States of water in poly(methyl methacrylate-*co*-*N*-vinyl-2-pyrrolidone) hydrogels during swelling

Mansor B. Ahmad and Malcolm B. Huglin*
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

(Received 14 September 1993; revised 28 October 1993)

Crosslinked copolymers of methyl methacrylate with *N*-vinyl-2-pyrrolidone of various compositions were prepared to high conversion by γ-irradiation and swollen in water to yield equilibrium water contents of 15–76 wt%. Differential scanning calorimetry was used to probe the states of water in the hydrogels prior to equilibrium swelling. Diffusion coefficients of water decreased about 100-fold as the effective crosslinking density of the polymers increased by the same factor. The relative uptake of the non-freezing water was found to be more rapid than that of the total freezing water.

(Keywords: hydrogel; differential scanning calorimetry; water sorption)

Introduction

The content and state of water in hydrogels are important determinants of the hydrogel interfacial properties, such as biocompatibility[1,2]. It is therefore useful to study the way in which water molecules are taken up by hydrogels. In a previous paper, differential scanning calorimetry (d.s.c.) analysis revealed the existence of three types of water in poly(methyl methacrylate-*co*-*N*-vinyl-2-pyrrolidone) (poly(MMA-*co*-VP)) hydrogels at equilibrium swelling, namely (i) free freezing water, (ii) freezable bound water and (iii) non-freezing water, which are defined in ref. 3. In this communication, attention is focused mainly on the states of water in the same systems but at various stages of swelling prior to final equilibrium swelling.

Experimental

Sample preparation. The purification of materials and mode of crosslinking copolymerization of VP with MMA via γ-irradiation have been described elsewhere[3]. As the bulk copolymerization was shown to proceed to 100% conversion, the overall composition of the xerogel is the same as that of the monomer mixture. Since ethylene dimethacrylate (EDMA) was incorporated in all copolymers at one fixed concentration of 1 wt%, based on the total weight of (VP + MMA + EDMA), the sample compositions are expressed in terms of the weight percentage of the principal monomers. Thus, the notation MMA15/VP85 indicates that MMA comprises 15 wt% of (MMA + VP). The solid rods were lathe cut into discs and pellets.

Swelling measurements. The xerogel discs (1 mm thickness, 10 mm diameter) were subjected to Soxhlet extraction with water as solvent. The weights and dimensions of the dried xerogels were determined before swelling. The xerogel was swollen in water at 298 K; at various times (t) it was surface-dried with filter paper and weighed. The degree of swelling, W, is expressed as the percentage water in hydrogel at any instant during swelling:

$$W = \frac{\text{weight of hydrogel} - \text{weight of xerogel}}{\text{weight of hydrogel}} \times 100 \quad (1)$$

At the time of equilibrium swelling, W becomes the familiar equilibrium water content (EWC). The latter was also obtained as the volume fraction of water in the hydrogel at equilibrium, which is equal to $(1-\phi_2)$, where ϕ_2 is the volume fraction of polymer in gel, i.e.

$$\phi_2 = \left(\frac{d_0}{d}\right)^3 \quad (2)$$

In equation (2) d_0 and d are the measured diameters of the dry xerogel and swollen gel, respectively. The photographic procedure of measuring swollen diameters has been given previously[4]. Stress–strain measurements were carried out on pellet samples (10 mm diameter, 10 mm thickness) which were swollen to equilibrium in water at 298 K. The detailed procedure has been described elsewhere[4].

Differential scanning calorimetry. A Mettler DSC 30 was used to measure the phase transition of water sorbed by the hydrogels using the procedure described previously[3]. The xerogel was swollen in water at 298 K, and at regular intervals the sample was surface-dried with filter paper and replaced in water after a small piece of about 10 mg weight had been cut from it. D.s.c. curves on the small sample were obtained by heating from 198 to 298 K at a rate of 2.5 K min^{-1}. Calibration of the instrument with pure water yielded the enthalpy of fusion of water, which was used to calculate the weight of freezing water in the gel. The percentage of non-freezing water (W_{nf}) was calculated by subtracting the total percentage of freezing water (W_{tf}) from the water content, W, in the hydrogel. As indicated in equation (1), W is calculated on the basis of the total mass of hydrogel; the same applies to W_{nf} and W_{tf}.

---

* To whom correspondence should be addressed

0032-3861/94/09/1997–04

Table 1 Swelling properties and network parameters of poly(MMA-*co*-VP) hydrogels at 298 K

Sample designation	Corrected composition[a]	*EWC* (wt%)	ν_e (mol dm^{-3})	χ	$D \times 10^{12}$ (m^2 s^{-1})
MMA75/VP25	MMA75.5/VP24.5	15.2	6.85	1.40	1
MMA60/VP40	MMA62.2/VP37.8	30.4	3.02	0.93	11
MMA45/VP55	MMA47.4/VP52.6	47.6	1.93	0.66	29
MMA30/VP70	MMA33.1/VP66.9	63.9	0.14	0.64	72
MMA15/VP85	MMA16.9/VP83.1	75.9	0.06	0.57	98

[a] Corrected by the measured sol fraction on the assumption that it comprises practically pure polyVP[20]

Results and discussion

Properties at swelling equilibrium. The compositions of the xerogels and the values of *EWC* are given in *Table 1*. Treatment of compression–strain results and values of ϕ_2, in conjunction with the Flory–Rehner equation[5], yielded values of Young's modulus of the hydrogels, the polymer–water interaction parameter (χ) and the effective crosslinking density (ν_e), the last two of which are also listed in *Table 1*. The values of χ decrease with increasing content of VP and approach the values reported for crosslinked polyVP[4,6]. Even though 1 wt% EDMA was used for the preparation of all the copolymers, there is about a 100-fold decrease in ν_e between the sample of lowest VP content and that of the highest content. This is a consequence of the influence of the different reactivity ratios in the terpolymerization up to high conversion[4,7]. High effective crosslinking is also a contributory factor to high values of χ.

Diffusion coefficient. When the fractional water uptake (W/EWC) is plotted vs. $t^{1/2}$, linearity up to a fractional uptake of 0.6 is observed for all samples, indicating a Fickian sorption process[8]. The diffusion coefficients (*D*), which are assumed to be constant, were determined from the following equation[9]:

$$D = \frac{0.0492\,L^2}{t_{1/2}} \qquad (3)$$

where $t_{1/2}$ is the time at $(W/EWC) = 0.50$ and the relevant film thickness is approximated to be that of the dry xerogel (*L*).

The values of *D* are given in *Table 1*, which shows that the diffusion coefficients increase about 100-fold as the values of ν_e decrease by the same factor. High crosslinking density has been indicated to increase restriction on water diffusion rates within hydogels[10]. The present results, however, are not in agreement with the earlier findings that the diffusion coefficients in some systems decrease linearly with crosslinking density[11,12]. The decrease in diffusion coefficient is due to the restraints of crosslinking on chain mobility and lower free volume. In addition, the low values of *D* at high contents of MMA are in accord with the proposition advanced by Takizawa *et al.*[13], who suggested that the hydrophobic interaction formed in the MMA90/VP10 and MMA73/VP27 systems is effectively a form of additional crosslinking, thereby reducing the diffusibility of water.

States of water at different swelling levels. D.s.c. melting curves of the MMA75/VP25 hydrogel at different swelling levels showed only one transition at 273 K throughout the swelling process, indicating a single state of freezing water. A single transition was also observed for MMA60/VP40, MMA45/VP55 and MMA30/VP70 at the early stages of swelling, and the second peak at 263 K emerged only after a certain swelling level. In contrast, two transitions were observed for the hydrogel of highest VP content from the very onset of swelling. In the ensuing semiquantitative treatment, the two states of freezing water are computed as simply total freezing water.

It has been suggested that only non-freezing water exists in the polymer network up to a certain percentage of water content before freezing water can be detected[14–18]. In a poly(MMA-*co*-VP) system, hydrogels with water contents up to 18% were reported to contain only non-freezing water[15]. The uptake of water into a polymeric network was also proposed to be in the following order: non-freezing, freezing bound and free freezing water[17,18], i.e. the free freezing is the last type of water emerging after the non-freezing and freezing bound types have reached their final maximum contents. However, our observations are not in accord with this proposal, since freezing water was detected in the early stage of swelling, even at a water content of less than 5%. Our findings are in agreement with those of Hori *et al.*[19] on acrylic fibres, in which freezing water exists in less porous samples even below a water content of 5%. The present results also demonstrate clearly that non-freezing water coexists with free freezing water even at low total water content, in which the non-freezing water has yet to reach its maximum.

In the early stage of swelling, the percentage of non-freezing water, W_{nf}, rises more rapidly than that of total freezing water, W_{tf}, as illustrated in *Figure 1*, which shows the relevant plots for MMA30/VP70. Similar trends were observed in all the other hydrogels, although the data for MMA75/VP25 are subject to some degree of uncertainty owing to the extremely small values of *W* and W_{tf} in the initial stages of swelling. In order to assess further the rates of subdivision of imbibed water during the initial stages, it is convenient to consider the ratio *R* defined in equation (4). At any time during swelling, the fraction of non-freezing water relative to its maximum value at equilibrium is $W_{nf}/W_{nf\infty}$ and the corresponding quantity for freezing water is $W_{tf}/W_{tf\infty}$. Hence the ratio (*R*) of the former to the latter is a measure of the relative fractional uptake of non-freezing water to that of freezing water:

$$R = \frac{(W_{nf}/W_{nf\infty})}{(W_{tf}/W_{tf\infty})} \qquad (4)$$

At swelling equilibrium, of course, $R = 1$. When *R* is plotted against time, the initially high ratio indicates that a significant fraction of water is taken up by the hydrogel as non-freezing water. For comparison, the mole fraction of VP units, X_{VP}, in the partially swollen hydrogel is calculated from the value of W at the particular stage of swelling in conjunction with the fixed composition of xerogel. A decreasing trend of X_{VP} with time was also observed. *Figure 2* gives an example of such plots, which provide some evidence for the correlation between the relative fraction of non-freezing water uptake and the hydrophilic component, VP, in the hydrogel. The same trends are observed in all polymers, except for the MMA75/VP25 hydrogel, in which the very small values of W and W_{tf} in the sample induce uncertainty in the values of R. A closer examination reveals that at any particular swelling time the relative fractional uptake of non-freezing water increases with decreasing VP content in the hydrogel. For example, at 5 min, the values of R for MMA15/VP85, MMA30/VP70, MMA45/VP55 and MMA60/VP40 are 1.4, 2.1, 3.6 and 3.9, respectively. Because of the low VP content associated with the low value of W in the MMA75/VP25 hydrogel, and the extremely slow uptake of freezing water, no transition peak was observed before 30 min.

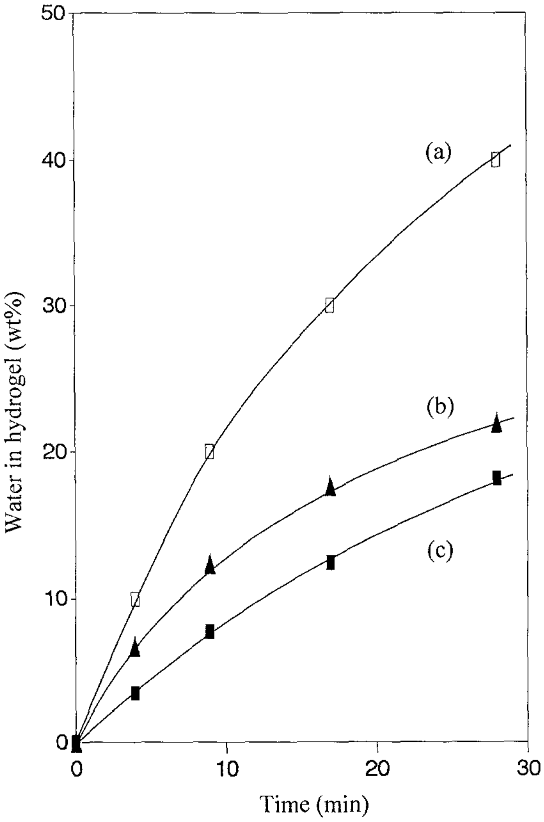

Figure 1 The percentages of different types of water in MMA30/VP70 at the initial stages of swelling: (a) W; (b) W_{nf}; (c) W_{tf}

It is pertinent to place the present procedure and findings within the overall context of those reported elsewhere. Thus the subdivision of states of water in hydrogels having water contents less than *EWC* has been examined after evaporation of water for various times from fully hydrated samples[15]; this device would tend to reduce the content of detectable free freezing water. Another procedure is to add various quantities of water to a fixed mass of polymer and to allow the system to equilibrate[16,17,19]; in this case the value of W is preset, but this value and subdivision of water do not necessarily correspond to those yielded by swelling prior to equilibrium in a large excess of water. A third expedient is the inclusion of various amounts of water in the monomer mixtures[18], which yields a product already swollen but to an extent constrained by the quantity of water included. Here the mass of water in hydrogel is fixed, whilst that of the polymer builds up during polymerization until it equals that of initial monomer. Also, regarding effective crosslinking it is necessary to consider not only the volume of polymer but also that of total initial mixture for the reference state[20]. All of these devices are useful but somewhat contrived. They also differ conceptually from the simpler, more common situation wherein dry xerogel is allowed to swell freely in a large excess of water at times up to that for swelling equilibrium. Hence the inclusion of 'during swelling' in the title of this communication. The authors believe that a study of this nature has not been reported previously.

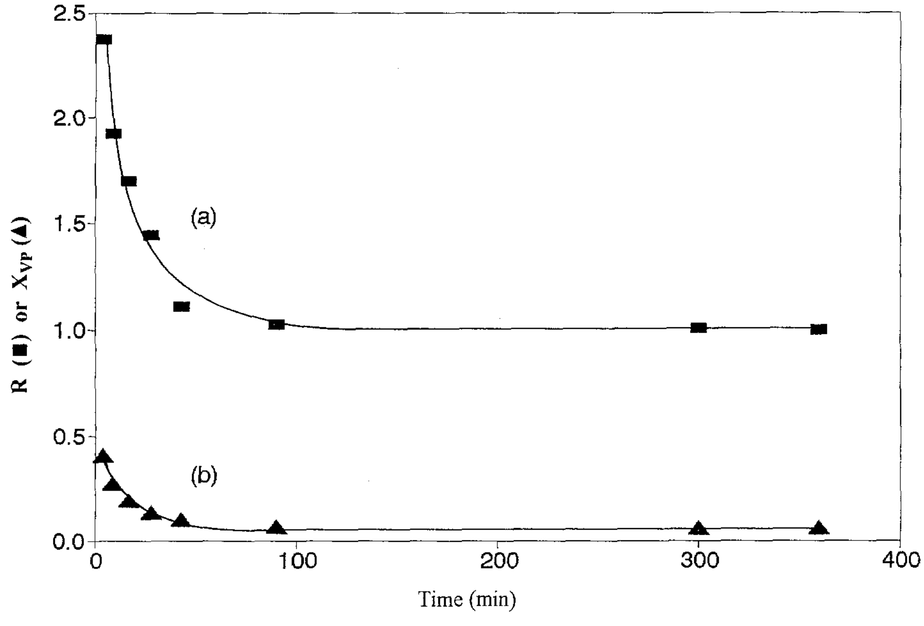

Figure 2 Variation with time during initial stages of swelling of (a) the ratio R (■), and (b) X_{VP} (▲) for MMA30/VP70

In summary, the present findings indicate: (i) water of the freezing type exists as a component of the hydrogels not only at equilibrium but also during the early stages of swelling; (ii) in the initial stages of swelling, the content of non-freezing water relative to its final equilibrium value is greater than the corresponding quantity for freezing water, i.e. $R > 1$; (iii) with increasing time of swelling, the decrease of VP content in the partly swollen hydrogel correlates well with the decrease in R.

Acknowledgement

M. B. A. thanks Universiti Pertanian Malaysia for financial support.

References

1 Jhon, M. S. and Andrade, J. D. *J. Biomed. Mater. Res.* 1973, **7**, 509
2 Rowland, S. P. (Ed.) 'Water in Polymers', ACS Symposium Series 127, American Chemical Society, Washington, DC, 1980
3 Ahmad, M. B. and Huglin, M. B. *Polym. Int.* in press
4 Davis, T. P., Huglin, M. B. and Yip, D. C. F. *Polymer* 1988, **29**, 701
5 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, New York, 1953, Ch. XIII
6 Good, W. R. and Cantow, H.-J. *Makromol. Chem.* 1979, **180**, 2605
7 Davis, T. P. and Huglin, M. B. *Macromolecules* 1989, **22**, 2824
8 Fujita, H. in 'Diffusion in Polymers' (Eds J. Crank and G. S. Park), Academic Press, London, 1968, p. 75
9 Crank, J. and Park, G. S. (Eds) 'Diffusion in Polymers', Academic Press, London, 1968, p. 1
10 Allen, P. E. M., Bennett, D. J. and Williams, D. R. G. *Eur. Polym. J.* 1992, **28**, 347
11 Rogers, C. E. in 'Polymer Permeability' (Ed. J. Comyn), Elsevier, London, 1985, p. 11
12 Meares, P. 'Polymers: Structure and Bulk Properties', Van Nostrand, London, 1965, Ch. 12
13 Takizawa, A., Kinoshita, T., Nomura, O. and Tsujita, Y. *Polym. J.* 1985, **17**, 747
14 Lee, H. B., Jhon, M. S. and Andrade, J. D. *J. Colloid Interface Sci.* 1975, **51**, 225
15 Quinn, F. X., Kampff, E., Smyth, G. and McBrierty, V. J. *Macromolecules* 1988, **21**, 3191
16 Nakamura, K., Hatakeyama, T. and Hatakeyama, H. *Polym. J.* 1991, **23**, 253
17 Nakamura, K., Hatakeyama, T. and Hatakeyama, H. *Polym. J.* 1983, **15**, 361
18 Sung, Y. K., Gregonis, D. E., Jhon, M. S. and Andrade, J. D. *J. Appl. Polym. Sci.* 1981, **26**, 3719
19 Hori, T., Zhang, H.-S. and Shimuzi, T. *Textile Res. J.* 1988, **58**, 227
20 Huglin, M. B. and Rego, J. M. *Macromolecules* 1993, **26**, 3118