Highly swollen hydrogels: Vinyl pyrrolidone copolymers*

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The objective was to prepare hydrogels which, though highly swollen, would have sufficient strength to allow crosslinked poly(vinyl pyrrolidone). Inclusion of tetraethyleneglycol dimethacrylate resulted in only a low physical (hydrophobic) crosslinks. The most successful results were achieved by gamma-irradiation of aqueous solutions of vinyl pyrrolidone plus methyl acrylate. Glass transitions of xerogels were characterized by differential scanning calorimetry. It was deduced that the hydrophobic comonomer (methyl acrylate or methyl methacrylate) is concentrated in microphase domains embedded in a matrix of almost pure crosslinked poly(vinyl pyrrolidone). Inclusion of tetraethylene glycol dimethacrylate resulted in only a low crosslinking efficiency but, nevertheless, had a marked influence in preventing phase separation, which gives hydrogels of improved clarity and mechanical strength.

(Keywords: hydrogels; poly(vinyl pyrrolidone) copolymers; differential scanning calorimetry; glass transition temperature; phase separation; chemical and physical crosslinks; hydrophobic crosslinks; mechanical strength)

INTRODUCTION

Applications of hydrogels are usually limited to materials with a water content up to about 80%[1-2]. If the water content is increased further, the decline in mechanical properties is unacceptable for most purposes. In a recent review of hydrogels, Wichterle emphasized how improved mechanical properties can be achieved by control of chemical (covalent) and physical (especially hydrophobic) crosslinking. It was pointed out that small clusters of hydrophobic groups in a predominantly hydrophilic network may serve to increase load bearing yet with avoidance of the embrittlement caused by carbon–carbon crosslinks[4]. Hydrophobic groups have been introduced by copolymerization of various hydrophobic monomers with hydrophilic monomers such as *N*,*N*-diethylacrylamide[5], vinyl pyrrolidone[6,7] and 2-hydroxyethyl methacrylate[8,9]. There are advantages in copolymerizing in an aqueous solution, although this may result in phase separation unless use is made of a solvent, which, subsequently, must be removed[5,8,9].

The purpose of the present work was, dispensing with any solvent, to make hydrogels which are much more highly swollen than those prepared previously and yet which have sufficient strength to be handled without collapse or tearing. In the past highly swollen hydrogels have been reported for poly(vinyl pyrrolidone) networks prepared both by copolymerization of vinyl pyrrolidone with diallyl[10,11] and by radiation crosslinking of aqueous solutions of poly(vinyl pyrrolidone)[12]. In preliminary experiments, highly swollen gels prepared by the latter technique were found to have unacceptable handling properties. Therefore attention was concentrated on hydrogels prepared by gamma-irradiation of aqueous mixtures of vinyl pyrrolidone with various hydrophobic monomers. The data to be presented here were obtained using methyl methacrylate and methyl acrylate. Previously vinyl pyrrolidone/methyl methacrylate copolymers, prepared by bulk polymerization, were swollen with water and evaluated as hydrogels for use as soft contact lenses[6,7].

EXPERIMENTAL

Inhibitors were removed either by vacuum distillation or by shaking with Amberlite IRA45 (Polysciences, Warrington, PA) from the following monomers: *N*-vinyl pyrrolidone, VP (Aldrich, Milwaukee, WI), methyl methacrylate, MMA, methyl acrylate, MA, and tetraethylene glycol dimethacrylate, TEGDM (Polysciences).

Purified monomers were mixed with distilled water to give clear one-phase solutions which were poured into moulds made from two vertical plane sheets of glass separated by a 0.2 cm rubber gasket. The glass had been preheated with a poly(tetrafluoroethylene) spray release agent (6075, Crown Industries). After flushing out air with nitrogen, the solutions were exposed to ^{60}Co gamma-rays until polymerization was complete: 20 h at 0.1 Mrad/h.

Hydrogels are sometimes difficult to separate from moulds[13] and this problem was compounded because poly(vinyl pyrrolidone) (PVP) adheres strongly to glass. Nevertheless, complete sheets (13 cm × 20 cm) could be removed even in the case of products made with large proportions of monomer. However, in bulk polymeri-

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* 1-(2-Oxo-1-pyrrolidinyl)ethylene

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zation, with 100% monomer, the rigid products could be removed only in fragments. Some of the hydrogels prepared as above (as polymerized) were dried in air (dried) while others were allowed to swell in water for several days (swollen).

Four dumbell specimens (gauge length = 2.54 cm; width = 0.5 cm) were cut from each sheet and load–extension traces recorded using an Instron machine at a cross-head rate of 10 cm/min. The tensile strength at break was calculated using the original (undeformed) cross-section of the specimen (4 specimens).

A strip of swollen hydrogel was immersed in water so as to cover a face of cuvete perpendicular to the instrument beam. Transmission (I), at $\lambda = 600$ nm, was compared with the value for the cell filled with water alone (I_0) to obtain the optical density $\log_{10}(I_0/I)$).

Fine cuttings (2–4 mg) of dried samples were scanned, in N_2 at 20°C/min, from room temperature to 200°C (DuPont 990 Thermal Analyzer, differential scanning calorimetry, d.s.c. mode, Wilmington, DE). Consecutive runs were made after quenching with liquid nitrogen. For some experiments samples were first purified by prolonged dialysis (many weeks) against distilled water, using dialysis tubes with a cut off at 6000–8000 D. More details about d.s.c. procedures are given in a previous report on PVP[14].

RESULTS

As-polymerized hydrogels approached equilibrium uptake of water after immersion for just a few days in water. The uptake of water was referred to the weight of polymer (xerogel) which remained after drying (*Figure 1*). Some xerogels prepared from aqueous solutions of VP alone took up almost 3000% water and yet retained their geometry in water, i.e. without collapsing into a jelly. However, such highly swollen gels were fragile and difficult to handle. Inclusion of a hydrophobic monomer reduced swelling and provided hydrogels which could be handled without tearing. Generally, swelling was smaller the larger the proportion of monomer in the aqueous reaction mixture.

The influence of TEGDM in reducing swelling appears to be small (*Figure 1*). An estimate of the expected influence can be obtained from Flory's swelling approximation (equation (1)) for highly swollen networks: V_0, volume of unswollen network; χ, polymer–solvent interaction constant; V, molar volume of solvent[15]. As a working hypothesis, it will be assumed that the number of elastically effective network chains, ν, is proportional to the concentration of crosslinker, C, so that two concentrations, C_1 and C_2, may be compared using equation (2). Then, with the approximation that the other terms[15] in equation (1) remain constant, the influence of C_1 and C_2 on corresponding volume swelling ratios, q_1 and q_2, is given by equation (3).

$$q^{5/3} = \left(\frac{V_0}{\nu}\right)(0.5 - \chi)V^{-1} \tag{1}$$

$$\frac{\nu_2}{\nu_1} = \frac{C_2}{C_1} \tag{2}$$

$$\frac{q_1}{q_2} = \left(\frac{\nu_2}{\nu_1}\right)^{3/5} = \left(\frac{C_2}{C_1}\right)^{3/5} \tag{3}$$

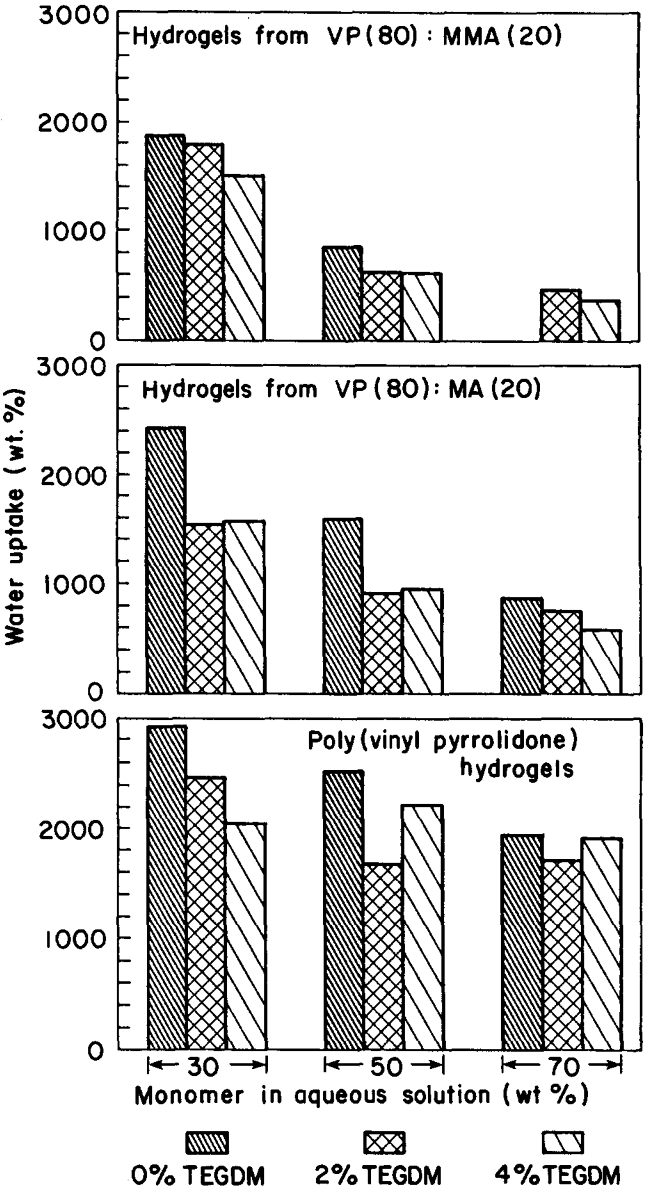

Figure 1 Water uptake of swollen hydrogels

From consideration of the results in *Figure 1* the small amount of crosslinking caused by irradiation may be neglected. The result then obtained is that halving the concentration of TEGDM should result in $q_1/q_2 = 1.5$. The experimental data are closer to $q_1/q_2 = 1.0$, which corresponds to a null effect (*Table 1*).

PVP hydrogels have only a faint yellow coloration and are transparent. Inclusion of MA as comonomer gives slightly hazy products while MMA gives ones which are white and opaque. The transparency of the copolymers can be increased by inclusion of TEGDM. The influence of TEGDM on optical density is particularly striking in the case of VP/MMA copolymers (*Figure 2*). However, at the lowest monomer feed (30%), opaque products were obtained even when TEGDM was included.

Load–extension curves of hydrogels all showed evidence of yielding. Yielding was most pronounced in as-polymerized specimens. Generally, the yield stress was increased by inclusion of TEGDM (*Figure 3*).

Ultimate tensile properties are given in *Table 2* for VP/MA copolymers of just one composition, i.e. with 20% MA, but made with variable feeds of water and TEGDM.

Table 1 Influence of changes in concentration of TEGDM on swelling ratios for VP/MA hydrogels

TEGDM in monomer (%)	*q* values % monomer in aqueous solution 30	 50	 70
0	30	20.3	11.9
2	19.2	12.1	10.1
4	19.4	12.4	8.0
$\frac{q(2\%)}{q(4\%)}$	0.99	0.98	1.26

q Values calculated using $\rho = 1.2\ \mathrm{g\ cm^{-3}}$ for density of polymer

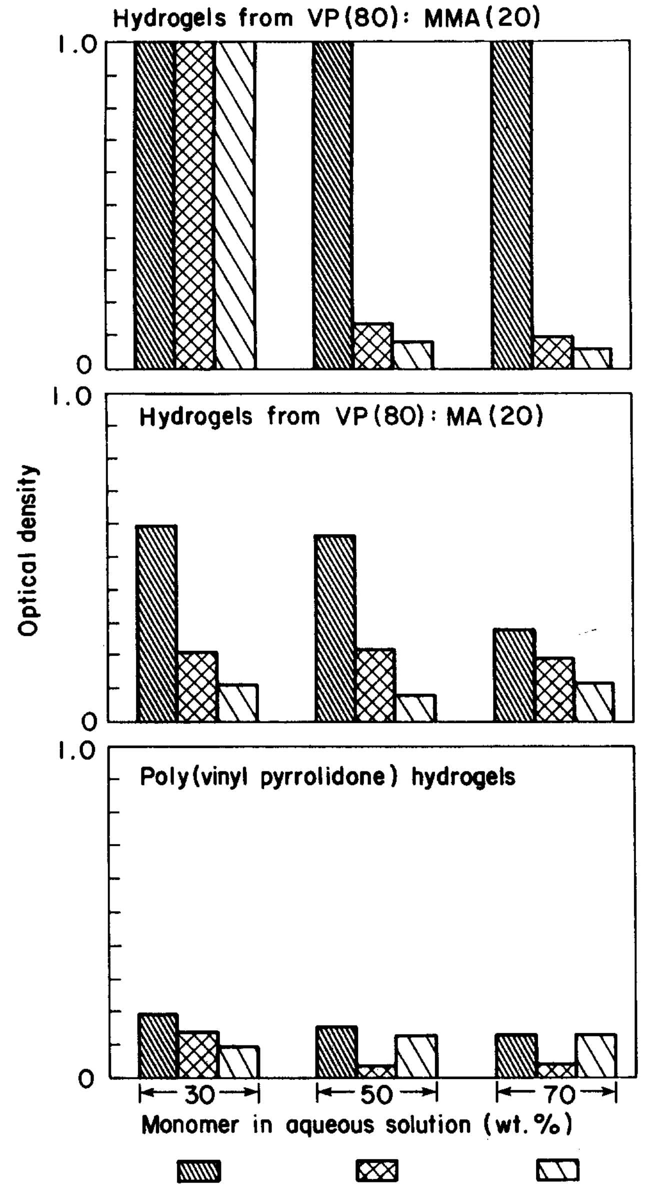

Figure 2 Optical density of swollen hydrogels

An interesting trend is discerned when strength values are adjusted from experimental values of S to S_0 on the assumption that the load is not borne by water but only by the volume fraction of polymer, V_p, according to equation (4)[5]:

$$S_0 = S V_p^{-2/3} \tag{4}$$

If equation (4) were adequate then S_0 should be independent of water content. Instead, S_0 decreases with increasing water content for both swollen and, much more markedly, for as-polymerized hydrogels (*Figure 4*). It will be noted that in *Figure 4* no distinction has been made concerning the feed of TEGDM.

Inclusion of TEGDM tends to reduce the elongation at break of hydrogels. This point is elaborated by a plot of data making an allowance for dilatation by water according to equation (5). This form of correction was introduced previously for analysis of swollen rubber networks[16,17].

$$\lambda = \lambda_0 V_p^{1/3} \tag{5}$$

λ and λ_0 are extension ratios at break for swollen and dry polymers, respectively. Values of λ were calculated from *Table 2* (% Elongation at break $\div 100 + 1$); values of λ_0 are hypothetical for the present hydrogels because vitrification occurs as V_p approaches unity. In *Figure 5* two lines have been drawn which distinguish between data for TEGDM = 0 and TEGDM = 2% or 4% (jointly). It will be noted that three compositions which include TEGDM lie well above the line drawn for the other crosslinked compositions. They had low monomer compositions in the aqueous feed (2 of only 20%, and 1 of 30%).

Dried copolymers have an elongation at break of 10–52% and a strength of 19–36 MPa. These results seem reasonable for polymers which, though well below the glass transition temperature, are plasticized by a few per cent of tenaciously held water (see below). Inclusion of TEGDM generally raises strength, which is in contrast to the negligible influence of EGDM on the strength of copolymers with MMA[18].

Figures 6 and *7* show d.s.c. runs for copolymers made by *bulk polymerization, i.e. without water.* A first run always exhibits a broad endotherm near 120°C, which is not observed in subsequent runs on the same sample. Similar results were reported in previous work on PVP and

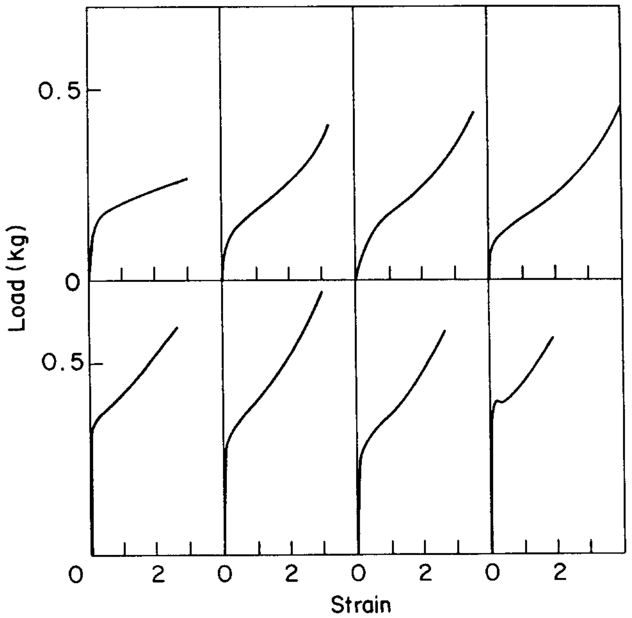

Figure 3 Load–extension traces of VP (80): MA (20) hydrogels, as polymerized with monomer (30): water (70). Key: without TEGDM; top 4 traces. With 2% TEGDM; bottom 4 traces. 1N = 0.102 kg

Table 2 Tensile properties at break of copolymers of VP (80%): MA (20%)

Reactant composition[a]		Properties of polymeric product				
TEGDM (%)	Monomer (%)	Condition	Water uptake (%)	Elongation (%)	Stress (kg cm^{-2})	Work (10^6 dyne cm)
0	30	Dried	–	23	187	1.34
		As polymerized	230	432	0.32	0.32
		Swollen	2430	198	0.08	0.04
0	50	Dried	–	33	256	4.41
		As polymerized	100	415	1.29	1.15
		Swollen	1590	282	0.27	0.18
0	70	Dried	–	25	279	4.88
		As polymerized	40	694	5.35	3.63
		Swollen	860	182	0.46	0.18
2.0	20	Dried	–	17	207	0.40
		As polymerized	400	396	0.27	0.11
		Swollen	2100	165	0.13	0.04
2.0	30	Dried	–	10	251	0.86
		As polymerized	230	237	0.91	0.30
		Swollen	1530	61	0.098	0.04
2.0	50	Dried	–	21	308	2.57
		As polymerized	100	210	1.69	0.46
		Swollen	910	99	0.52	0.03
2.0	70	Dried	–	17	360	3.13
		As polymerized	40	245	7.05	2.96
		Swollen	750	100	0.89	0.17
4.0	30	Dried	–	23	296	2.18
		As polymerized	230	246	0.65	0.20
		Swollen	1570	246	0.51	0.17
4.0	50	Dried	–	52	324	4.00
		As polymerized	100	314	2.98	1.12
		Swollen	960	77	0.55	0.07
4.0	70	Dried	0	18	240	3.74
		As polymerized	40	212	3.70	0.85
		Swollen	580	47	0.738	0.06

[a] TEGDM is expressed as a percentage of the total monomer of VP (80%) plus MA (20%). The monomer mixture is expressed as a percentage of the aqueous mixture. 1 MPa = 10.1884 kg cm^{-2}

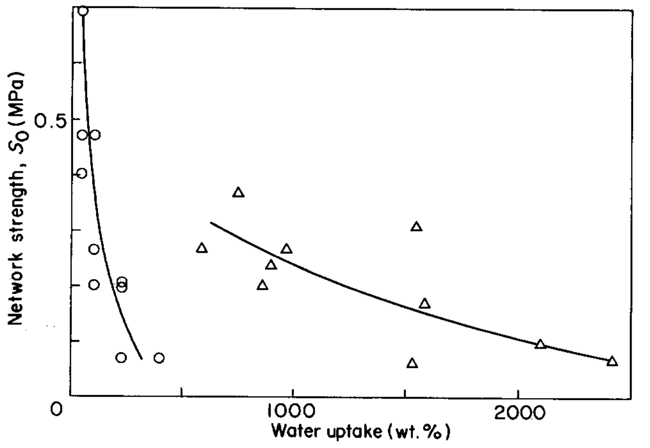

Figure 4 Network strength (S_0) *versus* water uptake. Calculated from *Table 2*. Key: ○, as polymerized; △, swollen

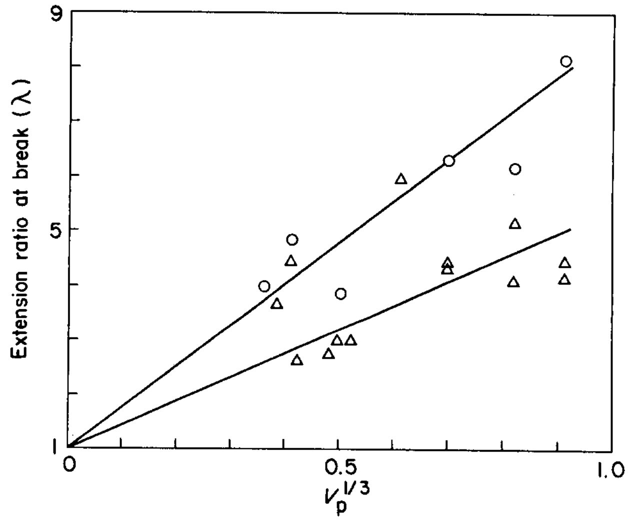

Figure 5 Extension ratio at break (λ) *versus* $V_p^{1/3}$. V_p is the volume fraction of polymer in the hydrogel (either as polymerized or swollen; from *Table 2* using $\rho = 1.2\,g\,cm^{-3}$ for the density of polymer). Key: ○, TEGDM = 0; △, TEGDM = 2 or 4%

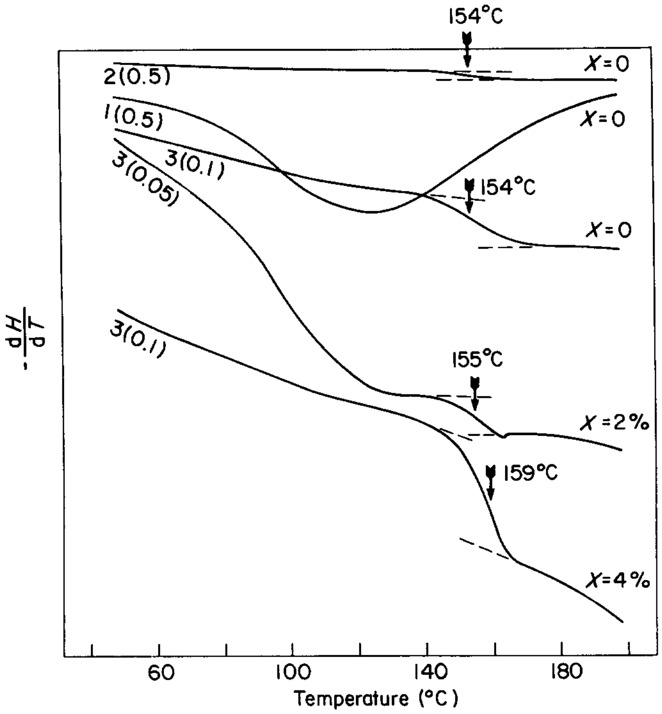

Figure 6 Runs (d.s.c.) on specimens made from VP (80): MMA (20), i.e. without water. The number of each run is followed by the sensitivity in parentheses (maximum sensitivity = 0.05 unit). % TEGDM is designated by X

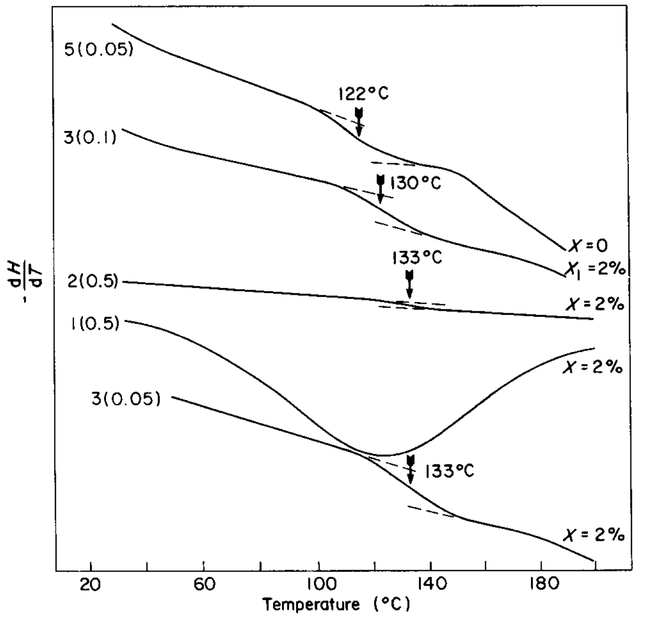

Figure 7 Runs (d.s.c.) on specimens made from VP (80): MA (20), i.e. without water. A run on a second specimen is designated by X_1

shown to be due to the presence, before run 1, of a few per cent water[14]. Such results were observed, too, in all the copolymers examined in the present work, but in subsequent figures, runs 1 and 2 generally will be omitted and glass transition temperatures defined by later runs made at higher sensitivity. Returning to the case of bulk copolymers, a single glass transition is observed. For the composition VP ($W_1 = 80$) with MMA or MA ($W_2 = 20$) the experimental values, reproducible to within a few degrees, are as follows: T_g (MMA copolymer) = 154°C (*Figure 6*), T_g (MA copolymer) = 122°C (*Figure 7*). Only slightly higher values, of T_g (MMA copolymer) = 161°C and T_g (MA copolymer) = 129°C, were calculated from the copolymer equation (6)[19-21] using the following values for homopolymers: T_{g_1} (PVP) = 453 K[14], T_{g_2} (PMMA) = 373 K[22], and T_{g_2} (PMA) = 276 K[23]. Inclusion of TEGDM slightly elevates experimental values into even closer agreement with calculations from equation (6).

$$\frac{100}{T_g} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \qquad (6)$$

Copolymers prepared from aqueous solutions of both MMA (*Figure 8*) and MA (*Figure 9*) differ from bulk copolymers in exhibiting two glass transitions. The higher transition occurs in the range 172°C–180°C, approaching the limiting value for PVP of high molecular weight reported previously, i.e. $T_g = 180°C$. The lower transition temperature is as follows:

T_g (MMA copolymer) = 132°C–134°C (*Figure 8*)
T_g (MA copolymer) = 103°C–106°C (*Figure 9*)

In each case the experimental value is lower than predicted by equation (6). This discrepancy cannot be due to depression of T_g by any low molecular weight components, such as residual VP, because a similar value is obtained in samples purified by prolonged dialysis (*Figures 8* and *9*).

DISCUSSION

The following copolymerization ratios have been reported for free radical reactions of VP (M_1) with MMA (M_2) and with MA (M_2):

MMA, at 60°C[24]; $R_1 = 0.005$; $R_2 = 4.7$
MA, at 50°C[25]; $R_1 = 0.041$; $R_2 = 0.27$

Thus, it is to be expected that copolymer formed in the initial stages of polymerization will be greatly enriched in

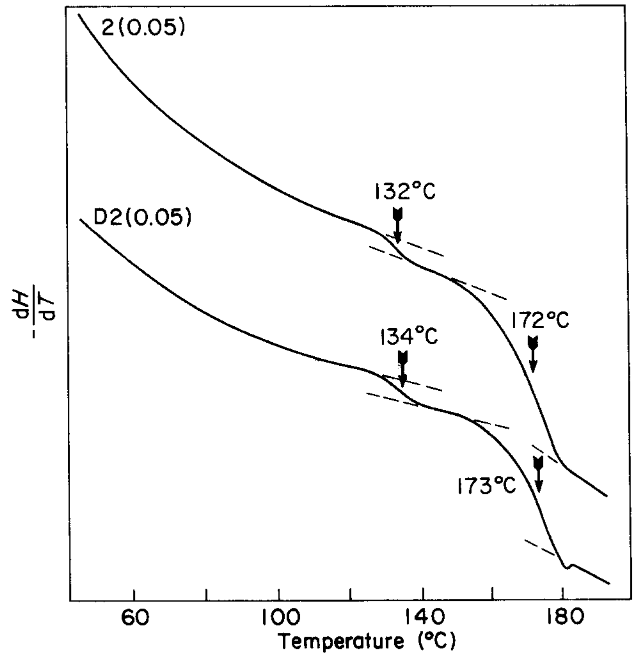

Figure 8 Runs (d.s.c.) on VP (80): MMA (20) xerogels: polymerized with monomer (30): water (70). $X = 0$. Lower curve (D) for a dialysed specimen

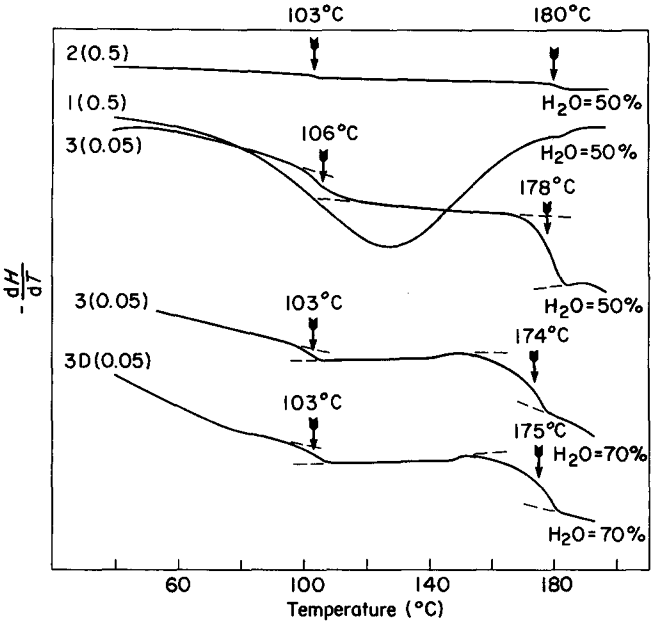

Figure 9 Runs (d.s.c.) on VP (80): MA (20) xerogels. $X=0$. Three consecutive runs are shown for specimens polymerized with monomer (50): water (50). Third runs alone are shown for specimens polymerized with monomer (30): water (70). D designates a dialysed specimen

MMA or in MA. Nevertheless, the observation of a single glass transition, with a T_g close to that predicted by equation (6), indicates complete mixing during bulk polymerization with formation of a single phase (*Figures 6* and *7*).

The locus of polymerization in an aqueous solution is influenced strongly by the water solubility of the reactants and products. MMA and MA are hydrophobic monomers which are sparingly soluble in water[26], while VP is miscible with all the reactants and products[27,28]. In this case there will be a tendency towards microphase separation of domains rich in MMA or MA at the beginning of the reaction. Further polymerization favours formation of a hydrogel matrix composed predominantly of PVP. Consistently xerogels exhibit two glass transition temperatures, one characteristic of almost pure PVP and the other of another phase enriched in either MMA or MA. An estimate of the degree of enrichment can be deduced by substituting experimental values of T_g of 407 K (*Figure 8*) or 376 K (*Figure 9*) in equation (6) to obtain a calculated value of W_1. In both cases the result indicates a copolymer phase with about 50% of either MMA or MA, as compared with a monomer feed containing only 20%.

Factors expected to favour phase separation include comonomer hydrophobicity (MMA > MA) and the proportion of water in the reaction mixture. On the other hand, crosslinking may reduce phase separation by immobilizing hydrophobic domains and thereby preventing their aggregation. The susceptibility of PVP to radiation crosslinking probably helps in this respect. Nevertheless, the further immobilization gained by inclusion in the monomer feed of 2% TEGDM is evident from its influence on optical density (*Figure 2*). But perhaps the single most impressive effect of including TEGDM is the way in which it suppresses the lower (copolymer) glass transition temperature in xerogels prepared from aqueous solutions (*Figure 10*). Presumably use of the crosslinker fixes a gradual change in copolymer composition extending from the nucleus of the hydrophobic domains into the predominantly PVP matrix. Corresponding to this model there would be a continuous range of glass transitions not discernible by the simple d.s.c. analysis used in this work.

In previous work stress–strain properties of some hydrogels were analysed simply by reference to the theory of rubber elasticity, as exemplified in the case of networks made by polymerization of solutions of 2-hydroxyethyl methacrylate[29–31]. However, when this same monomer was copolymerized with various hydrophobic monomers the resulting hydrogels gave more complex stress–strain curves with marked evidence of yielding. These results were 'tentatively explained by the nonhomogenous composition and structure of the copolymers'[5]. The stress–strain curves observed in the present work (*Figure 3*) are similar to those reported in ref. 5 and a similar general explanation is invoked. In more detail this explanation is supported by the arguments given above about phase structure and also is in line with the general comments of Wichterle about the load bearing possibilities of hydrophobic bonds. On his view such bonds occur between sequences of hydrophobic groups rather than between the small groupings characteristic of a random distribution[4]. A possible distinction between these two cases may be made by references to plots of extension at break according to equation (5): c.f. *Figure 5*. In previous studies of the influence of swelling liquids on rubber networks, upturns at high rubber contents were attributed to the effect of intermolecular cohesion[17]. As no such effect is observed in the present rubber-like networks, where hydrophobic bonding is believed to occur, it may be that such bonding has effects (physical crosslinking) which are distinct from ordinary intermolecular cohesion.

In the case of rubber networks, tensile strength goes through a maximum with increasing concentration of chemical crosslinks[32]. An original objective of the present work was to find whether this trend could be observed in hydrogels. From the limited data in *Table 2* it appears that

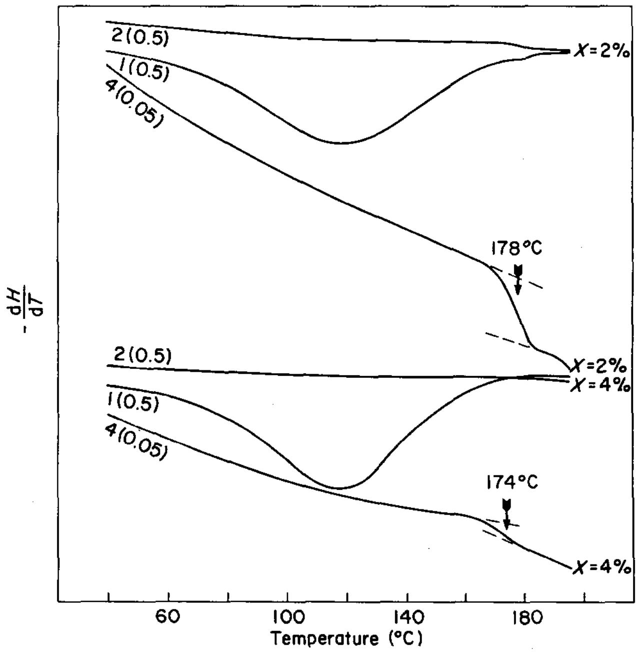

Figure 10 Influence of TEGDM on d.s.c. runs on xerogels. $X=2$. VP (80): MMA (20). Monomer (30): water (70). $X=4$. VP (80): MA (20). Monomer (50): water (50)

inclusion of TEGDM results in a relatively small and erratic increase in strength (c.f. ref. 5). A complicating factor is that the efficiency of potential crosslinking agents, such as TEGDM, is low and difficult to control. A low crosslinking efficiency has been stressed in previous work on other hydrogels and attributed to cyclization reactions which do not contribute to physical crosslinking. In the present system wastage of chemical crosslinking is compounded by their concentration in hydrophobic domains. On this view, the working hypothesis that physical crosslinking is proportional to the concentration of TEGDM, used in the analysis of swelling data (*Table 1*), is invalid for heterogenous systems. Other more refined factors which affect detailed analysis of swelling of hydrogels are of lesser importance[33-35].

The way in which an increase in the amount of water in the reaction system adversely affects properties is shown by its influence on strength (*Figure 4*). In previous work on hydrogels, polymerization in water resulted in inhomogeneous crosslinking and in phase separation with formation of spongy materials[36,37]. As mentioned above crosslinking helps to offset such changes but when the water content is too high, even this remedy fails (*Figure 5*).

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