ELSEVIER

PII: S0032-3861(97)10360-3

Polymer Vol. 39 No. 18, pp. 4453–4456, 1998

0032-3861/98/$19.00+0.00

In situ photon transmission technique for studying ageing in acrylamide gels due to multiple swelling*†

Ö. Pekcan[a,*], H. Çatalgil-Giz[a] and M. Çalişkan[b]
[a]*Departments of Physics and Chemistry, Istanbul Technical University, Maslak 80626, Istanbul, Turkey*
[b]*Department of Physics, Trakya University, 22030 Edirne, Turkey*
(Received 25 November 1997)

In situ photon transmission experiments were performed using an ultra-violet–visible (u.v.–vis) spectrometer during the multiple swelling of polyacrylamide (PAAm) gel in water. The transmitted light intensity, I_{tr} decreased continuously as the PAAm gel swelled. The decrease in I_{tr} was attributed to the increase in scattered light intensity which might have orginated from the contrast between 'frozen blob clusters' and holes in the swollen gel. It was observed that the correlation length, ξ_c, increased by 1/4 power of the swelling time. The sudden increase in the gel relaxation time, τ, was attributed to the rupture of the network structure after the eighth swelling step during multiple swelling of the PAAm gel. © 1998 Elsevier Science Ltd. All rights reserved

(Keywords: in situ photon transmission technique; ageing; acrylamide gels)

Introduction

The equilibrium swelling and shrinking processes of polyacrylamide (PAAm) gels in solvents have been extensively studied[1–3]. It has been reported that PAAm gels undergo continuous or discontinuous volume phase transitions with temperature, solvent composition, pH and ionic composition[1]. pH-induced volume phase transition of PAAm gels in an acetone/water mixture was studied using fluorescence techniques[2]. When an ionized PAAm gel is allowed to swell in water, an extremely interesting pattern appears on the surface of the gel, and the volume expansion is increased by adding sodium acrylate[3]. If PAAm gels are swollen in acetone–water mixture, gel ageing time plays an important role during the collapse of the network[4]. The kinetics of swelling of PAAm gels were studied by light scattering and the cooperative diffusion coefficient of the network was measured[5,6]. Small angle X-ray and dynamic light scattering were used to study the swelling properties and mechanical behaviour of PAAm gels[7,8]. It is known that the swelling and elastic properties of gels are strongly influenced by large scale heterogeneities in the network structure[9,10]. In the swollen state these imperfections manifest themselves in a non-uniformity of polymer concentration. These large scale concentration heterogeneities do not appear during the gelation but only in the gel swollen at equilibrium[11]. Light scattering experiments by Bastide *et al.* seem to confirm this picture[12].

The formation of the heterogeneities of crosslinked polymer gels has been the subject of great interest for many years. These structural inhomogeneities of a gel affect its physical properties such as optical and phase properties. Extensive studies have been conducted on the characterization of the gel heterogeneities. The effects of inhomogeneities of the polymer network on the swelling equilibrium of PAAm gels during the diffusion of water molecules were studied by Hsu *et al.*[13].

It is well known that the turbidity of a gel is a direct result of light scattered from the spatial inhomogeneities of its refractive index. It was proposed that when a polymer solution is in the phase separation regime, there appear two gel phases having two different concentrations. The domain sizes of these two phases depend on the condition of the gelation process and can sometimes have a size order of the wavelength of light and scatter tremendously, giving strong opacity to the gel[14].

In this paper in situ photon transmission experiments are reported during the swelling of PAAm gel in water. It was observed that the transmitted light intensity I_{tr} decreased continuously as the gel is swelled. Decrease in I_{tr} was attributed to the increase in scattered light intensity, I_{sc} from the gel due to spatial heterogeneities which appear during the swelling process. Multiple swelling and drying processes were applied to the PAAm gel and after each swelling process a continuous decrease in I_{tr} was observed.

Experimental

I_{tr} intensities were measured by ultra-violet–visible (u.v.–vis) spectrometric techniques. Swelling in PAAm gels was monitored in real time by using the time drive mode of the u.v.–vis spectrometer. The 'frozen blob' model[15] was employed to interpret the time (t) dependence of I_{tr} during the swelling of PAAm gel. The $t^{1/4}$ dependence on $(1 - I_{tr})$ was observed and the relaxation time, τ was measured in each swelling step and found to be around 2300 hr up to the eighth swelling step. Then it was observed that the τ values jumped to 4200 hr after the tenth swelling process. An increase in τ values is attributed to the ageing of gel due to multiple swelling and drying processes.

The gel was prepared by using 5 g of acrylamide (AAm), 0.133 g of *N,N*-methylenebisacrylamide (MBAAm) and 40 mg of ammonium persulfate (APS) as an initiator. This combination was dissolved in 100 ml of water in which 120 μl of tetramethylethylenediamine was added as an accelerator. Gelation was performed in 15 mm diameter tubes at room temperature. After 4 days the gel was

* To whom correspondence should be addressed
† Dedicated to Prof. Ö. Bekaroğlu on the occasion of his 65th birthday

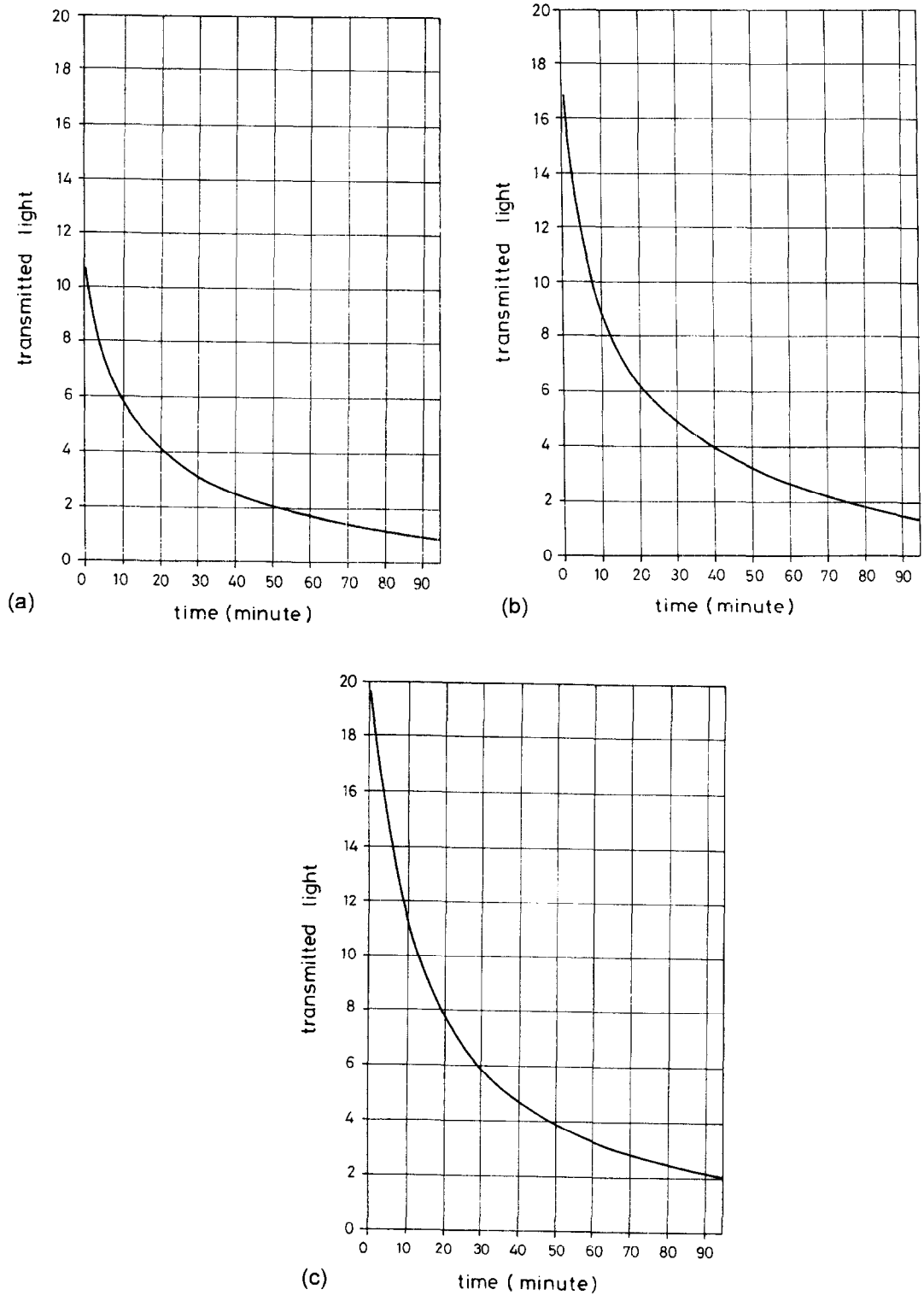

Figure 1 Plot of the transmitted light intensity *versus* swelling time for the PAAm gel sample in (a) first, (b) sixth, (c) ninth swelling steps

removed and left in air to dry. The dried PAAm gel was then cut in small pieces for the photon transmission experiments.

In situ photon transmission experiments were performed using a Perkin Elmer u.v.–vis Spectrometer. A PAAm gel sample was placed in the 1 × 1 cm u.v. cell, and water was added for the swelling process. The time drive mode of the spectrometer was turned on when the edges of the slightly swollen gel touched the walls of the cell. Then the I_{tr} intensity was monitored in real time, t, as the PAAm gel was swollen. During I_{tr} measurements, 350 nm was chosen as a fixed wavelength. Swelling curves (I_{tr} *versus* time) for the first, sixth and ninth swelling steps are presented in *Figure 1*. After each swelling step, samples were dried in the u.v. cell and reswelled again. All of these u.v. measurements were carried out at room temperature. Ten swelling and drying steps were performed and each swelling step was monitored in real time.

Results and discussion

The swelling curves in *Figure 1* present continuous decrease in I_{tr} intensity against time, t, which can be

quantified by taking into account the concentration heterogeneities in the randomly crosslinked lattice formed by the interchain contact points in solution. In this model, when two junctions are located on neighbouring lattice sites, a 'frozen blob' is formed. If this lattice swells the crosslinks cannot move apart from each other, because they are connected by a chain segment. These frozen blobs are often connected, and form clusters[11]. When the gel is in good solvent it swells and the frozen blob clusters expand less then the interstitial medium. In other words the swelling phenomenon can be represented as a dilution of the clusters of frozen blobs. When the gel swells, the frozen blobs clusters rearrange themselves in a way that small clusters are expelled from larger ones, creating low concentration regions[15]. Now the 'correlation length', ξ_c, can be the size of clusters which are not entangled with smaller ones, that is also the typical size of 'holes' in the frozen blob clusters. Due to polydispersity of the clusters, gel concentration, φ, is strongly depend on ξ_c and offers a relation[16] with $m = 5/3$

$$\xi_c = \varphi^{-m} \tag{1}$$

Now the mechanism of swelling leads to an excess scattering compared to a semidilute solution of linear chains of concentration, φ. This excess scattering originates from the contrast between frozen blob clusters and holes in the swollen gel. The scattered intensity, I_{sc}, now can be written[15,16] for $q \rightarrow 0$ and $m > 0$ as

$$I_{sc} \cong \varphi^{-m} \tag{2}$$

where q is the scattering vector amplitude. During swelling the partial separation of frozen blob clusters produces a strong increase in the scattering intensity.

In our case if we assume that the decrease in I_{tr} during swelling solely originates from the increase in scattering intensity I_{sc}, then combining equations (1) and (2) one can obtain the following useful relation to interpret our data

$$(1 - I_{tr}) \approx \xi_c \tag{3}$$

We tried to fit our swelling data in *Figure 1* to equation (3). The best fits were obtained when ξ_c was taken as proportional to $t^{1/4}$. In other words equation (3) becomes

$$(1 - I_{tr}) = t/\tau)^{1/4} \tag{4}$$

here τ is the time constant for each swelling experiment. *Figure 2* presents the fits of the digitized swelling data in *Figure 1* to equation (4). The slopes of straight lines in *Figure 2* produce τ values. Here τ can be considered as the relaxation time for the corresponding gel sample. The produced τ values are plotted against number of swelling in *Figure 3*. It is seen that τ values are suddenly increased after the eighth swelling step, which can be attributed to ageing of PAAm gel after multiple swelling processes (most probably due to the rupture of the network structure).

Conclusion

This work mainly introduces a novel method to measure the process of swelling in PAAm gels using u.v.–vis techniques. Besides that, a decrease in the transmitted photon intensity predicts the creation of large scale concentration heterogeneties in PAAm gels during swelling process. Here it has to be noted that these concentration heterogeneties can only be formed due to existing frozen blobs in these gels. The exponent 1/4 in equation (4) and its relation with the correlation length $\xi_c \approx t^{1/4}$ is highly

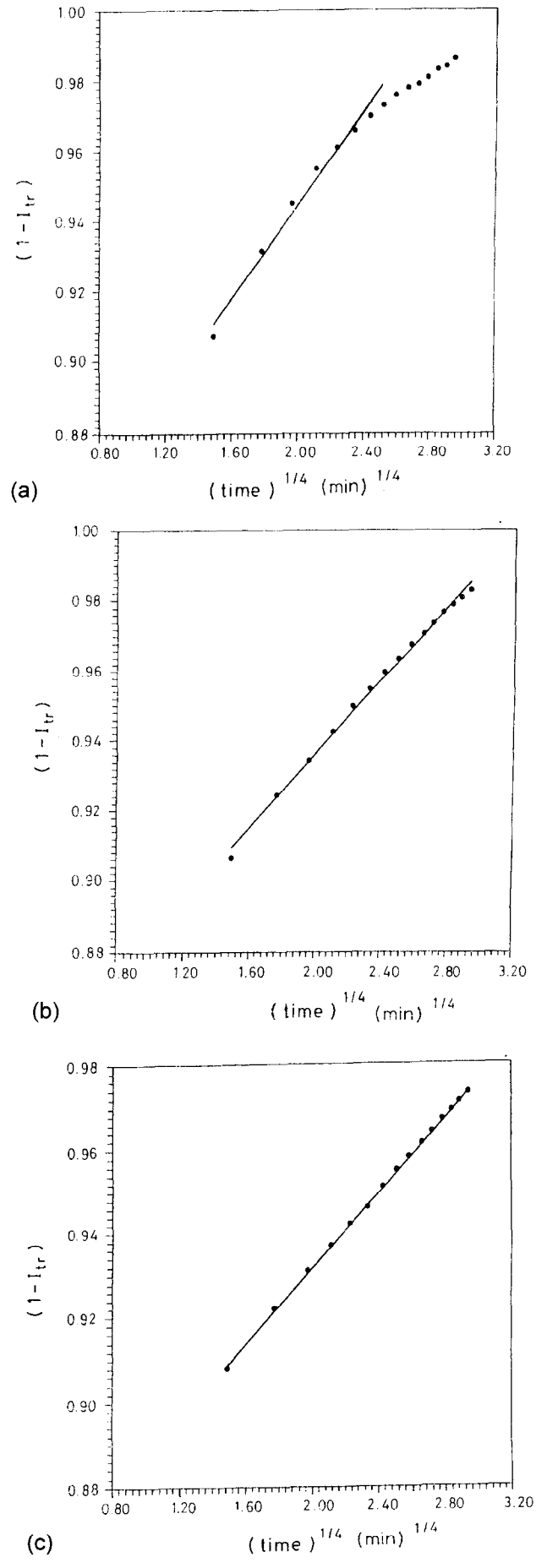

Figure 2 Fits of the digitized data in *Figure 1* to equation (4), where the slope of the curves produce τ values for (a) first, (b) sixth, (c) ninth swelling steps of PAAm gel sample

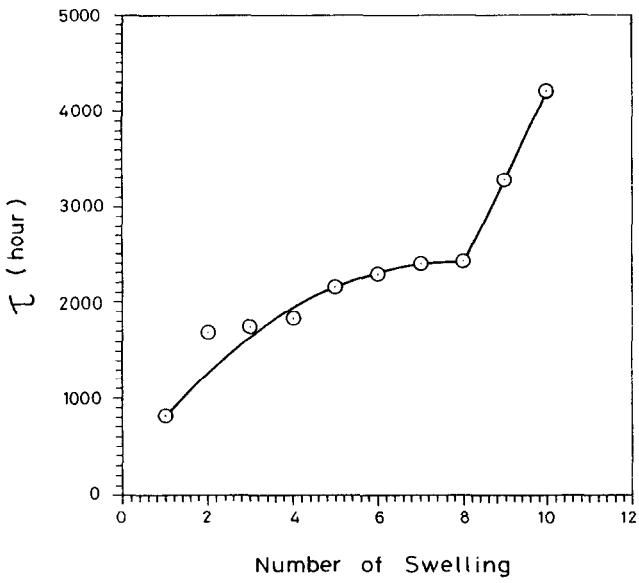

Figure 3 Plot of the τ values *versus* number of swelling

speculative. However one can argue that as the gel swells ξ_c increases due to the expansion of frozen blob clusters with $t^{1/4}$, which is much slower than the normal diffusion process ($\xi_c \approx t^{1/2}$), as expected.

In conclusion, we claim that simple u.v.–vis techniques are sufficient to observe all these interesting phenomenon.

Acknowledgements

Dr Giz thanks Dr Guia Kaslowsky and Organik Kimya A. Ş., who generously provided some of the chemicals used in this work.

References

1. Hirokawa, Y. and Tanaka, T., *J. Chem. Phys.*, 1984, **81**, 6379.
2. Hu, Y., Horie, K. and Ushiki, H., *Macromolecules*, 1992, **25**, 6040.
3. Tanaka, T., Sun, S. T., Hrokawa, Y., Katayama, S., Kucera, J., Hirose, Y. and Amiya, T., *Nature*, 1987, **325**, 796.
4. Tanaka, T., *Phys. Rev. Lett.*, 1978, **40**, 820.
5. Tanaka, T. and Fillmore, D., *J. Chem. Phys.*, 1979, **70**, 1214.
6. Peters, A. and Candau, S. J., *Macromolecules*, 1988, **21**, 2278.
7. Ilavsky, M., *Macromolecules*, 1982, **15**, 782.
8. Patel, S. K., Rodriguez, F. and Cohen, C., *Polymer*, 1989, **30**, 2198.
9. Duşek, K. and Prius, W., *Adv. Polym. Sci.*, 1969, **1**, 6.
10. Silberger, A., in *Biological and Synthetic Networks*, ed. O. Kramer. Elsevier App. Sci., Amsterdam, 1988.
11. Bastide, J. and Leibler, L., *Macromolecules*, 1988, **21**, 2649.
12. Bastide, J., Bove, F. and Busier, M., in *Molecular Basis of Polymer Networks*, ed. A. Baumgartner and C. Picot. Springer Verlag, Berlin, 1989.
13. Hsu, T. P., Ma, D. S. and Cohen, C., *Polymer*, 1983, **24**, 1273.
14. Duşek, K., in *Polymer Networks*, eds A.J. Chompff and S. Newman. Plenum, New York, 1971, pp. 245–260.
15. Bastide, J., Leibler, L. and Prost, J., *Macromolecules*, 1990, **1821**, 23.
16. Doud, M. and Leibler, L., *Macromolecules*, 1988, **21**, 1497.