 | 48.26 | 29.03 |
| 3 | SN (AAm) | 0.0 | 27.68 | 23.21 | 22.10 |
| 4 | SN (DMAPS-*co*-AAM) | 0.5 | 8.52 | 11.58 | 14.35 |
| 5 | DN (AMPS:DMAPS) | 0.95 | 6.56 | 6.96 | 10.01 |
| 6 | DN (AMPS:AAM) | 0.0 | 23.94 | 18.75 | 16.65 |
| 7 | DN (AMPS:DMAPS-*co*-AAM) | 0.65 | 9.07 | 10.27 | 16.83 |

DMAPS monomer units in the SN and DN (No 1, 4, 5, 7) results in the sharp decrease of the equilibrium degree of swelling ($Q_{eq}$) of these networks in water at an ambient temperature. This is in accordance with the mentioned in the Introduction poor PZ solubility in water and explains the striving for an increase this solubility (in this case the PZ $Q_{eq}$) through the copolymerization of zwitterionic monomers with hydrophilic ones, such as AAm, AMPS etc. The reason for small $Q_{eq}$ values of the DMAPS contained networks is the dipole-dipole cluster formation from the opposite oriented dipoles, playing a part of an additional physical networks nodes (Figure 1).[6]

The destruction of these clusters would increase both the PZ solubility,[4–7] and the $Q_{eq}$ of the zwitterion contained networks, DMAPS monomer units in this case. This destruction could be achieved by the increase of the temperature, ionic strength and the electrical field intensity.[7] The results presented in Table 1 are in accordance with the ionic strength effect on the physical crosslinking, and from here, on the $Q_{eq}$ values of the networks with DMAPS monomer units (1, 4, 5 and 7). $Q_{eq}$ of all of these networks increase at the transition from a swelling in water to a swelling in a 0.1 M and 0.5 M NaCl aqueous solutions. This result is a macroscopic expression of the antipolyelectrolyte effect of the PZ networks. Polyelectrolyte effect has an opposite macroscopic show, and one can see from the results in Table 1, it characterizes the networks in which mole fraction of the anionic AMPS monomer units dominates (No 2, 6).

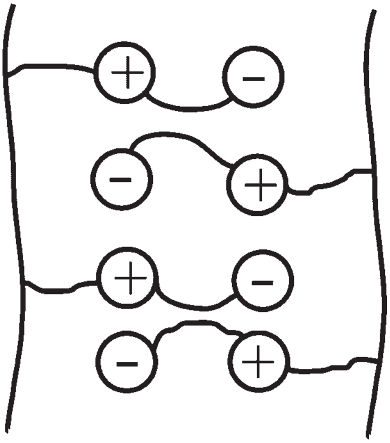

*Figure 1.*
Dipole-dipole self-assemblies of oppositely oriented dipoles - zwitterionic side groups of PZ macromolecules.

$Q_{eq}$ increase of the network No 5, which consist of both DMAPS and AMPS monomer units, and hence should express both polyelectrolyte and antipolyelectrolyte effects simultaneously, can be explained with that the $m_{DMAPS}$ is twenty times more than AMPS one. It is noteworthy that the effect of the ionic strength increase on the AAm SN swelling is a similar to a polyelectrolyte effect of the AMPS SN. This could be connected to the dehydration effect of the low molecular ions (salting effect) resulting in the association of the PAAm segments, as the association between the PAMP segment after the screening of the anionic repulsion by the low molecular counter ions.

Thought the obtained $Q_{eq}$ on the ionic strength are in accordance with its expected effects on the polyelectrolyte and antipolyelectrolyte network properties, it is important to note that these characteristic properties resulted from the density of the additional to the chemically produced nodes - physical ones. The chemical node density can be varied for different networks, especially for SN and DN, in spite of the same concentration of the cross-linking agent (MBAA) used. As the cross-linking reactions are copolymerization ones, the relative reactivity of MBAA in the propagation of the copolymer chain, the density and the distribution if the chemical nodes depend on both the nature and structure of other comonomers, and on the medium composition for the cross-linking copolymerization. Hence, the outlined tendencies from the results in Table 1 for $Q_{eq}$ dependence on the ionic strength are more reliable from those, which one could be derived from the $Q_{eq}$ comparison of the different types of networks. The heterogeneity of the chemical nodes distribution

***Table 2.***
Activation energy ($E_a$) of the hydrogels at different networks swelled in water and in aqueous 0.5 M NaCl solution at different degree of dehydration ($\alpha$), calculated by Eqn (1).

| No | Network | [NaCl], M | $E_a$ | | | |
|---|---|---|---|---|---|---|
| | | | $\alpha = 0.1$ | $\alpha = 0.3$ | $\alpha = 0.4$ | $\alpha = 0.7$ |
| 1 | **SN (DMAPS)** | 0.0 | $29.57 \pm 0.2$ | $27.31 \pm 0.2$ | $25.93 \pm 0.3$ | $24.19 \pm 0.1$ |
| | | 0.5 | $59.86 \pm 0.3$ | $46.07 \pm 0.1$ | $31.44 \pm 0.2$ | $24.11 \pm 0.3$ |
| 2 | **SN (AMPS)** | 0.0 | $67.96 \pm 0.2$ | $48.63 \pm 0.1$ | $39.19 \pm 0.2$ | $36.64 \pm 0.3$ |
| | | 0.5 | $46.93 \pm 0.2$ | $38.54 \pm 0.2$ | $27.45 \pm 0.3$ | $25.64 \pm 0.2$ |
| 3 | **SN (AAm)** | 0.0 | $55.44 \pm 0.2$ | $41.49 \pm 0.1$ | $34.89 \pm 0.2$ | $32.44 \pm 0.3$ |
| | | 0.5 | $39.92 \pm 0.3$ | $29.16 \pm 0.3$ | $23.40 \pm 0.1$ | $18.32 \pm 0.2$ |
| 4 | **SN (DMAPS-*co*-AAm)** | 0.0 | $31.06 \pm 0.3$ | $23.37 \pm 0.1$ | $21.09 \pm 0.1$ | $19.19 \pm 0.3$ |
| | | 0.5 | $84.75 \pm 0.2$ | $47.56 \pm 0.2$ | $40.15 \pm 0.2$ | $34.15 \pm 0.2$ |
| 5 | **DN (AMPS:DMAPS)** | 0.0 | $36.27 \pm 0.3$ | $26.27 \pm 0.1$ | $22.17 \pm 0.2$ | $19.93 \pm 0.3$ |
| | | 0.5 | $81.97 \pm 0.2$ | $68.31 \pm 0.2$ | $48.47 \pm 0.3$ | $37.82 \pm 0.2$ |
| 6 | **DN (AMPS:AAm)** | 0.0 | $48.03 \pm 0.2$ | $39.18 \pm 0.1$ | $36.64 \pm 0.1$ | $35.04 \pm 0.3$ |
| | | 0.5 | $38.40 \pm 0.1$ | $32.42 \pm 0.2$ | $30.61 \pm 0.2$ | $27.70 \pm 0.3$ |
| 7 | **DN (AMPS: DMAPS-*co*-AAm)** | 0.0 | $49.89 \pm 0.2$ | $46.56 \pm 0.3$ | $40.15 \pm 0.2$ | $34.17 \pm 0.1$ |

of the different networks should be accounted for more reliable conclusions.

## Dehydration Activation Energy of the SN and DN Hydrogels

There is not an information in available literature about the correlation between Qeq of the networks and the kinetic characteristics of their hydrogel dehydration. The attempt for correlation for the mentioned in Table 1 and 2 SN and DN is presented here. Using the described in the experimental part method, the temperature dependence for dehydration of these hydrogels at different rates of temperature increase are determined. Two of them (one for SN, and another for DN) are presented in Figure 2 and 3.

It is obvious that as far as the temperature rate is higher, the fixed hydrogel degree of dehydration ($\alpha$) is achieved at higher temperatures. This indicates the nonequilibrium character of the dehydration, characteristic for solid state destruction reactions.[11] The described in the experimental part isoconversional method for determination of the activation energy ($E_a$) of the solid-state degradation reactions is applied for the characterization of the dehydration of the discussed hydrogels. As one can see from Figure 2b and 3b the results obtained are linearized in the

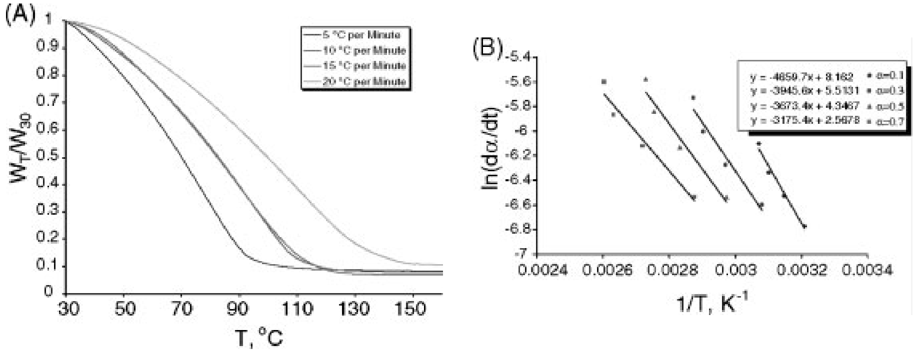

***Figure 2.***
TGA thermograms (A) of the SN (DMAPS) hydrogel dehydration, swelled in aqueous 0.5 M NaCl solution at the different rates of the temperature change ($W_T$ is the weight of the sample at temperature T) and the linearization of these data in the Friedman (Eqn 1) plot (B).

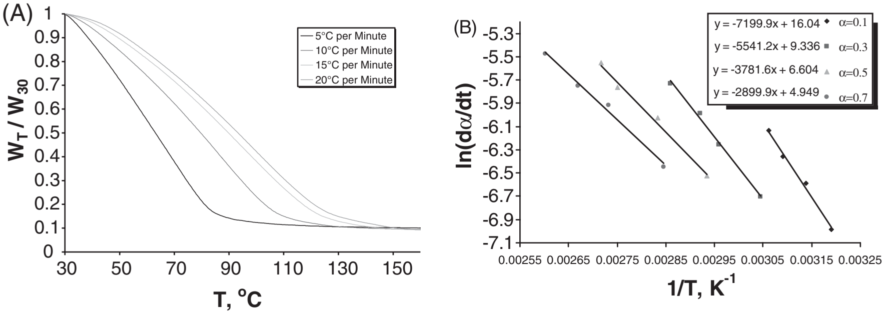

***Figure 3.***
TGA thermograms (A) of the DN (AMPS:DMAPS) hydrogel dehydration, swelled in aqueous 0.5 M NaCl solution at the different rates of the temperature change, and the linearization of these data in the Friedman (Eqn 1) plot (B).

Friedman equation (1) plot. This is in force for other investigated hydrogels also, and allows the Ea determination at different α values. The calculated $E_a$ values are included in Table 2.

The first consequence from the comparison of the presented in Table 1 and 2 results is a clear correlation between the $Q_{eq}$ values (Table 1) and those of Ea (Table 2) at the transition of the network swelling from a distilled water in NaCl aqueous solution. For the mentioned above networks, containing DMAPS monomer units (No 1, 4, 5, 7), $Q_{eq}$ (Table 1) increases together with the $E_a$ (Table 2) at this transition, while for the polyanionic networks (No 2, 6) $Q_{eq}$ (Table 1) and $E_a$ (Table 2) decrease. The impression is that $Q_{eq}$ and $E_a$ variations reflect the polyelectrolyte and antipolyelectrolyte hydrogel properties by the same way. Probably, this common ability of $Q_{eq}$ and $E_a$ is a result of the common reason for a $Q_{eq}$ and $E_a$ change: competitive interaction between the water molecules and the network monomer units. As far as this interaction is greater, the $Q_{eq}$ and $E_a$ values are higher. This natural at first sight correlation is derived for the first time, according to the available literature.

The more detailed comparison of the presented in the Table 1 and Table 2 data shows that the mentioned above $Q_{eq} - E_a$ correlation is in force for each network separately. It is not so strict at the comparison of $E_a$ and $Q_{eq}$ values for different networks. A possible reason for this deviation is the mentioned above difference between the density and distribution of the chemical junctions in different networks.

Another common relationship which one can reduce from the presented in Table 2 data is the Ea decrease with a α increase. It is in force for each network separately again. It is obvious that the greater $\alpha$, the smaller Ea values. The expectation that the Ea variation with α will outline the easier evaporation of the nonbound (''free'') water in contrast to the more involatile bound water does not support. The outlined $E_a$-$\alpha$ dependences have just reverse motion in comparison to the expected one, according to which at smaller α values the ''free'' water should be evaporated easier, i.e. with smaller $E_a$. There are two reason for the deviation from the expected dependence of $E_a$ and $\alpha$. The first one is the nonequilibrium character of the hydrogel dehydration at the high temperature rate used. This peculiarity of the process ''shades'' the expected two step character of the dehydration. The second reason is more essential . It is related to the application of the Arrhenius relationship (Eqn. (1) is derived from it) for the description of not only the hydrogel dehydration, but for the interpretation of the more general kinetic data of the solid-state reactions.[15] However, according to the modern theoretical models,[11,12] the determination of $E_a$ through Eqn. (1)

and obtained Ea dependence on α is acceptable and useful. The acceptability is a result of reduction of the bound strength between the water molecules and monomer units with $\alpha$, as the $\alpha$ increase of the iso-conversion method used for the $E_a$ estimation, means the temperature increase also.[13] The usefulness of the $E_a$-$\alpha$ relationship determination is in the possibility to unravel the complexity of the hydrogel dehydration as well as to gain an insight into its mechanism, and to reliably predict the kinetics of a process over a wide region of the temperatures.[11] It is important to note that the analysis of the kinetic mechanism based of determined Ea-α dependences is preferred to be presented as a model-free kinetic analysis.[11]

## Conclusion

$Q_{eq}$ end $E_a$ sensitivity to the opposite directed polyelectrolyte and polyelectrolyte behavior of polyelelectrolyte and PZ networks is proved. This is an important step for the production of the soft and biocompatible materials (hydrogels) with controlled swelling and deswelling characteristic. The established for the first time correlation between $E_a$ and $Q_{eq}$ reflects the common fundament for the values of the quantities – the strength of the interaction between the network monomer units and water molecules. The application of the developed for the solid-state destruction reaction characterization theoretical and applied approaches for such characterization of the soft materials (hydrogels) is performed for the first time. This is a useful transition from the solid-state material achievements to the soft material characterization.

*Acknowledgements:* This research was supported by DAAD Foundation (Germany) and Bulgarian National Scientific Fund (**Grant** No 06/2005 (24-04)).

[1] D. N. Schultz, D. G. Peiffer, P. K. Agarwall, J. Larabee, J. J. Kaladas, L. Soni, B. Handweker, R. T. Garner, *Polymer* **1986**, *27*, 1734.
[2] P. Koberle, A. Laschevsky, *Macromol. Symp.* **2002**, *179*, 209.
[3] P. Anton, P. Koberle, A. Laschevsky, *Macromol. Chem.* **1993**, *194*, 1.
[4] G. S. Georgiev, E. B. Kamenska, E. D. Vassileva, I. P. Kamenova, V. T. Georgieva, S. B. Iliev, I. A. Ivanov, *Biomacromolecules*, **2006**, *7*, 1329.
[5] G. S. Georgiev, A. A. Tzoneva, L. G. Lyutov, I. K. Petkov, *Nonlinear Opt. Quantumn Opt.* **2004**, *31*, 347.
[6] G. S. Georgiev, Z. P. Mincheva, V. T. Georgieva, *Macromol. Symp.* **2001**, *164*, 301.
[7] G. Georgiev, A. Tzoneva, L. Lyutov, S. Iliev, I. Kamenova, V. Georgieva, E. Kamenska, A. Bund, *Macromol. Symp.* **2004**, *210*, 393.
[8] C. Liu, J. Yu, X. Sun, J. Zhang, J. He, *Polym. Degr. Stab.* **2003**, *81*, 197.
[9] J. Cordoso, L. Rubio, M. Albores-Velasco, *J. Appl. Polym. Sci.* **1999**, *73*, 1409.
[10] J. H. Flynn, *J. Thermal Anal.* **1983**, *27*, 95.
[11] S. Vyazovkin, C. Wight, *Annu. Rev. Phys. Chem.* **1997**, *48*, 125.
[12] D. Dollimore, *Anal. Chem.* **1996**, *68*, 63.
[13] H. Friedman, *J. Polym. Sci.* **1964-65**, *C6*, 183.
[14] T. Ozawa, *Bull. Chem. Soc., Japan* **1965**, *38*, 1881.
[15] J. H. Flynn, L. A. Wall, *Polym. Lett.* **1966**, *4*, 323.