Swelling Behavior of Poly(N-vinyl-2-pyrrolidone) and Poly(N-vinyl-2-pyrrolidone)/ $K_2S_2O_8$ Hydrogels in Urea Solutions

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ABSTRACT: Hydrogels with varying cross-linking densities and average molecular weights between two consecutive cross-links were prepared from the binary poly(N-vinyl-2-pyrrolidone)/water and ternary poly(N-vinyl-2-pyrrolidone)/water/$K_2S_2O_8$ systems by irradiation with γ rays at ambient temperature. Both hydrogel systems were employed for diffusion and swelling experiments in various urea solutions at room temperature. Diffusion of urea solutions into hydrogels has been found to be of the non-Fickian type, except for the samples of PVP/$K_2S_2O_8$ hydrogels irradiated at higher doses in dilute urea solutions. The percent swelling, equilibrium swelling, initial rate of swelling, swelling rate constant, equilibrium water/urea content, and diffusion constant values were evaluated for PVP and PVP/$K_2S_2O_8$ hydrogel systems at two different urea concentrations. With regard to swelling data, it was determined that the dilute urea solution can penetrate much more effectively into the PVP/$K_2S_2O_8$ hydrogel system. © 2000 John Wiley & Sons, Inc. Adv Polym Techn 19: 210–217, 2000

Introduction

Charlesby and Alexander[1] first reported cross-linking of poly(N-vinyl-2-pyrrolidone) (PVP) under irradiation of aqueous solutions. In later

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studies, gel formation in irradiated solutions of PVP was investigated by many researchers. Chapiro and Legris[2,3] studied the effect of radiation dose, molecular weight, polymer concentration, and the influence of the nature of the solvent on crosslinking of PVP. Recently, the effects of radiation on the conversion of monomer and the gelation of polymer,[4] the gelation of PVP in the presence of agar and

poly(ethylene oxide),[5] preparation of PVP hydrogels in the presence of cross-linking agents (ethylene glycol dimethacrylate and trimethylolpropane triacrylate)[6] 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 evaluated.

Water-soluble polymers, poly(ethylene oxide) (PEO), dextran, and PVP are known to form association complexes in aqueous solutions. Obviously, different types of additives (inorganic and organic cosolutes) can change molecular association already existing between polymer and solvent molecules. Previously, the effects of inorganic salts on dynamic and thermodynamic properties of PEO[7,8] and PVP,[9–11] and the effects of special organic cosolutes (namely, denaturing agents; urea, thiourea, and guanidinium salts) on different solution properties of PEO[12] and PVP,[13–16] dextran[17] and periodate-oxidized dextran[18] were studied in aqueous solutions. These studies revealed that the dynamic and thermodynamic behavior of water-soluble polymers mainly depend on the nature of cosolute, their concentrations, and the temperature.

Persulfate anion has a different behavior on PVP and its monomer. It is commonly known that the persulfate anion is an initiator for the polymerization of vinyl type monomers and exhibits a more distinguished behavior than the other initiators.[19] Another unusual behavior is the effect of persulfate anion on the polymer chain structure in aqueous solutions. Two different trends; that is, cross-linking and chain scission of PVP, can be observed in aqueous solutions of polymer in the presence of persulfate anion, depending on the content of persulfate in the mixture.[20,21] In addition, some other reactions, oxidative degradation and ring opening lactam ring, were also proposed by the same research groups. The interaction mechanism of persulfate anion with PVP chains has not been explained until now. Recent studies have revealed that significant changes occur in the hydrodynamic volume of PVP, which may be interpreted by probable chain scission in the polymer chain in the presence of persulfate anion.[22] This observation is also supported by the gelation of PVP in aqueous solutions in the presence of different concentrations of persulfate.[23]

Urea is a toxic substance and has a great importance in biological systems. Our previous studies revealed that urea was not effective on certain solution properties, such as molecular association, viscometric characteristics, reduction of the theta

temperatures, polymer dimensions, and thermodynamic characteristics of water-soluble polymers compared with the other denaturing agents. However, studies are being widely carried out on binding and/or interactions of urea with PVP due to its biological importance.[24,25]

In this study, the effect of urea (at two concentrations of 0.01 M and 0.03 M aqueous urea solutions) on swelling characteristics of PVP and PVP/K$_2$S$_2$O$_8$ hydrogels has been investigated.

Experimental

CHEMICALS

The PVP sample used in this study was obtained from British Drug House (BDH) with nominal molecular weight of 700,000 g mol^{-1}. The weight average molecular weight of the sample was determined from light scattering measurements in chloroform at 30°C by Brice–Phoenix Light Scattering Photometer, 2000 series. The specifications of instrument and determined characteristics and second virial coefficient, root-mean-square radius of gyration were reported previously.[9,15] The interpretation of light scattering data was based on the Zimm method. It has a weight average molecular weight of 548,000 g mol^{-1}. Potassium persulfate (K$_2$S$_2$O$_8$) and urea were obtained from Merck and aqueous urea solutions were prepared after recrystallization of urea.

PREPARATION OF PVP HYDROGELS

Aqueous solutions of PVP (6%) and PVP aqueous solutions containing 4% potassium persulfate were prepared using double distilled deionized water. The prepared polymer solutions (PVP/water and PVP/water/K$_2$S$_2$O$_8$) were then placed in PVC straws and irradiated with a dose of 24, 64, 96, and 124 kGy in air at ambient temperature in a Gamma Cell 220 type[60] Co γ irradiator at a fixed dose rate of 0.40 kGy h^{-1}, the radiation dose being determined by Fricke dosimeter previously. The PVP, K$_2$S$_2$O$_8$ ratio value and the irradiation doses mentioned previously, were preferable since the exact cylindrical geometry of the gels had been obtained under these optimum conditions.

MEASUREMENT OF SWELLING

Cross-linked PVP samples have been obtained in long cylindrical shapes cut into pieces ~ 0.5 cm long and stored for later studies. Gels thus prepared were immersed in distilled water for a week to remove uncross-linked polymers and low molecular-weight substances, and dried to constant weight. Dried hydrogels were left in urea solutions at room temperature (20°C) to determine the parameters of swelling which were removed from the urea solutions, dried with filter paper, weighed, and placed in the same solutions. The percentage swelling (S) was determined gravimetrically by the following equation,

$$S\% = [(M_t - M_o)/M_o] \times 100 \qquad (1)$$

where M_o is the initial weight and M_t is the weight of swollen gel at time, t.

In this study, measurements have been achieved at two optimum urea concentrations, since at low urea concentrations (<0.01 M) concentration dependence of swelling has not been observed. Similarly, at higher urea concentrations (>0.03 M) no effective swelling has occurred for either hydrogel system.

DENSITY MEASUREMENTS

Density measurements of PVP and PVP/K₂S₂O₈ gels were carried out 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 systems in both solvents was excellent within 0.02 g mL⁻¹.

NETWORK STRUCTURE CHARACTERIZATION OF PVP AND PVP/K₂S₂O₈ HYDROGELS

Average molecular weights between two consecutive cross-links ($\overline{M}_c$) for PVP and PVP/K₂S₂O₈ hydrogel systems were determined by Flory and Rehner eq.[26] and evaluated. $\overline{M}_c$ values were reported in the previous part of this study.[27] It was found that the number average molecular weight between cross-links of hydrogel decreased with the irradiation dose and the results obtained showed that $\overline{M}_c$ is affected by persulfate content. The $\overline{M}_c$ values of the PVP/K₂S₂O₈ hydrogel system were found to be higher than the values of the PVP hydrogel systems.

The cross-link densities of both hydrogel systems were also determined by the mole fraction or the cross-linked units.[28] The calculated values exhibited that the cross-linking density increased with irradiation dose and the values of cross-link density of PVP hydrogel were higher than those of PVP/K₂S₂O₈ hydrogels.[27]

Results and Discussion

SWELLING

A fundamental relationship exists between the swelling of a cross-linked polymer in a solvent and the nature of the polymer and the solvent. Swelling of the cross-linked polymers in the chosen and/or suitable solvent is the most important parameter (especially since one of the most important parameters is mass swelling[29,30]) for swelling studies. The intake of initially dry hydrogels was followed for a long period of time in urea solutions. Swelling curves of PVP and PVP/K₂S₂O₈ hydrogels are plotted and representative swelling curves at two urea concentrations are shown in Figure 1. As can be seen from this figure, swelling capabilities of PVP and PVP/K₂S₂O₈ hydrogels are increased by time, reaching constant swelling (equilibrium swelling) after a certain period of time.

Another observation is the swelling of the gels depends on the irradiation dose. It is obvious that increasing the total radiation dose increases the cross-linking density, resulting in lower maximum swelling percent. As shown in these curves, the swelling capabilities of PVP and PVP/K₂S₂O₈ hydrogels vary in the range 440–1420% in urea solutions. In order to make a better comparison, the determined equilibrium swelling percentages are given in Table I. It is clearly seen that the highest swelling percentages are observed in the PVP/K₂S₂O₈ hydrogel system at the lower concentration of urea aqueous solution. On the other hand, the swelling behaviors of PVP hydrogels in 0.01 M of urea, PVP hydrogels in 0.03 M of urea, and PVP/K₂S₂O₈ hydrogels in 0.03 M of urea yield almost the same percentages. Before explanation of the swelling of hydrogels in the presence of urea, it is better to discuss the effect of additives on the structure of water and interactions between polymer and solvent molecules.

It is known that the Mark-Houwink exponent, **a,**
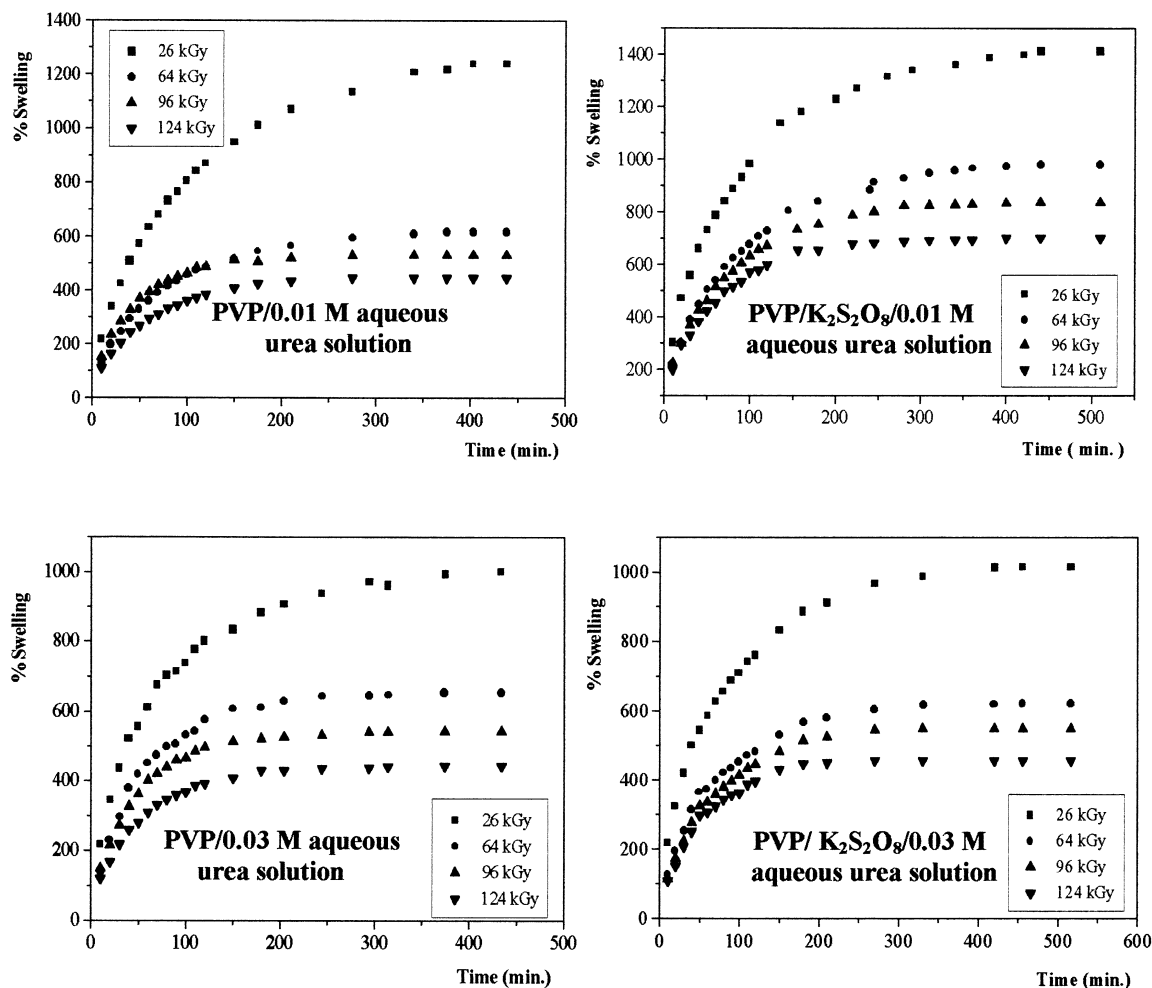
FIGURE 1. Swelling % values of PVP and PVP/K$_2$S$_2$O$_8$ gels in 0.01 and 0.03 M aqueous urea solution at different radiation doses.

depends on the nature of solvent, temperature, and the molecular weight of the polymer. At the theta temperature, **a** is equal to 0.50. This exponent has been found as 0.55 in the Mark-Houwink equation for the system PVP/H$_2$O, which is close to 0.50, showing the characteristic of a theta solvent.[31] It is obvious that the additives can change and/or disturb the hydrogen-bonded structure of water and the molecular association of the water-soluble polymer in aqueous media, as well as the swelling behavior of cross-linked PVP chains.

In the presence of urea, swelling of hydrogels can easily follow the change of the hydrogen-bonded structure of water and polymer-solvent interaction. Equilibrium swelling percentages were indicated as 1300, 700, 600, and 500% for PVP/K$_2$S$_2$O$_8$ hydrogel systems in aqueous solutions.[27] However, in the

case of 0.01 M of aqueous urea solutions, these percentages are increased to 1420, 980, 810, and 720% for the same hydrogel system, respectively. The variation in the nature of solvent has positively affected the swelling behavior of hydrogels. It is interesting that swelling percentages of PVP and PVP/K$_2$S$_2$O$_8$ in 0.03 M aqueous urea solution are nearly the same as the swelling values of PVP and PVP/K$_2$S$_2$O$_8$ hydrogels in water. This behavior mainly indicates the probability of interaction of urea molecules among themselves through hydrogen bonding at high urea concentration.

DIFFUSION

The swelling curves of PVP and PVP/K$_2$S$_2$O$_8$ hydrogels in aqueous urea solutions were used for the

Equilibrium Swelling (%) of PVP and PVP/$K_2S_2O_8$ Hydrogels in 0.01 and 0.03 M Aqueous Urea Solutions

Dose (kGy)	0.01 M Aqueous Urea Solution		0.03 M Aqueous Urea Solution	
	PVP	PVP/$K_2S_2O_8$	PVP	PVP/$K_2S_2O_8$
26	1240	1420	1020	1000
64	620	980	620	640
96	520	840	540	540
124	440	720	450	440

calculation of certain diffusion characteristics. The following equation was used to determine the nature of diffusion of urea solution into hydrogels,[32]

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

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 numerical value 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.[33] Equation 2 was applied to various stages of swelling and plots of $\ln F$ against $\ln t$ yielded straight lines from which the exponents n and k were calculated from the slope and intercept of the lines listed in Table II at 0.01 M and 0.03 M aqueous urea solutions. It is clearly seen from the table that the values of the diffusion exponent range between 0.52 and 0.65 and are found to be over 0.50. Hence, the diffusion of urea solutions into PVP and PVP/$K_2S_2O_8$ hydrogels was assumed to be non-Fickian in character. It can also be noticed from Table II that in dilute urea solution and at higher irradiation doses (96 and 124 kGy) of PVP/$K_2S_2O_8$, that is, the higher the crosslinking density is, the more the transport of urea solutions into the hydrogels becomes.

For extensive swelling of PVP and PVP/$K_2S_2O_8$ hydrogels in urea solutions the following equation[34,35] can be used,

$$t/S = A + Bt \qquad (3)$$

where $B = 1/S_{eq}$ is the reciprocal of the maximum or equilibrium swelling, $A = 1/(k_sS_{eq}^2)$ is the reciprocal of the initial swelling rate of the gel, and k_s is

Diffusion Characteristics of PVP and PVP/$K_2S_2O_8$ Hydrogels in 0.01 and 0.03 M Aqueous Urea Solutions

	0.01 M Aqueous Urea Solution			
	PVP		PVP/$K_2S_2O_8$	
Dose (kGy)	n	$k \times 10^2$	n	$k \times 10^2$
26	0.58	4.72	0.52	6.69
64	0.56	5.86	0.52	6.79
96	0.58	6.85	0.46	9.28
124	0.56	7.43	0.46	10.08

	0.03 M Aqueous Urea Solution			
	PVP		PVP/$K_2S_2O_8$	
Dose (kGy)	n	$k \times 10^2$	n	$k \times 10^2$
26	0.59	4.08	0.56	4.57
64	0.60	5.61	0.63	4.78
96	0.55	7.31	0.65	5.80
124	0.56	7.89	0.60	5.92

the swelling rate constant. This relation represents second order kinetics.[34] Figure 2 exhibits the linear regression of the swelling curves obtained by means of eq. (3) for PVP and PVP/$K_2S_2O_8$ hydrogels in two different urea concentrations. The initial rate of swelling (r_i), swelling rate constant, and equilibrium swelling (or as commonly used, theoretical equilibrium swelling) of PVP and PVP/$K_2S_2O_8$ hydrogels are calculated from the slope and intersection of the lines given in Table III for both hydrogel systems in 0.01M urea solutions. The values of theoretical equilibrium swelling of the hydrogels are in good agreement with the results of equilibrium

Calculated r_1 {(g water/g gel)/min}, k_s {(g gel/g water)/min}, and S_{eq} {(g water/g gel)} Values of PVP and PVP/$K_2S_2O_8$ Hydrogels in 0.01 M Aqueous Urea Solution

	PVP			PVP/$K_2S_2O_8$		
Dose (kGy)	r_i	$k_s \times 10^3$	S_{eq}	r_i	$k_s \times 10^3$	S_{eq}
26	0.193	0.91	14.55	0.285	1.14	15.79
64	0.132	2.70	7.00	0.224	1.58	11.06
96	0.131	5.36	5.67	0.213	2.48	9.26
124	0.127	7.21	4.94	0.193	3.86	7.62
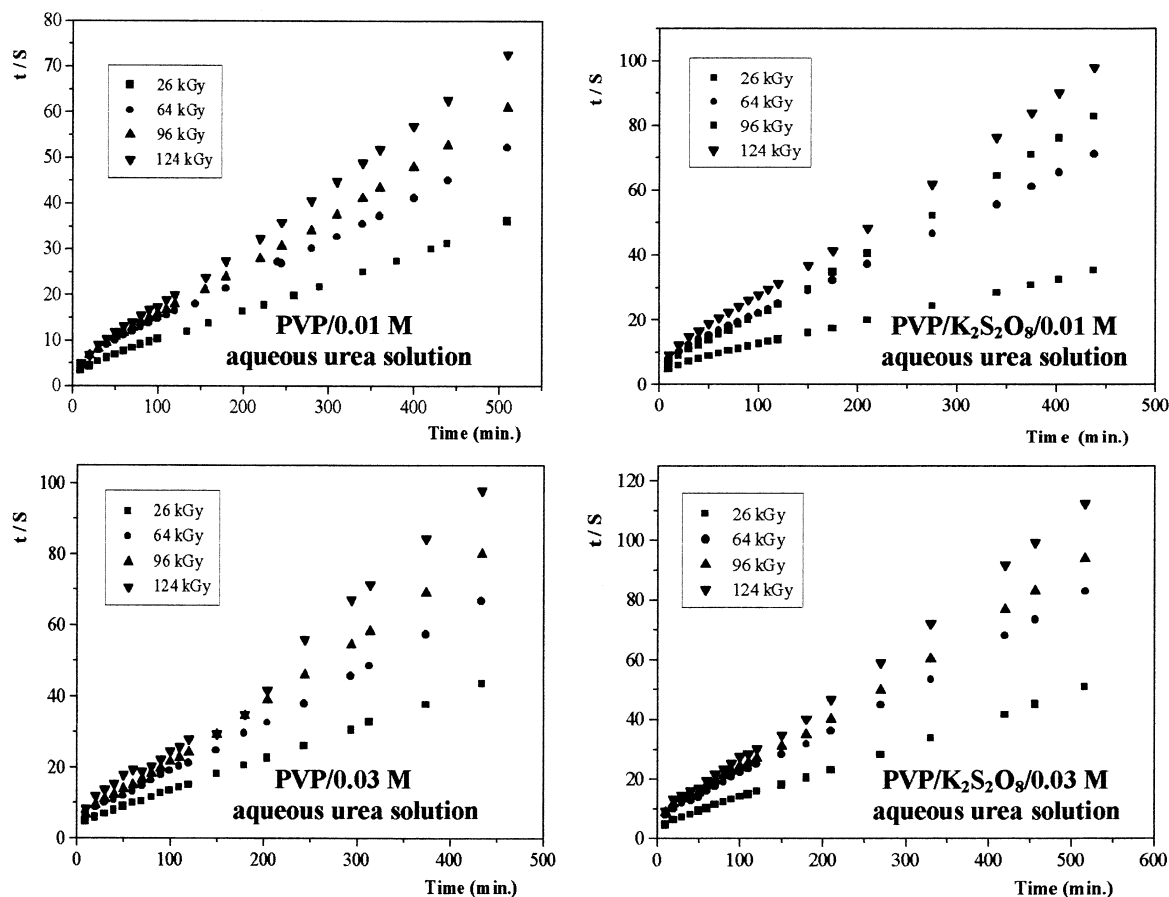
FIGURE 2. t/S vs. t graphs plotted for PVP and PVP/K$_2$S$_2$O$_8$ gels in 0.01 and 0.03 M aqueous urea solution.

swelling of PVP and PVP/K$_2$S$_2$O$_8$ hydrogels (Figure 1). Swelling process of PVP/K$_2$S$_2$O$_8$ hydrogels is quicker than the swelling rate of PVP hydrogels. It is well known that swelling is directly related to the structure of the cross-linked polymer and/or the density of the hydrogel. Initial swelling rate, rate constant, and equilibrium swelling values given above were lower in 0.03 M aqueous urea solution than those in 0.01 M aqueous urea solution. The initial swelling rates of PVP/K$_2$S$_2$O$_8$ hydrogels in the same urea solution were determined as 0.212, 0.144, 0.143, and 0.135 with increasing radiation dose, respectively, and the swelling rate constants were found to be lower in the same urea solution. S_{eq} values were determined as 11.11, 7.21, 5.87, and 4.87 for PVP hydrogels, whereas the values appeared as 11.33, 6.92, 6.10, and 4.99 for PVP/K$_2$S$_2$O$_8$ hydrogels.

The study of diffusion phenomenon in hydrogel and solvent is of importance as it clarifies the polymer behavior.[36] For the characterization of hydro-

gels, the diffusion coefficient (D) can be determined by different methods.[37, 38] 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 cross-linked polymers in a chosen solvent. Commonly, the diffusion coefficient of cylindrical hydrogel is determined by the following equation,

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

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

The diffusion coefficients of PVP and PVP/K$_2$S$_2$O$_8$ hydrogels were also calculated from the slope of the lines of F against $t^{1/2}$ by a computational

program in urea solutions. The results are listed in Table IV for two different hydrogel systems. It can be seen from the table that the values of the diffusion coefficients of PVP/K$_2$S$_2$O$_8$ hydrogels in 0.01 and 0.03 M aqueous urea solutions vary from 3.36×10^{-7} to 5.09×10^{-7} cm^2 min^{-1} and 5.24×10^{-7} to 6.29×10^{-7} cm^2 min^{-1}, respectively. With regard to the values in Table IV, it can be proposed that 0.01M urea solution can penetrate more easily into the PVP/K$_2$S$_2$O$_8$ hydrogel system. However, it has been found that D values determined for PVP hydrogels change between the range 7.0×10^{-7} to 9.0×10^{-7} cm^2 min^{-1} and are higher than the value observed for PVP/K$_2$S$_2$O$_8$ hydrogels. This result implies that PVP/K$_2$S$_2$O$_8$ hydrogels swell much more in urea solutions (being more efficient at 0.01M aqueous urea solution) compared to that in water, thus increasing diffusion.

EQUILIBRIUM WATER/UREA CONTENT (EWUC)

Equilibrium water/urea content has been calculated from Eq. (5),

$$EWUC = [(W_{dry} - W_{eq})/W_{eq}] \times 100 \qquad (5)$$

where W_{eq} is the water/urea content diffused into the gel at equilibrium state and W_{dry} is the weight of initially dried gel. The determined EWUC values are presented in Table V. Along with the increase of irradiation dose, the equilibrium water/urea content is decreased for both hydrogel systems. Equilibrium water/urea content, as well as the swelling behavior of hydrogel, mainly depends on the nature of network structure, that is, hydrophilicity, crosslinking density, and the average molecular weight between two consecutive cross-links. When two different hydrogel systems are compared, it is clearly

TABLE IV ■
Diffusion Coefficient (cm^2 min^{-1}) of PVP/K$_2$S$_2$O$_8$ Hydrogels in 0.01 and 0.03 M Aqueous Urea Solutions

Dose (kGy)	$D \times 10^7$, 0.01 M Aqueous Urea Solution	$D \times 10^7$, 0.03 M Aqueous Urea Solution
26	5.09	6.29
64	4.09	6.05
96	3.76	5.21
124	3.36	5.24

TABLE V ■
Equilibrium Water/Urea Content (%) of PVP and PVP/K$_2$S$_2$O$_8$ Hydrogels in 0.01 and 0.03 M Aqueous Urea Solutions

Dose (kGy)	0.01 M Aqueous Urea Solution		0.03 M Aqueous Urea Solution	
	PVP	PVP/K$_2$S$_2$O$_8$	PVP	PVP/K$_2$S$_2$O$_8$
26	92.5	93.5	90.9	91.0
64	86.1	90.7	86.7	86.2
96	84.1	89.3	84.4	84.6
124	81.7	87.5	81.6	82.1

seen that the values of EWUC of PVP/K$_2$S$_2$O$_8$ hydrogels in 0.01M aqueous urea solution are higher than the values of EWUC for PVP hydrogels and of both hydrogels in 0.03 M aqueous urea solutions. This observation is also in good agreement with the swelling results of these two hydrogel systems and with that of equilibrium swelling and initial swelling rate values mentioned previously.

Conclusion

The Swelling capabilities of PVP and PVP/K$_2$S$_2$O$_8$ hydrogels, followed for a long period of time in urea solutions, increase with immersion time. On the other hand, irradiation dose increase the crosslinking density, resulting in lower swelling percent. In 0.01 M urea solution, the PVP/K$_2$S$_2$O$_8$ system showed optimum swelling capability with regard to kinetic swelling magnitudes. The diffusion of urea solutions into PVP and PVP/K$_2$S$_2$O$_8$ hydrogels was assumed to be non-Fickian in character. The theoretical equilibrium swelling of the hydrogels fitted quite well with those of PVP and PVP/K$_2$S$_2$O$_8$ hydrogels, where the swelling rate of the PVP/K$_2$S$_2$O$_8$ system was faster than that observed in PVP hydrogels. Penetration of 0.01 M urea solution into PVP/K$_2$S$_2$O$_8$ hydrogels is the most efficient, implying that aqueous solutions of urea facilitate and consequently increase the diffusion process compared to that in water.

Acknowledgments

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