Effect of composition on properties of copolymeric *N*-vinyl-2-pyrrolidone/methyl methacrylate hydrogels and organogels

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Gamma irradiation has been used to copolymerize *N*-vinyl-2-pyrrolidone with methyl methacrylate to high conversion in both the presence and absence of ethyleneglycol dimethacrylate. The resultant solid xerogels were swollen to equilibrium in water and in dioxane to yield hydrogels and organogels respectively. The gels were characterized by uniaxial compression measurements and by determination of sol fraction, equilibrium solvent content, dimensions, effective crosslink density (ν_e) and polymer–solvent interaction parameter (χ). The *Q–e* scheme was used to compute instantaneous compositions of the terpolymer components at all stages of conversion, and compositional drift served to interpret the heterogeneous crosslinking at some compositions. No measurable effect of temperature on ν_e could be discerned. When the temperature was increased from 278 to 343 K, the hydrogels underwent deswelling with an increase in χ, whereas, over a similar increase in temperature, the opposite behaviour was exhibited by the organogels.

(Keywords: γ-irradiation; hydrogel; organogel; crosslink density; Young's modulus; *N*-vinyl-2-pyrrolidone-*co*-methyl methacrylate; ethyleneglycol dimethacrylate)

INTRODUCTION

Copolymers and terpolymers containing *N*-vinyl-2-pyrrolidone (VP) find wide application in the field of hydrogels[1]. We have reported previously on VP copolymerized with n-butyl acrylate (BA)[2–5], 2-hydroxyethyl methacrylate (HEMA)[5,6], a siloxanyl methacrylate[5,7] and ethyleneglycol dimethacrylate (EDMA)[8]. These and other similar copolymeric hydrogels are used as contact lens materials[1,9,10] or as possible matrices for drug release[1,11]. When methacrylates or dimethacrylates are used as comonomers, there is considerable compositional drift during the course of copolymerization, and, as demonstrated earlier[5], this effect is due to the disparate reactivities between VP and its comonomer. The present paper deals with copolymers of VP with methyl methacrylate (MMA) and with terpolymers comprising VP, MMA and the tetrafunctional monomer EDMA. The VP component of these copolymers affords swelling in water to produce hydrogels, while the MMA content gives rise to swelling in dioxane to yield organogels. The main objectives of this work are: (i) to compare the mechanical behaviour of the hydrogels and organogels; (ii) to compare the efficiency of crosslinking by the EDMA in the terpolymeric xerogels with the theoretically predicted, compositional drift of the EDMA content; (iii) to compare the properties of these gels with those of other VP-containing gels, which have been described previously.

The abbreviations already adopted are prefixed sometimes by P to denote the polymeric forms. Except where indicated otherwise, a temperature of 294 K applies, viz. to copolymerization, terpolymerization, swelling and stress(compression)–strain measurements. Compositions are expressed on a weight per cent (wt%) basis relative to the total weight of the principal monomers for MMA and VP, and relative to the total weight of the three components for EDMA. Thus, the designation MMA85/VP15 indicates that MMA/VP = 85/15 (wt/wt). The designation MMA85/VP15/EDMA1 means that MMA/VP = 85/15 (wt/wt) and that EDMA comprises 1 wt% of (MMA + VP + EDMA).

Because preparations of the xerogels were conducted to almost 100% conversion, these designations apply not only to the monomer feed but also to the overall compositions of the copolymers and terpolymers.

EXPERIMENTAL

Materials

VP[5] (Aldrich Chemical Co.) and MMA (Fisons Plc) were dried over anhydrous $MgSO_4$ and distilled under reduced pressure. EDMA (Ancomer ATM3) was purified by column chromatography as before[6,12]. Dioxane, purified as described previously[13], and deionized water were used for swelling.

Polymerization

The method of polymerization, described in full elsewhere[2,4], may be summarized as follows. Mixtures of monomer were made up gravimetrically and outgassed in siliconized[14] glass ampoules, which were sealed under vacuum and then subjected to γ-irradiation from the 9000 Ci ^{60}Co source at Salford University to a total dose of 1 Mrad at a dose rate of 0.01 Mrad h^{-1}. After their removal from the ampoules the resultant solid rods of

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xerogel were oven cured for 24 h at 378 K. The small weight loss on oven curing indicated that conversion of monomers was always in excess of 99%. The xerogels were cut finally into discs (diameter ~10 mm, thickness ~0.5 mm) and pellets (diameter ~10 mm, length ~10 mm).

Swelling

The cut specimens of xerogel were swollen separately in water and in dioxane, the swelling medium being changed regularly to remove any material extracted during the swelling process. Equilibrium was attained generally in 2 weeks for discs and 4–6 weeks for pellets.

The degree of swelling at equilibrium is expressed as the equilibrium solvent content W_1:

$$W_1 = 100(m - m_2)/m \qquad (1)$$

In equation (1) m_2 and m denote respectively the weights of dry xerogel and swollen gel, the latter being obtained after lightly surface drying the swollen gel.

The degree of swelling was also obtained as the volume fraction of solvent in swollen gel, which is equal to $(1 - \phi_2)$ where ϕ_2 is the volume fraction of polymer in gel:

$$\phi_2 = (D_2/D)^3 \qquad (2)$$

In equation (2) D_2 and D are the measured diameters of dry xerogel and swollen gel respectively. To obtain D and hence ϕ_2 at different temperatures, a photographic technique was employed. A Minolta X300 35 mm camera fitted with a Tamron 90 mm *f*/2.5 lens was used to photograph swollen discs placed in a thermostated bath of the swelling medium[2,8]. Dimensions of the gel were magnified 2–4 times in the print, thus yielding accurate measurements of D at each temperature.

Uniaxial compression

Stress(compression)–strain measurements were made on swollen pellets immersed continuously in the thermostated swelling medium at each of several temperatures. Details of the compression rig and exact procedure have been given elsewhere[8].

RESULTS AND DISCUSSION

Swelling at 294 K

Swelling was conducted in both water and dioxane, the former being a solvent for linear PVP and the latter a solvent for linear PMMA. Although water is certainly a non-solvent for PMMA, there is a some divergence of opinion regarding the solubility of PVP in dioxane. In some references dioxane is stated to be a solvent for desiccated PVP[15,16], while elsewhere it is classified as a non-solvent[17]. Some measure of polymer–solvent interaction must certainly occur, as evidenced by a value of $W_1 = 37.4$ wt% reported by Breitenbach[18] for crosslinked PVP swollen in dioxane. Against this, it should be borne in mind that a very similar value of W_1 obtains for crosslinked PHEMA swollen in water[13], but linear PHEMA is insoluble in water. From the considerations above, coupled with our own rough solubility tests, we are of the opinion that dioxane should not be regarded as a solvent for PVP.

Initially copolymers were prepared in the absence of crosslinker (EDMA). After swelling in water, the hydrogels of these possessed different water contents (*Table 1*). The higher the content of VP in the xerogel, the greater is the value of W_1 and the higher is the sol fraction. The copolymers having the highest VP content, i.e. MMA15/VP85 and MMA10/VP90, were extremely weak; the former broke up on measurement of W_1 and the latter disintegrated during the swelling process. No data corresponding to those in *Table 1* were obtainable for the organogels of samples prepared in the absence of crosslinker. On swelling in dioxane all of these samples across the compositional range lost their coherent structure, becoming jelly-like or, at high MMA content, appearing to dissolve.

Subsequently, terpolymeric xerogels of varying composition with respect to MMA and VP but at a fixed content of 1 wt% EDMA were prepared and swollen separately in water and dioxane. In *Table 2* it is seen that the hydrogels exhibit lower values of W_1 than the corresponding ones prepared in the absence of crosslinker. However, the sol fractions remain of very similar magnitudes. With regard to swelling in dioxane (*Table 3*), the crosslinked xerogels retained their structure and gave no sol fractions. The equilibrium dioxane content of the organogels is small at low contents of MMA, but the value of W_1 shows only a small increase (from ~65 to 67 wt%) over a wide range of higher MMA contents (45–95 wt%).

Table 1 Sol fractions and equilibrium water contents for MMA/VP gels of different composition prepared in the absence of crosslinker

Sample	Sol fraction (wt%)	W_1 (wt%)	ϕ_2
MMA15/VP85	broke up on measurement		
MMA30/VP70	14.8	80.0	0.204
MMA45/VP55	9.7	60.0	0.429
MMA60/VP40	6.1	34.9	0.559
MMA70/VP30	2.5	23.6	0.776
MMA85/VP15	0.6	8.5	0.909
MMA95/VP5	0.6	3.2	0.979

Table 2 Sol fractions and equilibrium water contents for MMA/VP gels of different composition prepared in the presence of a fixed concentration of crosslinker

Sample	Sol fraction (wt%)	W_1 (wt%)	ϕ_2
MMA15/VP85/EDMA1	28.5	88.6	0.152
MMA30/VP70/EDMA1	14.6	66.8	0.336
MMA45/VP55/EDMA1	9.9	49.2	0.537
MMA60/VP40/EDMA1	6.2	32.9	0.753
MMA75/VP25/EDMA1	2.4	16.2	0.869
MMA85/VP15/EDMA1	0.8	8.7	0.954
MMA95/VP5/EDMA1	0.6	3.5	0.988

Table 3 Sol fractions and equilibrium dioxane contents for MMA/VP gels of different composition prepared in the presence of a fixed concentration of crosslinker

Sample	Sol fraction (wt%)	W_1 (wt%)	ϕ_2
MMA15/VP85/EDMA1	0	35.5	0.698
MMA30/VP70/EDMA1	0	59.6	0.338
MMA45/VP55/EDMA1	0	64.7	0.309
MMA60/VP40/EDMA1	0	67.1	0.281
MMA75/VP25/EDMA1	0	67.6	0.284
MMA85/VP15/EDMA1	0	67.5	0.280
MMA95/VP5/EDMA1	0	66.9	0.298

A value of $W_1 = 80$ wt% has been reported by Patel[19] for a MMA20/VP80/EDMA0.91 hydrogel. Although a terpolymer of exactly this composition was not prepared here, interpolation from the present data in *Table 2* to a very similar composition, i.e. MMA20/VP80/EDMA1, also yields a value of $W_1 = 80$ wt%. Loshaek and Shen[20] have reported that both W_1 and the sol fraction decrease with increasing content of MMA in MMA/VP crosslinked with diallyl itaconate.

In the present work, the increase in sol fraction from 0.6 to 28.5 wt% (*Table 2*) as the VP content increases from 5 to 85 wt% can be interpreted on the basis of terpolymerization compositional drift. Relevant equations and methodology of the calculations have been described in a previous communication[6], where they were applied to the system HEMA/VP/EDMA. The procedure requires a knowledge of the copolymerization parameters Q and e, the following values[21] of which were adopted for the present study:

MMA:	$Q = 0.74$	$e = 0.40$
VP:	$Q = 0.14$	$e = -1.14$
EDMA:	$Q = 0.88$	$e = 0.24$

These values in conjunction with the appropriate equations[6] show the existence of a compositional drift in the terpolymer, which is very similar in form to that found for the HEMA/VP/EDMA system[6]. It should be noted that, because the calculations involves mole fractions rather than weight fractions of the monomers in feed and terpolymer, due allowance must be made for the two double bonds in each molecule of EDMA. The drift is illustrated in *Figure 1* for the terpolymer of feed composition MMA30/VP70/EDMA0.5. The interesting feature of this plot is that the MMA and EDMA originally in the feed are totally consumed when $\theta = 0.63$ (where θ is the fractional conversion of monomers). Thereon at higher conversions the product obtained is almost pure PVP. At $\theta = 1.0$, i.e. at complete conversion, the polymer is predicted to comprise crosslinked MMA/VP copolymer (relatively rich in MMA and EDMA with respect to the initial feed) and a considerable quantity of PVP. *Figure 2* shows the instantaneous mole fractions F_i of MMA ($i = 1$) and EDMA ($i = 3$) in the terpolymer as $F_i \rightarrow 0$ for four different feed compositions in which the concentrations of MMA and VP are varied but that of EDMA is maintained constant. The plots show the overall conversion at which MMA and EDMA are completely incorporated into the terpolymer, and hence indicate equivalently also the quantity of PVP generated in the later stages of conversion. As the quantity of MMA in the initial feed is increased from 15 to 75 wt% (*Figures 2a–2d*), the conversion at which $F_1 = 0$ and $F_3 = 0$ becomes greater, thereby reducing the quantity of PVP produced in the final stages of polymerization.

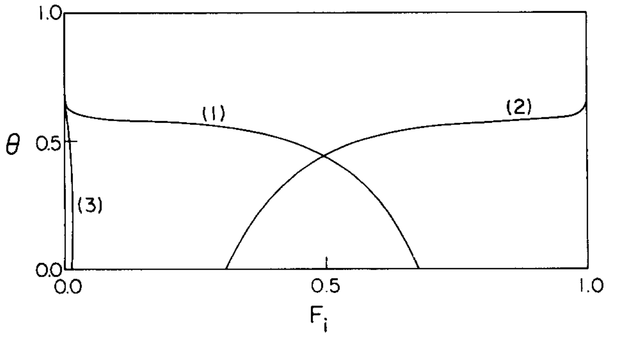

Figure 1 Computed theoretical plots of fractional conversion (θ) of monomers vs. instantaneous mole fraction (F_i) of (1) MMA ($i = 1$), (2) VP ($i = 2$) and (3) EDMA ($i = 3$) in the terpolymer of initial weight feed composition MMA30/VP70/EDMA0.5

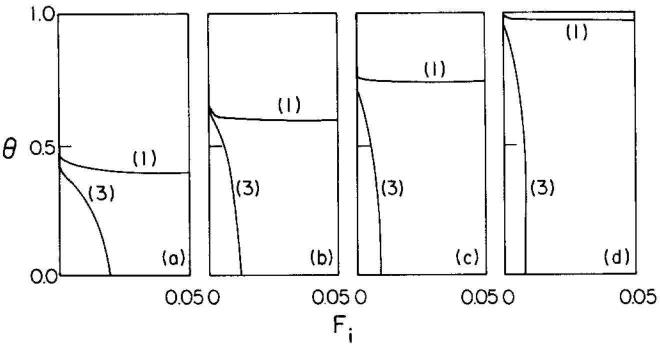

Figure 2 Computed theoretical plots of fractional conversion (θ) of monomers vs. instantaneous mole fraction (F_i) of (1) MMA ($i = 1$) and (3) EDMA ($i = 3$) over the interval $F_i = 0$–0.05 for the terpolymerization of initial feed mixtures (a) MMA15/VP85/EDMA0.5, (b) MMA30/VP70/EDMA0.5, (c) MMA45/VP55/EDMA0.5 and (d) MMA75/VP25/EDMA0.5

The quantity of PVP present in the polymer may be identified with the sol fraction obtained on swelling in water. The absence of a sol fraction for gels swollen in dioxane provides confirmatory evidence for this assertion. As indicated in an earlier section, dioxane is a non-solvent for PVP and therefore it is incapable of effecting its removal. In contrast, dioxane is a good solvent for PMMA, so that the absence of any extractable material confirms that MMA is completely incorporated into the network structure, as predicted by the treatment of terpolymer compositional drift. Thus, at equilibrium swelling, the organogels differ fundamentally from the hydrogels in the respect that the latter consist mainly of crosslinked copolymer, which is richer in MMA than the initial feed composition would suggest. Some of the gels swollen in dioxane also contain a significant proportion of uncrosslinked (but unextractable) PVP, which may affect the properties subsequently exhibited by them.

For MMA/VP gels prepared in the absence of EDMA, the loss of coherent physical structure on swelling in dioxane suggests that these gels are only lightly chemically crosslinked. When these same xerogels are swollen in water, they owe their structure to physical, hydrophobic, intermolecular interactions, which remain intact on swelling. (In this connection not only is water a non-solvent for PMA but it is also a thermodynamically poor one for PVP; large values of the interaction parameter χ for MMA/VP xerogels swollen in water are given later in the text.) For hydrogel samples crosslinked with EDMA there is a smooth decrease in W_1 with increasing content of MMA (*Table 2*). This contrasts markedly with the situation in dioxane (*Table 3*), for which the increase in W_1 with increasing MMA content is followed by a region ($\sim$45–85 wt% MMA) of fairly constant swelling values and then a slight fall in W_1 at the highest content of MMA (95 wt%). Because samples of even higher MMA content were not prepared or studied, it is not possible to confirm if this tendency for a final fall in W_1 is a real one. The solubility parameters δ ($\mathrm{kJ^{1/2}\,dm^{-3/2}}$) in the literature are 20.5 for dioxane and 18.4–19.4 for PMMA. From the density of PVP and molar attraction contributions we have calculated δ for this polymer to be 20.7 or 21.0 depending on whether the attraction constants of Small[22] and Hoy[23] respectively are adopted. Thus the solubility parameters of the swelling medium and copolymers are of a similar magnitude and W_1 accordingly undergoes little significant change over quite a wide range of copolymer composition. Nonetheless, despite the uncertainty in δ values, δ(PVP) > δ(dioxane) > δ(PMMA) and maximum swelling would be anticipated for a particular copolymer composition for which δ(copolymer) = δ(dioxane). The shallowness of the curve of W_1 vs. copolymer composition (according to data of *Table 3*) precludes any accurate location of this maximum swelling.

Effect of temperature on swelling

To examine the influence of temperature in swelling for hydrogels, two samples of moderately high water content were selected, viz. MMA15/VP85/EDMA1 and MMA30/VP70/EDMA1. For these, increases in ϕ_2 of 70% and 41% respectively were measured when the temperature was raised from 278 to 343 K. Kuriaki and Harata[24] have similarly noted exothermic swelling within the range 273–323 K for MMA/VP hydrogels. For organogels, swelling in dioxane was examined for three compositions, viz. MMA15/VP85/EDMA1, MMA45/VP55/EDMA1 and MMA85/VP15/EDMA1. Decreases in ϕ_2 of 46%, 19% and 18% respectively were obtained on raising the temperature from 288 to 334 K. Breitenbach[18] reported that swelling for pure crosslinked PVP in dioxane was also endothermic; over the interval 293–324 K, the percentage decrease in ϕ_2 per degree increase in temperature was slightly greater than the corresponding decrease of 1.0% per degree for the organogel of highest VP content in the present studies, MMA15/VP85/EDMA1.

Uniaxial compression

The use of compression–strain measurements to derive network parameters has been described by us in detail earlier[2]. Densities[25] of the swelling media at different temperatures T (K) were employed to give the following expressions for molar volumes V_1 (dm^3 mol^{-1}):

water: $V_1 = 18.05 \times 10^{-3} + 3.6 \times 10^{-6}(T-298)$
dioxane: $V_1 = 85.8 \times 10^{-3} + 95.5 \times 10^{-6}(T-298)$

Young's moduli (E) of the gels were obtained as the slopes of linear plots of stress vs. strain, where the stress is the applied force per unit area of swollen gel. Values of the effective crosslink density (ν_e) were derived from the slopes of linear plots of stress (τ) vs. $(\lambda - \lambda^{-2})$ according to equation (3):

$$\begin{aligned} \tau &= G(\lambda - \lambda^{-2}) \\ G &= RT\nu_e\phi_2^{-1/3} \end{aligned} \qquad (3)$$

in which τ denotes the applied force per unit area of dry xerogel, λ is the ratio of the deformed length to the initial undeformed length of swollen pellet and RT has its usual meaning.

Examples of the plots used to obtain ν_e are not given here, since they were of similar form to those shown in previous papers[2,26]. The densities of the xerogels were determined from their weights and volumes, the latter being obtained micrometrically. The molar mass per crosslink M_c equals the ratio of density to ν_e. The polymer–swelling medium interaction parameter (χ) was calculated from equation (4), in which f is the functionality of crosslinker (for EDMA, $f = 4$):

$$\ln(1-\phi_2) + \phi_2 + \chi\phi_2^2 + \nu_e V_1(\phi_2^{1/3} - 2\phi_2 f^{-1}) = 0 \quad (4)$$

The value of ϕ_2 is the most dominant factor in the calculation of χ from equation (4) and hence, as seen from equation (2), the values of D_0 and D assume prime importance. Previous comment has been made on assessment of precision[4] and accuracy[2], which are both considered satisfactory. However, it is difficult to assign an overall value to the uncertainty in ϕ_2 (and hence in χ), because this is a quantity that increases with decrease in D and thus with increase in ϕ_2. For unfavourable cases of low swelling the uncertainty in ϕ_2 is estimated to be ~4%. Isotropic swelling was verified by measuring not only the diameters of dry and swollen discs but also their thicknesses and the lengths of pellets. In the very few instances wherein swelling was not isotropic (possibly on account of incomplete annealing of xerogel rods), the samples and data relating to them were discarded.

For the hydrogels, the values of E, ν_e, M_c and χ are listed in *Table 4*. Because of the increasingly glassy nature of the hydrogels with increasing content of MMA, no mechanical measurements could be made on samples of very high MMA content; the range covered was 15–60 wt% MMA in xerogel. Increasing content of MMA produces enhanced hydrophobic bonding and consequently both the effective crosslink density and Young's modulus increase. The efficiency of chemical crosslinking also may be expected to increase at high MMA contents, since the compositional heterogeneity, with respect to the EDMA component, diminishes. This is a consequence of the terpolymerization compositional drift referred to earlier in the text. However, with regard to elastic behaviour, the dominant factor is considered to be the increasing hydrophobic, physical interaction among the MMA units in the chains, which occurs eventually to such an extent that water is unable to penetrate sufficiently to allow elastic behaviour. Yokota *et al.*[27] employed a different experimental approach (^{13}C n.m.r.) to study VP/MMA xerogels swollen separately in water and in chloroform. The structure proposed from their analysis was one in which VP and MMA constitute separate domains within the gel and, specifically with regard to the hydrogels, it was suggested that the MMA-rich domains might contain a rigid disordered crystalline region that contributes to effective crosslinking. This analysis, which predicts a structure of a blend-type system having PVP dispersed within a MMA-rich copolymer matrix, lies in full accord with the analysis proposed in the present work. Here the same structure is predicted as a consequence of compositional drift, and hydrophobic bonding is shown to make a significant contribution to the high modulus or rigidity of the gel. Starodubstev *et al.*[28] have reported that the tensile strength and elastic

Table 4 Network parameters and polymer–water interaction parameters for MMA/VP hydrogels of different composition prepared in the presence of a fixed concentration of crosslinker

Sample	E (MN m^{-2})	ν_e (mol dm^{-3})	M_c (kg mol^{-1})	χ
MMA15/VP85/EDMA1	0.15	0.004	32.4	0.544
MMA30/VP70/EDMA1	1.23	0.205	5.9	0.634
MMA45/VP55/EDMA1	6.92	1.09	1.1	0.771
MMA60/VP40/EDMA1	13.1	2.04	0.6	1.10

the content of VP is increased in both MMA/VP and HEMA/VP hydrogels crosslinked with a small fixed concentration of EDMA. No meaningful analysis of the variation of χ with copolymer composition is warranted for the hydrogels because of the small number of samples in *Table 4*. However, curve fitting indicates that $\chi \sim 0.48$–0.52 at zero content of MMA, which agrees well with the value obtained previously for crosslinked PVP hydrogels[8].

For some VP-containing copolymeric hydrogels (*Table 4* of the present paper and HEMA/VP/EDMA hydrogels in a previous paper[6]) the values of ν_e are observed to increase as χ increases. Thus, as the solvent becomes poorer, physical interactions assume more importance and contribute to the effective crosslink density. However, in contrast, from the present compression–strain measurements on organogels (*Table 5*) it is seen that the values of ν_e increase as χ decreases. It will be recalled that decrease in χ means an increase in thermodynamic goodness of solvent, which parallels an increase in content of MMA. In dioxane, therefore, physical interaction between the chains does not contribute to ν_e. The same copolymers prepared in the absence of EDMA were found to lose their coherent structure. Hence the increase in ν_e must be a direct consequence of chemical crosslinking. For each of the seven samples in dioxane (*Table 5*) the EDMA content is constant (1 wt%) and only the ratio of MMA to VP is varied. Calculated terpolymerization compositional drift (*Figure 2*) demonstrates that the higher the MMA content in the initial feed the lower is the quantity of PVP homopolymer generated in the final stages of polymerization, and at the same time a reduced compositional drift of EDMA is evident.

With regard to the effect of temperature (T) on ν_e, the latter can be assessed from compression–strain measurements and determination of ϕ_2 at each T (see equation (3)). The effect of T on ϕ_2 for hydrogels and organogels of different compositions has been noted earlier in the text. Over the range $T = 278$–343 K, the compression modulus G was also measured. The derived values of ν_e displayed some scatter but no discernible trend to either increase or decrease with T. Consequently, the value of ν_e measured at 294 K was adopted at all temperatures. For MMA/VP hydrogels Kuriaki and Harata[24] found that the retractive force at small strains ($\leqslant 50\%$) increased with increase in T, but for larger strains a minimum in the refractive force occurred at ~ 343 K. This behaviour is at variance with the independence of ν_e on T observed in the present study, for which the measurements were restricted to very low strains ($\leqslant 7\%$). However, any change in elastic modulus with T may well be insignificant at such low strains or, if the change is a finite but small one, difficult to detect by the experimental techniques used here.

Table 5 Network parameters and polymer–dioxane interaction parameters for MMA/VP organogels of different composition prepared in the presence of a fixed concentration of crosslinker

Sample	E (MN m^{-2})	ν_e (mol dm^{-3})	M_c (kg mol^{-1})	χ
MMA15/VP85/EDMA1	0.15	0.002	62.4	1.02
MMA30/VP70/EDMA1	0.58	0.009	12.9	0.615
MMA45/VP55/EDMA1	0.66	0.116	10.4	0.581
MMA60/VP40/EDMA1	0.73	0.136	8.9	0.543
MMA75/VP25/EDMA1	0.96	0.176	6.8	0.524
MMA85/VP15/EDMA1	1.01	0.191	6.2	0.511
MMA95/VP5/EDMA1	1.18	0.217	5.5	0.520

Table 6 Coefficients in polynomial ($\chi = a_0 + a_1 T + a_2 T^2$) of polymer–solvent interaction parameter as a function of temperature for MMA/VP hydrogels and organogels of different composition prepared in the presence of a fixed concentration of crosslinker

Sample	Swelling medium	a_0	$-a_1 \times 10^3$ (K^{-1})	$a_2 \times 10^5$ (K^{-2})
MMA15/VP85/EDMA1	Water	1.20	4.78	88.2
MMA30/VP70/EDMA1	Water	1.29	5.75	1.19
MMA15/VP85/EDMA1	Dioxane	19.1	10.8	0.16
MMA45/VP55/EDMA1	Dioxane	2.83	0.13	1.89
MMA85/VP15/EDMA1	Dioxane	2.95	0.14	2.03

Thermodynamic aspects

The plots of χ vs. T given in *Figure 3* for the hydrogel MMA30/VP70/EDMA1 and in *Figure 4* for the organogel MMA45/VP55/EDMA1 are similar in general form to those obtained for other xerogel compositions in water and dioxane, respectively. The dependences of χ on T (K) could be fitted well to polynomials of the second degree, viz.:

$$\chi = a_0 + a_1 T + a_2 T^2 \tag{5}$$

The values of the coefficients a_0, a_1 and a_2 for two different hydrogels and three different organogels are listed in *Table 6*.

The total interaction parameter χ is the sum of its enthalpic (χ_H) and entropic (χ_S) contributions, which are given by:

$$\chi_H = -T(\mathrm{d}\chi/\mathrm{d}T) \tag{6}$$

$$\chi_S = \chi + T(\mathrm{d}\chi/\mathrm{d}T) \tag{7}$$

Because $\mathrm{d}\chi/\mathrm{d}T = a_1 + 2a_2T$ (cf. equation (5)), the enthalpic and entropic contributions are readily calculated from the coefficients tabulated. Moreover, as described previously[2], the dimensionless parameters can be used to calculate the actual partial molar enthalpy ($\Delta\bar{H}_1$) and partial molar entropy ($\Delta\bar{S}_1$) of dilution at specific temperatures, viz.:

$$\Delta\bar{H}_1 = RT\phi_2^2\chi_H \tag{8}$$

$$\Delta\bar{S}_1 = R\phi_2(0.50 - \chi_S) \tag{9}$$

The plots of χ_H and χ_S vs. T together with the corresponding plot for the variation of χ with T are shown in *Figure 3*, which relates to hydrogels. The forms of these curves are similar to those for hydrogels of crosslinked PVP[8] and of crosslinked VP/n-butyl acrylate copolymers[2]. For these systems and the present one χ_H is negative in sign and increases in magnitude with increasing T. Because ϕ_2 increases with rise in T, it follows also (cf. equation (8)) that $\Delta\bar{H}_1$ is negative and increases in magnitude with T. The numerically largest value of $\Delta\bar{H}_1$ at a particular T obtains in the VP/n-butyl acrylate system; an intermediate one occurs in the present copolymers; and the numerically smallest enthalpy of dilution obtains for crosslinked PVP, the swelling of which is almost athermal. The same sequence holds for the numerical values of $\Delta\bar{S}_1$ and these negative values (cf. equation (9)) also increase in magnitude with T. A decrease in entropy is postulated to arise from structuring of water. From sorption, permeation and d.s.c. measurements on uncrosslinked copolymeric MMA/VP membranes, Takizawa *et al.*[29] concluded that the water present consists of water that is tightly bound on the polar VP residues and also water that is associated in

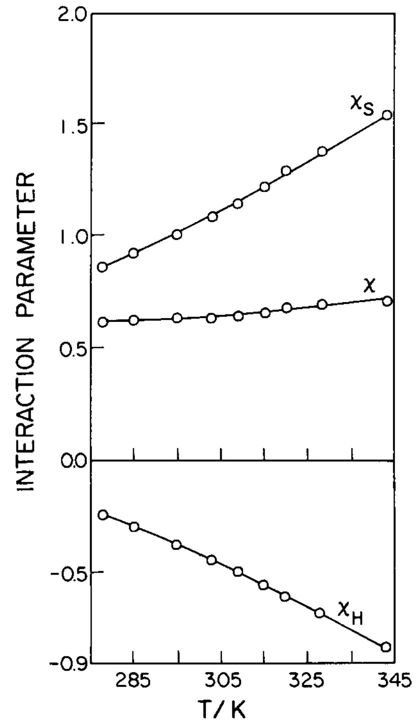

Figure 3 Variation of the interaction parameters χ, χ_H and χ_S with temperature for the terpolymeric xerogel MMA30/VP70/EDMA1 swollen in water

the vicinity of hydrophobic MMA moieties. For different VP-containing crosslinked copolymeric hydrogels we have postulated that the reduction in swelling with increase in T is due to the loss of mainly free water, thus leaving a higher proportion of bound (or structured) water in the hydrogel at lower values of W_1. It was confirmed via d.s.c.[30] that the proportion of non-freezing water increases with increasing hydrophobic interaction or crosslinking, both of which are accompanied by reduced values of W_1. The values of χ decrease towards a value of 0.50 as the temperature is lowered, and the deswelling of these hydrogels may be considered to be analogous to the behaviour of linear polymers in solution, which exhibit a lower critical solution temperature (*LCST*). This phenomenon is due in part to hydrogen bonding between polymer and solvent, which enhances solubility. As such bonds are thermally labile, the number of them is reduced on raising T.

In dioxane the thermodynamic aspects are entirely different. Thus (see *Figure 4*) χ decreases towards a value of 0.50 on raising the temperature and the values of χ_H are positive, as are also the derived values of $\Delta\bar{H}_1$, which decrease with temperature. Although χ_S exhibits negative values in the low-temperature region, positive values of the entropy of dilution prevail at all the temperatures. Swelling is thus endothermic and enhanced swelling at elevated temperatures for these organogels is analogous to normal upper critical solution temperature (*UCST*) behaviour exhibited by solutions of linear polymers such as PMMA itself[31].

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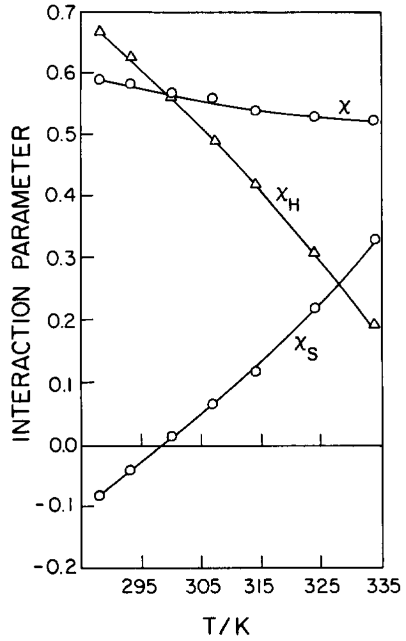

Figure 4 Variation of the interaction parameters χ, χ_H and χ_S with temperature for the terpolymeric xerogel MMA45/VP55/EDMA1 swollen in dioxane

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