

Characterization and Determination of Swelling and Diffusion Characteristics of Poly(*N*-vinyl-2-pyrrolidone) Hydrogels in Water

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ABSTRACT: Hydrogels in the form of rods with varying crosslink densities and three-dimensional network structures were prepared from Poly(*N*-vinyl-2-pyrrolidone) (PVP)/water and PVP/water/persulfate systems by irradiation with γ rays at ambient temperature. Average molecular weights between crosslinks, percent swelling, swelling equilibrium values, diffusion/swelling characteristics (i.e., the structure of network constant, the type of diffusion, the initial swelling rate, swelling rate constant), and equilibrium water content were evaluated for both hydrogel systems. Water diffusion to the hydrogel is a non-Fickian type diffusion and diffusion coefficients vary from 6.56×10^{-7} to $2.51 \times 10^{-7} \text{cm}^2 \text{min}^{-1}$ for PVP and 6.09×10^{-7} to $2.14 \times 10^{-7} \text{cm}^2 \text{min}^{-1}$ for PVP/persulfate hydrogel systems. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 994–1000, 2000

Key words: swelling behavior; poly(*N*-vinyl-2-pyrrolidone) hydrogel; poly(*N*-vinyl-2-pyrrolidone)/persulfate hydrogel; water

INTRODUCTION

Hydrogels have been widely used in different application fields from agriculture to controlled drug delivery systems. Generally, the preparation of hydrogels is performed by direct crosslinking of polymers or copolymers in solution using a small amount of a crosslinking agent or beginning from monomer in the presence and/or absence of some comonomers or treating the aqueous solutions of a chosen water-soluble polymer with γ rays. In these preparation techniques, γ ray-induced crosslinking is an effective and simple method for hydrogel formation and has some advantages over the other techniques. It is known as a clean

technique, because it does not require any extra substances, does not leave some unwanted residues, and does not need any further purification.

Poly(*N*-vinyl-2-pyrrolidone) (PVP) is a water-soluble polymer, which exhibits a series of interactions toward dissolved small molecules and ions in aqueous solutions.^{1–7} Aqueous PVP solutions are permanently gelled when crosslinked by reaction with certain chemical reagents⁸ or irradiation with γ rays.⁹ PVP hydrogels, as well as its aqueous solutions have been commonly used in various technologies.

Potassium persulfate is a well-known initiator for the polymerization of vinyl type monomers. However, persulfate anion exhibits a behavior distinguished from the other ions and initiators. It is known that the thermal decomposition of persulfate anion produces sulfate ion radical, which causes chain propagation. However, different types of reaction mechanisms [formation of 1,1 bis(1'-pyrrodonyl) ethane and cationic poly-

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merization] were indicated depending on the content of water in aqueous solutions.¹⁰

Another interesting point is the effect of persulfate anion on the polymer chain structure in aqueous solutions. Crosslinking and/or chain scission of PVP can be observed in aqueous solutions of polymer in the presence of persulfate depending on the content of persulfate in the mixture.^{11,12} On the other hand, some other competing reactions, such as oxidative degradation and ring opening of lactam ring have also been proposed by the same studying groups. As far as we know, the interaction mechanism of persulfate with polymer chains has not been explained clearly until now. However, the kinetic investigations of PVP/persulfate system (in the first few hours of experimentation) have revealed that significant changes occur in the hydrodynamic volume of the polymer which may be interpreted by probable chain scission and/or degradation in the polymer chain.¹³ This idea is also supported by the gelation behavior of PVP in aqueous solutions in the presence of different amounts of persulfate content.¹⁴

The aim of the present study is to investigate the network structure, swelling behavior, and the diffusion of water for hydrogels of PVP and PVP/persulfate prepared by γ -irradiation from their aqueous solutions.

EXPERIMENTAL

Chemicals

The PVP sample used in this study was obtained from British Drug House (BDH; UK) with nominal molecular weight of 700,000 g mol⁻¹. The weight average molecular weight of polymer was determined from light scattering measurements in chloroform at 30°C by Brice-Phoenix Light Scattering Photometer, 2000 Series. The evaluation of the data was achieved by the Zimm method, and the weight average molecular weight, M_w , was calculated as 548,000 g mol⁻¹. Potassium persulfate (K₂S₂O₈) was obtained from Merck and used without further purification.

Preparation of Hydrogels

Aqueous solutions of PVP and persulfate containing PVP aqueous solutions were prepared in different persulfate content (1.0, 1.5, 3.0, and 3.5%) in double-distilled deionized water. The prepared

solutions were then placed in PVC straws and irradiated with a dose of 26, 64, 96, and 124 kGy in air at ambient temperature in a Gamma Cell 220 type of ⁶⁰Co- γ irradiator at a fixed dose rate of 0.40 kGy h⁻¹, the dose being determined by Fricke dosimeter previously.

Measurement of Swelling

Crosslinked polymer samples obtained in long cylindrical shapes were cut into pieces ≈ 0.5 cm long and stored for later evaluations. Gels thus prepared were immersed in distilled water for 1 week to remove uncrosslinked polymers and low molecular-weight substances, and dried to constant weight. Dried hydrogels were left to swell in distilled water at room temperature to determine the parameters of swelling which were removed from the water bath, dried with filter paper, weighed, and placed in the same bath. The percentage swelling (S) was determined gravimetrically by the following equation:

$$S \% = [(m_t - m_o)/m_o] \times 100 \quad (1)$$

where m_o is the initial weight and m_t is the weight of swollen gel at time t .

Density Measurements

Density measurements of PVP and persulfate containing PVP gels were performed by a picnometer for unswollen and swollen samples in two different solvents (*n*-hexane and 1,2-dichloro methane) at room temperature. Reproducibility of the density measurements for all hydrogel system in two solvents was excellent within 0.02 g mL⁻¹.

RESULTS AND DISCUSSION

Charlesby and Alexander¹⁵ first reported crosslinking of PVP, under irradiation of aqueous solutions. Later, gel formation in irradiated solutions of PVP was investigated by many research groups. Chapiro and Legris^{16,17} studied the effect of radiation dose, molecular weight, polymer concentration, and the influence of the nature of the solvent. In recent years, the effects of radiation on the conversion of monomer and the gelation of polymer,¹⁸ the gelation of PVP in the presence of agar and poly(ethylene oxide),¹⁹ preparation of PVP hydrogels in the presence of crosslinking agents (ethylene glycol dimethacrylate and trim-

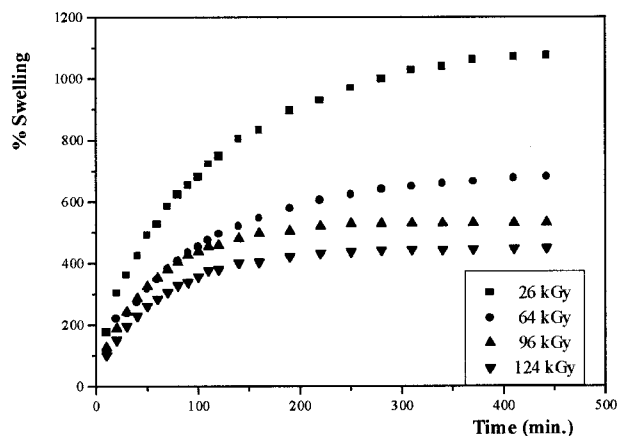


Figure 1 Swelling % values of PVP gels in water at different doses.

ethylolpropane triacrylate)²⁰ were studied and various characteristics (gelation dose, degree of swelling, equilibrium water content, elongation at break, tensile strength, diffusion behavior, etc.) of PVP hydrogels were determined.

Swelling

A fundamental relationship exists between the swelling of a crosslinked polymer in a solvent and the nature of polymer and the solvent. Swelling of the three-dimensional network structure in a suitable solvent is the most important parameter (especially one of the most important parameters is mass swelling^{21–23}) for swelling measurements. The intake of initially dry hydrogels was followed for a long period of time. Swelling curves of PVP and persulfate containing PVP hydrogels are plotted and representative swelling curves are shown in Figures 1 and 2, respectively. As shown in these figures, swelling capabilities of PVP and persulfate containing PVP hydrogels are increased by time, but after a certain period, they show constant swelling (equilibrium swelling).

Another observation is the swelling of gels by irradiation time. It is obvious that increasing the total dose increases the crosslinking density resulting in lower maximum swelling ratio. These two figures also exhibit the equilibrium swelling differences of PVP and persulfate containing PVP hydrogels irradiated at these doses: 26, 64, 96 and 124 kGy. Equilibrium swelling values are indicated as 1070, 670, 530, and 430% for PVP hydrogels at four different doses. However, in the case of persulfate containing PVP hydrogel system, these values are increased to 1300, 700, 600, and

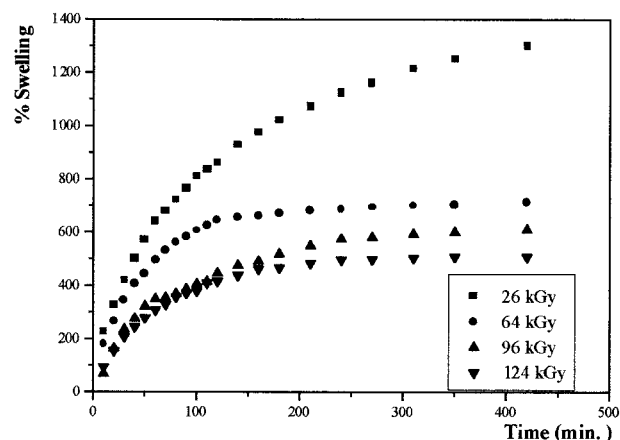


Figure 2 Swelling % values of PVP/K₂S₂O₈ gels in water at different doses.

500%, respectively (Table I). The results obtained from the swelling behavior simply reflect the probability of network structure differences of these two hydrogel systems.

Characterization of Network Structures

Another structural parameter characterizing the crosslinked polymers is the average molecular weight between two consecutive crosslinks (\bar{M}_c) and is directly related to the crosslink density. The magnitude of the \bar{M}_c affects the mechanical, physical and thermal properties of crosslinked polymers. The determination of \bar{M}_c has great practical significance and can be determined by swelling studies according to Flory and Rehner,²³ for a network.

$$\bar{M}_c = -\{V_1 d_p (\phi_p^{1/3} - \phi_p/2)\} / \{[\ln(1 - \phi_p) + \phi_p + \chi \phi_p^2]\} \quad (2)$$

where V_1 is the molar volume of solvent (for water, 18 mL mol⁻¹), d_p is the density of polymer (determined previously as 1.16 g mL⁻¹ for PVP²,

Table I Equilibrium Swelling Percents of PVP and PVP/K₂S₂O₈ Hydrogels in Water

| Dose (kGy) | PVP | PVP/K ₂ S ₂ O ₈ |
|------------|------|--|
| 26 | 1070 | 1300 |
| 64 | 670 | 700 |
| 96 | 530 | 600 |
| 124 | 430 | 500 |

Table II The \bar{M}_c Values of PVP and $K_2S_2O_8$ Containing PVP Hydrogels

| Dose (kGy) | PVP | PVP/ $K_2S_2O_8$ |
|------------|---------|------------------|
| 26 | 273,200 | 317,500 |
| 64 | 116,600 | 132,000 |
| 96 | 16,400 | 23,000 |
| 124 | 16,200 | 11,000 |

ϕ_p is the volume fraction of polymer in the swollen gel and finally, χ is the Flory–Huggins interaction parameter between polymer and solvent molecules which is assumed to be 0.49 for PVP/water system.²⁴

The \bar{M}_c values thus determined from Eq. (2) for PVP and persulfate containing PVP hydrogels are given in Table II. It is shown that number average molecular weight between crosslinks of hydrogels decreased with the irradiation dose. The results obtained also exhibited that \bar{M}_c is affected by persulfate. The \bar{M}_c values of PVP/ $K_2S_2O_8$ hydrogels are higher than the values of PVP hydrogels. This behavior mainly shows that the crosslinking ability of polymer chains is more dominant than persulfate containing PVP chains.

The crosslink density, ρ , is defined as the mol fraction of crosslinked units²⁵:

$$\rho = M_o/\bar{M}_c \quad (3)$$

where M_o is the molecular weight of the polymer repeating unit, and the calculated density values are given in Table III for two hydrogel systems. The obtained results show that the crosslink density increased with irradiation dose and the values of crosslink density of PVP hydrogel are higher than the values of persulfate containing PVP hydrogels.

Diffusion

The swelling curves of PVP and PVP/ $K_2S_2O_8$ hydrogels were used for the calculation of some

Table III The Crosslink Densities (mol/cm³) of PVP and $K_2S_2O_8$ Containing PVP Hydrogels

| Dose (kGy) | PVP | PVP/ $K_2S_2O_8$ |
|------------|-----------------------|-----------------------|
| 26 | 4.07×10^{-4} | 3.50×10^{-4} |
| 64 | 9.53×10^{-4} | 8.43×10^{-4} |
| 96 | 6.78×10^{-3} | 4.82×10^{-3} |
| 124 | 6.87×10^{-3} | 1.01×10^{-3} |

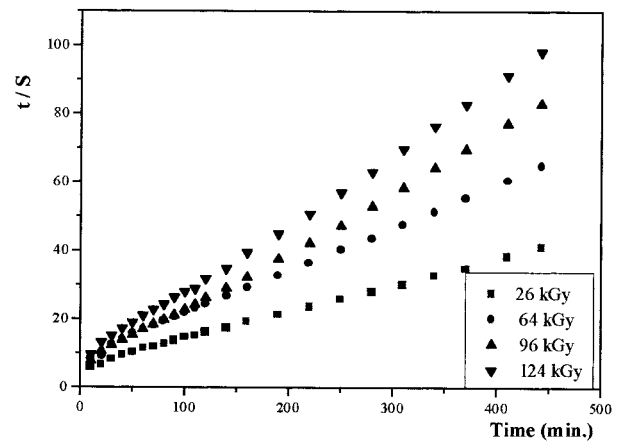
Table IV Diffusion Characteristic of PVP and PVP/ $K_2S_2O_8$ Hydrogels

| Dose (kGy) | PVP | | PVP/ $K_2S_2O_8$ | |
|------------|------|-----------------|------------------|-----------------|
| | n | $k \times 10^2$ | n | $k \times 10^2$ |
| 26 | 0.59 | 6.40 | 0.57 | 6.77 |
| 64 | 0.59 | 6.16 | 0.58 | 5.25 |
| 96 | 0.59 | 5.92 | 0.67 | 4.72 |
| 124 | 0.59 | 4.49 | 0.81 | 4.03 |

characteristic parameters. The following equation was used to determine the nature of diffusion of water into hydrogels²⁶:

$$F = M_t/M_\infty = kt^n \quad (4)$$

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 $0.50 < n < 1.00$ indicates that diffusion is non-Fickian.²⁷ Equation 4 was applied to the stages of swelling and plots of $\ln F$ against $\ln t$ yielded straight lines from which the exponent n and k were calculated from the slope and intercept of the lines listed in Table IV. It is clearly seen from the table that the values of the diffusion exponent range between 0.57 and 0.81 and are found to be over 0.50. Hence, the diffusion of water into PVP and PVP/ $K_2S_2O_8$ hydrogels was taken as a non-Fickian


Figure 3 t/S versus t graphs for PVP hydrogels in water at different doses.

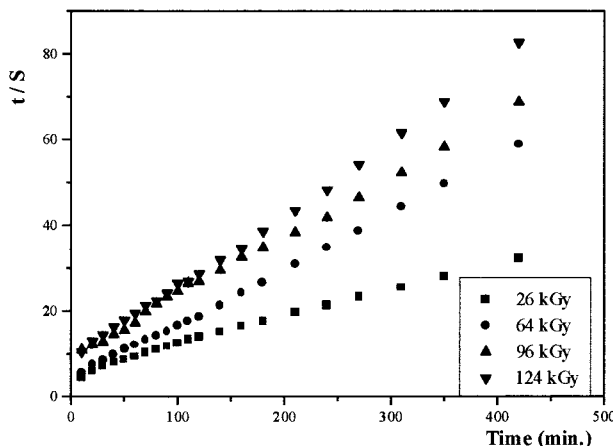


Figure 4 t/S versus t curves for PVP/K₂S₂O₈ hydrogels in water at different doses.

character. It can also be noticed from this table that at higher irradiation doses (96 and 124 kGy) of PVP/K₂S₂O₈, i.e., the higher the crosslink density, the more the transport of water into the hydrogels becomes non-Fickian. This behavior is generally explained as a consequence of slow relaxation rate of polymer matrix.

For extensive swelling of PVP and PVP/K₂S₂O₈ hydrogels, the following equation^{28,29} can be written:

$$t/S = A + Bt \quad (5)$$

where $B = 1/S_{\text{eq}}$ is the reciprocal of the maximum or equilibrium swelling, $A = 1/(k_s S_{\text{eq}}^2)$ is the reciprocal of the initial swelling rate of the gel and k_s is the swelling rate constant. This relation represents second order kinetics.²³ Figures 3 and 4 exhibit the linear regression of the swelling curves obtained by means of Eq. (5) for PVP and PVP/K₂S₂O₈ hydrogels. The initial rate of swell-

ing (r_i), swelling rate constant, and theoretical equilibrium swelling of PVP and PVP/K₂S₂O₈ hydrogels are calculated from the slope and intersection of the lines, presented in Table V.

The values of theoretical equilibrium swelling of the hydrogels are in good agreement with the results of equilibrium swelling of PVP and PVP/K₂S₂O₈ hydrogels (Figs. 1 and 2). Swelling process of PVP/K₂S₂O₈ hydrogels is quicker than the swelling rate of PVP hydrogels. It is well known that the swelling phenomena are directly related to the structure of crosslinked polymer and/or density of the hydrogel.

The study of diffusion phenomenon in hydrogel and water is of importance as it clarifies polymer behavior.³⁰ For the characterization of hydrogels, the diffusion coefficient (D) can be determined by different methods.^{31,32} The short-time approximation method is used for the calculation of diffusion coefficients of hydrogels. This method is used for the first 60% of swelling of crosslinked polymers in a chosen solvent. Commonly, the diffusion coefficient of cylindrical hydrogel is determined by the following equation:

$$F = M_t/M_\infty = 4[Dt/\pi r^2]^{1/2} - \pi[Dt/\pi r^2] - \pi/3[Dt/\pi r^2]^{3/2} + \dots \quad (6)$$

where D is the diffusion coefficient (cm²min⁻¹), t is the time (min), and r is the radius (cm) of cylindrical polymer samples. The graphical comparison of Eqs. (4) and (6) shows the semi-empirical Eq. (4) with $n = 0.50$, and $k = 4 [Dt/\pi r^2]^{1/2}$.

The diffusion coefficients of PVP and PVP/K₂S₂O₈ hydrogels were calculated from the slope of the lines of F against $t^{1/2}$ by a computational program. The results are listed in Table VI for two different hydrogel systems, from which it can

Table V The Swelling Characteristic of PVP and PVP/K₂S₂O₈ Hydrogels

| Dose (kGy) | PVP | | | PVP/K ₂ S ₂ O ₈ | | |
|------------|---------|----------------------|-------------------|--|-------------------|-----------------|
| | r_i^a | $k_s \times 10^{3b}$ | S_{eq}^c | r_i | $k_s \times 10^3$ | S_{eq} |
| 26 | 0.164 | 1.01 | 12.72 | 0.245 | 0.78 | 15.29 |
| 64 | 0.162 | 1.64 | 8.03 | 0.182 | 1.07 | 7.75 |
| 96 | 0.123 | 4.76 | 5.87 | 0.119 | 1.88 | 7.27 |
| 124 | 0.106 | 4.94 | 4.99 | 0.114 | 3.33 | 5.86 |

^a (g water/g gel)/min.

^b (g gel/g water)/min.

^c (g water/g gel).

be seen that the values of the diffusion coefficients of PVP and PVP/K₂S₂O₈ hydrogels vary from 2.14×10^{-7} to 6.56×10^{-7} cm²min⁻¹. The obtained results also exhibit that the diffusion coefficient is highly affected by the crosslink density and the nature of the three-dimensional network structure of the gel system.

Equilibrium Water Content (EWC)

Equilibrium water content has been calculated from the following equation¹⁸:

$$EWC = [(W_{eq} - W_{dry})/W_{eq}] \times 100 \quad (7)$$

where W_{eq} is the water content diffused into the gel at equilibrium state and W_{dry} is the weight of initially dried gel, and determined EWC values are presented in Table VII.

Along with the increase of irradiation dose, the equilibrium water content is decreased for two hydrogel systems. Equilibrium water content, as well as the swelling behavior of hydrogel mainly depend on the nature of the network structure, i.e., hydrophilicity, crosslink density, and the average molecular weight between two consecutive crosslinks. When two different hydrogel systems are compared, it is clearly seen that the values of EWC of PVP/K₂S₂O₈ hydrogels are about 2.0% higher than those for PVP hydrogels. This observation is in agreement with the swelling results of these two hydrogel systems.

CONCLUSION

In this study, the swelling behavior of two hydrogels (PVP and PVP/K₂S₂O₈) with differing crosslink densities and average molecular weights between two consecutive crosslinks has been investigated. It has been detected that, when two hydrogel systems are compared, the PVP/K₂S₂O₈ hydrogel system with lower crosslink density has higher equilibrium swelling, initial rate of swelling, theoretical equilibrium swelling, and equilibrium water content values in water. Comparison of obtained diffusion coefficients for both hydrogel systems proves that the diffusion coefficient of PVP/K₂S₂O₈ hydrogel is much smaller as expected according to Eq. 6. Enhancement and/or facility of diffusion result in a decrease in diffusion coefficient value.

Table VI Variation of the Diffusion Coefficient (cm² min⁻¹) for PVP and PVP/K₂S₂O₈ Hydrogels

| Dose (kGy) | $D \times 10^7$ (PVP) | $D \times 10^7$ (PVP/K ₂ S ₂ O ₈) |
|------------|-----------------------|---|
| 26 | 2.51 | 2.14 |
| 64 | 3.46 | 3.29 |
| 96 | 4.60 | 4.46 |
| 124 | 6.56 | 6.09 |

Table VII Equilibrium Water Content (%) of PVP and PVP/K₂S₂O₈ Hydrogels

| Dose (kGy) | PVP | PVP/K ₂ S ₂ O ₈ |
|------------|------|--|
| 26 | 91.5 | 93.0 |
| 64 | 87.0 | 89.0 |
| 96 | 84.0 | 86.0 |
| 124 | 82.0 | 84.0 |

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