

Swelling Studies in Electrochemically Prepared Acrylamide/*N,N'* Methylene Bisacrylamide Gels

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ABSTRACT: Acrylamide/*N,N'* methylene bisacrylamide gels were prepared at different voltages electrochemically. The dependence of the swelling properties on the preparation voltage was investigated. A set of gel samples was swollen as prepared and another set was swollen after being dried to constant weight. Swelling versus time curves were all in stretched exponential form, rather than pure exponen-

tial form, indicating that the gels are of heterogeneous nature. Maximum swelling increased with the preparation voltage in both gel types. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 1398–1401, 2006

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INTRODUCTION

Polyacrylamide gels have diverse applications. Their ability to absorb solvents 50–100 times more than their original weight and retain their durability enhances their use in holding aqueous solutions. They are used extensively as sieving systems in column chromatography and electrophoresis in analytical separation processes. They also have biomedical applications in artificial organs, contact lenses, and controlled drug release systems for both human and animal therapy.^{1–6} In recent years, acrylamide and *N,N'* methylenebisacrylamide copolymeric gels prepared with ionic comonomers having polyelectrolyte nature have received considerable attention.^{7–10} The formation and properties of polyacrylamide gels and the gelation processes have been extensively studied.

Li and Tanaka¹¹ predicted that in a heterogeneous system, with various processes with their own time constants, swelling and shrinking can be represented by

$$(W_{\infty} - W_t) = (W_{\infty} - W_0) \times (B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2} + B_3 e^{-t/\tau_3} + \dots) \quad (1)$$

Here, W_{∞} , W_t , and W_0 are the infinite weight of swollen gel at equilibrium and the weights of the gel at time t and time 0, respectively. B_i 's are the corresponding fractions within the gel such that their sum is equal

to 1 and τ_i 's are the time constants of various processes.

This equation can be written in terms of the relative swelling $S_t = (W_t - W_0)/W_0$ as

$$S_t = S_{\infty}(1 - (B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2} + B_3 e^{-t/\tau_3} + \dots)) \quad (2)$$

where S_{∞} is the equilibrium swelling approached at long times. When the system is homogenous and can be described by a single time constant, first order kinetics apply.

$$S_t = S_{\infty}(1 - \exp(-t/\tau)) \quad (3)$$

In logarithmic form this gives a linear plot,

$$\ln(1 - S_t/S_{\infty}) = -t/\tau \quad (4)$$

When the system is heterogeneous, $\ln(1 - S_t/S_{\infty})$ does not vary linearly with t . A common approximation used in these cases is to replace the sum with a stretched exponential of the form

$$S_t = S_{\infty}(1 - \exp(-(t/\tau)^{\beta})) \quad (5)$$

where β is a constant less than one and $(1 - \beta)$ is a measure of the heterogeneity of the system.

In many chemically prepared gel systems, swelling behavior satisfactorily fitted the exponential form of Li and Tanaka equation.^{11–13} Especially, the longer times fitted very well as noted by Pekcan and Yilmaz.^{14,15}

Electrochemical preparation of gels were first described in our previous work.¹⁶ The electrochemical method for gelation is very simple to operate and

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control and can be performed at room temperature. Electrochemical preparation is a new way and it was observed that by changing only the preparation voltage it is possible to change the gel properties. Electrochemical gelation reaction is a free radical crosslinking copolymerization, but here voltage application decomposes the initiator at the initiation stage (details of the reaction are given in ref. 16).

Purpose of this study was to investigate the effect of voltage on the properties of the resulting gels, such as the amount and rate of swelling. Gel composition was kept constant during this work. In previous work,¹⁶ crosslinker content less than 0.045M resulted in very soft gels, which were impossible to work with. Crosslinker content between 0.045 and 0.09M resulted in flexible gels useful for swelling. Crosslinker content equal to or higher than 0.18M resulted in brittle gels, which crumbled when swelled.

Gels used in this study were all prepared with 0.09M crosslinker concentration, which the previous work indicated to be optimal. The synthesis voltage was varied from 0.5 to 0.8 V. Voltages higher than this caused oxygen evolution and appearance of abundant bubbles.

A set of electrochemically prepared gel samples was swollen as prepared, and another set was swollen after being dried to constant weight. The dependence of the swelling properties on the preparation voltage was investigated.

EXPERIMENTAL

Equipment

Electrochemical experiments were carried out using an Autolab PGSTAT 30 computer-controlled potentiostat. Electrolytic solutions were prepared from ultrapure water (Millipore milli Q system). All experiments were performed in a classic three electrode cell with a platinum wire as counter electrode and a calomel electrode as reference. The working electrode was a silver wire with a geometric surface of 1.5 cm².

Materials

Acrylamide (AAm; Sigma, Steinheim, Germany), *N,N'* methylene bisacrylamide (bis; Sigma), and ammo-

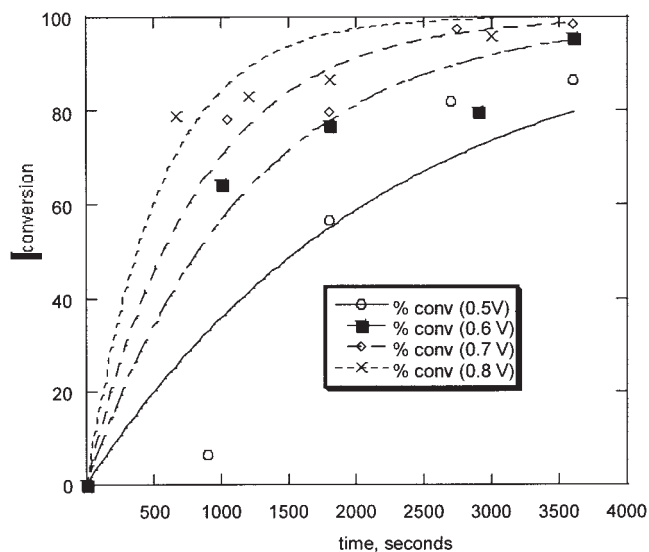


Figure 1 % conversion vs time values at different voltages.

nium persulphate (Merck, Darmstadt, Germany) were used as supplied.

Polymerization procedure

The gels were prepared using 50 mL solution of 0.62M AAm, 0.09M bis, and 0.005M ammonium persulfate. The reaction solution was deoxygenated by nitrogen bubbling for 15 min prior to the voltage application. In all voltammetric experiments, the solution was stirred continuously using a magnetic stirrer at constant speed. Gels were prepared at 0.5, 0.6, 0.7, and 0.8 V. The reactions were stopped when the magnetic stirrer slowed down, which is a rough guide of the gel point.¹⁷

Swelling

Swelling experiments were conducted in two different ways. In the first part, the gels were swollen immediately as prepared. In the second batch, gels dried up to a constant weight and then placed in the water. Swelling measurements were continued up to 10 days. The gels were in the form of small cylinders of 35 mm height and 6 mm diameter. The cylinders were cut into three equal pieces and swelling was followed separately to obtain fluctuations. The average of the three measurements is used in the calculations.

RESULTS AND DISCUSSION

Gel preparation voltages and gelation times are given in Table I. As indicated, gelation times decreased as voltage increased. The gelation times indicate that the reaction rates are higher at higher voltages.

Figure 1 shows the conversion versus time results in

TABLE I
Gel Preparation Voltage and Resulting Gelation Times and Corresponding Conversion Values

Gel preparation voltage (V)	Gelation time (min)	Approx. conv. at gel point (%)
0.5	30	55
0.6	26	70
0.7	20	75
0.8	13	75

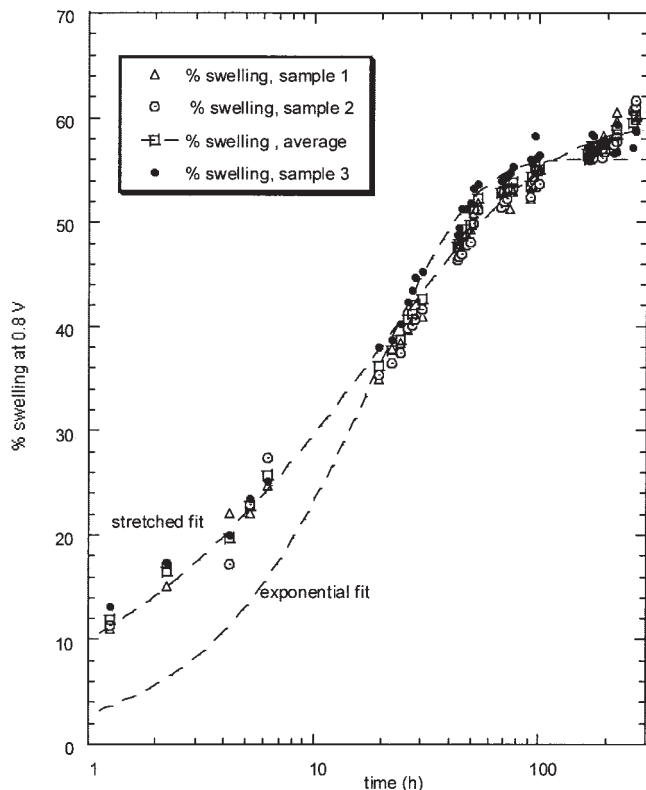


Figure 2 Percent swelling versus time at 0.8 V for gels swollen as prepared.

separate gelation experiments conducted up to the 2 h for all voltages. The conversions at the gel point ranged from 55% for the gel prepared at 0.5 V to 75% for the gel prepared at 0.8 V. The conversion at the gel point increases as the voltage increases, indicating higher reaction rates at higher voltages.

Figure 2 shows the amount of swelling as a function of time at 0.8 V for three different samples and their average. In all samples, it is seen that eq. (3) with a single time constant τ is not satisfied, but rather there is a distribution of time constants so that the relaxation toward the equilibrium swelling is in the stretched exponential form. This is because faster processes have not relaxed within 10 h. Subsequent data follow the exponential relation rather well. Stretched exponential fit to the same data shows good match at both early and late times. Observed values of the exponent β ranged from 0.47 to 0.67. Since best-fit values of β are significantly less than one, the gels are heterogeneous in nature. In most studies of acrylamide gels prepared by chemical initiation, exponential fits have been found to be adequate.^{14,15}

In Figure 3 voltage dependence of swelling in the case of swollen as prepared gels and in Figure 4 voltage dependence of dried gels are shown.

The stretched fit results are given in Tables II and III. Table II shows the final swelling ratio of the gels swollen as prepared without drying, and it shows that

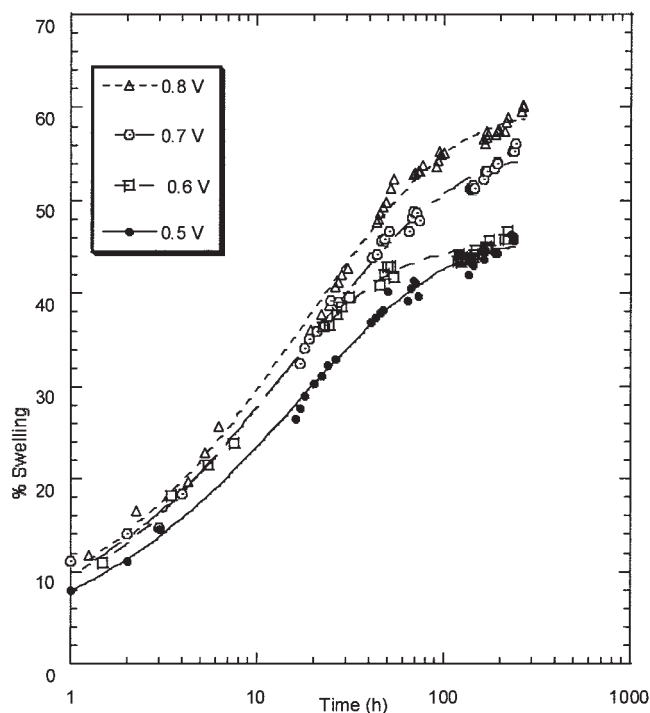


Figure 3 Voltage dependence of % swelling of gels swollen as prepared.

the gels prepared at higher voltages can swell more. Since the gel point occurred at higher conversion in gels prepared at higher voltages, these samples have more polymer and therefore a greater density of crosslinks. Since these added chains would tend to hinder the swelling, one would expect higher conversion material to swell less. Thus the differences in their

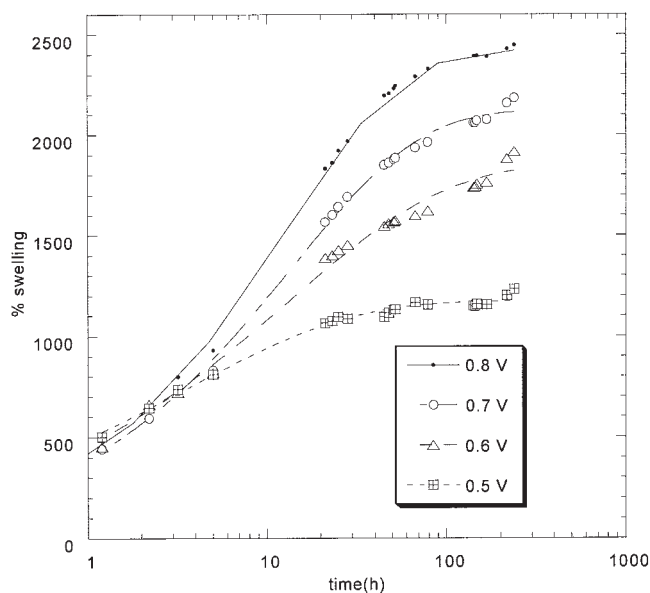


Figure 4 Voltage dependence of % swelling of gels swollen after being dried.

conversions cannot account for the higher swelling ability of the higher voltage gels. This indicates that the swelling ability of the gels is a function of their structures.

Richard and Temple¹⁸ noted that the more regular gels swell less. Nonideal gels as called clustered and crumpled swell more. Based on their conjecture, it can be seen that the gels prepared at higher voltages and therefore at a higher reaction rate are less regular than gels prepared at lower voltages.

Table III shows that this observation is also valid for gels swollen after being dried until constant weight. The gels prepared at higher voltages were swollen more. Note that the gels were dried to ~5% of their original mass. Those prepared at 0.5 and 0.6 V did not swell to their original mass. This indicates that the dried gels have additional hindrances to swelling. The gel structure is likely to have many unterminated dangling chain ends. During the drying process, some of the active chain ends can get in contact with each other and form additional crosslinks. These new links tend to further restrict swelling. Thus one can surmise that additional crosslinks occurred while the gels were crumpled during their drying.

Swelling times τ , in the range of 10 h, showed a rather large scatter and were not sensitive to preparation voltage. The power indices β were also not sensitive to the preparation voltage in gels swollen as prepared. On the other hand, the power indices in the gels swelled after drying showed a monotonic increase with preparation voltage. The low power indices and low equilibrium swelling of the gels prepared at 0.5 and 0.6 V may both be due to formation of additional crosslinks during the drying process.

Nagash and Okay¹⁷ had noted the inhomogeneity of chemically prepared acrylamide gels also. The electrochemically prepared gels are also showing inhomogeneity. However, the dependence of the equilibrium

TABLE II
Gel Preparation Voltage and Swelling Properties of As Prepared Gels

Preparation voltage (V)	Equilibrium swelling, S_{∞} (%)	Time constant, τ (h)	Exponent (β)
0.5	45.5	17.3	0.58
0.6	44.9	10.5	0.65
0.7	55.0	18.7	0.56
0.8	59.4	19.0	0.58

TABLE III
Gel Preparation Voltage and Swelling Properties of Dried Gels

Preparation voltage (V)	Equilibrium swelling S_{∞} (%)	Time constant τ (hr)	Exponent (β)
0.5	1170	3.62	0.47
0.6	1850	13.2	0.49
0.7	2120	13.8	0.60
0.8	2420	12.9	0.67

swelling on the preparation voltage implies that the degree of inhomogeneity depends on this parameter.

CONCLUSION

The results show that the electrochemically initiated gels prepared at higher voltages swell more than those prepared at lower voltages, indicating that the gels prepared at lower voltages have more regular nature. It is also seen that for these gels a single swelling time constant is inadequate and the heterogeneity of their structure leads to a stretched exponential form.

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