Preparation and characterization of poly(n-vinyl 2-pyrrolidone) hydrogels

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Hydrogels in the form of rods were prepared from the ternary systems n-vinyl 2-pyrrolidone/crosslinking agent/water, in composition ranges where the three components were completely miscible. Gelation was achieved by irradiating the systems with γ rays at ambient temperature. The incorporation of water into the binary system of monomer/crosslinking agent reduced the gelation dose 120-fold. The influence of dose, functionality of the crosslinking agent, and relative amounts of crosslinking agent and water on the swelling properties, diffusion behaviour of water and mechanical properties of the hydrogels were investigated. Hydrogels with swelling capabilities in the range 140–420% were obtained with tensile strength values between 0.721 and 2.717 MN m^{-2}.

(Keywords: poly(n-vinyl 2-pyrrolidone); characterization; hydrogels; gelation)

INTRODUCTION

Crosslinked hydrophilic polymers capable of imbibing large volumes of water (i.e. > 20%) are termed hydrogels. Interest in the preparation of hydrogels with various properties has increased considerably in recent years, due to their versatile applications in biomedicine, biotechnology and in a vast field where controlled release of chemicals is required. The first step in the preparation of hydrogels is the selection of a highly hydrophilic or even water-soluble polymer. The number of polymers suitable for this purpose is quite limited compared to the enormous number of synthetic polymers available. The polymers used in the preparation of hydrogels comprise mainly homopolymers of polyacrylamide (PAAm), poly(n-vinyl 2-pyrrolidone) (PVP), poly(hydroxy ethyl methacrylate) (PHEMA), poly(acrylic acid) (PAA), poly(ethylene oxide) (PEO) etc. and their copolymers with some hydrophobic monomers.

Highly crosslinked PVP hydrogels are generally prepared from the monomer, with or without some comonomers, in the presence of crosslinking agents[1]. Lightly crosslinked hydrogels of PVP are prepared by treating the aqueous solutions of PVP with γ rays[2], persulphate[3], hydrazin or hydrogen peroxide[4]. Although PVP hydrogels prepared in this way show very high biocompatibility, their mechanical properties are rather poor.

Among the methods listed above, γ ray-induced simultaneous polymerization and crosslinking has some advantages over the others. This technique is generally termed a 'clean technique', not requiring any extra chemicals and leaving some unwanted residues. It can be applied at any temperature and dose rate. Huglin and co-workers[5,6] used this method in the preparation of copolymeric hydrogels of vinyl pyrrolidone and butyl acrylate and determined that, depending on the amount of crosslinking agent used and monomer feed ratio, it was possible to obtain hydrogels with a wide range of mechanical, swelling and optical properties.

In the present work ternary systems composed of vinyl pyrrolidone/water/crosslinking agent were prepared at varying compositions and irradiated with γ rays to different total doses. The hydrogels thus prepared were characterized with respect to their swelling properties, network structures, and the mechanism of diffusion in addition to their mechanical properties. The gels will later be evaluated for potential enzyme immobilization systems.

EXPERIMENTAL

n-Vinyl 2-pyrrolidone (VP) was obtained from Merck. The crosslinking agents were ethylene glycol dimethacrylate (EGDMA) from BDH Chemicals Ltd, and trimethylolpropane triacrylate (TMPTA) from Aldrich. Three components were used in the preparation of hydrogels, namely vinyl pyrrolidone, crosslinking agent and water. Ternary phase diagrams of these systems were first constructed for two different crosslinking agents[7]. Various compositions were prepared where the three components showed complete miscibility. In the notations used for the identification of samples, the numbers preceding the abbreviations denote the percentage compositions by weight. Pure VP monomer and the solutions thus prepared were placed in PVC straws of 4 mm diameter and irradiated in air at ambient temperature in a Gammacell 220 type γ irradiator at a fixed dose rate of 1.5 kGy h^{-1}, the dose rate being determined by the conventional Fricke dosimeter. Hydrogels obtained in long cylindrical shapes were cut into pieces $\sim$4–5 mm long and stored for later evaluations. Conversions to gels were determined gravimetrically after removing the uncrosslinked polymer by extracting with water. Extracted gels were dried in vacuum ovens at 315 K to constant weights. Percentage

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gelation, i.e. percentage conversion of monomer-crosslinking agent into insoluble networks, was based on the total weight of the crosslinking agent and monomer in the initial mixture.

Dried hydrogels with initial weights w_0 were left to swell in distilled water at $35 \pm 0.1°C$. Swollen gels removed from the water bath at regular intervals were dried superficially with Whatman No. 1 filter paper, weighed and placed in the same bath. Percentage swelling was calculated from the following relation:

$$\% \text{ swelling} = \frac{w_t - w_0}{w_0} \times 100 \qquad (1)$$

where w_t is the weight of the swollen gel at time t.

The mechanical tests were performed on freshly prepared gels by using Instron 1185 model mechanical testing equipment. Samples prepared for tensile strength and elongation tests were cylinders of 3 mm diameter and 15 cm long.

RESULTS AND DISCUSSION

PVP hydrogels

When pure vinyl pyrrolidone monomer was irradiated with γ rays, polymerization and crosslinking reactions took place simultaneously. The total dose required for the onset of gelation was determined to be 3 kGy for this system, see *Figure 1*. The hydrogels prepared at relatively low irradiation doses showed low mechanical stability and ruptured upon swelling. This is most probably due to the presence of polymerized, but not crosslinked, PVP chains entrapped within the gel structure. Their loss as sol fractions upon contact with water will naturally weaken the mechanical stability of gels. Only hydrogels prepared at very high doses, i.e. 180 kGy, retained their shapes and integrity in the swollen state.

PVP/EGDMA hydrogels

To decrease the gelation dose and increase the crosslink density at the same time, a difunctional crosslinking agent was added to monomer. The hydrogels obtained in the presence of 1–2% EGDMA behaved similarly to pure PVP gels, i.e. upon swelling the geometric shape of the gels was distorted. This is probably due to insufficient
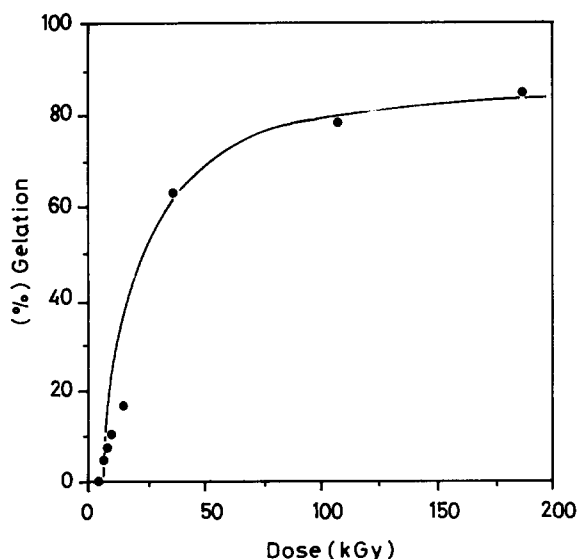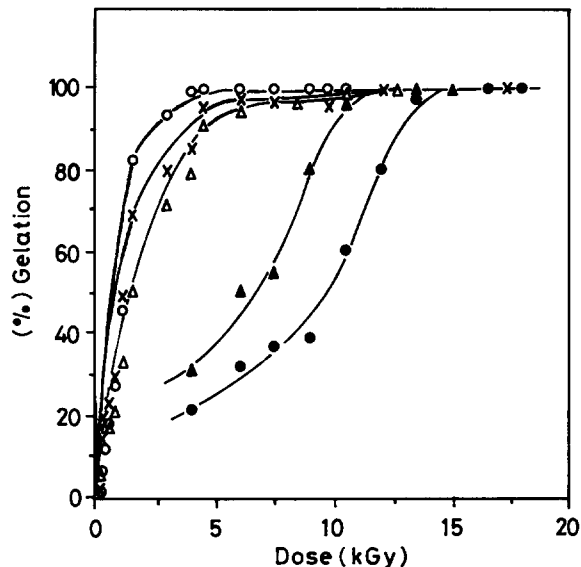
Figure 2 Effect of crosslinking agent and water on the percentage gelation of vinyl pyrrolidone: (●) 3EGDMA97VP; (▲) 5EGDMA95VP; (○) 8EGDMA30W62VP; (×) 6EGDMA30W64VP; (△) 4EGDMA30W66VP

formation of crosslinks. The gels prepared with 3–5% EGDMA, however, were very stable and showed uniform swelling properties and improved mechanical stability in the swollen state. These observations are in agreement with the results obtained by Davis *et al.*[8], who studied the influence of low concentrations of EGDMA on the properties of PVP hydrogels. When EGDMA was added in 6–7%, the gels again ruptured when in contact with water, which is most probably due to inhomogeneous distribution of crosslinks within the hydrogel. The internal pressures developed upon swelling of inhomogeneous network structures may be responsible for the poor mechanical properties of these gels.

PVP/EGDMA/H₂O hydrogels

In order to make use of the indirect effect of radiation and to minimize its possible degradative effect on the ingredients of the mixture, such as chain scission effects in enzymes or other biologically active substances used in immobilization studies, water is added to VP/EGDMA binary systems. When percentage gelation *versus* dose curves are compared for these two systems (see *Figure 2*) it can be seen that gelation is achieved at relatively low total doses, around 0.025 kGy in these ternary systems. Water acts to promote both polymerization and crosslinking reactions[9]. The enhancing effect of water on crosslinking reactions is strikingly observed for some samples where no sol fraction was detected, even at relatively low doses. Hydrogels obtained were mechanically stable.

PVP/TMPTA/H₂O hydrogels

The substitution of a trifunctional crosslinking agent, TMPTA, instead of a difunctional one, EGDMA, would be expected to enhance the crosslinking effect of radiation[10]. In the presence of equal amounts of crosslinking agents, less total dose is required for the onset of gelation or higher crosslink density obtained for the same absorbed dose in the presence of TMPTA. Optically clear hydrogels showing homogeneous swelling properties were obtained when TMPTA and water were used in concentrations of 4–8% and 30–36% respectively.

Figure 1 Conversion of vinyl pyrrolidone monomer into gel with dose

Characterization of hydrogels

Swelling. The water intake of initially dry hydrogels was followed for a long period of time. Representative swelling curves are shown in *Figure 3* for 3 EGDMA/ 97 VP and 5 EGDMA/95 VP gels. Increasing the amount of crosslinking agent increases the crosslinking density resulting in lower maximum swelling ratio.

Swelling behaviour of hydrogels prepared from PVP/EGDMA/H_2O mixtures irradiated with 6–16 kGy doses were also followed gravimetrically. The maximum swelling values reached with these gels were relatively low compared with those prepared in the absence of water, both irradiated to the same dose. This is due simply to enhanced crosslinking brought about by the radiolysis products of water. Such an effect was previously observed by Charlesby and Alexander[11] in the radiolysis of aqueous solutions of PVP. Increasing the irradiation dose further causes a decrease in the final extent of swelling. By keeping the water content fixed at 30% and increasing the amount of crosslinking agent from 4 to 8%, equilibrium swelling decreased by a factor of 3.5, again due to increased crosslink density, as can be seen from *Figure 4*. The use of TMPTA instead of EGDMA required lower irradiation doses, namely 4–12 kGy, and the hydrogels prepared were swollen to lower equilibrium values as a consequence of the trifunctionality of the crosslinking agent. Data relating maximum swelling in these systems with total dose is given in *Table 1*. The data shows that by varying the amount of crosslinking agent and water, and changing the dose, it is possible to prepare PVP hydrogels with swelling capabilities in the range 140–420%. It should be mentioned at this point that the principal control over swelling is derived from the nature and amount of crosslinking agent but not from the total dose.

Diffusion. The following equation was used to determine the nature of diffusion of water into hydrogels[12]

$$M_t/M_\infty = kt^n \qquad (2)$$

where M_t and M_∞ denote the amount of solvent diffused into the gel at time t and infinite time (at equilibrium) respectively, k is a constant related to the structure of the network, and the exponent n is a number to determine the type of diffusion. For cylindrical shapes, $n = 0.45$–0.50 and corresponds to Fickian diffusion whereas $0.50 < n < 1.0$ indicates that diffusion is non-Fickian[13]. This equation is applied to the initial stages of swelling and plots of log M_t/M_∞ versus log t yield straight lines up to almost 20% increase in the weight of hydrogels. For the hydrogels prepared by ternary systems, such plots were drawn using the kinetics of swelling and some
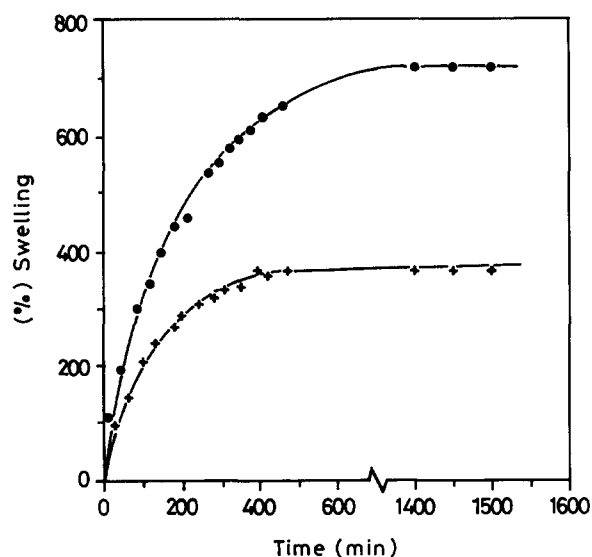
Figure 3 Effect of the amount of ethylene glycol dimethacrylate on the percentage swelling of PVP hydrogels. Total dose given 13.5 kGy: (●) 3EGDMA97VP; (+) 5EGDMA95VP
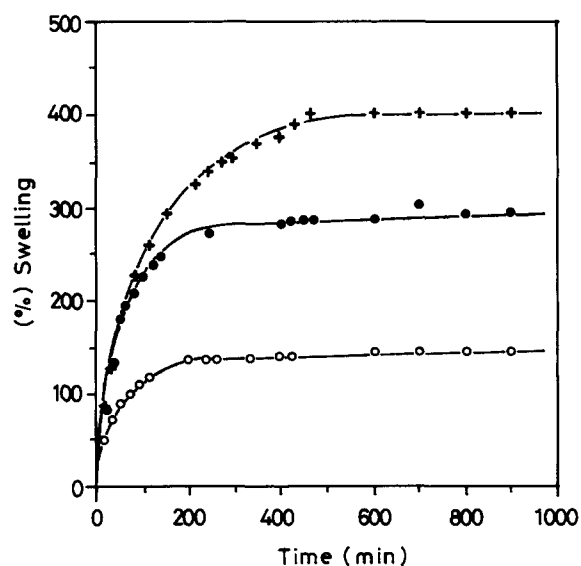
Figure 4 Combined effect of water and crosslinking agent on the percentage swelling of PVP hydrogels. Total dose given 13.5 kGy: (O) 8EGDMA30W62VP; (●) 6EGDMA30W64VP; (+) 4EGDMA30W66VP

Table 1 Dependence of equilibrium swelling of various PVP hydrogels on the dose and composition

8 EGDMA/ 30 W/62 VP		6 EGDMA/ 30 W/64 VP		4 EGDMA/ 30 W/66 VP		8 TMPTA/ 30 W/62 VP		6 TMPTA/ 30 W/64 VP		5 TMPTA/ 30 W/66 VP	
Dose (kGy)	Swelling (%)	Dose (kGy)	Swelling (%)	Dose (kGy)	Swelling (%)	Dose (kGy)	Swelling (%)	Dose (kGy)	Swelling (%)	Dose (kGy)	Swelling (%)
7.5	187	7.5	330	7.5	422	4.5	153	4.5	211	4.5	316
9.0	190	9.0	315	9.0	418	6.0	146	6.0	206	6.0	311
10.5	187	10.5	300	10.5	416	7.5	150	7.5	203	7.5	319
12.0	180	12.0	296	12.0	405	9.0	142	9.0	192	9.0	304
13.5	183	13.5	293	13.5	418	10.5	145	10.5	208	10.5	296
15.7	144	15.7	287	15.7	403	12.0	141	12.0	192	12.0	292
						13.5	143	13.5	198	13.5	285

Table 2 Values of n and k determined from equation (2) for the three-component systems

Dose (kGy)	8 EGDMA/ 30 W/62 VP		6 EGDMA/ 30 W/64 VP		4 EGDMA/ 30 W/66 VP		8 TMPTA/ 30 W/62 VP		6 TMPTA/ 30 W/64 VP		4 TMPTA/ 30 W/66 VP	
	n	k	n	k	n	k	n	k	n	k	n	k
6.0	0.42	10.52	0.50	7.25	0.55	7.41	0.35	16.71	0.45	10.23	0.34	11.67
9.0	0.46	9.68	0.58	5.83	0.53	5.18	0.32	20.95	0.41	12.39	0.38	12.49
10.5	0.48	8.61	0.60	5.22	0.56	4.59	0.30	21.48	0.40	13.73	0.35	14.11
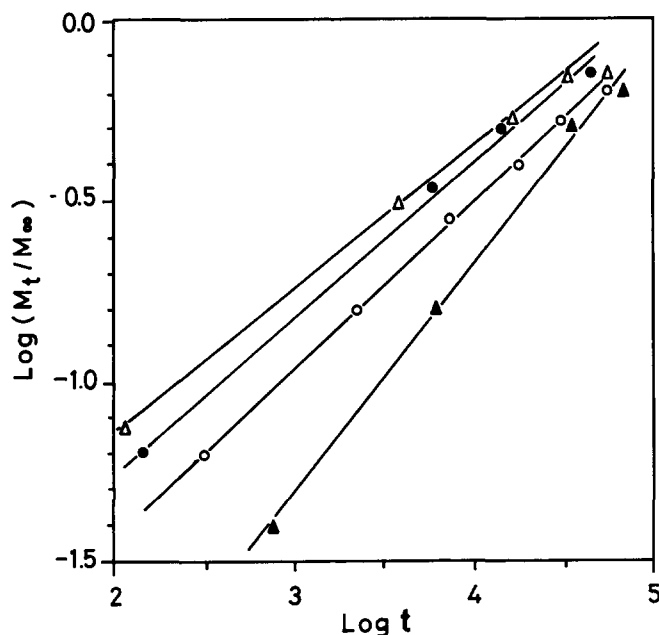
Figure 5 Plots of log M_t/M_∞ *versus* log t for various PVP hydrogels. Total dose given 10.5 kGy: (○) 8EGDMA30W62VP; (▲) 6EGDMA30W64VP; (●) 8TMPTA30W62VP; (△) 6TMPTA30W64VP

Table 3 Values of M_c for the initial hydrogel systems

Hydrogels	M_c
8 EGDMA/30 W/62 VP	2050
6 EGDMA/30 W/64 VP	3650
4 EGDMA/30 W/66 VP	4550
8 TMPTA/30 W/62 VP	1050
6 TMPTA/30 W/64 VP	2200
4 TMPTA/30 W/66 VP	3400

representative results are shown in *Figure 5*. The exponents in equation (2) were calculated from the slope of the lines and are listed in *Table 2*. The values given in this table show that at low concentrations of EGDMA (4–8%), n takes values between 0.42 and 0.60. It can be seen from this table that the lower the amount of EGDMA, i.e. the lower the crosslink density, the more non-Fickian becomes the transport of water into the hydrogels. This is generally explained as a consequence of slow relaxation rate of the polymer matrix. For hydrogels prepared with TMPTA, n is generally smaller than 0.45, with values between 0.30 and 0.45. Substitution of TMPTA, a trifunctional crosslinking agent, instead of the difunctional EGDMA, will eventually result in higher crosslink density for the gels obtained under similar conditions. Increasing the crosslink density of hydrogels caused a substantial decrease in the n value. From the point of view of this decrease in n value we can interpret this behaviour in the following way: when the crosslink density, i.e. the average molecular weight between the crosslinks decreases, the diffusion rate becomes less than the relaxation rate and diffusion of water takes a more Fickian character.

Molecular weight between crosslinks. The average molecular weight between two consecutive crosslinks can be determined by swelling experiments according to the Flory–Rehner[14] equation:

$$\frac{1}{M_c} = \frac{V_s + \chi V_s^2 + \ln(1 - V_s)}{d_p V_1 [V_s^{1/3} - (2V_s/f)]} \quad (3)$$

where M_c denotes the average molecular weight between the crosslinks, V_s is the volume fraction of polymer in the swollen gel, χ is the polymer–solvent interaction parameter, V_1 is the molar volume of solvent, d_p is the specific volume of polymer and f is the functionality of the crosslinking agent. V_s was determined after measuring the dimensions of dry and swollen cylindrical hydrogels using a micrometer (precision ± 0.01 mm) and the following equation:

$$v_s = v_0/v_\infty \quad (4)$$

where v_0 and v_∞ are the volumes of hydrogel in the dry and swollen state respectively. The polymer–solvent interaction parameter, χ, was calculated using the relation:

$$B = 2v^2[1/2 - \chi]/N_A V_1 \quad (5)$$

where B is the Stockmayer–Fixman type interaction parameter determined experimentally by Gargallo and Radic[15], v is the specific volume of polymer, V_1 is the molar volume of solvent (for water 18 ml g^{-1}) and N_A is Avogadro's number. The specific volume of PVP was determined by picnometry to be 0.86 g ml^{-1}.

The M_c values thus determined from equation (3) for every hydrogel system are given in *Table 3*. The results obtained show that the average molecular weight between the crosslinks is affected by the amount and functionality of crosslinking agent. It is therefore possible to control the average dimensions of meshes produced on the crosslinked PVP chains by changing these parameters. This so-called mesh size becomes a very important factor in the design and production of hydrogels used for immobilization purposes[16].

Mechanical properties. The mechanical tests were performed immediately after the preparation of hydrogels and without applying a drying procedure. Freshly prepared hydrogels contained 30% water and were easily clamped for tensile measurements. Highly swollen hydrogels, however, were not easily clamped, and those that could be clamped gave inconsistent results. Mechanical stability of the hydrogels was determined by plotting the stress–strain curves of various samples. The cross-sectional areas of unstretched cylindrical hydrogels were all the same, namely 7 mm². The tensile strength
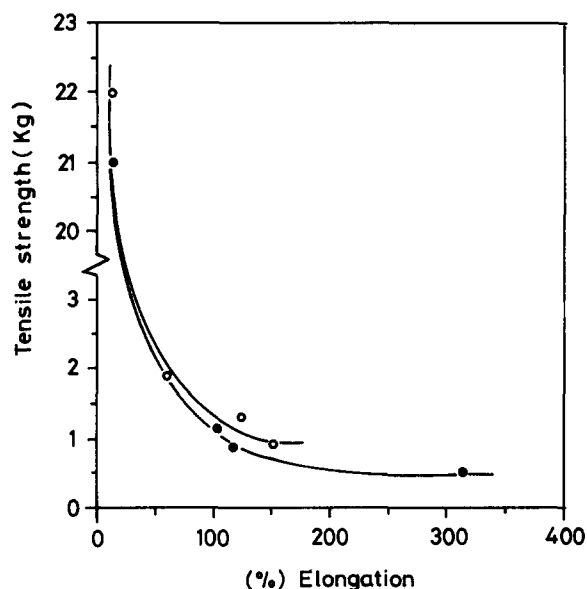
Figure 6 Variation of tensile strength of two hydrogel systems with strain: (○) 6EGDMA(X)W64VP; (●) 4EGDMA(Y)W66VP. The two points in the upper left corner refer to anhydrous systems

Table 4 Tensile strength values for selected hydrogels

Initial water content (%)	Tensile strength (MN m^{-2})	
	4% EGDMA	6% EGDMA
0	29.11	30.50
30	1.608	2.717
34	1.262	1.844
36	0.721	1.303

and elongation to break values were used for comparison. The gels prepared from PVP/EGDMA systems showed the highest tensile strength and lowest elongation to break. With the inclusion of water in these binary systems, the gels prepared had significantly higher elongation to break and consequently lower tensile strength values. The typical effects of crosslinking and plasticization of water on the mechanical properties are observed in gel systems with different compositions. Although increasing the water content of initial mixtures increases the crosslinking efficiency and density, see *Figure 6*, it also shows a plasticization effect which becomes increasingly important, as seen from *Figure 6*. The higher the water content, the longer the elongation

to break values. A similar effect is observed when the EGDMA content is lowered at fixed initial water contents. Tensile strength values calculated for these hydrogels are given in *Table 4*. The values are reported for hydrogels prepared at 4 and 6% EGDMA concentrations with 30, 34 and 36% water content.

CONCLUSION

A different approach to the preparation of PVP hydrogels was followed in this study. Three component mixtures composed of VP monomer, crosslinking agent and water were prepared and irradiated to various total doses at a fixed dose rate. Incorporation of water at the preparation stage of hydrogels enormously decreased the dose required for the formation of insoluble network structures. The resulting hydrogels were later investigated with respect to their swelling properties, diffusion of water into the gels and their mechanical properties. We observed that by changing the relative amounts of water and crosslinking agent and irradiating to various doses it is possible to obtain hydrogels with quite different properties. The swelling of the gels thus prepared was determined to be in the range 140–420% with the tensile strength values varying from 0.721 to 2.717 MN m^{-2}.

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