Mechanical and thermodynamic properties of butyl acrylate–N-vinylpyrrolidone hydrogels

Malcolm B. Huglin and Mahmoud M. A.-M. Rehab
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, UK

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Copolymerization to almost 100% conversion has been effected by the γ-irradiation of mixtures of n-butyl acrylate (BA) and *N*-vinyl-2-pyrrolidone (VP) in the presence of a crosslinking agent, 1,1,1-trimethylolpropane trimethacrylate (TPT). Swelling in water at 294 K yielded hydrogels having equilibrium water contents in the range 1–89%, the corresponding extension ratios and volume fractions of water being obtained from dimensional changes on swelling. Stress(compression)–strain measurements yielded the compression and Young's moduli, the effective crosslinking density (ν_e) and the copolymer–water interaction parameters (χ). From the linear dependence of ν_e on the theoretical value based on the concentration of TPT, the efficiency of crosslinking was found to increase with increasing BA content; a finite ν_e was also interpolated to exist even in the absence of added TPT. Increasing the VP content of xerogels produced a corresponding increase and decrease in the fractional contents of water and BA respectively within the hydrogels, whereas the fractional content of VP displayed an increase followed by a decrease. This latter behaviour mirrors that exhibited by ν_e and the elastic moduli. Possible explanations are proposed.

(Keywords: hydrogel; crosslinking density; elastic modulus; γ-irradiation; equilibrium water content; butyl acrylate–N-vinylpyrrolidone copolymer)

INTRODUCTION

Polymers and copolymers that exhibit the ability to absorb a considerable quantity of water without actual dissolution are termed hydrogels. Such materials are usually crosslinked. One of the basic properties of a hydrogel is its equilibrium water content W_1, which is defined (as a percentage) by:

$$W_1 = [(m - m_0)/m] \times 100 \quad (1)$$

where m_0 and m are the weights of initial dry xerogel and of the hydrogel respectively. Several useful applications require not only a suitable value of W_1, but also that the swollen material possesses favourable elastic and mechanical properties in the swollen state[1,2]. This requirement can be achieved by the use of copolymers in which, for example, a hydrophilic monomer is grafted via γ-irradiation to a hydrophobic backbone[3]. Alternatively, and with greater versatility with regard to the possible range of properties, the copolymer can be produced by free-radical copolymerization of a pair of monomers in the presence of a crosslinking agent.

Recent studies in the authors' laboratory have been directed towards the preparation and properties of such a series of copolymers afforded by the bulk copolymerization of a hydrophobic monomer, n-butyl acrylate (BA), with a hydrophilic monomer, *N*-vinyl-2-pyrrolidone (VP), in the presence of a hexafunctional crosslinking agent, 1,1,1-trimethylolpropane trimethacrylate (TPT). Aspects investigated include the optical and compositional homogeneity[4–6], permeability of dissolved oxygen[7] and overall swelling behaviour[5]. For a copolymer of one fixed composition the effect of varying the crosslinker concentration on copolymer–water interaction was also studied[8]. The present communication is similar in overall aims, but is extended in scope to include (i) BA/VP copolymers over the whole range of composition all at a fixed concentration of added TPT and (ii) the influence of varying contents of TPT for copolymers of both higher and lower hydrophilicity (i.e. contents of VP) than that in the previous investigation[8].

The use of γ-irradiation enabled copolymerization to be effected to practically 100% conversion. Accordingly, the predetermined weight composition of the feed is the same as that of the resultant xerogel. For the latter, the designation BA20/VP80, for example, means that BA comprises 20% of (BA + VP). The content of crosslinking agent relates to the whole mixture; for example, in BA20/VP80/TPT1.5, TPT comprises 1.5% of (BA + VP + TPT) and the ratio by weight of BA to VP remains 20/80. Unless specified otherwise all concentrations are expressed as a percentage by weight with w and W relating to concentrations in xerogel and hydrogel respectively. A temperature of 294 K applies to the copolymerization, swelling and compression measurements.

EXPERIMENTAL

Materials

BA (Aldrich, UK) and VP (Aldrich, UK) were purified as described elsewhere[4–6], TPT[9] (Polyscience) was used as received and deionized water was used for swelling.

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Preparation of xerogels

The techniques employed for preparing the crosslinked xerogels have been described previously[4–8]. Essentially, mixtures of BA, VP and TPT in the absence of any added solvent were outgassed in siliconized[10] glass ampoules, which were sealed off under vacuum (10^{-4} mmHg) and then subjected to γ-irradiation to a total dose of 1 Mrad at 0.01 Mrad h^{-1} rom a ^{60}Co source at Salford University. The resultant solid xerogel rods were cured finally for 24 h at 378 K. They ranged in form from glassy to leathery to rubbery with increasing content of BA. For the glassy and leathery samples thin discs (diameter ~ 10 mm, thickness ~0.5 mm) and pellets (diameter ~10 mm, length ~ 10 mm) of uniform dimensions were lathe cut as before[10]. The procedure for the more rubbery samples, i.e. those of BA contents $\gtrsim 60\%$, was more difficult and required cooling of the sample in liquid nitrogen prior to cutting and then further cooling at stages during the cutting. The dimensions of the pellets were similar to those quoted above, but because of the anticipated low degrees of swelling, the discs were larger (diameter ~20 mm, thickness ~0.7 mm). All discs and pellets were dried exhaustively in a vacuum oven at 308 K.

Preparation of hydrogels

Dried discs of initial weight m_0 and initial diameter d_0 were placed in vials and water was added. At swelling equilibrium the weight (m) and diameter (d) were determined, the latter quantity by means of a micrometer or via a photographic technique. Full details have been reported earlier[5,8]. The equilibrium water content was obtained from equation (1) and also from:

$$W_1 = 100\frac{\phi_1\rho_1}{\phi_1\rho_1 + \phi_2\rho_2} \qquad (2)$$

in which ϕ_1 and ϕ_2 are the volume fractions of water and copolymer respectively in the hydrogel and ρ_1 and ρ_2 denote the corresponding densities. The values of ρ_2 were obtained from the mass and the volume, the latter being calculated from the measured thickness and diameter.

The volume fraction ϕ_2 of copolymer in the hydrogel was calculated from:

$$\phi_2 = (d_0/d)^3 \qquad (3)$$

on the basis of isotropic volumetric swelling.

Measurement of sol fraction

During swelling and subsequent drying of discs after attainment of swelling equilibrium a reduction in weight of xerogel was noted in some cases. The same reduction in weight due to loss of a sol fraction could be obtained more rapidly (24 h) by a Soxhlet extraction with boiling water. For this purpose three or four discs were used, which were dried finally to constant weight m_s in a vacuum oven at 308 K. The sol fraction S (expressed as a percentage) was obtained from:

$$S = 100[(m_0 - m_s)/m_0] \qquad (4)$$

All measurements were made on extracted samples and the water contents, for example, relate to the true rather than apparent values.

Stress–strain measurements

Stress–strain measurements were made on swollen pellets immersed continuously in water. The apparatus and procedure adopted for the uniaxial compression were as before[8].

RESULTS

Three types of system were examined:

(i) BA/VP copolymers covering a wide range of composition, but all comprising a fixed content (1% w/w) of added TPT.

(ii) BA20/VP80 copolymers containing different concentrations of TPT.

(iii) BA60/VP40 copolymers containing different concentrations of TPT.

System (i) will be dealt with separately, whilst systems (ii) and (iii) will be considered together.

For (i), (ii) and (iii) the extent of linear expansion (LE) on swelling was calculated as a percentage from $LE = 100[(d - d_0)/d_0]$. Young's modulus of elasticity (E) was obtained as the slope of stress (τ) *versus* strain ($\lambda - 1$), where λ is the ratio of the deformed length (l) of hydrogel to its undeformed length (l_0). Such plots were accurately linear within the range studied, i.e. for strains between 0 and −0.19. The compression modulus (G) was obtained by linear regression analysis as the slopes of τ *versus* ($\lambda - \lambda^{-2}$) according to the following expressions[11]:

$$\tau = G(\lambda - \lambda^{-2}) \qquad (5)$$

$$G = RT\nu_e\phi_2^{1/3} \qquad (6)$$

For hydrogels from xerogels containing up to 60% BA, linearity in plots according to (5) was obtained over the range of strains used, i.e. for strains between 0 and −0.07; for the remaining samples of higher BA content the corresponding range of strain was 0 to −0.12.

Determination of G thus allowed the effective crosslinking density (ν_e) to be evaluated, thereby yielding the molar mass between crosslinks (M_c) via:

$$M_c = \rho_2/\nu_e \qquad (7)$$

The theoretical crosslinking density (ν_t) is given by:

$$\nu_t = Cf/2 \qquad (8)$$

in which C (mol dm^{-3}) is the concentration of added crosslinking agent of functionality f. In the present preparations with hexafunctional TPT as crosslinking agent, equation (8) reduces to:

$$\nu_t = 3C \qquad (9)$$

The values of C were calculated from the known weights of TPT in the feed mixture, in conjunction with ρ_2 and the molar mass of TPT (388 g mol^{-1}). The copolymer–water interaction parameter χ was calculated from equation (10)[12]:

$$\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 + \nu_e V_1(\phi_2^{1/3} - 2\phi_2 f^{-1}) = 0 \qquad (10)$$

where V_1 (mol dm^{-3}) is the molar volume of water at a temperature T (K), which was obtained via[13]:

$$V_1 = 10^{-3}[18.05 + 3.6 \times 10^{-3}(T - 298)] \quad (11)$$

Gels of different composition

Data relating to copolymers of 15 different compositions, BA2/VP98/TPT1–BA95/VP5/TPT1, all at a fixed concentration of 1% TPT, are summarized in *Table 1*. The densities of xerogels ρ_2 (kg dm^{-3}) do not vary linearly with weight per cent of BA (w_{BA}) but fit a dependence of the third degree:

$$.\rho_2 = 1.220 - 3.6 \times 10^{-3} w_{BA} + 3.98 \times 10^{-5} w_{BA}^2 - 1/67 \times 10^{-7} w_{BA}^3$$

Table 1 Swelling data for BA/VP/TPT1 hydrogels of different copolymer composition, but constant TPT congtent of 1%

BA/VP (w/w)	ρ_2 (kg dm^{-3})	LE (%)	ϕ_2	W_1 (via (1)) (%)
2/98	1.220	115.4	0.100	89.0
5/95	1.203	95.1	0.135	85.5
10/90	1.190	71.9	0.197	78.6
20/80	1.167	53.8	0.275	73.7
30/70	1.147	35.8	0.398	62.7
40/60	1.131	24.0	0.524	49.2
50/50	1.122	16.5	0.633	38.0
60/40	1.115	9.7	0.758	22.5
65/35	–	6.5	0.826	15.1
70/30	1.108	4.8	0.870	9.5
75/25	–	2.9	0.917	5.1
80/20	1.101	1.6	0.952	3.3
85/15	–	0.8	0.976	2.2
90/10	1.100	0.3	0.990	1.4
95/5	–	–	–	0.8

The sol fractions S of xerogels are not tabulated, but are shown in *Figure 1a* to decrease from 20.8% for BA2/VP98/TPT1 to 1% for BA60/VP40/TPT1. At $w_{BA} > 60\%$ the value of S is zero. The linear expansion coefficients on swelling increase markedly with increasing content of the hydrophilic component, VP, and interpolation from the listed values of LE shows that the dimensions double in magnitude (i.e. $LE = 100\%$) on swelling when the VP content of xerogel is 96%. A very wide range of water contents is exhibited by these hydrogels, viz. $W_1 = 0.8$ to 89%. In general the values of W_1 obtained via (2) agreed to within ~1% with those determined from (1). However, because the estimated uncertainty in the measured values of d for gels of very high BA content was somewhat greater than the corresponding uncertainty in m, we have listed in *Table 1* only the values of W_1 determined via (1).

Figure 2 shows the plots according to equation (5) and *Table 2* gives the data derived either directly or indirectly from these stress–strain measurements on 11 of the samples. Although all the copolymers contained the same weight percentage of TPT, the values of C and v_t exhibit a small decrease with increasing concentration of BA. This is due to the previously noted decrease in ρ_2 with increase in w_{BA}. The most elastic hydrogels, i.e. those of smallest moduli, are those of highest water content and of lowest v_e. However, the trend for the moduli and v_e to increase holds only up to BA content of ~60% in the xerogel. At higher contents corresponding to lower total swelling the trend is reversed. Comment on this point will be made in the 'Discussion' section. It is noteworthy that the thermodynamic parameter χ manifests a consistent increase with BA content of xerogel over the whole range of composition.

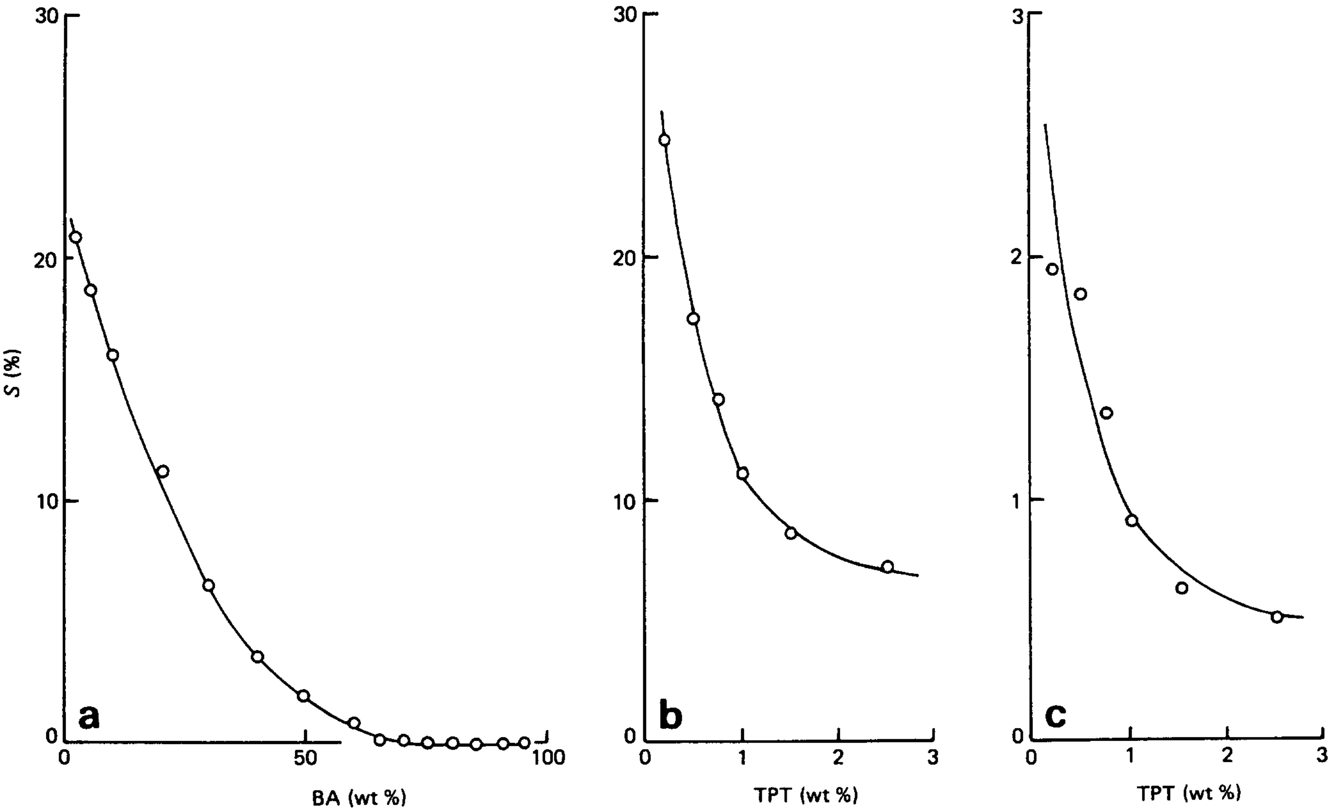

Figure 1 Variation of sol fraction with (a) BA content of xerogels containing 1% TPT, (b) concentration of TPT in BA20/VP80 xerogels and (c) concentration of TPT in BA60/VP40 xerogels

Gels of different content of crosslinking agent

Similar measurements to those indicated in the subsection above were made on BA20/VP80 gels in which TPT was incorporated at six different concentrations, viz. 0.2–2.5%, and on the less hydrophilic series of BA60/VP40 gels in which the same six contents of TPT were included.

The effect of TPT concentration on *S* is shown in *Figure 1b* for series (ii) and in *Figure 1c* for series (iii). The significant sol fraction in BA20/VP80 xerogels is decreased markedly by the presence of crosslinking agent, the latter also effecting a reduction in the small *S* values for the BA60/VP40 copolymers. In neither system is *S* reduced to zero within the range of TPT used. Other properties of these two sets of gels are given in *Table 3*. Comparison of these data with those of *Table 1* shows that the swelling properties are reduced by TPT to a smaller extent than they are by changing the composition at a fixed concentration of TPT.

Results derived from stress–strain measurements are given in *Table 4*, which shows that for each of these two systems an increase in the concentration of TPT results in a continuous increase in G, E, ν_e and χ. The dependence of ν_e on ν_t (not illustrated) was found to be accurately linear as was also true previously[8] for the BA30/VP70 system. The linear dependences are given by the following equations (in which the crosslinking densities are expressed in mol dm^{-3}):

$$\text{BA20/VP80} \qquad \nu_e = 0.024 + 0.49\nu_t \qquad (12)$$

$$\text{BA30/VP70} \qquad \nu_e = 0.035 + 0.54\nu_t \qquad (13)$$

$$\text{BA60/VP40} \qquad \nu_e = 0.064 + 0.60\nu_t \qquad (14)$$

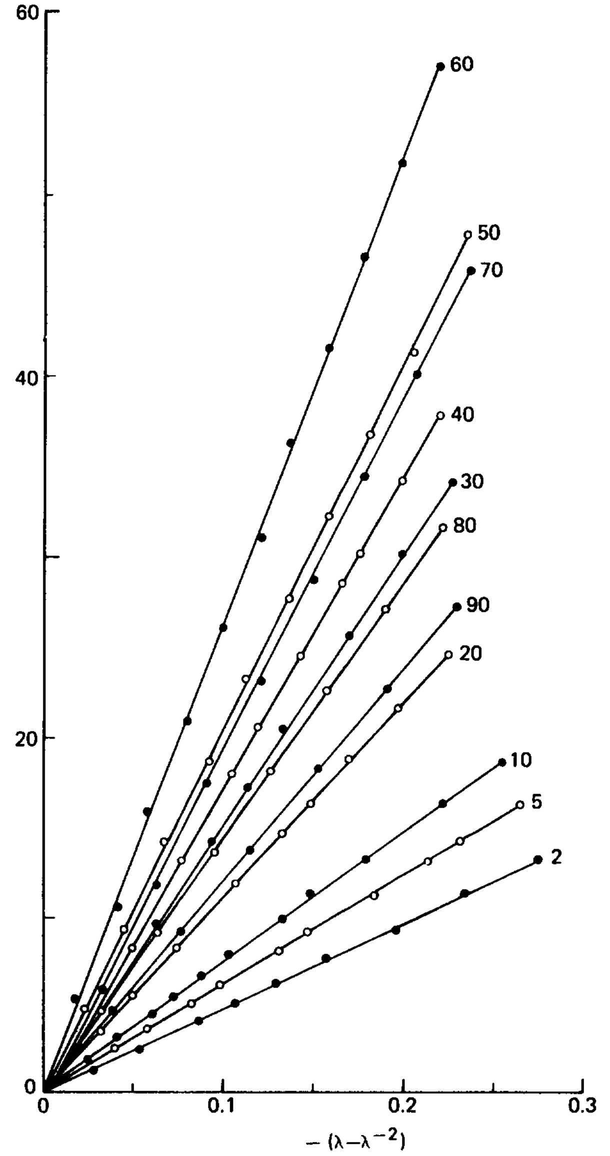

Figure 2 Plots according to equation (5) from compression–strain data for BA/VP/TPT hydrogels containing 1% TPT. The weight percentages of BA in xerogels are indicated

Table 3 Swelling data for BA20/VP80 and BA60/VP40 hydrogels at different contents of TPT

Sample	*LE* (%)	ϕ_2	W_1 (via (1)) (%)
BA20/VP80/TPT0.2	77.5	0.179	80.2
BA20/VP80/TPT0.5	67.0	0.214	77.7
BA20/VP80/TPT0.75	58.9	0.249	74.4
BA20/VP80/TPT1	53.8	0.275	73.7
BA20/VP80/TPT1.5	43.8	0.337	64.4
BA20/VP80/TPT2.5	34.7	0.409	58.5
BA60/VP40/TPT0.2	11.4	0.714	27.5
BA60/VP40/TPT0.5	11.1	0.727	25.4
BA60/VP40/TPT0.75	10.0	0.733	24.1
BA60/VP40/TPT1	9.7	0.758	22.5
BA60/VP40/TPT1.5	8.7	0.779	21.2
BA60/VP40/TPT2.5	8.5	0.782	20.2

Table 2 Network parameters from stress–strain measurements for BA/VP/TPT1 hydrogels of different copolymer composition, but constant TPT content of 1%

BA/VP (w/w)	$\nu_t \times 10^3$ (mol dm^{-3})	$\nu_e \times 10^3$ (mol dm^{-3})	G (MN m^{-2})	E (MN m^{-2})	$M_c \times 10^{-3}$ (g mol^{-1})	χ
2/98	94.3	40.4	0.046	0.148	30.2	0.507
5/95	93.0	46.3	0.058	0.187	26.0	0.529
10/90	92.0	50.5	0.072	0.234	23.5	0.565
20/80	90.2	68.5	0.109	0.349	17.0	0.607
30/70	88.8	86.0	0.149	0.475	13.3	0.655
40/60	87.4	90.1	0.177	0.562	12.5	0.786
50/50	86.7	96.7	0.201	0.648	11.6	0.890
60/40	86.2	114.8	0.256	0.829	9.7	1.148
70/30	85.7	84.3	0.197	0.653	13.2	1.548
80/20	85.1	55.0	0.132	0.431	20.0	2.334
90/10	85.1	50.3	0.123	0.407	21.9	3.787

Table 4 Network parameters from stress–strain measurements for BA20/VP80 and BA60/VP40 hydrogels at different contents of TPT

Sample	$\nu_t \times 10^3$ (mol dm^{-3})	$\nu_e \times 10^3$ (mol dm^{-3})	G (MN m^{-2})	E (MN m^{-2})	$M_c \times 10^{-3}$ (g mol^{-1})	χ
BA20/VP80/TPT0.2	18.1	32.7	0.045	0.156	35.8	0.560
BA20/VP80/TPT0.5	45.1	47.1	0.069	0.234	24.8	0.575
BA20/VP80/TPT0.75	67.7	57.2	0.088	0.295	20.4	0.593
BA20/VP80/TPT1	90.2	68.5	0.109	0.349	17.0	0.607
BA20/VP80/TPT1.5	135.4	88.7	0.151	0.510	13.1	0.643
BA20/VP80/TPT2.5	225.6	135.0	0.245	0.787	8.6	0.690
BA60/VP40/TPT0.2	17.2	74.6	0.163	0.536	15.0	1.053
BA60/VP40/TPT0.5	43.1	90.0	0.198	0.660	12.4	1.079
BA60/VP40/TPT0.75	64.7	106.1	0.234	0.766	10.5	1.091
BA60/VP40/TPT1	86.2	114.8	0.256	0.829	9.7	1.148
BA60/VP40/TPT1.5	129.3	141.3	0.318	1.040	7.9	1.201
BA60/VP40/TPT2.5	215.6	194.8	0.439	1.399	5.7	1.208

DISCUSSION

Certain hydrogels exhibit values of W_1 which exceed ~99.9%. They are termed 'super-sorbers'[14]. The present crosslinked copolymers do not come into this category, but afford water contents extending up to a maximum of ~89% according to their content of hydrophilic monomer, VP, which is capable of binding with water. Alternatively, at a particular content of VP, the water content decreases with increasing concentration of added TPT. Thus, a reduction from 2.5% to 0.2% in the TPT concentration raises W_1 by a factor of 1.36 for both the BA20/VP80 and BA60/VP40 systems. However, for the latter system the value of W_1 still remains rather small (27.5%) even at the low TPT concentration of 0.2%, because of the small VP content. In this connection we note that inclusion of crosslinker into xerogels of VP/methyl methacrylate (80/20 w/w) has been reported[15] to produce only a small decrease in W_1.

Removal of a sol fraction is a matter of some inconvenience and, as is evident from *Figure 1a*, the samples for which this is necessary are those of most potential use, i.e. those of highest VP content. We have examined the compositional heterogeneity at all stages of conversion throughout the BA/VP copolymerization[6] and have also identified as practically pure poly-VP the extracted material produced during the final stages of reaction[5]. The effects are dependent on the feed composition. The fall in S up to a BA content of ~65% and the absence of any sol fraction in xerogels of higher BA contents are entirely consistent with the theoretical analysis. The possibility of reducing S by increasing the TPT concentration is shown in *Figures 1b* and *1c*, but neither of these curves indicates that S can be reduced to zero. Moreover, this procedure has the disadvantage that it concomitantly increases the elastic moduli and decreases the water contents of the hydrogels.

At any specified concentration of TPT, the effective crosslinking density is larger the higher the BA content (for w_{BA} < ca. 60%). Thus, at $w_{TPT} = 1\%$ the elasticity of the hydrogels follows the sequence:

BA20/VP80/TPT1 > BA30/VP70/TPT1
> BA60/VP40/TPT1

the values of Young's modulus being 0.156, 0.475 and 0.836 MN m^{-2} respectively and the values of ν_e also increasing in the same order. In all cases considered here ν_e differs from ν_t. The linear interrelations between these quantities for three systems are given by equations (12)–(14), which are of the form $\nu_e = \alpha + \beta \nu_t$.

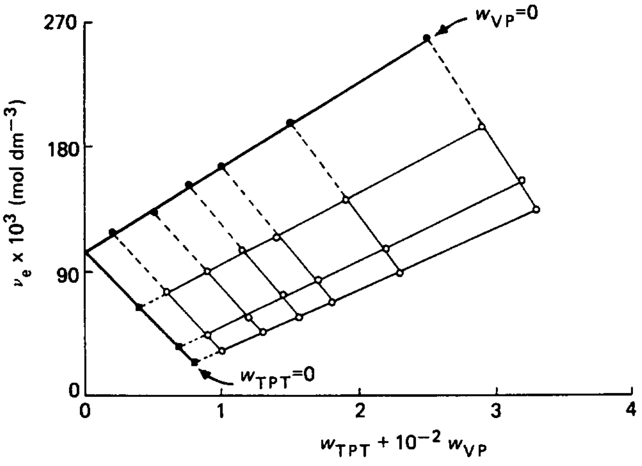

Figure 3 Interrelation among ν_e, w_{VP} and w_{TPT} for BA20/VP80, BA30/VP70 and BA60/VP40 hydrogels each containing six different concentrations of TPT

The coefficients β are all less than unity. They signify the efficiency of crosslinking and their values (0.49, 0.54 and 0.60) increase with increasing BA content. The term α denotes the value of ν_e when $\nu_t = 0$. These values also increase with increasing BA content. There are thus strong indications of crosslinking even in the absence of any added TPT. Poly(acrylates) are known to have a high tendency to crosslink under γ-irradiation[16,17] and moreover, acrylic acid for example undergoes chain transfer and crosslinking when polymerized by γ-irradiation[18,19]. *Figure 3* is a representation in a Zimm-type plot of the interrelation among ν_e, w_{VP} and w_{TPT} where the latter two symbols denote the weight percentages of VP and TPT in the xerogels. A double extrapolation, as indicated, yields a significant value of 0.103 mol dm^{-3} for ν_e at $w_{TPT} = 0$ and $w_{VP} = 0$, i.e. for pure poly-BA. This polymer would not, of course, yield a swollen hydrogel in water. Similarly, in *Figure 4* the same type of plot is given with ν_e, w_{BA} and w_{TPT} as variables. The common intercept at $w_{TPT} = 0$ and $w_{BA} = 0$ yields a very small value (cf. that for poly-BA) of $\nu_e = 0.005$ mol dm^{-3} for the effective crosslinking density of poly-VP in the absence of added TPT. Davis and Senogles[20] have reported a low radiation crosslinking G-value of 0.10–0.16 heV^{-1} for irradiated poly-VP and Shultz and Bovey[17] obtained ~1.00–1.25 heV^{-1} as the correspond-

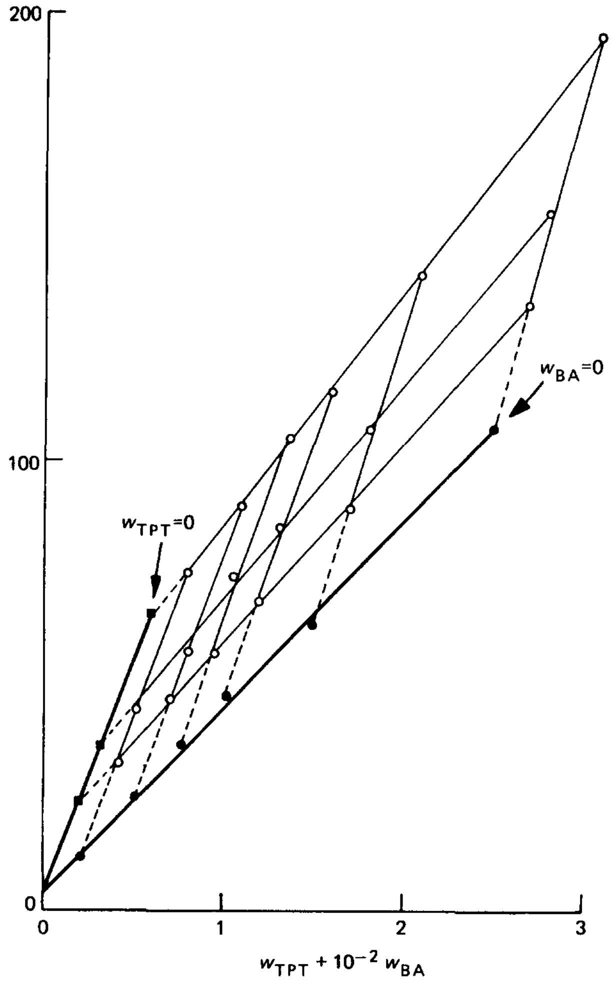

Figure 4 Interrelation among ν_e, w_{BA} and w_{TPT} for BA20/VP80, BA30/VP70 and BA60/VP40 hydrogels each containing six different concentrations of TPT

ing G-value for crosslinking in poly-BA. The relevant temperatures were different from each other and different from the one used here for measurement of ν_e. With allowance for this and also for the uncertainty limits of the G-values, the possible ratio of 1.25/0.1 for the relative crosslinking tendencies in the two homopolymers may be considered to be of an acceptably similar order of magnitude to the ratio 0.103/0.005 obtained here for the relative ν_e values of these polymers in the absence of TPT.

Starodubstev and coworkers[21] have found increased swelling in water and decreasing elastic moduli in hydrogels based on VP with 2-hydroxyethyl methacrylate (HEMA); the latter comonomer has a definite hydrophobic character despite the ability of its polymer to swell in water. For the present systems, the data in *Table 2* relating to a fixed concentration of TPT show the expected high elasticity (small E and small ν_e) at low BA contents, i.e. with only small hydrophobic interaction. The increase in ν_e and E continues, however, only up to hydrogel BA60/VP40/TPT1. Thereafter there is an amelioration in the elastic behaviour and the values of the moduli and ν_e fall. The values of W_1 in conjunction with the known compositions of the xerogels allow one to calculate the composition of the hydrogels in terms of their components, viz. per cent water (W_1), per cent BA units (W_{BA}) and per cent VP units (W_{VP}). *Figure 5* shows that W_{BA} and W_1 increase and decrease respectively in a smooth manner with increasing content (w_{BA}) of BA in the xerogel. However, although W_{VP} increases with w_{BA}, this occurs only up to w_{BA} ~60%; at higher values of w_{BA} there is a fall in W_{VP}. The stress–strain results show that the behaviour of Young's modulus (also indicated in *Figure 5*) follows a similar pattern to that of W_{VP}, and highly elastic hydrogels are obtainable from xerogels of both high and low contents of BA, but not from those of intermediate composition. Although it has not proved possible to provide a definite and unequivocal explanation for this behaviour, some relevant factors are now discussed.

(1) In the region of low w_{BA} flexibility and low moduli are possible because of the high content of water (W_1 ~ 70–90%) which plasticizes the copolymer.

(2) In the region of high w_{BA} the fractional contents of VP and water are both small, but the magnitude of W_{BA} becomes large. The glass transition temperatures (T_g) of poly-BA and poly-VP are about −55°C[22] and 172°C[23,24] respectively. In this region one can reasonably neglect the small water content in calculating the T_g of the copolymer and specifically one finds that at the temperature of these measurements (21°C) the copolymers are already above their T_g provided $w_{BA} \gtrsim 65\%$. In this region, therefore, it is the flexibility of the BA region of the hydrogel that causes the low moduli.

(3) Differential scanning calorimetry is currently being used here to determine the mass of freezing (sometimes termed 'free') water and hence, by difference, that of non-freezing (sometimes called 'bound') water in a fixed mass of hydrogel. The percentage by weight of non-freezing water within the whole hydrogel is denoted by $(W_1)_{nf}$. Coverage of samples of different TPT concentrations and of 15 different compositions has not yet been completed. However, the findings to date[24] indicate clearly that the variation of $(W_1)_{nf}$ with w_{BA} is of a similar general form to that assumed by W_{VP}, ν_e and the elastic moduli, i.e. small fractions of non-freezing water at both ends of the copolymer composition range and large values in the

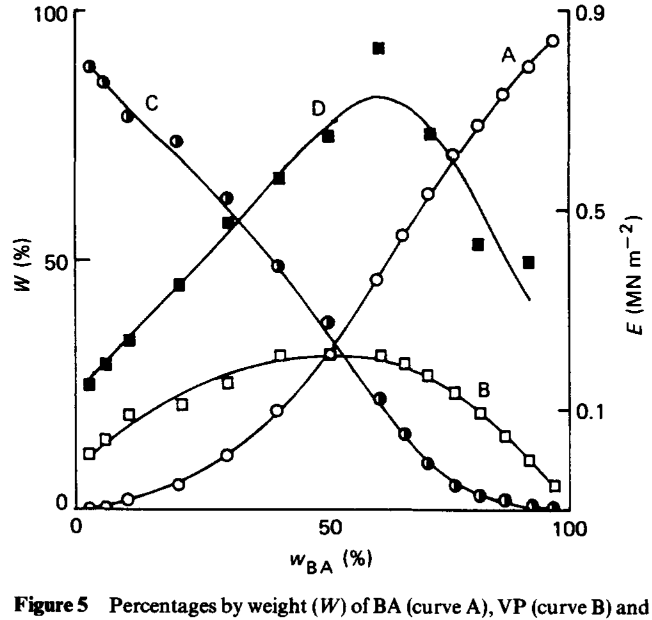

Figure 5 Percentages by weight (W) of BA (curve A), VP (curve B) and water (curve C) within hydrogels at swelling equilibrium as a function of the percentage by weight of BA (w_{BA}) of the parent xerogels. Curve D gives the corresponding Young's moduli (E) of the hydrogels

intermediate region. In this intermediate region ($w_{BA} \sim 50$–65%) it is reasonable to presume that the high fraction of non-freezing water represents binding, i.e. an additional form of effective crosslinking involving a water molecule and the carbonyl groups (or possibly the nitrogen atoms[25,26]) of VP units.

Water is a non-solvent for poly-BA, a fact which is emphasized by the increase in χ with increasing BA at any particular TPT concentration. At medium–high w_{BA} there is a second-degree dependence of χ on composition, but for $w_{BA} = 2$–30% linear extrapolation of the data (*Table 2*) yields $\chi \sim 0.50$ for poly-VP, which does of course represent the homopolymer in the presence of 1% TPT. Some χ values of a similar magnitude to this have been determined[27,28] by compression–strain measurements on poly-VP prepared in the presence of crosslinking agents different from TPT. We have been unable to find any published values of χ for aqueous solutions of linear poly-VP. However, since water is thermodynamically a rather poor solvent for this polymer[29], the value of χ might be expected to be ~ 0.48–0.49 and the slightly higher value of 0.50 derived above for the crosslinked polymer would thus appear to be a reasonable one. Interpolation from the data in *Table 4* shows that at zero concentration of TPT the χ values for hydrogels from xerogels of 20% and 60% BA are 0.55 and 1.02 respectively. The corresponding value obtained from previous results[8] relating to an intermediate content of 30% BA is 0.61. These three values of χ also demonstrate the net overall reduction in copolymer–water interaction induced by inclusion of the hydrophobic monomer.

Finally, it is interesting to note the apparent stability of the gels discussed here. There was no evidence of any bacterial growth either on the hydrogels or in the deionized water in which they were immersed in stoppered vials, even after a period of 12 months. No suppressants such as sodium azide or thymol were incorporated in the swelling liquid. In contrast, under the same conditions of swelling medium and swelling time, green algae were apparent both in the water and on the immersed discs and pellets of more common hydrogels of VP-*co*-HEMA.

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