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Effective crosslinking densities and elastic moduli of some physically crosslinked hydrogels

Yan Liu and Malcolm B. Huglin*
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK
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Samples of poly(*N*-vinyl-2-pyrrolidone (VP)-*co*-methyl methacrylate (MMA)), containing 41–76.5 wt% MMA, have been prepared by a controlled, semicontinuous copolymerization procedure and swollen to equilibrium in water at various temperatures T (283–343 K) to yield hydrogels in which the network structure is maintained by physical crosslinking involving sequences of MMA units. The effective crosslinking densities (ν_e) and Young's moduli (E) were determined by compression–strain measurements. Values of ν_e and E decreased with decreasing content of MMA in copolymer, this effect being more pronounced the lower the temperature. For a particular composition, ν_e and E decreased with increasing T to an extent which was greater the higher the MMA content of copolymer. The findings are compared with the behaviour of corresponding chemically crosslinked hydrogels of poly(VP-*co*-MMA).

(Keywords: linear copolymer; hydrogel; physical crosslinking)

Introduction

Many hydrogels are based on chemically crosslinked copolymers, the composition and crosslinking density being controlled in order to effect changes in the swelling and mechanical behaviour of the hydrogel. The effective crosslinking density (ν_e) must be measured, since it normally differs in magnitude from the theoretical density calculated from the concentration of multifunctional crosslinking monomer included in the preparation. It has been shown that not only the concentration of crosslinker but also its hydrophilicity influence the properties of the hydrogel. Similar considerations apply to the principal components, which are commonly a hydrophilic and a hydrophobic monomer. *N*-vinyl-2-pyrrolidone (VP) and methyl methacrylate (MMA), respectively, are typical examples, and detailed studies on the behaviour of hydrogels of their copolymers in a chemically crosslinked form have been made[1,2]. Disadvantages of such systems include difficulty of processing and presence of a significant sol fraction of pure or nearly pure polyVP homopolymer.

Under the impetus of an earlier report by Brook[3], we have prepared linear poly(VP-*co*-MMA) samples by a carefully controlled semicontinuous procedure and have demonstrated that they are homogeneous with respect to the composition, but polydisperse in molecular mass[4]. They exhibit the following useful properties: (1) ability to be compression moulded; (2) film-forming capacity by casting from solution in chloroform and a few other solvents; (3) swellability of the films in water to form elastic hydrogels provided the VP content is not too high, otherwise the films dissolve in water; (4) minimal sol fraction. Semiquantitative observations on the states of imbibed water within the hydrogel have been made recently[5]. The swollen network structure of these hydrogels must be due, at least in part, to physical crosslinking imparted by hydrophobic MMA sequences. The main purpose of this work is to quantify this crosslinking and to determine whether it is sensitive to temperature. In this connection it may be noted that no discernible influence of temperature on ν_e was found for the corresponding copolymers in their chemically crosslinked form[1]. Elastic moduli at various temperatures are also determined as a further aspect of comparison with the corresponding chemically crosslinked hydrogels.

Experimental

Materials. The purification of materials, synthesis of a graft dispersant copolymer (GDP) based on poly(lauryl methacrylate), and the use of GDP in the preparation of poly(VP-*co*-MMA) samples via a semicontinuous procedure have been described fully elsewhere[4].

Volume fraction of copolymer in hydrogel. Thin discs (thickness ~ 1 mm and diameter ~ 10 mm) were cut from dry films obtained by casting from dilute solutions in chloroform and allowing the solvent to evaporate at ambient temperature. They were swollen in water to equilibrium at different temperatures. Details and relevant times have been reported[5].

Although the times to attain swelling equilibrium at a constant temperature, say 303 K, were quite long when starting from the dry state, a subsequent change of temperature of the hydrogel afforded swelling equilibrium more quickly (~ 1–2 h) at each of the new temperatures used within the range 283–343 K. Accordingly, the time of 4 h actually allowed was more than adequate.

Diameters (d_2) of xerogel were measured with a micrometer, and diameters (d) of hydrogels at swelling equilibrium were determined, while the disc was still immersed in water, by an image magnification technique using a microscope. The diameter of each was measured across at least 10 positions and the average value was used to calculate the volume fraction of copolymer in hydrogel (ϕ_2) according to:

$$\phi_2 = (d_2/d)^3$$

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* To whom correspondence should be addressed

Table 1 Compositions of copolymers and effective crosslinking densities at various temperatures

Copolymer	Composition (wt% VP)	ν_e (mol m^{-3}) 283 K	299 K	303 K	323 K	343 K
C4	59.0	0.42	0.40	0.40	0.37	0.36
C5	53.0	3.7	2.9	2.6	1.4	0.8
C6	50.0	193	100	81.8	12.0	6.1
C7	36.5	412	193	150	24.0	9.2
C8	23.5	924	407	290	111	38

Uniaxial compression. Attempts to produce solid xerogel pellets from powdered copolymer by compression moulding at elevated temperature (courtesy ICI Runcorn Research Centre, UK) yielded products with some pale brown coloration and which contained some very small (probably air) bubbles. Since these pellets were not considered satisfactory, an alternative lengthy procedure was adopted. A small quantity of copolymer solution in chloroform was introduced into a polypropylene cap and the solvent was allowed to evaporate. Prior to attainment of complete dryness, a further small quantity of solution was introduced and the procedure repeated until sufficient thickness had built up (~2.5 months). The solid was removed from the cap, heated for 8 h at 318 K and finally heated to constant weight at 353 K. Pellets (diameter ~10 mm and length 8–10 mm) were lathe cut and swollen to equilibrium in water at ambient temperature (~2.5 months). Stress (compression)–strain measurements on the resultant hydrogel immersed continuously in water were conducted at each of several temperatures. Full details of the apparatus and procedure have been given elsewhere[6].

Results and discussion

Composition of hydrogel. The compositions of the five copolymers, denoted here as samples C4–C8, are given in *Table 1*. For each of these, the value of ϕ_2 was measured at 283, 299, 303, 323 and 343 K. The variations of ϕ_2 with swelling temperature (T) are shown in *Figure 1*, which displays the following main features: (a) the smallest value of ϕ_2 (=0.239) is exhibited by the copolymer of largest VP content at the lowest temperature, and the largest value of ϕ_2 (=0.880) is obtained for the sample of smallest VP content at the highest temperature; (b) at any particular swelling temperature T, the value of ϕ_2 increases with increasing hydrophobicity, i.e. with decreasing content of VP; this increase is much more pronounced at the lowest T (ϕ_2 goes from 0.239 to 0.857 at 283 K) than at the highest swelling temperatures (ϕ_2 increases from 0.512 to 0.880 at 343 K); (c) for a particular copolymer composition, the deswelling (i.e. increase in ϕ_2) on heating is very considerable for copolymer C4, whereas for the most hydrophobic copolymer C8, this increase in ϕ_2 is only from 0.857 at 283 K to 0.880 at 343 K.

Table 2 Young's moduli of the hydrogels at various temperatures (for compositions of copolymers see *Table 1*)

Copolymer	E (kPa) 283 K	299 K	303 K	323 K	343 K
C4	5	5	5	4	4
C5	35	29	27	14	9
C6	1890	937	740	120	60
C7	3230	1658	1300	220	90
C8	7390	4027	2600	940	350

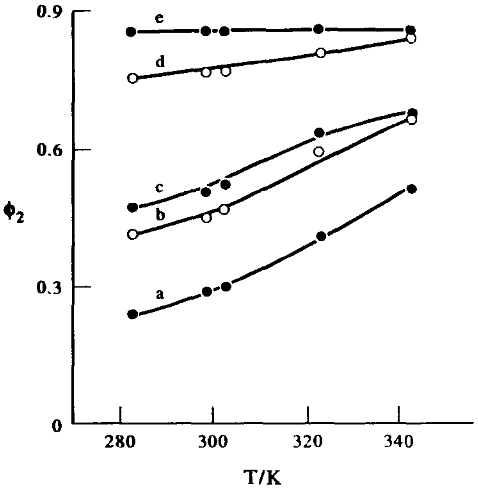

Figure 1 Variation of volume fraction of copolymer in hydrogel with temperature. Hydrogels of copolymers C4, C5, C6, C7 and C8 are denoted by a, b, c, d and e, respectively

Network parameters. The stress (τ), expressed as applied force per unit area of undeformed hydrogel, and resultant strain (λ), expressed as ratio of deformed to undeformed length of swollen hydrogel, were obtained from compression–strain measurements. Young's moduli (E) were yielded directly as the slope of the plot of τ *versus* λ. For affine deformation, the shear modulus (G) is a function of λ:

$$G = \nu_e R T \phi_2^{1/3} (\bar{r}_i^2/\bar{r}_0^2)(\lambda - \lambda^{-2}) \qquad (1)$$

In equation (1), ν_e is the crosslinking density and $(\bar{r}_i^2/\bar{r}_0^2)$ is termed the front factor (which can alternatively be expressed in terms of corresponding volumes), $\bar{r}_i^2$ being the mean square isotropic, unstrained, end-to-end distance and $\bar{r}_0^2$ being the mean square end-to-end distance of the equivalent free chain.

The present hydrogels were prepared by swelling existing preformed copolymers and, moreover, the effective functionality of crosslinking is unknown. Accordingly it is not possible to evaluate independently the front factor. Although the front factor has been implicitly taken to be unity in simple treatments, this assumption is likely to be erroneous in the general case. With awareness of the approximation, made of necessity, in assigning a value of unity here to the front factor, values of ν_e were obtained from plots of τ *versus* $(\lambda - \lambda^{-2})$ according to equation (1). The plots affording E and G were linear within the range of low strain examined, namely from 0 to −7%. The ratio (E/G) was around 3 in all cases, as required theoretically for elastic gels at low strain. The values of ν_e and E are listed in *Tables 1* and *2*, respectively, in which the following main features are evident: (a) at any particular temperature, the values of E and ν_e decrease with decreasing content of MMA in the copolymer; (b) the highest modulus and crosslinking density are exhibited by the sample (C8) of highest MMA content at the lowest temperature; (c) for any particular copolymer composition, ν_e and E decrease in magnitude on heating; analysis shows this decrease to be exponential. The effect is more pronounced the higher the MMA content of copolymer. Thus for sample C4, having the lowest MMA content, the change in ν_e is only from 0.42 to 0.36 mol m^{-3} on going from 283 to 343 K, and for the same decrease in temperature the change in E is from 5 to 4 kPa.

Although measurements of modulus of biopolymeric gels in water and thermoreversible gels of certain synthetic polymers in non-aqueous media have been made (see for example, reviews by Clarke and Ross-Murphy[7] and Guenet[8], respectively), there has been little, if any, reported work comparable in scope to the present study focusing on physical crosslinking in water-swollen synthetic copolymers. It is, however, instructive to make comparisons, where possible, with the properties of the corresponding chemically crosslinked poly(VP-*co*-MMA) hydrogels for which the composition, nature and concentration of crosslinker have been found to be important factors. Copolymerization of VP with MMA by γ-irradiation alone, in the absence of a crosslinker such as ethylene glycol dimethacrylate (EDMA), produces water-swellable products in which the crosslinking is due mainly to γ-irradiation. However, when the VP content is too high, these materials disintegrate during swelling just as the present physically crosslinked gels dissolve (rather than swell) when the VP content is >62 wt%. Inclusion of EDMA in the γ-ray-initiated copolymerization yields hydrogels that are stable over an unrestricted range of copolymer composition. However, they are mechanically unstable at very high contents of EDMA. Evidence has been adduced of a finite contribution to the measured ν_e and E by some hydrophobic physical interactions in stable, chemically crosslinked poly(VP-*co*-MMA), even in the absence of EDMA[1,2]. Moreover, the ^{13}C n.m.r. data of Saitô and co-workers show that the MMA component comprises a rigid disordered region as a form of additional crosslinking[9]. The absence of EDMA and the mode of synthesis of the present copolymers are such as to promote this avenue as the major means of crosslinking, and indeed phase segregation is manifested by opacity in the swollen state.

The precise nature and functionality of junction points cannot be ascertained. Whilst Takizawa *et al.*[10] emphasize the 'hydrophobic hydration' role of water in chemically crosslinked poly(VP-*co*-MMA), we prefer to focus attention more on crosslinking zones involving regions in which hydrophobic interaction among MMA units prevails, as indicated in *Figure 2*. It should be noted that VP units will also exist within the crosslinking zone and that the elastic chains between junction zones, designated as VP-rich, will also contain MMA units. In this connection it is also relevant to point out that overall, average, cumulative sequence lengths (n) range from $\bar{n}_{\mathrm{MMA}}/\bar{n}_{\mathrm{VP}} \approx 3.5$ (for sample C8) to $\bar{n}_{\mathrm{MMA}}/\bar{n}_{\mathrm{VP}} \approx 1.1$ (for sample C4). However, there must inevitably be a wide distribution of sequence lengths, and for this reason it is quite feasible for hydrophobic junction zones to involve even longer sequences of MMA. The crosslinking densities and moduli are markedly smaller than those reported for the corresponding chemically crosslinked systems[1,2]. Thus, for a hydrogel of the latter type prepared in the presence of 1 wt% EDMA and having an MMA content of 45 wt%, the values of ν_e and E at 294 K are 1.09 mol dm^{-3} and 6.92 MPa, respectively. Interpolation to this composition and temperature from the present data yields $\nu_e = 0.024$ mol dm^{-3} and $E = 0.02$ MPa.

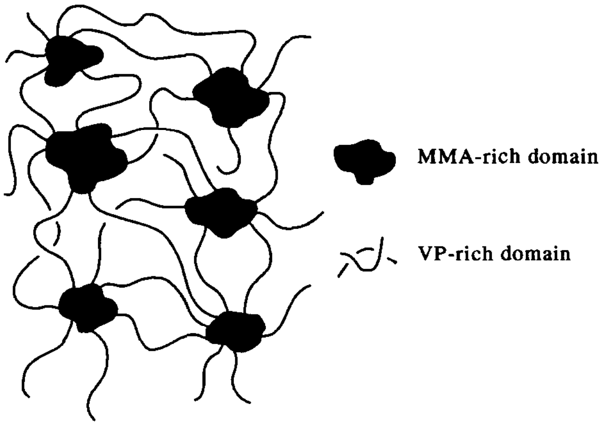

Figure 2 Possible representation of flexible chains and crosslinking junction zones in linear poly(VP-*co*-MMA)

No discernible influence of temperature (278–343 K) on ν_e and E has been found for the chemically crosslinked hydrogels[1], which contrasts with the situation in *Tables 1* and *2* where it is evident that physical crosslinking is very temperature sensitive. Essentially, the higher the MMA content of copolymer (e.g. sample C8), the higher the propensity for crosslinking involving MMA sequences and the greater the absolute reduction in ν_e per degree.

The total copolymer–water interaction parameters (χ) were calculated from the Flory–Rehner equation, in which V_1 (dm^3 mol^{-1}) is the molar volume of water at a temperature T(K):

$$\ln(1-\phi_2)+\phi_2+\chi\phi_2^2+\nu_e V_1[\phi_2^{1/3}-(\phi_2/2)]=0 \quad (2)$$

$$V_1 = 18.05\times10^{-3}+3.6\times10^{-6}(T-298) \quad (3)$$

The values of χ in conjunction with $\mathrm{d}\chi/\mathrm{d}T$ yielded the enthalpic (χ_H) and entropic (χ_S) contributions[1,11,12]. These quantities for the present copolymers were all positive, negative and positive, respectively, and were temperature dependent to an extent increasing with VP content of copolymer. For sample C8, these thermodynamic parameters were found to undergo only a small change with temperature, which must be attributable, at least in part, to closer proximity to the lower critical solution temperature of this most hydrophobic of the copolymers. Although the general thermodynamic behaviour is similar to that noted for the hydrogels of the corresponding chemically crosslinked copolymers, one significant difference lies in the small temperature dependence of the interaction parameters reported[9] for the hydrogel of the chemically crosslinked polymer of maximum VP content, i.e. polyVP. The opposite would have been anticipated from extrapolation to 100 wt% VP content from the present findings on the physically crosslinked system. With regard to the principal focus of this work, it would appear that there is no obvious correlation between the mechanical and thermodynamic properties of these new copolymeric hydrogels.

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