screening of hydrodynamic interactions and as such does not address the issue of molecular topology directly.

A more quantitative interpretation of these results will be appropriate after several related studies have been conducted. In addition to the measurements of linear PS diffusion in this matrix referred to previously,[25] measurements are in progress on linear and 3-arm-star PS in other PVME matrices. Light scattering studies are being undertaken to determine the PS coil dimensions as a function of matrix concentration, as is further rheological characterization of semidilute and concentrated PVME solutions. Nevertheless, it is evident from these data that reptation must be considered as a significant contribution to diffusion of linear polymers in thoroughly entangled solutions. However, it is equally clear that coil overlap is not a sufficient condition for reptation to be the dominant mechanism of diffusion.

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Thermodynamic Interactions in Copolymeric Hydrogels

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ABSTRACT: Xerogels comprising *n*-butyl acrylate and *N*-vinyl-2-pyrrolidone (30/70 wt/wt) and varying small amounts of a hexafunctional cross-linking agent have been prepared by γ-ray-initiated copolymerization to complete conversion and then swollen in water to equilibrium at several different temperatures (T) within the range 284–349 K. Photographic determination of the sample dimensions afforded the volume fractions of polymer (ϕ_2) and water within the resultant hydrogels, and the effective cross-linking densities (ν_e) were obtained via stress–strain measurements. Values of ϕ_2 increased with increasing T and with increasing ν_e. The elastic moduli at 294 K lay within the range 0.21–1.07 MN m^{-2}. Although the enthalpic components (χ_H) were negative, the large entropic components (χ_S) were positive and dominant in the overall increase with T of the polymer–water interaction parameter (χ). The negative values for the enthalpy and entropy of dilution are compatible with structuring of water via enhanced hydrogen bonding and by hydrophobic interaction.

Introduction

In previous reports[1,2] we have shown that by means of γ-irradiation *n*-butyl acrylate (BA) can be copolymerized with *N*-vinylpyrrolidone (VP) to more than 99.9% conversion to yield a series of xerogels having a range of hydrophilicity. These materials are insoluble in liquids that are capable of dissolving the corresponding low-conversion copolymers. Hence it is inferred that the γ-irradiation not only effects initiation but also induces some cross-linking into the copolymers. Incorporation of a hexafunctional cross-linking agent, 1,1,1-trimethylolpropane trimethacrylate (TPT),[3] into the feed mixture enhances the cross-linking and also reduces the water content of the hydrogels produced by swelling the xerogels in water. The influence of composition, dose, and dose rate on the swelling characteristics[4] of the copolymers and observations on the dissolved oxygen permeability coefficient[5] in the hydrogels have been reported.

In this paper an attempt is made to characterize some of these hydrogels more fully, with specific reference to (a) copolymer–water interaction and (b) the influence of temperature on the degree of swelling.

In addition to those abbreviations already indicated, PEO, PTFE, PU, and PVAL are used to denote poly-

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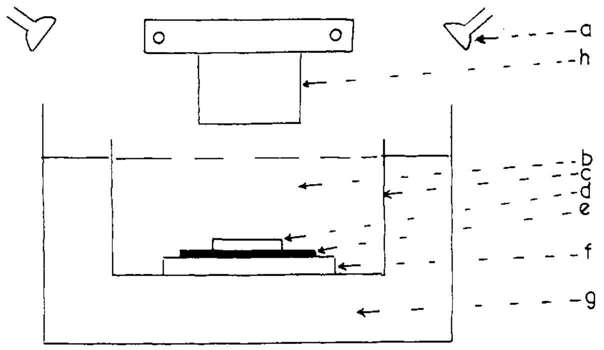

Figure 1. Mode of measuring diameter of swollen hydrogels at different temperatures: (a) lamp; (b) water; (c) glass container; (d) disk of swollen hydrogel; (e) graph paper; (f) glass plate; (g) water thermostat; (h) camera.

(ethylene oxide), poly(tetrafluoroethylene), polyurethane, and poly(vinyl alcohol), respectively. The following are also adopted either alone or prefixed by P- for the polymeric form: DHPM, 2,3-dihydroxypropyl methacrylate; EDMA, ethylene glycol dimethacrylate; HEMA, 2-hydroxyethyl methacrylate; HPA, hydroxypropyl acrylate; HPM, hydroxypropyl methacrylate; HPMA, (hydroxypropyl)methacrylamide; MMA, methyl methacrylate.

Experimental Section

Materials. The purification of monomers and the modes of outgassing and irradiation (1 Mrad at a dose rate of 0.01 Mrad/h) as well as the post-treatment of the copolymers have been described elsewhere.[1-4] The particular hydrogels selected for this work were those of fairly high water content, viz., hydrated xerogels prepared from a feed mixture of 30 wt % BA with 70 wt % VP. To effect changes in the swelling of xerogels, TPT at overall concentrations between 0.185% and 5% were included in the bulk feed mixture. Since polymerization proceeded to >99.9% conversion, the compositions of the seven resultant xerogels can be denoted as BA30/VP70/TPT0.185, BA30/VP70/TPT0.5, BA30/VP70/TPT0.75, BA30/VP70/TPT1, BA30/VP70/TPT2, BA30/VP70/TPT3, and BA30/VP70/TPT5.

Volume Fraction of Xerogel in Hydrogel. Thin (ca. 0.2 mm) disks of xerogel were swollen to equilibrium at ambient temperature (ca. 294 K). Details and relevant times have been reported in another paper,[4] wherein the degree of swelling was expressed on a weight basis. Hence we are concerned with the degree of volumetric swelling q and the volume fraction ϕ_2 of copolymer within the hydrogel.

In eq 1, d_0 is the diameter of the dry disk of xerogel (generally

$$\phi_2 = 1/q = (d_0/d)^3 \qquad (1)$$

ca. 12 mm), and d is the corresponding diameter in the swollen state at equilibrium. Although the times to attain swelling equilibrium at 294 K were quite long when starting from the dry state, a subsequent change of temperature of the hydrogel afforded swelling equilibrium more quickly (ca. 1–2 h) at each of the new temperatures used within the range 284–348 K. Accordingly the time of 4 h actually allowed was more than adequate.

Values of d_0 were measured with a micrometer, and those of d were determined by an image magnification technique using a standard SLR camera with a 50-mm lens. A 56-mm extension tube between the lens and the film (Kodak B/W, 100 ASA) yielded a magnification of ca. 4× on 3R prints. The arrangement is shown schematically in Figure 1. On the prints measurements were made with a ruler of the image diameter D(image) of the hydrogel disk and the length D(graph) of an actual 10-mm portion on the graph paper, which was positioned below the gel during attainment of swelling equilibrium. Hence d (expressed in millimeters) is given by

$$d = 10 \times D(\text{image})/D(\text{graph})$$

Excellent accuracy of the procedure was verified by using coins in place of hydrogel disks and comparing d for them with the diameter measured directly with a micrometer.

Stress–Strain Experiments. Initially, stress (extension)–strain measurements were made on three hydrogels, BA30/VP70/TPT0.185, BA30/VP70/TPT0.5, and BA30/VP70/TPT1. These samples, cut from a large swollen disk, were in the form of a strip 1 × 7 × 20 mm and were extended between the fiber grips of the Instron Table Model 1026 at room temperature (294 K).

Subsequently, it proved more convenient to conduct stress–strain measurements by uniaxial compression at 294 K. This procedure was highly reproducible, allowed the sample to remain immersed in water during the measurements, afforded accurate strains even at very low stresses, and permitted constant temperature control over a range of temperatures (although the present compression measurements were conducted at only one temperature). The apparatus was constructed here and was basically of a form similar to that reported elsewhere by Cluff et al.[6] Cylindrical pellets (ca. 7–10 mm in diameter and 7–10 mm in length) were cut on a lathe from xerogel rods and were exhaustively dried in an oven at 378 K. After their dimensions had been measured accurately with a micrometer, they were swollen to equilibrium in deionized water. This required ca. 2 months. The dimensions in the swollen state (length and cross-sectional area) were calculated from those in the dry state in conjunction with values of d/d_0 already obtained for the corresponding thin hydrogel disks. A swollen pellet was placed between two parallel PTFE cylinders, the upper one of which was connected to a load pan. The assembly was immersed in deionized water within a double-jacketed container through which water from an external thermostat was passed. The pellet was covered completely with water during the course of the measurements of strain (on a gauge) at preset stresses.

Results

Network Cross-Linking Density. The theoretical cross-linking density (ν_t) in the xerogel is given[7] by eq 2,

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

in which C is the concentration of cross-linking agent with a functionality f. In the present systems with TPT as cross-linking agent $f = 6$, and hence eq 2 reduces to

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

The values of C were calculated by using 388 g mol^{-1} as the molar mass of TPT and by taking the density of the xerogel as 1.148 kg dm^{-3}. This latter value is the average of densities obtained individually from direct weighings and micrometrically determined dimensions of 98 exhaustively dried xerogel disks of BA30/VP70/TPT1 (standard deviation 1.7%).[4] It is assumed that the density is not altered significantly in the other six samples wherein the concentration of TPT differed from 1 wt %.

With regard to the effective cross-linking density (ν_e), which frequently differs in magnitude from ν_t, Tobolsky et al.[8] have shown that this may be made from stress–strain data in accord with eq 4. In eq 4, RT carries its normal

$$\tau = RT\nu_e\phi_2^{1/3}(\lambda - \lambda^{-2}) \qquad (4)$$

meaning, τ is the applied stress, and λ is the ratio of the deformed length (l) to the undeformed length (l_0) of hydrogel.

As indicated previously, extension measurements were made on only three of the hydrogels. Compression measurements were made on these same three samples as well as on samples BA30/VP70/TPT0.75, BA30/VP70/TPT2, and BA30/VP70/TPT3. By neither technique could wholly reliable data be obtained for the hydrogel of highest cross-linker content (BA30/VP70/TPT5) because this sample was too brittle. In general, the compression technique was found to be preferable with respect to its excellent reproducibility and linearity of the appropriate plots. For these reasons, coupled with availability of results for six (rather than three) samples, we present and consider

Table I
Characteristics of the Hydrogels Obtained from Swelling Equilibrium and Stress–Strain Measurements at 294 K

sample	$C \times 10^3$, mol dm^{-3}	$\nu_t \times 10^3$, mol dm^{-3}	$\nu_e \times 10^3$, mol dm^{-3}	$M_c \times 10^{-3}$, g mol^{-1}	Young's modulus E, MN m^{-2}	ϕ_2
BA30/VP70/TPT0.185	5.5	16.4	41.3	27.8	0.212	0.279
BA30/VP70/TPT0.5	14.8	44.4	57.5	20.0	0.313	0.329
BA30/VP70/TPT0.75	22.2	66.6	74.3	15.5	0.410	0.342
BA30/VP70/TPT1	29.6	88.8	85.4	13.4	0.475	0.356
BA30/VP70/TPT2	59.2	178	129	8.9	0.785	0.426
BA30/VP70/TPT3	88.8	266	180	6.4	1.076	0.472
BA30/VP70/TPT5	148	444	240[a]	4.8		0.492

[a] Interpolated from eq 5.

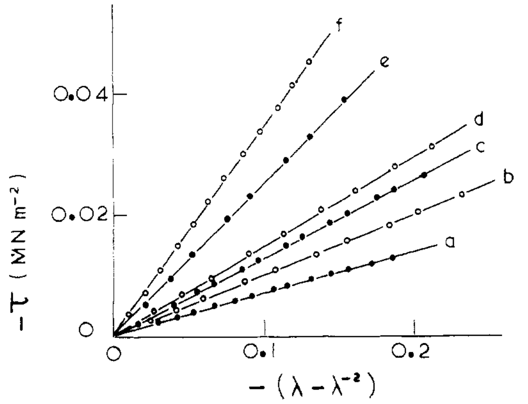

Figure 2. Plots of stress (τ) vs. $(\lambda - \lambda^{-2})$ at 294 K for the hydrogels: (a) BA30/VP70/TPT0.185; (b) BA30/VP70/TPT0.5; (c) BA30/VP70/TPT0.75; (d) BA30/VP70/TPT1; (e) BA30/VP70/TPT2; (f) BA30/VP70/TPT3.

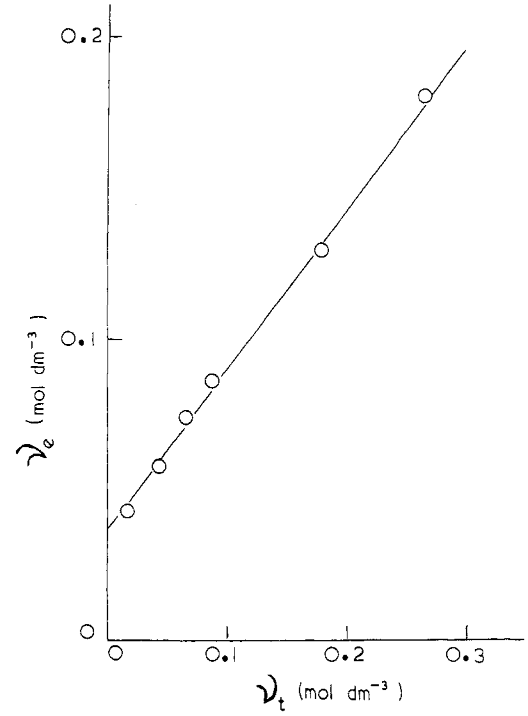

Figure 3. Dependence of effective cross-linking density (ν_e) on theoretical cross-linking density (ν_t) for BA/VP/TPT hydrogels at 294 K.

henceforth only data derived via compression measurements.

The plots of τ vs. strain are not reproduced here. They were accurately linear over the range studied, i.e., for strains between 0 and −0.07. Young's moduli of elasticity (E) were obtained as the slopes. Plots of τ vs. $(\lambda - \lambda^{-2})$ according to eq 4 are shown in Figure 2. Over the range of deformation actually covered, these plots too were linear. The gradients were obtained by linear regression analysis and were used to calculate the values of ν_e via eq 4. The linear dependence of ν_e on ν_t is indicated in Figure 3 from which least-squares analysis yielded the following relationship in which ν_e and ν_t are both expressed in moles per cubic decimeter:

$$\nu_e = 0.035 + 0.54\nu_t \qquad (5)$$

From the values of ν_e the molar mass per cross-link (M_c) was calculated via eq 6, in which ρ denotes the density of

$$M_c = \rho/\nu_e \qquad (6)$$

the xerogel. The values of C, ν_t, ν_e, M_c, and E as well as ϕ_2 at 294 K are given in Table I. Note that for sample BA30/VP/70/TPT5 the value of ν_e could not be determined and was obtained by interpolation from eq 5.

Volume Fraction of Polymer in Hydrogel. For four of the samples (BA30/VP70/TPT0.185, BA30/VP70/TPT0.5, BA30/VP70/TPT1, and BA30/VP70/TPT5) the volume fractions of polymer and water within the hydrogel were measured at 15 temperatures. At a fixed temperature ϕ_2 increased with increasing content of cross-linking agent. At a fixed content of TPT, ϕ_2 increased with increasing T. Thus at the lowest temperature used (284 K) the values of ϕ_2 for BA30/VP70/TPT0.185, BA30/VP70/TPT0.5, BA30/VP70/TPT1, and BA30/VP70/TPT5 were 0.261, 0.294, 0.324, and 0.457, respectively. At the highest temperature used (348 K) the corresponding values of ϕ_2 were 0.452, 0.517, 0.566, and 0.656, respectively.

Interaction Parameters. For a gel at swelling equilibrium in a liquid of molar volume V_1 the following interrelation among the composition, the cross-linking density, and the polymer–solvent interaction parameter (χ) obtains:[9]

$$\ln(1 - \phi_2) + \phi_2 + \chi\phi_2^2 + \nu_e V_1(\phi_2^{1/3} - 2\phi_2 f^{-1}) = 0 \qquad (7)$$

For water as swelling medium the values of V_1 (dm^3 mol^{-1}) at temperature T (K) are given by[10]

$$V_1 = (18.05 \times 10^{-3}) + 3.6 \times 10^{-6}(T - 298) \qquad (8)$$

Values of χ were thereby calculated for each of the four samples at the fifteen different temperatures. The change of χ with the system variables followed the same general trend as that indicated previously for ϕ_2. Water is a thermodynamically poor solvent for the polymers, and all values of χ exceeded 0.60. The lowest value of χ (~0.60) was exhibited at the lowest TPT content at the lowest temperature (284 K). Conversely, at the highest TPT content at the highest temperature (348 K), χ attained its largest value (~0.94). The dependences of χ on T at a fixed percent TPT and of χ on percent TPT at a fixed T are illustrated in Figure 4.

The plot of χ vs. T for sample BA30/VP70/TPT5 was linear and thus exceptional, the plots for the other three

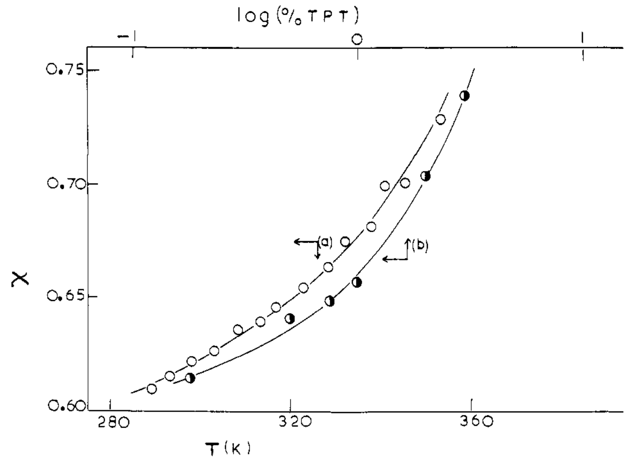

Figure 4. Variation of the interaction parameter χ with (a) temperature for hydrogel BA30/VP70/TPT0.185 and (b) content of cross-linker in xerogel for hydrogels at a fixed temperature of 294 K.

Table II
Coefficients a_i of Equation 9 for the Dependence of χ on T for BA/VP/TPT Hydrogels

sample	a_0	$a_1 \times 10^3$, K^{-1}	$a_2 \times 10^6$, K^{-2}
BA30/VP70/TPT0.185	2.89	−15.9	27.8
BA30/VP70/TPT0.5	3.21	−18.6	33.2
BA30/VP70/TPT1	3.09	−17.9	32.8
BA30/VP70/TPT5	−0.316	3.61	0

hydrogels of lower TPT content being of the form shown in Figure 4a for one of the other samples. The data points were fed into a computer for curve fitting to a polynomial; best fit was afforded by a polynomial of second degree. Fitting for sample BA30/VP70/TPT5 was obtained by linear regression. The general dependence of χ on T (K) was represented by eq 9, and the derived coefficients a_0, a_1, and a_2 are listed in Table II.

$$\chi = a_0 + a_1T + a_2T^2 \quad (9)$$

Further analysis of polymer–solvent interaction was made by separating χ into its enthalpic (χ_H) and entropic (χ_S) components, viz.[11]

$$\chi = \chi_H + \chi_S \quad (10)$$

$$\chi_H = -T(\mathrm{d}\chi/\mathrm{d}T) \quad (11)$$

$$\chi_S = \chi + T(\mathrm{d}\chi/\mathrm{d}T) = \mathrm{d}(\chi T)/\mathrm{d}T \quad (12)$$

Values of χ are not listed, since they are obtainable via Table II. Similarly, the values of χ_H and χ_S are obtainable via eq 9, 11, and 12, which show that

$$\chi_H = -a_1T - 2a_2T^2$$

$$\chi_S = a_0 + 2a_1T + 3a_2T^2$$

The variations of χ, χ_H, and χ_S with temperature are illustrated together in Figure 5 for the hydrogel BA30/VP70/TPT1. Similar forms of plot are exhibited by the other samples.

Discussion

The linear relationship between ν_e and ν_t accords with the findings of Janáček and Hasa[7] on P-HEMA hydrogels cross-linked by EDMA. In the plot of ν_e vs. ν_t these workers obtained a slope of 0.52, which is close to the value of 0.54 (cf. eq 5) found for the present systems. This indicates that the efficiencies of these two cases of chemically induced cross-linking are similar since the slope, being a proportionality constant, is a measure of such an efficiency. The finite value of ν_e even when $\nu_t = 0$ shows that BA/VP xerogels prepared under γ-irradiation are clearly being cross-linked also if TPT is excluded (as evidenced by the present findings in conjunction with earlier ones on solubility on sol fractions[4]).

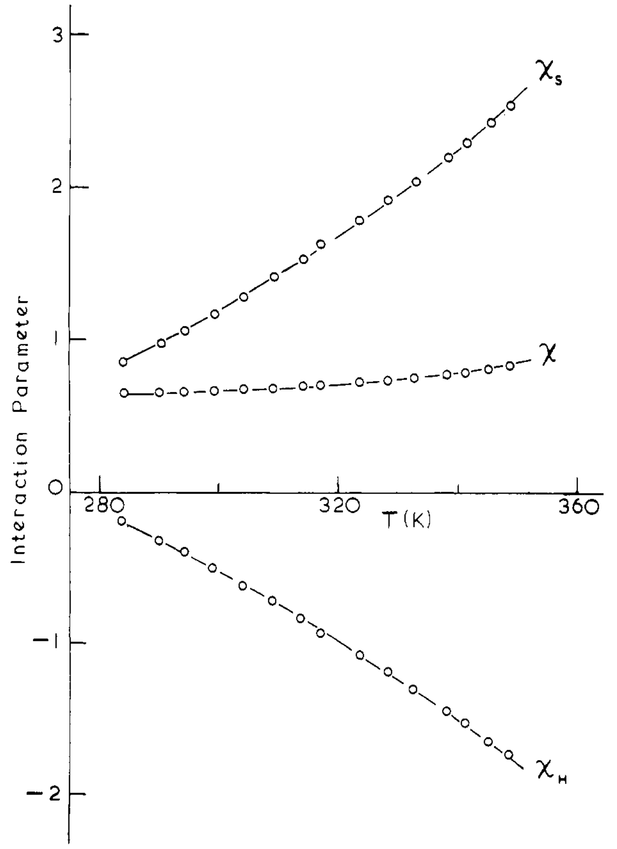

Figure 5. Variation with temperature of the interaction parameter χ and its enthalpic (χ_H) and entropic (χ_S) contributions for hydrogel BA30/VP70/TPT1.

The intercept on the ordinate of ν_e vs. ν_t has been related to the number of network entanglements extrapolated to infinite molar mass.[12] However, the present xerogels were prepared by irradiation from monomer mixtures (instead of from an existing polymer). Hence, it is more plausible to relate the value of the intercept to the actual cross-linking density existing in the absence of any TPT as well as to the physical entanglements. The lower value of 0.035 mol dm^{-3} (cf. eq 5) compared with 0.064 mol dm^{-3} for P-HEMA/EDMA[7] seems likely to be due to the fact that BA/VP/TPT was prepared in bulk, whereas a diluent was present in P-HEMA/EDMA gels. This accords with the finding that the value of ν_e decreases with decreasing content of diluent.[7]

In general, linearity in stress vs. strain holds only up to a certain strain. Yannes[13] has suggested a lower limit of ca. 0.20 as characteristic of rubbery networks, threshold strains for linearity which are very much below this value being indicative of materials in a glassy or glassy–elastomeric intermediate state. Westman and Lindstrom,[14,15] for example, have obtained linearity up to strains in excess of 0.20 for cross-linked cellulosic hydrogels and considered this in conjunction with the estimated ultimate tensile strain of 0.40 to provide evidence for the rubbery network nature of these gels. For the present BA/VP/TPT hydrogels the ultimate tensile strain was not reached, and measurements were only extended up to low strains. Hence it is not possible to invoke the criteria of these authors to assess the present hydrogels as rubbery networks. However, some aspects of rubbery networks are shown in the Appendix to apply to these hydrogels.

With regard to the stress–strain modulus (E) it is difficult to make meaningful comparison with published values for other hydrogels, because such values differ according to (1) mode of preparation (chemical or radiation initiation), (2) presence or absence of cross-linker and diluent during preparation, (3) whether they are made from a preformed polymer or by polymerization, and (4) composition in the case of copolymers. Among the most elastic hydrogels (i.e., of low E) are the very hydrophilic HEMA/DHPM copolymers cross-linked with EDMA[16] for which $E \sim 0.1–0.2$ MN m^{-2}. P-HEMA prepared in solution in the presence of EDMA[16] yields a slightly higher E of ca. 0.2 MN m,$^{-2}$ while the present BA/VP/TPT hydrogels are marginally less elastic, having $E \sim 0.2–1.1$ MN m^{-2} (Table I). The absence of cross-linking agent affords much higher moduli of 1.1–1.4 and $\sim$1.6 MN m^{-2} for hydrogels of P-HEMA and a VP/MMA copolymer, respectively.[17] The widest range of E values (ca. 0.002–0.46 MN m^{-2}) is probably exhibited by PU networks based on PEO,[18] at the lower end of which range these materials are significantly more elastic than the BA/VP/TPT hydrogels.

At constant temperature the observed decrease in swelling (i.e., increase in ϕ_2) with increasing cross-linker concentration is consistent with the behavior of most hydrogels. P-HEMA is rather exceptional in this respect, and the effect of cross-linker for this polymer is very small.

Reported influences of temperature on the dimensions of hydrogels are quite diverse and may be categorized into types a, b, and c. In (a), typified by P-DHPM,[19] the swelling increases with T; in (b) the swelling decreases with T, as found for P-HPA,[20–22] P-HPMA,[23] and PVA[24,25]; in (c) there is a combined effect of swelling decreasing with T down to a minimum value and thereafter increasing at higher temperatures. This has been observed for P-HEMA[20–22] and a VP/HPM copolymer.[26] The present BA/VP/TPT hydrogels thus fall into category b. Investigations have currently commenced here to ascertain if the same situation prevails when the content of VP in the copolymers is reduced to $\ll$70 wt %. Viscometric data on aqueous solutions of linear P-VP have demonstrated a reduction in solvent power with increasing T, and an estimate of ca. 413 K has been made for the lower critical solution temperature.[27] Type b behavior has also been observed for P-VP cross-linked with diallyl compounds.[28,29] Swelling not only in water but also in ethanol and chloroform was found to decrease at increasing T, but the opposite effect prevailed for swelling in non-hydrogen-bonding liquids.[28,29] The value of χ is large for PVP and BA/VP/TPT, and for both systems it increases with T.

Since the original introduction of χ as a reduced excess free energy of mixing parameter, several modifications and amplifications have been proposed.[11,30–33] These include its dependence on concentration (or composition of a gel) and, in polar systems, the subdivision into polar and nonpolar contributions, the latter of which, in turn, may comprise combinatorial and free-volume contributions. Allowing for all these possibilities, it is possible to propose the general form of the dependence of χ on T; appropriate diagrams have been given by Patterson.[32,33] However, it does not yet seem feasible to isolate all the contributions unambiguously and quantitatively (unlike the situation for the general interpretation of the dependence of intrinsic viscosity on T, for example[34]). Consequently, we shall resort to the simple subdivision of χ according to eq 10.

It will be recalled that χ_H and χ_S are related to the dimensionless enthalpy (κ) and entropy (ψ) of dilution parameters of Flory[35] by $\chi_H \equiv \kappa$ and $\chi_S = 0.50 - \psi$. The actual partial molar enthalpy of dilution ($\overline{\Delta H}_1$, J mol^{-1}) and partial molar entropy of dilution ($\overline{\Delta S}_1$, J K^{-1} mol^{-1}) are given by[35]

$$\overline{\Delta H}_1 = RT\phi_2{}^2\kappa$$

$$\overline{\Delta S}_1 = R\phi_2\psi$$

Hence the dimensionless contributions χ_H and χ_S assume the forms

$$\chi_H = \overline{\Delta H}_1/RT\phi_2{}^2$$

$$\chi_S = 0.50 - \overline{\Delta S}_1/R\phi_2$$

Because χ_H is negative, $\overline{\Delta H}_1$ is also negative, and since χ_S is positive and >0.50, $\overline{\Delta S}_1$ is also negative.

These findings are similar to the qualitative ones noted and discussed by Warren and Prins[23] for the behavior of P-HEMA hydrogels at $T < 328$ K (because P-HEMA belongs to type c referred to above, the situation for it is different at $T > 328$K). Despite the lowering of enthalpy on dilution with water, the swelling remains limited and actually decreases, and the entropy of dilution must be unfavorable, i.e., $\overline{\Delta S}_1 < 0$. This decrease in entropy might be attributable to structuring of water, which becomes more pronounced upon solvation of hydrophobic groups ("the hydrophobic interaction"). Concomitantly, the increase in water structure leads to a reduced enthalpy via enhanced hydrogen bonding in accord with the negative $\overline{\Delta H}_1$. The largest values of $|\overline{\Delta H}_1|$ ($\sim$−1.6 kJ mol^{-1}) and $|\overline{\Delta S}_1|$ ($\sim$−9.3 J K^{-1} mol^{-1}) obtain at the highest temperature or, equivalently, at the highest values of ϕ_2. In this connection it is pertinent to note that the fraction of water within the gel which is structured or bound water has been shown[36] to increase with decreasing total water content, i.e., with increasing ϕ_2.

Finally, it has been suggested that the action of water of gels with this type of behavior is a cooperative one, i.e., one in which hydrophobic backbone portions of several chains are compressed together to minimize the hydrophobically induced structuring of water. Warren and Prins[23] tentatively infer the existence of so-called hydrophobic bonds in P-HEMA, inducing the formation of ribbonlike micelles comprising alternating regions of hydrophobic backbone and hydrophilic side chains.

We do not consider that an exact parallel can be drawn with the present hydrogels in which a hydrophobic backbone of α-methyl groups is absent. The main source of hydrophobicity lies in the side-chain n-butyl groups of the BA units. The monomer reactivity ratios are $r_1 = 0.02$ and $r_2 = 0.80$ for VP and BA, respectively.[37] From these values in conjunction with the composition of initial feed and of unreacted monomer at each stage of fractional conversion (F), one can calculate the sequence length distributions for each of the two monomeric units within the copolymer.[38] The fractions of VP units occurring as single units, diads, triads, etc. are denoted by $(X_1)_1$, $(X_1)_2$, $(X_1)_3$, etc. and the corresponding sequences of BA units by $(X_2)_1$, $(X_2)_2$, $(X_2)_3$, etc. It is found that

(a) at $F = 0.1$

$(X_1)_1 = 0.94$ $\quad$ $(X_1)_2 = 0.056$ $\quad$ $(X_1)_3 = 0.003$

$(X_2)_1 = 0.80$ $\quad$ $(X_2)_2 = 0.16$ $\quad$ $(X_2)_3 = 0.032$

(b) at $F = 0.5$

$(X_1)_1 = 0.62$ $\quad$ $(X_1)_2 = 0.24$ $\quad$ $(X_1)_3 = 0.09$

$(X_1)_4 = 0.034$

$(X_2)_1 = 0.97$ $\quad$ $(X_2)_2 = 0.025$ $\quad$ $(X_2)_3 = 0.0006$

(c) at $F = 0.6$

$$(X_1)_1 = (X_1)_2 = (X_1)_3 = (X_1)_4 = 0.0007$$

$$(X_2)_1 = 0.999 \qquad (X_2)_2 = (X_2)_3 = (X_2)_4 \sim 0$$

(d) at $F = 0.9$

$$(X_1)_1 = (X_1)_2 = (X_1)_3 = (X_1)_4 \sim 0$$

$$(X_2)_1 = 0.999 \qquad (X_2)_2 = (X_2)_3 = (X_2)_4 \sim 0$$

The situation at low conversion is seen to differ from that prevailing at high conversion. Data for the interval $F = 0.5$–0.6 are included, since this is the short region over which there is a wide spread in compositional heterogeneity.[37]

On a cumulative basis, i.e., considering the final copolymer comprising species formed at all stages of conversion, it is apparent from the values above that (1) BA segments occur predominantly as single units and (2) even though VP units occur mainly as single ones in the first stages, overall they encompass a very wide spread of sequence sizes. It should be recalled also that for this particular BA/VP composition the reaction is conducted to $F = 1.0$, and only 28% of the monomer units (corresponding to 30 wt %) are BA. This, together with observations 1 and 2 above, tends to render it unlikely from the spatial and statistical standpoints that hydrophobic portions of several chains are compressed together to promote the formation of ribbonlike micelles.

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Appendix: Young's Modulus and Equilibrium Compression Modulus of Elasticity

The strain (positive in extension and negative in compression) is $\Delta l/l_0$, where $\Delta l = l - l_0$. Also $\Delta l/l_0 = \lambda - 1$. Hence in the initial linear region of a plot of stress (τ) vs. strain, Young's modulus (E) is given as the slope, viz.

$$E = \mathrm{d}\tau/\mathrm{d}(\Delta l/l_0) = \mathrm{d}\tau/\mathrm{d}\lambda \tag{A1}$$

In the initial linear region of the plot according to eq 4, the slope is the equilibrium modulus of elasticity G (where $G = RT\nu_e\, \phi_2{}^{1/3}$) and is thus given by

$$G = \mathrm{d}\tau/\mathrm{d}(\lambda - \lambda^{-2}) \tag{A2}$$

Also

$$\mathrm{d}\tau/\mathrm{d}(\lambda - \lambda^{-2}) = \frac{\mathrm{d}\tau/\mathrm{d}\lambda}{\mathrm{d}(\lambda - \lambda^{-2})/\mathrm{d}\lambda} = \frac{\mathrm{d}\tau/\mathrm{d}\lambda}{(1 + 2\lambda^{-3})} \tag{A3}$$

Combination of eq A1, A2, and A3 yields

$$G = E/(1 + 2\lambda^{-3}) \tag{A4}$$

In the limit of extremely small deformations when $\lambda \to 1$, eq A4 shows that $(E/G) \to 3$. In extension, $\lambda > 1$, and for small deformations (E/G) should be slightly less than 3, whereas in compression for which $\lambda < 1$ the value of (E/G) should be rather greater than 3. For the six different hydrogels studied here by compression the value of (E/G) was 3.2. Accordingly, in view of the theoretical basis of eq 4, some corroboration for the rubbery nature of the hydrogels is afforded.

Registry No. (BA)(VP)(TPT) (copolymer), 91442-56-7.

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