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Swelling Behavior of Chemically Ion-Doped Hydrogels

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Summary: Poly(acrylamide-*co*-*N,N′*-methylenebisacrylamide) gels were synthesized in the presence of pyranine fluoroprobe (trisodium 8-hydroxypyrene-1,3,6-trisulfonate). Pyranine binds to polymer chains through its OH group via radical addition. Thus, the final gels were doped with the pyranines having SO_3^- ions as side groups and Na^+ as counter-ions. The swelling behavior of gels prepared with varying amounts of pyranine and monomer concentrations were studied. The swelling ratio of the synthesized gels did not exceed 35 except the 2 M gel containing 10^{-2} M pyranine which are the concentrations for the abnormal swelling behavior. At this particular concentration of monomer (acrylamide) and pyranine, the mass ratio m/m_0, the mass of the swollen gel to the mass of the dried gel, reaches about 1300; a stepwise behavior was observed in the swelling kinetics. The swelling kinetics of polyacrylamide gels containing unbound (free) pyranine were compared with the swelling behavior of the gels containing chemically bound pyranine.

Keywords: ion doped polyacrylamide; microstructure; swelling

Introduction

Polymer gels are three-dimensional cross-linked polymer networks which may contain a large amount of solvent.[1,2] One of the most important properties of these materials is the substantial swelling and collapse which can be induced by temperature, pH, ionic strength.[3] This volume transition property of the polymer gels has prompted researchers to investigate gels as sensors, membranes for separations, drug delivery agents, artificial muscles and actuators.[4–7] Since the polymer gels can simulate biological tissues, they have an enormous importance in biomedical applications.[8–10]

Polyacrylamide (PAAm) hydrogels are widely used because of this biocompatibility, and unique chemical and physical properties. Therefore they attract attention of researchers who investigate the use of PAAm hydrogels as superabsorbents,[11] electrophoresis matrices, encapsulating agents for drugs, enzymes and proteins in drug delivery systems, biosensors, etc.[12,13]

The network structure, which is directly related to swelling properties of the PAAm hydrogels prepared with *N,N′*-methylenebisacrylamide (BIS), is described in literature. It was observed that the structure contains inhomogeneous crosslink distribution due to the different reactivity ratios of AAm-AAm and AAm-BIS monomers.[14,15] The reactivity of AAm-BIS is higher than that of AAm-AAm. The difference in the reactivities results in crosslink-rich regions which causes the local heterogeneity in PAAm gels. It was also shown that partially hydrolyzed PAAm hydrogels undergo a phase transition as a result of changes in solvent composition, temperature and pH of the solution.[16]

The swelling behavior of PAAm hydrogels have been studied extensively for different solvent compositions and the ionic groups that are free in solution.[17–25] The swelling experiments on PAAm gels were initiated by Tanaka and co-workers in 1970's.[26] They observed that the final swelling ratio of the PAAm gels changes as a function of solvent composition, i.e.

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with the water/alcohol ratio. In addition, the effects of free ionic groups on the swelling behavior of the hydrogels have been studied.[27–29] It has been shown that the gels containing free ions undergo discontinuous transition during swelling, depending on the ionic group concentration.

Even though much valuable work has been done on swelling of PAAm gels, the effect of the ions bonded to PAAm gels has not been studied in detail, only a few papers were published on this topic.[19,20] In these studies the swelling kinetics have not been evaluated from the viewpoint of internal morphology (the effect of heterogeneity) of the gels, only the osmotic pressure produced by the difference between the ion concentrations inside and outside of the gels was taken into account.

In the present work we studied the swelling kinetics of PAAm gels with or without pyranine (trisodium 8-hydroxypyrene-1,3,6-trisulfonate), which were chemically bound or entrapped (free) in the gel. The effect of the free and bonded ions on the swelling of PAAm gels were examined in detail. We have observed a stepwise behavior, which has not been put forward previously, in the swelling for a certain monomer and bonded-ion concentration.

Experimental Part

Crosslinked copolymers of acrylamide (PAAm gels) were synthesized with various amounts of AAm as monomer (Merck) and pyranine as trivalent anion (Fluka). *N,N′*-Methylenebisacrylamide (BIS, Merck) was used as crosslinking agent and the ratio of AAm to BIS was kept fixed, AAm/BIS = 31, for all samples. Three main groups of gels were synthesized. Four gels in the first group were synthesized with 0.5 M, 1 M, 2 M and 4 M AAm without pyranine (neat gels, NG). In the second group the samples were prepared via diffusion of pyranine into the neat gels of the first group (pyranine diffused gels, DG). The concentrations of diffused pyranine for each AAm concentration were varied - 10^{-6} M, 10^{-4} M and 10^{-2} M. In the third group the gels were synthesized in the presence of pyranine where pyranines bind to the strands of the gel during the polymerization (pyranine bonded gel, BG). In this group AAm and pyranine concentrations were kept the same as those in the second group. Here it is important to note that the pregel solutions including 10^{-2} M pyranine and 0.5 or 1 M AAm did not turn into gel.

The samples were deoxygenated by bubbling nitrogen for 10 min and the gelation was performed in cylindrical glass tubes of radius 0.9 cm and length 3.5 cm. On sealing the samples with Teflon stoppers they were put in a 60 °C heat bath. After 24 h they were cut into slabs of 1 mm thickness. Later, these samples were dried at 40 °C. Then, the dried gels were swollen in excess of pure water and the masses of the swelling gels were measured with a balance (Precisa) at certain times. The times for weighing were kept at the minimum (less than 20 s) compared with equilibrium swelling times.

Results and Discussion

Figure 1 shows the mass ratio of NG, m/m_0, the mass of the swollen gel to the mass of the dried gel, for different AAm contents

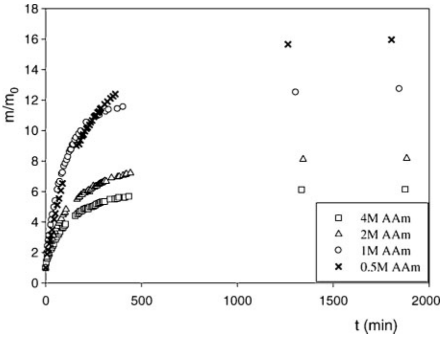

Figure 1.
The ratio, m/m_0, vs. swelling time, t, for different NG samples of varying polymer concentrations. Samples were swollen in pure water at room temperature.

where swelling kinetics accelerates as the monomer concentration is decreasing. The results given in Figure 1 confirm the literature data; it is well known that the elasticity is inversely proportional to the monomer concentration. Increasing monomer concentration results in an increasing number of entanglements of polymer chains, which suppress junction fluctuations and affects the swelling by acting as additional cross-links.[19,20,30]

Figure 2 shows the mass ratios of polymers NG and DG for varying AAm and pyranine concentrations. As seen from this figure, the equilibrium mass ratios increase again with decreasing monomer concentrations. In addition, the swelling rate and the difference in the osmotic pressure of DG are obviously bigger than those of NG. This difference is due to the entrapped charges in DG.[27–29]

The mass ratios of NG and BG are compared in Figure 3 for varying AAm and pyranine concentrations. The results from Figure 3 can be summarized as follows: (*i*) for 4 M gel, the final mass ratio increases and the swelling rate in the initial periods decreases with increasing pyranine concentration (Figure 3a), (*ii*) for 0.5 and 1 M PAAm gels both the final mass ratios and the swelling rates in the initial periods increase with increasing pyranine concentration (Figure 3c and d), (*iii*) for 2 M gel, the final mass ratio and the swelling rates in the initial period increase again with increasing pyranine concentration (Figure 3b). For 2 M BG with 10^{-2} M pyranine, an unexpected behavior in the swelling is observed as seen in the inset of Figure 3b. In this case, the final mass increases excessively to the ~1300 multiple of its initial value. At the same time a "stepwise" behavior appears in the swelling kinetics. As seen from the inset of Figure 3b, the gel "wants" to swell more after the 1300 fold initial value but it could not keep its own shape, breaking into pieces above this mass ratio.

The bonded ions in the gel make probably the gel more homogeneous[30] and cause an abrupt increase in the

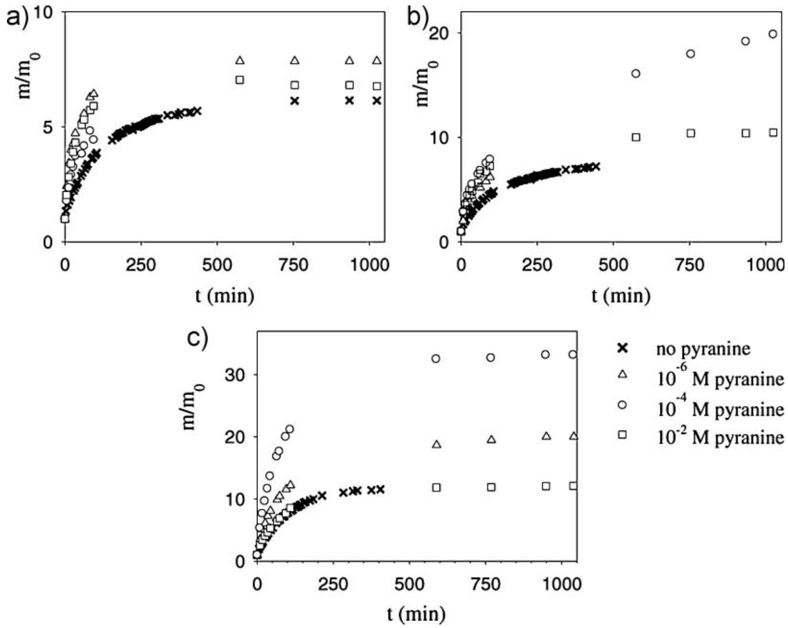

Figure 2.
The ratio, m/m_0, vs. swelling time, t, for different DG samples of varying polymer concentrations, a) 4 M, b) 2 M and c) 1 M. Each sample contained varying amounts of free pyranine, 10^{-6}, 10^{-4}, 10^{-2} M. The samples were swollen in pure water at room temperature.

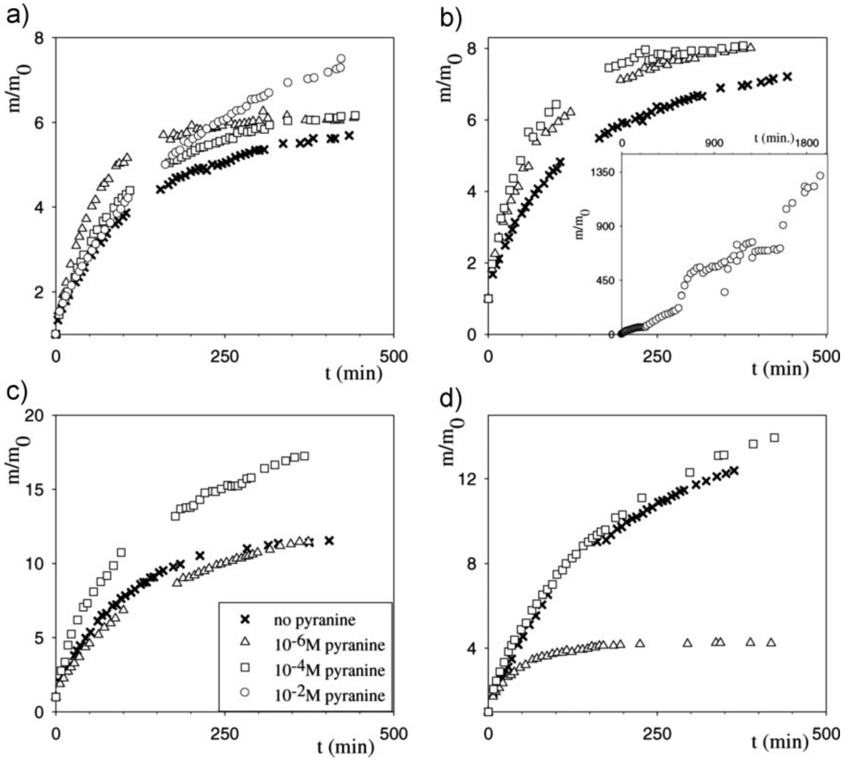

Figure 3.
The ratio, m/m_0, vs. swelling time, t, for different BG samples of varying polymer concentrations, a) 4 M, b) 2 M, c) 1 M and d) 0.5 M. Each sample contained varying amounts of bound pyranine, 10^{-6}, 10^{-4}, 10^{-2} M. The samples were swollen in pure water at room temperature.

equilibrium swelling degrees especially at certain pyranine and monomer concentrations, 10^{-2} M and 2 M, as seen in the inset of Figure 3b. This is probably due to the fact that the bonded ions repel the crosslinker (BIS) molecules during the polymerization and inhibit the formation of BIS-rich regions and inhomogeneous crosslink distribution. This is supported by the fact that no gelation occurred for 1 M and 0.5 M PAAm gels containing 10^{-2} M pyranine concentrations. Because in these cases the monomer concentration is comparably low and the monomer molecules have not the chance to come close and react with BIS molecules which are repelled by the bonded ions. The fact that an abrupt increase in the swelling degree was not observed for 4 M BG including 10^{-2} M pyranine is probably due to the screening effect of high monomer concentration against the repulsion between bonded ions and BIS molecules.

Each of the steps in swelling kinetics of 2 M BG with 10^{-2} M pyranine shown in the inset of Figure 3b corresponds probably to a different morphology of the charged gel. These steps are related to the distribution of dense polymer regions: they are defined as the ‘‘blobs’’ appearing in the microstructure of a given PAAm gel. For the charged gel, the heterogeneity of the gel decreases due to the internal electric field of the charged sites; there still exist dominant generations of the blobs the sizes or densities of which are different from each other. This characteristic behavior in the swelling can be seen apparently for 2 M BG with 10^{-2} M pyranine. The stepwise behavior is not observed for the neat and other charged gels, because a continuous size distribution of heterogeneous regions was probably formed during the gelation process, as recently reported for electric properties of charged and uncharged gels.[31]

In the following part experimental data given in Figure 1, 2 and 3 will be evaluated using the Li-Tanaka equation;[26–29,32]

$$\frac{W_t}{W_\infty} = 1 - \sum_{n=1}^{\infty} B_n \mathrm{e}^{-\frac{t}{\tau_n}} \tag{1}$$

where W_t and W_∞ are the swelling (solvent uptake) at time t and at equilibrium, respectively. W_t can be considered as volume difference of the gel in time t and zero. B_n represents a constant related to the ratio of shear modulus G and longitudinal osmotic modulus; M is defined by the combination of shear and osmotic bulk moduli, $M = (4/3)G + K$.[33,34] τ_n is the time constant, which is independent of time t. For large t or if τ_1 is much larger than the rest of τ_n, all high-order terms ($n \geq 2$) in Equation (1) can be neglected. Then Equation (1) becomes

$$\frac{W_t}{W_\infty} = 1 - B_1 \mathrm{e}^{-\frac{t}{\tau_1}} \tag{2}$$

Here B_1 is given by Equation 3

$$B_1 = \frac{2(3-4R)}{\alpha_1^2 - (4R-1)(3-4R)} \tag{3}$$

where $R = G/M$ and α_1 is given as a function of R, i.e.

$$R = \frac{1}{4}\left[1 + \frac{\alpha_1 J_0(\alpha_1)}{J_1(\alpha_1)}\right] \tag{4}$$

In Equation (2) τ_1 is related to the collective cooperative diffusion coefficient D_c of a gel disk at the surface and is given by Equation 5 [35]

$$\tau_1 = \frac{3a^2}{D_c \alpha_1^2} \tag{5}$$

Here a represents the half of the disk thickness in the final infinite equilibrium that can be experimentally determined. The collective diffusion coefficient D_c of the swelling is given by Equation (5).

Equation (2) can be written in terms of the masses of the gels measured as function of the swelling times,

$$\frac{W}{W_\infty} = \frac{m(t \to \infty) - m(t)}{V_0 + m(t \to \infty) - m(0)} = B_1 \mathrm{e}^{-t/\tau_1} \tag{6}$$

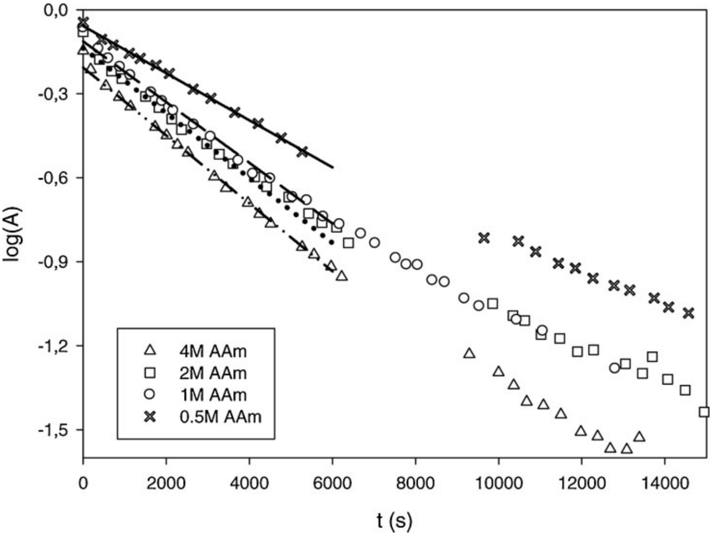

Figure 4.

Linear regressions of the data given in Figure 1 according to Equation 7 for NG.

Table 1.
Measured parameters of NG.

Parameter	4 M AAm	2 M AAm	1 M AAm	0.5 M AAm
τ_1 (s)	8305	8635	10000	11877
B_1	0.8132	0.8712	0.8930	0.9433
α_1	1.6	1.2	1.02	0.5
a (cm)	0.19	0.16	0.15	0.09
$D_c{}^*10^{-6}$ (cm^2/s)	5.04	6.17	6.48	8.38
m_∞/m_0	6.16	8.23	14.54	15.95

where V_0 is the initial volume of gel, $m(t)$ and $m(t \to \infty)$ are the total masses of gel at time t and infinity, respectively. Here the density of water was taken as 1 g/cm^3. Defining $A = \frac{m(t\to\infty)-m(t)}{V_0+m(t\to\infty)-m(0)}$, and taking the logarithm of Equation (6) gives Equation 7

$$\log(A) = \log B_1 - \frac{t}{\tau_1} \tag{7}$$

B_1 and τ_1 values were calculated from the $\log A - t$ plots (as shown in Figure 4 for neat gels) derived from the data given in Figure 1–3. The calculated D_c values are given in Table 1–3 together with other parameters.

Using the same procedure, the parameters given in Table 1 were calculated and listed in Table 2 and 3 for DG and BG, respectively.

As seen in the tables the collective diffusion coefficients, D_c, increase with decreasing monomer concentration and with increasing pyranine concentrations as expected. At a certain composition (2 M monomer and 10^{-2} M pyranine concentrations) the D_c goes almost to infinity.

Table 2.
Measured parameters of DG.

Parameter	4 MAAm			2 M AAm			1 M AAm		
	pyronine			pyronine			pyronine		
	10^{-6} M	10^{-4} M	10^{-2} M	10^{-6} M	10^{-4} M	10^{-2} M	10^{-6} M	10^{-4} M	10^{-2} M
τ_1 (s)	3262	3147	3009	9132	2572	6289	8032	5243	6481
B_1	0.676	0.643	0.660	0.869	0.763	0.680	0.773	0.917	0.806
α_1	1.85	1.95	1.90	1.30	2.00	1.80	1.40	1.00	1.43
a (cm)	0.11	0.12	0.14	0.18	0.21	0.25	0.13	0.12	0.2
$D_c{}^*10^{-6}$ (cm^2/s)	3.25	3.61	5.41	4.15	12.8	9.20	1.6	8.2	9.05
m_∞/m_0	7.85	5.34	6.81	6.80	22.47	10.46	20.36	33.16	12.22

Table 3.
Measured parameters of BG.

Parameter	4 M AAm			2 M AAm			1 M AAm		0.5 M AAm	
	pyronine			pyronine			pyronine		pyronine	
	10^{-6} M	10^{-4} M	10^{-2} M	10^{-6} M	10^{-4} M	10^{-2} M	10^{-6} M	10^{-4} M	10^{-6} M	10^{-4} M
τ_1 (s)	3745	6548	14493	5681	4926	NA	11422	8992	3080	17889
B_1	0.836	0.824	0.854	0.815	0.791	NA	0.904	0.897	0.733	0.935
α_1	1.4	1.4	1.3	1.5	1.6	NA	0.6	0.9	1.7	0.82
a (cm)	0.130	0.175	0.245	0.152	0.178	0.205	0.130	0.171	0.180	0.240
$D_c{}^*10^{-6}$ (cm^2/s)	6.90	7.15	7.38	7.219	7.53	$\sim\infty^*$	12.3	12.04	10.91	14.36
m_∞/m_0	6.12	6.47	9.21	8.58	8.47	$>$1300	14.85	21.28	4.3	22.28

*Extremely big since α is close to zero. NA: Not applicable.

Conclusion

In this work we have studied the swelling kinetics of PAAm hydrogels and observed for the first time an abrupt and a stepwise behavior during the swelling processes for a certain monomer and bonded ion concentration, 2 M AAm and 10^{-2} M pyranine. The swelling kinetics of this special gel does not obey the classical Li-Tanaka model. It seems that the Li-Tanaka equation can be applied only to the gels where the gel is completely homogenous or gel is so heterogeneous that the generations of the blobs are not distinguishable, i.e., all sizes of the blobs exist at the same time. It seems that evaluation of the kinetics of this special gel needs some new theoretical approaches concerning the local heterogeneity.

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