Proceedings of the World Congress on Mechanical, Chemical, and Material Engineering (MCM 2015)
Barcelona, Spain – July 20 - 21, 2015
Paper No. 265

Studying on the Effect of Ph on Volume Phase Transition for Composite Hydrogel Using by Fluorescence Technique

Demet Kaya Aktaş
Istanbul Technical University, Department of Physics,
Maslak 34469 Istanbul- Turkey
demet@itu.edu.tr

Abstract **-**Steady-state fluorescence (SSF) technique was employed for studying swelling of poly(acrylamide-co-acrylic acid) (P(AAm-co-AAc)) composite gels in various pH. Disc shaped composite gels were prepared by free-radical crosslinking copolymerization of P(AAm-co-AAc). N, N'- methylenebis (acrylamide) (BIS) and ammonium persulfate (APS) were used as crosslinker and initiator, respectively. Pyranine 4 was introduced as a fluorescence probe. P(AAm-co-AAc) composite gels dried before using for swelling experiments. Fluorescence intensity of pyranine 4 was monitored during in situ swelling processes of composite gels. It was observed that fluorescence intensity values decreased as swelling is proceeded. Gravimetrical and volumetrical experiments were also performed. Li-Tanaka equation was used to determine the swelling time constants, τ and cooperative diffusion coefficients, *D* from intensity variations during the swelling processes. It was shown that swelling time constants, τ decreased and diffusion coefficients, *D* increased as the pH values are increased.

Keywords: Hydrogels, swelling, pH, fluorescence

1. Introduction

Hydrogels can be defined as three-dimensional networks of polymers which can swell several hundred times in relation to the dry network mass, when in contact with water or aqueous solutions[1]. Their swelling and deswelling ability can be tuned by the interaction between the polymeric network and the solvent. Properties of the gel are studied by varying the stimuli such as solvent composition [1], temperature [2], electric field [3], ionic strength [4], and pH [5] that perturb their swelling and deswelling behaviour. In case of anionic polymeric networks, ionization takes place as the pH of the external medium rises above the pKa of the ionizable moiety [6]. The polymeric network becomes more hydrophilic as the degree of ionization increases and the drug release is accomplished as the polymer swells. Because many of the potentially most useful pH-sensitive polymers swell at high pH values and collapse at low pH values, the delivery of active agent occurs upon an increase in the pH of the environment. Such materials are ideal for systems such as oral delivery, in which the drug is not released at low pH values in the stomach but rather at high pH values in the upper small intestine [7-9].The swelling, shrinking and drying kinetics of gels are important in many technological applications. Especially in pharmaceutical industries in designing controlled release of drugs and in using cosmetic ingredients, understanding the kinetics of gels is highly desirable. The knowledge of the gel kinetics is an important requirement for producing storable foods in agricultural industry and developing artificial organs in medical applications. In general the elastic and swelling properties or permanent networks can be understood by considering two opposing effects: osmotic pressure and restraining force [10], [11] and [12]. Usually the total free energy of a chemically crosslinked network can be separated into two terms: bulk and shear energies. In a swollen network the characteristic quantity of the bulk free energy is the osmotic bulk modulus, K. The shear energy as the other important energy, keeps the gel in shape by minimizing the non-isotropic deformation. The characteristic coefficient of these forces is the shear modulus, μ which can be most directly evaluated by stress–strain measurements [13]. Li and Tanaka [14] have developed a model where the shear modulus plays an important role by keeping the gel in shape due to coupling of any change in different directions. This model predicts that the geometry of the gel is an important factor and swelling is not a pure diffusion process. Many different experimental techniques have been used to study the kinetics of swelling and shrinking of chemical and physical gels such as neutron scattering, quasielastic light-scatterin, macroscopic experiments and in situ interferometric measurements. Experimental techniques used for monitoring this transition must be very sensitive to the structural changes, and should not disturb the system mechanically. In this work we focus on fluorescence technique that is of particularly useful for elucidation of detailed structural aspects of the gels. This technique is based on the interpretation of the change in anisotropy, emission and/or excitation spectra, emission intensity, and viewing the lifetimes of injected aromatic molecules to monitor the change in their microenvironment [15, 16].

2. Results

We studied the effect of pH on the swelling of poly(acrylamide-co-acrylic acid) (P(AAm-co-AAc)) composite gels using by Steady-state fluorescence (SSF) technique. Disc shaped composite gels were prepared by free-radical crosslinking copolymerization of P(AAm-co-AAc). N, N'- methylenebis (acrylamide) (BIS) and ammonium persulfate (APS) were used as crosslinker and initiator, respectively. Pyranine 4 was introduced as a fluorescence probe. P(AAm-co-AAc) composite gels dried before using for swelling experiments. The fluorescence intensity measurements were carried out using the Model LS-50 spectrometer of Perkin-Elmer. All measurements were made at 90^o position and slit widths were kept at 5 nm. A disc-shaped gel samples were placed on the wall of 1x1 quartz cell filled with different pH solutions for the swelling experiments. Fluorescence intensity of pyranine 4 was monitored during in situ swelling processes of composite gels. Emission and scattered intensity of P(AAm-co-AAc) composite gel were monitored during the swelling process in different pH solutions. It can be seen that as the water uptake is increased fluorescence intensity, I_{em} decreased and the scattered light intensity, I_{sc} increased. Since the increase in I_{sc} corresponds to increase in turbidity of the swelling gel, then we have defined corrected fluorescence intensity, I as I_{em}/I_{sc}. It was observed that fluorescence intensity values decreased as swelling is proceeded. Plots of water uptake, W versus swelling time are presented in Figure 1a and b for swelling in pH 4 and pH 9, respectively. It has been suggested [14] that the kinetics of swelling and shrinking of a polymer network and/or gel should obey Li-Tanaka relation,

$$\frac{W_t}{W_f} = 1 - \sum_{n=1}^{\infty} B_n e^{\frac{-t}{\tau_n}} \qquad (1)$$

Here W_t and W_f are the solvent uptakes at time t and at infinite equilibrium, respectively.

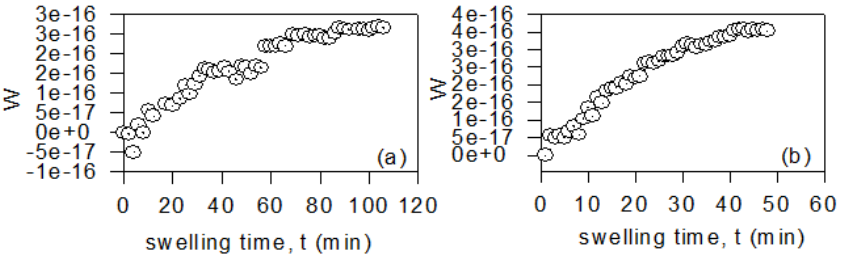

Fig. 1. The plots of water uptake, W versus swelling time, t for composite gel swollen in a) pH=4 and b) pH=9.

The logarithmic forms of the data in Figure 1 are fitted to the logarithmic form of equation (1) as follows.

$$\ln\left(1 - \frac{W}{W_f}\right) = \ln B_1 - \frac{t}{\tau} \qquad (2)$$

Using equation (2) linear regressions of curves in Figure 2and b provide us with B_1 and τ values. Taking into account the dependence of B_1 on R, one obtains R values and from α_1-R dependence α_1 values were produced [17]. Then cooperative diffusion coefficients D were determined for these disc-shaped composites and found to be around 10^{-9} m^2/s. Experimentally obtained τ and D values found from both fluorescence and gravimetric techniques are summarized in Table 1, where *a* and *r* values are also presented for each gel sample. It was shown that swelling time constants, τ decreased and diffusion coefficients, D increased as the pH values are increased.

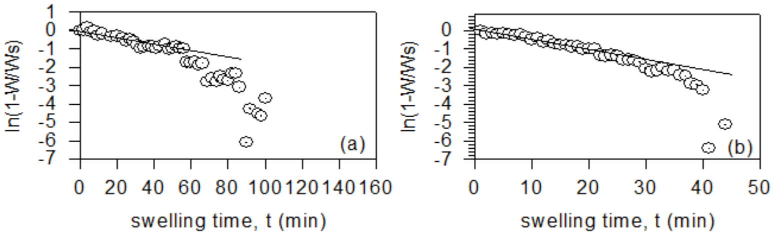

Fig. 2. Logarithmic form of water uptake, W versus swelling time, t for composite gel swollen in a) pH= 4 and b) pH=9.

Table. 1. Experimental values determined both fluorescence and gravimetric techniques for P(AAm-AAc) copolymerization for various pH.

pH	τ_F(min)	τ_G (min)	$D_{c\,F}$($x10^{-8}$ m^2/s)	$D_{c\,G}$($x10^{-8}$ m^2/s)
2	82	161.29	3.9	1.98
4	60	50	25.5	30.6
7	57	48	73.8	87.6
9	18.75	46.15	240	97.5
10	15	44.11	300	102

Here it is seen in Table 1 that D_c values measured by using fluorescence technique are much larger than the values measured by gravimetric technique, which interested different behaviours of the gel. It is obvious that the fluorescence technique measure the behaviour of the microstructure of the gel. *i.e* segmental motion can be measured by fluorescence because pyranine molecules are bounded to the polymer chains. However, gravimetric measurements may provide us with the behaviour of the macroscopic environment. According to above argument, one may suggest that chain segments move much faster than the bulk polymeric material during swelling process.

3. Conclusion

In conclusion these results have shown that the direct fluorescence method can be used for real-time monitoring of P(AAm-co-AAc) composite hydrogel swelling process. Li-Tanaka equation was used to determine the swelling time constants, τ_c and cooperative diffusion coefficients, D_c for the swelling processes. In this method *in situ* fluorescence experiments are easy to perform and provide us with quite sensitive results to measure the swelling parameters.

References

Almdal, K., Dyre, J., Hvidt, S., & Kramer, O. (1993). What is a gel? *Macromolecular Symposia*, 76, 49-51.

Jeong, S., Park, S.J., Shin, M.S., & Kim, S.I. (2002). Characteristics of Electrical Responsive Chitosan/Polyallylamine Interpenetrating Polymer Network Hydrogel. *Journal of Applied Polymer Science,* 86, 2290-2295.

Kim, S.J., Shin, S.R., Lee, Y.M., & Kim, S.I. (2003). Swelling Characterizations of Chitosan and Polyacrylonitrile Semi-Interpenetrating Polymer Network Hydrogels. *Journal of Applied Polymer Science, 87*, 2011-2015.

Frank, S., & Lauterbur, P.C. (1993). Voltage-Sensitive Magnetic Gels as Magnetic Resonance Monitoring Agents. *Nature*, 363, 334-336.

Peppas, N.A., & Colombo, P. (1997). Analysis of Drug Release Behavior from Swellable Polymer Carriers Using the Dimensionality Index. *Journal of Controlled Release,* 45, 35-40.

Tanaka, T. (1992). Phase Transitions in Polyelectrolyte Gels: Properties, Preparation and Applications. *American Chemical Society,* 480, 1-21.

Suzuki, A., Ishii, T., & Maruyama, Y. (1996). Optical Switching In Polymer Gels. *Journal of Applied Physics,* 80, 131-136.

Khare, A.R., & Peppas, N.K. (1995). Swelling/Deswelling Of Anionic Copolymer Gels. *Biomaterials,* 16, 559-567.

Zhong, X., Wang, Y.X., & Wang, S.C. (1996). Pressure Dependence of the Volume Phase-Transitions of Temperaturesensitive Gels. *Chemical Engineering Science*, 51, 3235-3239.

Tanaka, T., Filmore, D. Kinetics of Swelling of Gels. *J. Chem. Phys,* 70, 1214-1218.

Peters, A., & Candau, S.J. (1986). Kinetics of Swelling of Polyacrylamide Gels**.** *Macromolecules***,** 19, 1952-1955.

Chiarelli, P., & De Rossi, D. (1988). Determination Of Mechanical Parameters Related To The Kinetic Of Swelling In An Electrically Activated Contractile Gel**.** *Prog. Colloid Polym. Sci***,** 78, 4-8.

Candau, S.J., Bastide, J., & Delsanti, M. (1982). Structural, Elastic and Dynamic Properties of Swollen Polymer Networks. *Adv. Polym. Sci,* 44, 27-71.

Li, Y., Tanaka, T. Kinetics of Swelling and Shrinking Of Gels. *J. Chem. Phys.*, 92, 1365-1371.

Barrow, G.M. (1962). Introduction to Molecular Spectroscopy, McGraw-Hill, New York.

Birks, J.B. (1965). Photophysics of Aromatic Molecules, Willey, (Interscience), London**.**

Shibayama, M., & Tanaka, T. (1993). Volume Phase Transition and Related Phenomena of Polymer Gels. *Adv. Polym. Sci,* 109, 1-62.