Swelling Properties of Copolymeric Hydrogels Prepared by Gamma Irradiation

MALCOLM B. HUGLIN and MAT B. ZAKARIA* *Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, England*

Synopsis

Crosslinked xerogels in the form of rods have been prepared to $> 99.9\%$ conversion by the γ-ray initiated copolymerization in vacuo of n-butyl acrylate (BA) with N-vinyl-2-pyrrolidone (VP) in the presence and absence of a crosslinking agent. Thin (about 0.5 mm) disks were swollen in water at 21°C, the final equilibrium swelling being the true water content only for copolymers of high BA content. At low-medium BA content, swelling was accompanied by the release of a small water-soluble fraction, leading to a slightly reduced apparent value for the water content. True water contents could be obtained more rapidly by prior Soxhlet extraction with boiling water. For xerogels containing ⩾ about 75% VP by weight, the resultant hydrogels had water contents ⩾ about 80%. The influences of dose, dose rate copolymer composition, and concentration of crosslinker on the water content, sol fraction, and extension ratio were investigated. A high level of reproducibility in properties of the hydrogels was obtained by numerous replicate experiments. The feasibility of scaling up the preparation to produce long (60 cm) xerogel rods of uniform properties has been demonstrated. For these copolymers, swelling in several common organic solvents generally exceeds that in water.

INTRODUCTION

A xerogel is a crosslinked polymer or copolymer, which is capable of imbibing a considerable quantity of liquid up to swelling equilibrium. With water as swelling agent, the product is termed a hydrogel.[1,2] The final water content is dependent on the chemical composition and also, in the majority of cases, on the crosslinking density. A straightforward means of effecting a range of water contents is by copolymerizing a hydrophobic monomer with a hydrophilic one, an example of the latter being N-vinyl-2-pyrrolidone (VP). The hydrogel of poly-VP itself is of limited applicability because of its inferior mechanical properties. This polymer finds its principal uses in the form of its uncrosslinked, water-soluble homopolymer.[3,4] Copolymerized VP occupies a significant role within the field of hydrogels as biomedical materials, such as soft contact lenses.[5,6]

Previously we have described the preparation of copolymers of VP with n-butyl acrylate (BA) as a comonomer in the presence of 1,1,1-trimethylolpropane trimethacrylate (TPT) as crosslinking agent.[7,8] γ-ray initiation was found to afford a convenient means of effecting 100% conversion at ambient temperature. The optical homogeneity of the resultant xerogels was shown to be dependent on the composition and on the concentration of TPT. The

* Present address: Jabatan Kimia, Universiti Kebangsaan Malaysia, Bangi, Selangor, Malaysia

measurement of dissolved oxygen permeability through the swollen xerogels (i.e., hydrogels) has also been described.[9] The present communication is devoted to aspects of the swelling of these polymers in water with some consideration also to the swelling in other liquids.

Since the copolymerizations in bulk proceeded to 100% conversion, the overall composition of xerogel is the same as that of the monomer feed mixture. Thus the designation BA 20-VP 80 indicates that BA comprises 20% by weight of (BA + VP). Exactly the same contents obtain in a copolymer designated as BA 20-VP 80-TPT 1. However, here TPT is also present and comprises 1% by weight of (BA +VP + TPT).

EXPERIMENTAL

Materials

BA, VP, and TPT, as well as methyl methacrylate (MMA), were purified as described elsewhere.[8] Deionized water was used for swelling. The organic liquids used for subsidiary swelling experiments were of a high-purity grade and were used as received

Preparation of Xerogels

Bulk copolymerization of monomer mixtures in vacuo was effected by γ-irradiation from a 9000-Ci ^{60}Co source. The dose rate was 0.01 Mrad/h and the total dose, 1 Mrad. Postirradiation treatment and other relevant details have been published previously.[7-9] From the resultant solid xerogel rods, thin disks were lathe cut[7] and exhaustively dried in a vacuum oven at 35°C.

Swelling

Dry disks of measured weight and diameter were placed in vials and solvent added. The swelling time was taken from the moment of addition of solvent, and swelling proceeded at ambient temperature (21 ± 1°C). At various times the swollen disks were removed, surface dried with Whatman No. 1 filter paper, weighed in a stoppered weighing bottle, and then replaced in the vials quickly. Swelling characteristics were expressed as

$$\text{Water content} = C = \frac{W - W_0}{W}$$

$$\text{Fractional extension} = E = \frac{d - d_0}{d_0}$$

where W_0 and W are the weights of xerogel and hydrogel, respectively, and d_0 and d are the corresponding diameters. Values of d_0 (generally about 12 mm) were measured with a micrometer and are accurate to within 0.001 mm. The main uncertainty in E lies in the values of d, which relate to nonrigid hydrogels. For these a ruler was used, giving values of d accurate

to within ± 0.5 mm. The values of d ranged from 12 mm (at low VP content) to 24 mm (at high VP content). The relative errors in d thus range from $(0.5/12) \equiv 4\%$ to $(0.5/24) \equiv 2\%$.

Measurement of Sol Fraction

Dry xerogel disks were subjected to Soxhlet extraction with water at 100°C and then dried to a constant weight in a vacuum oven at 35°C. No further extraction was found after 24 h, and this Soxhlet extraction time was adopted for all samples. The sol fraction S was expressed as the fractional loss in weight of xerogel.

RESULTS AND DISCUSSION

BA/VP Gels

The poly-VP (in the absence of BA) was glassy at room temperature. With or without TPT during the polymerization, this polymer did not dissolve in water but formed a highly swollen hydrogel. The poly-BA (in the absence of VP) was elastomeric. With and without TPT during the polymerization, this product formed a highly swollen organogel in toluene, but did not dissolve. There are strong indications, therefore, that both homopolymers had been crosslinked during polymerization even without the incorporation of a crosslinking agent. The physical states were dictated by the composition. Glassy xerogels obtained for BA contents below about 50% by weight. At higher BA contents the copolymers were leathery, extending to elastomeric at very high BA content.

Swelling Properties

Typical hydration curves of C versus swelling time are illustrated in Figure 1 for copolymers of three different compositions (with no TPT). The swelling times extend to 27 h. For the same systems, swelling during a total
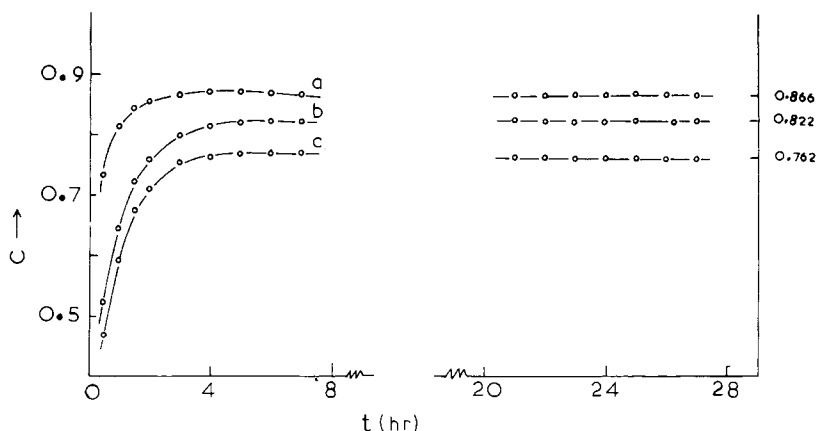

Fig. 1. Water contents at different times for swollen xerogels: (a) BA 20-VP 80, (b) BA 25-VP 75, and (c) BA 30-VP 70 (temperature = 21°C).

period of about 1 month is shown in Figure 2. Overall, swelling attains a maximum and then levels off to a slightly lower value. A very high initial rate of swelling is evident by the attainment of maximum C within the first 6 h, and indeed most of the water is absorbed within the first 2 h. The shape of the curves indicates a release of water-soluble materials during swelling.[10] These effects are small but nonetheless definite. Since attainment of the final equilibrium water content is slow, that is, about about 2 weeks, the release rate of water-soluble species is low. For one of the samples (BA 25-VP 75), considered in Figures 1 and 2, the effect of disk thickness was investigated, as shown in Figure 3. Here the thicknesses are 0.95 and 1.85 mm, the final equilibrium water contents being practically identical, namely, 0.822 and 0.813, respectively. The water uptake here is expressed relative to the dry weight, that is, $C/(1 - C)$, and the abscissa is (time).[1/2] On this basis, diffusion-controlled swelling is demonstrated[11] by the linearity extending almost to the point at which a constant equilibrium value is reached. The higher rate and shorter time to equilibrium for the thinner disk are typical effects of thickness on swelling behavior.[11-13]

Since the dry thicknesses of disks used in this work were nearly all about 0.5 mm, a time of 24 h can be regarded as sufficient for maximum swelling and a time of 2 weeks for attainment of a final equilibrium swelling. However, the water content after 2 weeks is only an apparent value, because it does not take into account the weight fraction W_S of any material leached out during swelling. Nevertheless, these two values of C are useful as guidelines for examining further factors that influence the swelling. They will be distinguished by C_d (after 1 day) and C_f (after a fortnight). The variation of C_d and E with composition of the xerogels is shown in Figure 4. The sharp decrease in both quantitities with content of BA becomes less pronounced at very high contents of this hydrophobic monomer unit.
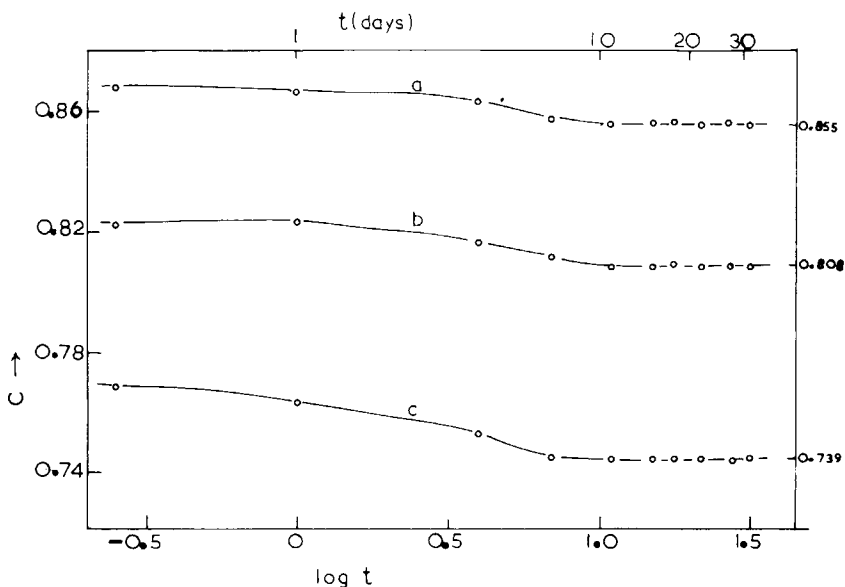

Fig. 2. Water contents at extended times of swelling for hydrogels (a), (b) and (c) of Figure 1 (temperature = 21°C).
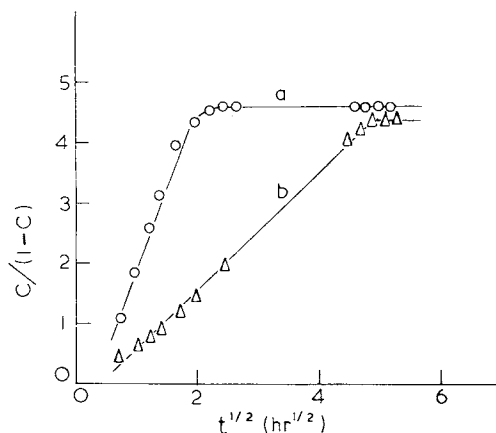
Fig. 3.   Degree of swelling as a function of (time)$^{1/2}$ for xerogel BA 25-VP 75 disks of thickness (a) 0.95 mm and (b) 1.85 mm.

Sol Fraction

Slow release of water-soluble species at 21°C having been evidenced, the effect was examined separately by means of Soxhlet extraction at 100°C. The results in Figure 4c show that S decreases markedly with increasing content of BA in the xerogel. For BA contents $\geqslant$ 80% by weight the sol fraction S was zero.
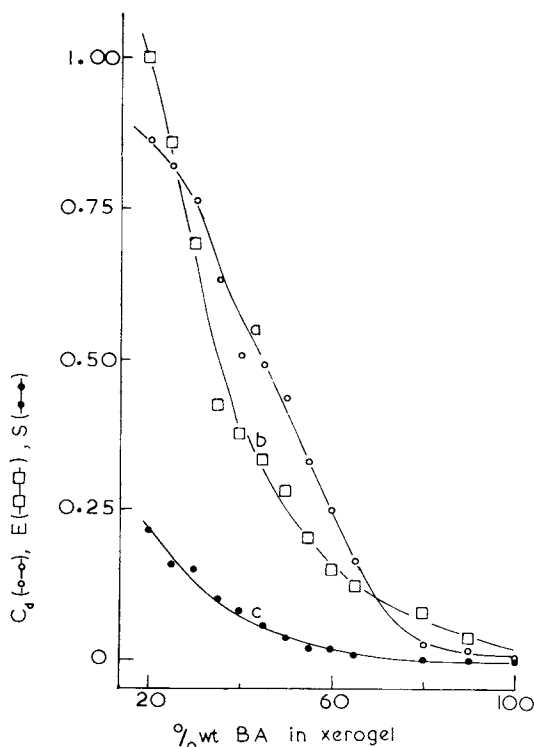

Fig. 4.   Variations of (a) water content, (b) fractional extension, and (c) sol fraction with composition of xerogel.

The true nature of the sol fraction is not known. Frequently, solubility increases with decrease in chain length, and indeed although poly (tetrahydrofuran), for example, is insoluble in water, a significant solubility is exhibited by its oligomers. However, in the present system there is no absolute necessity to invoke solely the role of oligomers, since theoretical analysis[8,14] of compositional drift with conversion during copolymerization of BA with VP has shown effects compatible with the results on Soxhlet extraction. On approaching 100% conversion, the copolymer has an instantaneous composition of very high VP content when the feed mixture comprises low-medium contents of BA. Although copolymer produced in the final stages of conversion comprises only a small weight fraction of the whole, such material might be expected to be water soluble. In contrast, at high contents of BA in the feed, the compositional drift with conversion is rather small and, on approaching 100% conversion, the instantaneous composition is not of very high VP content.

These comments are based on analysis invoking reactivity ratios r_1 (for VP) and r_2 (for BA), which were estimated[8] via the Q-e scheme. Subsequent to the completion of the present work, we have obtained experimentally[15] the values of $r_1 = 0.02$ and $r_2 = 0.80$. This value of r_1 is nearly the same as estimated, but r_2 (experimental) is larger than r_2 (estimated). However, the general tenor of the argument above remains essentially unaltered by the use of the new reactivity ratios.

Also subsequent to the completion of this work, some corroborative evidence on the nature of the sol fraction has been adduced in this laboratory by Rehab.[16] Xerogel BA 20-VP 80-TPT 1 was obtained by irradiation in the normal way from a feed mixture of the same composition. The mole fraction f_1 of VP in the feed is thus 0.822. The initial instantaneous copolymer composition expressed as mole fraction F_1 of VP is calculated from f_1, r_1, and r_2 to be 0.482, but calculation of instantaneous composition at different stages of conversion[15] yields values of F_1 increasing in value to 0.98, 0.99, and tending to 1.00 at 100% conversion. The overall value of F_1 for the copolymer comprising species formed at all stages of conversion is, of course, 0.822. A large number of disks cut from this xerogel were Soxhlet extracted with boiling water, and the extracted sol fraction was retained as an aqueous solution, which was concentrated by slow evaporation at atmospheric pressure and room temperature. Complete evaporation left an optically clear, colorless film, which was subjected to Kjeldahl analysis. The resultant nitrogen content of 12.35% (12.6% by weight in pure poly-VP) corresponds to $F_1 = 0.981$ in the sol fraction. Like pure poly-VP, this extract was soluble not only in water but also in ethanol and chloroform. There was insufficient material for a molar mass determination. The refractive index $n_D{}^{20}$ measured on an Abbé refractometer was 1.526. Values of $n_D{}^{20}$ for pure poly-VP samples of different molar mass M showed a slight decrease with decreasing M, the value at high M (7×10^5 g mol^{-1}) being 1.522.[15] Consequently, the extract exhibited a value of $n_D{}^{20}$ slightly greater than 1.522 rather than an anticipated value slightly less than this (the small content of BA units in the extracted copolymer does not resolve this point, since $n_D{}^{20} = 1.467$ for poly-BA).[16] Although the extraction was made with water, the sol fraction could nonetheless have been lightly branched or crosslinked.

There is a precedent for the solubility of quite highly branched polymers, especially where such specific interactions as hydrogen bonding can exist.[17] In the present instance, this could have the effect of increasing the density and n_D^{20} over the values for the linear polymer. This conjecture apart, it seems reasonably well established that (1) the sol fraction is removed from the high-conversion copolymer because compositional drift produces species of composition approaching that of pure poly-VP, and (2) the physical form, refractive index, and slow release rate at 21°C suggest that the sol fraction is probably not oligomeric.

Effect of Dose

The effect of irradiation dose (at a constant dose rate of 0.01 Mrad h^{-1}) on the swelling characteristics and sol fraction for xerogel BA 30-VP 70 is indicated in Figure 5. Within the range of dose examined the dose has only a slight effect in decreasing the value of both swelling parameters. These reductions must arise from a small amount of crosslinking of the copolymer already produced to complete conversion at 1 Mrad; they are insignificant in comparison with the effect of deliberately introducing a crosslinking agent (see later). The effect on the sol fraction is more pronounced, S being reduced from a value of 0.15 at 1 Mrad to about 0.07 at 3 Mrad.
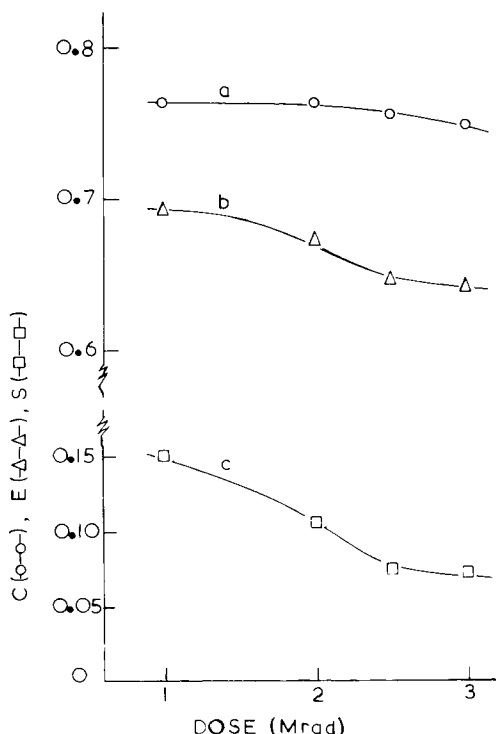

Fig. 5. Influence of absorbed irradiation dose (at a fixed dose rate of 0.01 Mrad h^{-1}) used to prepare xerogel BA 30-VP 70 on the parameters: (a) water content of hydrogel, (b) fractional extension of hydrogel, and (c) sol fraction.

Effect of Crosslinking Agent

From the standpoint of ultimate end use, special interest is centered on hydrogels of high water content. Introduction of TPT into the feed mixture has been shown to influence considerably the optical homogeneity of the resultant xerogels.[8] Regarding swelling characteristics, attention has been focused on xerogels of high VP content (70 and 80%).

For each of these two systems, the decrease in C_d, E, and S with concentration of TPT is shown in Figure 6. For BA 20-VP 80-TPT 1 and BA 30-VP 70-TPT 1 the water contents C_d are 0.697 and 0.622, respectively, which represent significant decreases from the corresponding values of 0.860 and 0.763 for BA 20-VP 80 and BA 30-VP 70, respectively. Data relating to an extremely high concentration of TPT have been excluded from Figure 6. For BA 30-VP 70-TPT 5 the value of C_d falls even further to 0.479, and the values of E and S are 0.245 and 0.022, compared with those of 0.691 and 0.15, respectively, for BA 30-VP 70.

In contrast to the present systems, the swelling properties of the more widely known hydrogel poly-(2-hydroxyethyl methacrylate) (PHEMA) are not affected drastically by crosslinking and in this respect are atypical.[1] The water content of PHEMA is reduced from 0.42 to 0.38 on inclusion of 1% TPT, the value at 5% TPT being 0.32.[18]
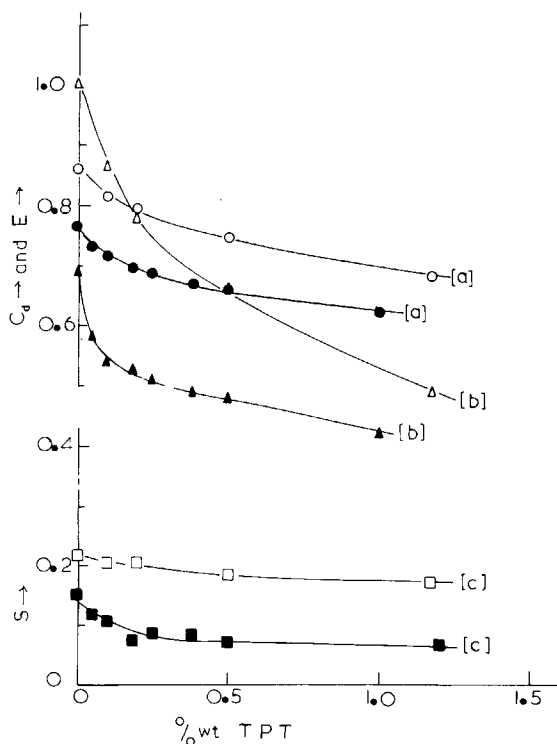

Fig. 6.   Effect of concentration of crosslinker used in preparation of xerogel on the parameters: (a) water content of hydrogel, (b) fractional extension of hydrogel, and (c) sol fraction. Open symbols: BA 20-VP 80; filled symbols: BA 30-VP 70.

Hydration and Rehydration

As a further investigation into the effect of extractable materials on the water content, three treatments were adopted:

1. The original dry xerogel was swollen to obtain its hydration curve, as already described.

2. The disk from treatment 1 at its final swelling equilibrium was dehydrated and the rehydration curve established on the resultant completely dry disk.

3. A sample of the original dry xerogel was subjected to Soxhlet extraction, and dried completely. Its hydration curve was then obtained.

The relevant curves are not reproduced here (for case 1 they have already been illustrated in Figs. 1 and 2). The main points emerging from them are summarized as follows for BA 30-VP 70-TPT 1. For case 1 the value of $C = 0.530$ at $t = 0.5$ h increases to a maximum of $C = 0.636$ at $t = 2$ h. Thereafter, C decreased slowly to a value of 0.597 at $t = 15$ days and remained at this value for the remainder of the period of observations, that is, until $t = 32$ days. This final equilibrium value of $C = 0.597$ is lower than the true water content, because of the slow release of water-soluble species. No such release was evident for cases 2 and 3. In case 2 the value of $C = 0.593$ at $t = 0.5$ h rose to 0.632 at $t = 2$ h and remained at this value up to $t = 32$ days. In case 3 the value of $C = 0.561$ at $t = 0.5$ h increased to 0.632 at $t = 4$ h and also remained thereat up to $t = 32$ days.

For application as a biomaterial it is preferable and convenient that the xerogel should be free from water-soluble extractable materials. Unfortunately, in the present copolymers, such a situation obtains only for those xerogels of low hydration (i.e., of high BA content). In the useful composition BA 30-VP 70, the level of extractable materials can be minimized by inclusion of TPT in the feed mixture or by increasing the irradiation dose. The former approach does, however, have the effect of also reducing the water content and the fractional extension.

The most rapid means of removing the soluble fraction is Soxhlet extraction at high temperature. As verified here, the same final properties (including C_T) can be achieved by the swelling at ambient temperature for a prolonged period. For xerogels BA-VP-TPT of thickness = 0.5 mm, the required time is approximately 2 weeks.

Equilibrium Water Content

As indicated earlier, neither C_d nor the water content at equilibrium after 2 weeks (C_f) constitutes the true water content C_T, on account of the release of the sol fraction and the adoption of the initial dry weight of unswollen xerogel W_0. The value of C_T can be calculated from the following expression:

$$C_T = 1 - (1 - C_f)(1 - S) \tag{1}$$

Here S may be taken as the fractional loss in weight of gel by release of extractables. It is obtainable by either Soxhlet extraction or swelling at ambient temperature.

Effect of Dose Rate

We have shown previously[7,8] that the use of very low dose rates during the γ-ray-initiated copolymerization can lead to textural inhomogeneity in the form of popcorn formation in the xerogels produced. However, no such inhomogeneity ensued at the dose rate used here. The effect of this dose rate and two higher ones on the properties of the homogeneous gels is presented in Table I. After polymerization there is virtually no loss in weight due to removal of unreacted monomers. The oven recovery (24 h at 100°C) is ⩾99.9% in each case. Within the accuracy of measuring the dimensions of cut disks to give their volume, the resultant calculated density is also the same for each dose rate. At any particular dose rate there is good agreement between W_S and S. However, the values of these increase with increasing dose rate, and there is a corresponding fall in the values of the water contents C_d and C_f (although the true value C_T remains unchanged).

Qualitatively these observations can be explained on the basis of (1) presence of copolymer of high instantaneous content of VP at high conversion (already discussed), and (2) the effect of dose rate on chain length. With regard to the latter, the kinetic chain length is inversely proportional to radiation intensity. Hence the chains of lowest chain length and maximum solubility will be produced at the highest dose rate.

BA-VP-MMA Hydrogels

In our previous work[8] it was shown that inclusion of MMA in the feed mixture improved the overall optical homogeneity of the resultant terpolymeric xerogels relative to that of the BA-VP copolymers. However, hydrophobic interaction and microsyneresis led to a deterioration in the clarity of these terpolymers when swollen to hydrogels. In the six different terpolymers the content of BA was maintained constant at 20%, the remaining 80% comprising VP and MMA in varying proportions. The highest content of MMA was 50%, viz, that in the terpolymer BA 20-VP 30-MMA 50. The xerogels in this series are glassy, but the hydrogels are less elastic compared

TABLE I
Effect of Dose Rate on the Properties of BA 30-VP 70-TPT 1 Gels (1 Mrad, 294 K)

Properties	Dose rate (Mrad h^{-1})		
	0.01	0.053	0.285
Oven recovery (wt %)	99.93	99.98	99.90
Density (g cm^{-3})	1.15	1.13	1.14
Water contents			
C_d	0.624	0.611	0.593
C_f	0.600	0.588	0.568
C_T	0.626	0.628	0.622
Fractional extension E	0.413	0.433	0.412
Fractional loss in weight during swelling W_S	0.067	0.098	0.123
Sol fraction S after Soxhlet extraction	0.068	0.092	0.113

with the hydrogels of BA-VP. The elasticity of the hydrogels decreases with increasing content of MMA and is extremely small in the composition of maximum MMA content.

The plots of C_d, E, and S versus MMA content are not reproduced here. They are of a similar general form to those in Figure 4 and display a decrease in all these parameters with increasing content of the hydrophobic comonomer MMA. To afford comparison with the systems not containing MMA, we may take hydrogel BA 20-VP 60-MMA 20 as an example. For this, the values of C_d and E are 0.65 and 0.47, respectively. The ratio of BA to VP is $20{:}60 = 1{:}3$. The same ratio in the absence of MMA would occur in the copolymer BA 25-VP 75, for which hydrogel much higher values of 0.83 and 0.86 obtain for C_d and E, respectively.

Reproducibility Test

For the potentially useful composition BA 30-BP 70-TPT 1, an experiment was conducted to test the reproducibility of its measured properties. From a purified batch of each of the purified components, six mixtures of composition BA 30-70VP-TPT 1 were prepared gravimetrically. They are designated as V_1 through V_6. The actual slight variations in composition among these, which arose during weighing, are BA: range, 29.99–30.01%: mean, 30.00%; SD, 0.01 (0.03%); VP: range, 69.99–70.01%; mean, 70.00%; SD, 0.01 (0.01%); TPT: range, 1.00–1.03%; mean, 1.01%; SD, 0.01 (1.3%).

The six monomer mixtures were divided among 14 ampoules. After outgassing, irradiation, and postcure, the number R of resultant xerogel rods was thus also 14. Each rod is designated as V_iR_j, where i indicates the designated number of the monomer mixture (1–6) and j is the designated number of the rod itself (1–14).

From each rod about 15 disks were cut. Each was numbered to correspond to its original relative position in the rod. In each rod the designated numbers for the discs are D_1, D_2,..., D_k, where k is the maximum number of disks obtained from the rod. The numbering is taken from the top of the rod in its original upright position during irradiation. Thus D_1 is the disk from the uppermost part, followed by D_2, D_3, and so on.

From the k (≈ 15) disks cut from each rod, only 7 were selected for the swelling measurements. These were not taken at random but were selected to represent the whole region of the rod, that is, its top, middle, and bottom. Out of the remaining 8 disks cut from each rod, 4 were selected at random for measurement of sol fraction. The systematic selection of the $7 \times 14 = 98$ disks used for swelling is summarized in Table II. Here, for example, the column on the extreme right side indicates that disks numbered 1, 3, 5, 7, 10, 13, and 15 were selected from the total cut from rod number 14, which had been prepared from monomer feed mixture number 6.

The detailed results of the measurements of all the relevant parameters for each of the 98 disks (as well as the additional ones of S) are not given here. The grand means are quoted in Tables III and IV, and analysis of data on S is summarized in Table V. The means of the weight (W_o) and thickness (d_o) of the xerogels have no statistical significance but serve only to indicate the sampling domain. The density of the xerogel lay within the

TABLE II
Specification and Sources of Disks Used in Test on Reproducibility for Preparation of BA 30-VP 70-TPT 1

Designation of disk used	Source of disk used; monomer mixture V_i and xerogel rod R_j													
D_1	V_1R_1	V_2R_2	V_3R_3	V_3R_4	V_3R_5			V_4R_8	V_5R_9	V_5R_{10}	V_5R_{11}	V_6R_{12}	V_6R_{13}	V_6R_{14}
D_2		V_2R_2	V_3R_3	V_3R_4	V_3R_5	V_4R_6	V_4R_7		V_5R_9	V_5R_{10}	V_5R_{11}	V_6R_{12}	V_6R_{13}	V_6R_{14}
D_3	V_1R_1	V_2R_2	V_3R_3	V_3R_4	V_3R_5	V_4R_6	V_4R_7	V_4R_8	V_5R_9	V_5R_{10}	V_5R_{11}	V_6R_{12}	V_6R_{13}	V_6R_{14}
D_4		V_2R_2	V_3R_3	V_3R_4	V_3R_5	V_4R_6	V_4R_7	V_4R_8	V_5R_9		V_5R_{11}	V_6R_{12}	V_6R_{13}	V_6R_{14}
D_5	V_1R_1	V_2R_2	V_3R_3	V_3R_4	V_3R_5	V_4R_6	V_4R_7	V_4R_8	V_5R_9	V_5R_{10}		V_5R_{12}		V_6R_{14}
D_6	V_1R_1										V_5R_{11}	V_6R_{12}	V_6R_{13}	V_6R_{14}
D_7	V_1R_1	V_2R_2	V_3R_3	V_3R_4	V_3R_5	V_4R_6	V_4R_7	V_4R_8	V_5R_9					
D_8										V_5R_{10}	V_5R_{11}	V_6R_{12}	V_6R_{13}	
D_9	V_1R_1	V_2R_2	V_3R_3	V_3R_4	V_3R_5	V_4R_6	V_4R_7	V_4R_8	V_5R_9	V_5R_{10}			V_6R_{13}	
D_{10}		V_2R_2	V_3R_3	V_3R_4	V_3R_5	V_4R_6	V_4R_7	V_4R_8	V_5R_9	V_5R_{10}	V_5R_{11}	V_6R_{12}	V_6R_{13}	V_6R_{14}
D_{11}	V_1R_1			V_3R_4	V_3R_5		V_4R_7				V_5R_{11}	V_6R_{12}	V_6R_{13}	
D_{12}					V_3R_5		V_4R_7							
D_{13}		V_2R_2	V_3R_3	V_3R_4		V_4R_6		V_4R_8	V_5R_9		V_5R_{11}	V_6R_{12}		V_6R_{14}
D_{14}										V_5R_{10}			V_6R_{13}	
D_{15}							V_4R_7	V_4R_8	V_5R_9		V_5R_{11}	V_6R_{12}		V_6R_{14}
D_{16}						V_4R_6								
D_{17}										V_5R_{10}				

TABLE III
Grand Mean of Swelling Parameters for BA 30-VP 70-TPT 1 Hydrogels Prepared in the
Reproducibility Test (1 Mrad, 0.01 Mrad h^{-1}, 294 K)[a]

Rod	100 × Water content			100 × W_S
	C_d	C_f	C_T	
V_1R_1	61.9 (0.5)	59.7 (0.5)	62.5 (0.3)	7.0 (5.3)
V_2R_2	62.1 (0.3)	59.7 (0.4)	62.3 (0.4)	6.5 (5.3)
V_3R_3	62.4 (0.3)	60.2 (0.3)	62.8 (0.2)	6.5 (2.6)
V_3R_4	62.1 (0.2)	59.7 (0.2)	62.8 (0.6)	7.2 (2.6)
V_3R_5	62.3 (0.3)	60.0 (0.3)	62.5 (0.3)	6.3 (2.0)
V_4R_6	62.4 (0.5)	59.8 (0.6)	62.5 (0.3)	6.7 (4.8)
V_4R_7	62.3 (0.3)	59.9 (0.3)	62.6 (0.2)	6.8 (2.4)
V_4R_8	62.6 (0.3)	60.1 (0.4)	62.9 (0.4)	7.0 (3.7)
V_5R_9	62.5 (0.6)	60.1 (0.6)	62.7 (0.4)	6.4 (3.3)
V_5R_{10}	62.4 (0.5)	60.0 (0.5)	62.6 (0.3)	6.7 (4.3)
V_5R_{11}	62.3 (0.8)	59.8 (0.7)	62.7 (0.4)	7.0 (4.3)
V_6R_{12}	62.7 (0.4)	60.3 (0.4)	62.9 (0.3)	6.6 (4.6)
V_6R_{13}	62.7 (0.3)	60.3 (0.5)	62.9 (0.4)	6.6 (2.1)
V_6R_{14}	62.3 (0.4)	60.0 (0.4)	62.8 (0.4)	7.0 (2.2)
Range	61.6–63.1	59.3–60.7	62.0–63.5	6.1–7.6
Mean	62.4	60.0	62.7	6.7
Standard deviation	0.2 (0.3%)	0.2 (0.4%)	0.2 (0.3%)	0.3 (4.0%)

[a] Numbers in parentheses are % standard deviation.

range 1.047–1.175 g cm^{-3}, the mean being 1.148 g cm^{-3} with a standard deviation of 0.019 g cm^{-3} (1.7%).

The reproducibility and precision of the swelling parameters are very high, the standard deviation being <1% in most cases. The rather higher standard deviation (SD) of 3.2% for E can be attributed to insufficient accuracy in measuring the diameters d of the hydrogels. Similarly, the value of SD = 4% for W_S is a consequence of the very small values of the actual weight losses during swelling. The statistical analysis also confirms the previous assertion that W_S is equal to S; hence, swelling a xerogel in water for about 2 weeks at ambient temperature or extraction for about 24 h in a Soxhlet apparatus serve as equivalent alternatives for removing any sol fraction.

Scaling-Up Scheme

The laboratory-scale preparation of the xerogels was made in glass ampoules, the resultant rods being of length 5 cm, approximately. To assess the uniformity of properties in a large-scale preparation, experiments were conducted to simulate the production of a rod of length of about 60 cm. The system was BA 30-VP 70-TPT 1.

For the normal small-scale preparations, the ampoule was placed on a circular table at the center of which the source assembly was located. The midpoint of the rod produced was thus about 2.5 cm above the level of the table. For the simulation experiment, several similar ampoules containing

TABLE IV
Parameters of BA 30-VP 70-TPT 1 Gels Prepared in the Reproducibility Test
(1 Mrad, 0.01 Mrad h^{-1})

Rod[a]	Oven recovery (wt %)	d_0 (mm)	$100 \times E$
V_1R_1 (11) (6)	99.95	11.388	40.5
V_2R_2 (13) (7)	99.95	10.680	40.5
V_3R_3 (13) (7)	99.97	10.000	40.0
V_3R_4 (13) (7)	99.98	10.519	42.6
V_3R_5 (12) (7)	99.98	10.644	40.9
V_4R_6 (16) (8)	99.84	11.113	44.0
V_4R_7 (15) (8)	99.96	10.480	43.1
V_4R_8 (16) (8)	99.97	10.659	40.7
V_5R_9 (16) (8)	99.89	10.686	40.4
V_5R_{10}(17) (8)	99.93	10.963	41.4
V_5R_{11}(15) (7)	99.90	10.133	43.1
V_6R_{12}(15) (7)	99.92	10.659	40.7
V_6R_{13}(14) (7)	99.90	10.005	39.9
V_6R_{14}(15) (10)	99.93	10.043	40.4
Range	99.84–99.98	10.000–11.388	39.9–44.0
Mean	99.93	10.569	41.3
Standard deviation	0.04 (0.04%)	0.420 (4.0%)	1.3 (3.2%)

[a] The number in the first set of parentheses is the total number of disks obtained from this rod. The number within the second parentheses denotes the disk used for the measurement of fractional extension on swelling E. For example, in rod V_4R_8, the total number of disks was 16 and, of these, disk D_8, was used for the measurement, yielding $E = 0.407$.

the same feed mixture were positioned above each other in a vertical stand at a fixed distance from the center of the table. The sample in the lowest position (midpoint of rod 2.5 cm above the table) was identical with that in the normal small-scale experiments. The sample at the highest position yielded a rod with a midpoint 59.5 cm above the table. Thus, overall, the series of separated small ampoules simulates the preparation in a single extremely long ampoule of a rod of length 59.5 + 2.5 = 62 cm. The spherical symmetry of the radiation envelope meant that samples at higher position were further from the source than that at the normal, lowest position; the dose rates for them were correspondingly somewhat lower. Irradiation times were adjusted to afford a dose of 1 Mrad for all samples.

As shown in Table VI, the properties of the xerogels and hydrogels yielded by this simulation are satisfactorily similar. Thus a xerogel rod at least 62 cm long and capable of affording about 200–300 thin disks of similar properties is demonstrated to be a viable preparation.

Swelling of Xerogels in Other Liquids

Disks of xerogel BA 30-VP 70-TPT 1 prepared by 1 Mrad of irradiation at 0.01 Mrad h^{-1} were extracted with water, dried, and then left to attain swelling equilibrium at 393 K in several common organic solvents of

TABLE V
Results of Soxhlet Extraction in Boiling Water on BA 30-VP 70-TPT 1 Xerogels Prepared
in the Reproducibility Test (1 Mrad, 0.01 Mrad h^{-1})

Rod	W_0 (g)	S (wt%)
V_1R_1	0.25435	7.8
V_2R_2	0.27205	8.1
V_3R_3	0.25605	6.5
V_3R_4	0.24400	6.2
V_3R_5	0.25660	6.0
V_4R_6	0.29085	6.0
V_4R_7	0.23965	6.2
V_4R_8	0.24160	7.4
V_5R_9	0.27415	8.0
V_5R_{10}	0.21000	6.7
V_5R_{11}	0.22575	5.7
V_6R_{12}	0.22080	5.8
V_6R_{13}	0.28590	6.9
V_6R_{14}	0.25690	7.4
Range	0.22080–0.29085	5.7–8.1
Mean	0.25205	6.8
Standard deviation	0.02381 (9.4%)	0.8 (12.5%)

known[19] solubility parameter δ_1. The value of C_f and E for these organogels are reported in Table VII. The gels were then dried and reswollen in water to obtain the values of C_T for the hydrogels. Calculation of C_T was made via equation (1).

The equilibrium water contents of hydrogels obtained by hydrating the dried organogels are slightly lower than the corresponding values obtained

TABLE VI
Properties of BA 30-VP 70-TPT 1 Gels Prepared in a Scaling-up Simulation
(1 Mrad, 0.01 Mrad h^{-1}, 294 K)

Position of midpoint of rod above source level (cm)	2.5	18	31.5	44.5	59.5
Length of rod (cm)	5.0	4.5	5.0	5.0	5.0
Oven recovery (wt %)	99.93	99.90	99.94	99.94	99.93
Density (g cm^{-3})	1.15	1.13	1.12	1.12	1.12
Water contents					
C_d	0.624	0.627	0.628	0.626	0.622
C_f	0.600	0.600	0.599	0.597	0.593
C_T	0.627	0.627	0.627	0.624	0.623
E	0.413	0.417	0.406	0.433	0.401
Fractional weight loss during swelling W_s	0.067	0.068	0.068	0.066	0.073
Sol fraction S during Soxhlet extraction	0.068	0.063	0.062	0.067	0.066

TABLE VII
Swelling Properties of BA 30-VP 70-TPT 1 in Common Solvents

Solvent	δ_1 (kJ dm^{-3})$^{1/2}$	C_f	W_s	C_T	E	C_T in water for hydration of dried organogel
Chloroform	19.0	0.918	0.054	0.922	1.06	0.602
Ethyl acetate	18.6	0.838	0.012	0.840	0.996	0.609
Ethanol	26.0	0.832	0.005	0.833	1.00	0.618
Methanol	29.7	0.824	0	0.824	0.920	0.616
Formamide	39.3	0.757	0	0.757	0.693	0.622
Water	47.9	0.627	0	0.627	0.413	0.627

from hydrogels that had not been preswollen in organic solvents. The lowest value ($C_T = 0.602$) is found for the hydrogel obtained from the most highly swollen organogel, that is, in chloroform. In the latter solvent the weight loss of xerogel during swelling in the organic liquid also exhibits its maximum value (5.4%). It is significant that, of the liquids used, including water, chloroform is a good solvent for both poly-BA and poly-VP and is the only one capable of dissolving the BA-VP copolymers in their uncrosslinked form.

The order of swelling capacity of the present solvents for BA 30-VP 70-TPT gel is different from that of PHEMA for which the order has been found to be[20]

Formamide > methanol > ethanol > water

> chloroform > ethyl acetate

Although swelling measurements were not made in any solvents of very low δ_1, the present results, when plotted in the usual manner[21] of equilibrium solvent content versus δ_1, exhibit a maximum that indicates that the solubility parameter of the copolymeric xerogel δ_2 has a value of about 20 (kJ dm^{-3})$^{\frac{1}{2}}$. Neglecting the small contribution of TPT, the average molar mass M of the repeating unit is calculated to be 116 g mol^{-1}. The mean density ρ was 1.148 g cm^{-3}. Using these, the value of δ_2 may be calculated from the sum of the molar attraction constants G of the groups in the repeating unit, according to equation (2):

$$\delta_2 = \frac{\rho}{M}\Sigma G \qquad (2)$$

The revelant values of G listed by Small[22] yield $\delta_2 = 19.8$ (kJ dm^{-3})$^{\frac{1}{2}}$: the slightly different and more recent tabulation of Hoy[23] gives a value of $\delta_2 = 20.0$ (kJ dm^{-3})$^{\frac{1}{2}}$.

CONCLUSIONS

γ Irradiation has been shown to provide a convenient mode of effecting high conversion in the bulk copolymerization of BA with VP. Several properties were measurable in a precise and reproducible manner, and the preparative procedure was demonstrated to be amenable to scaleup.

Within the range of compositions prepared, water contents of the hydrogels extended to more than 80%. For the possibly less useful compositions (high BA content) affording low-medium water contents, there was no extractable sol fraction, and such materials are capable of being used directly as hydrogels. More attention has been focused on high-water-content hydrogels (xerogels of low BA concentration). For these, some form of preextraction is necessary on account of the release of water-soluble species during swelling. This sol fraction was shown to comprise a BA-VP copolymer of very high VP content, the presence of which accords with the calculated compositional drift during high conversion. Breakdown by hydrolysis was discounted as the source of the sol fraction because (1) the sol fraction after

extended swelling at 21°C had the same value as that obtained after a short Soxhlet extraction at 100°C, and (2) after extraction by either means no further loss in weight occurred on further reswelling and the true corrected degree of swelling could be obtained reproducibly on dried sol-free disks. There was no evidence of any bacterial growth either on the hydrogels or in the water after prolonged swelling (about 1 month). Consequently, such suppressants as sodium azide, thymol, or mercuric salts were not incorporated in the swelling liquid. Indeed, their presence would have altered the thermodynamic activity of the water and hence the final degree of swelling (see, for example, ref. 24).

Biomedical and other applications of hydrogels are extensively documented in the literature. It is relevant that the ability of the present xerogels to swell in both aqueous and nonaqueous media offers potential for imbibition of drugs from solutions prior to drying and subsequent release from the xerogel matrix.

Finally, it is pointed out that the water contents reported here constitute only total overall values and work has not yet commenced on a more detailed investigation into the subdivision into free, bound, and interfacial water. In a similar vein, the concentration of TPT has been quoted here on a weight percentage basis, which cannot be taken to represent the effective crosslink density. This and other aspects of the network structure in BA-VP-TPT hydrogels are currently being investigated, and results will be reported in a later communication.

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