

## DIFFUSION IN POLYVINYLPYRROLIDONE HYDROGELS PREPARED BY RADIATION TECHNIQUE

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**Abstract**—Hydrogels of polyvinylpyrrolidone (PVP) were prepared by using polymer aqueous solutions at 10% w/w and gamma radiation. The swelling experiments were carried out in water at 30° and followed by weighing. The concentration of effective chains ( $V_e$ ) and the number-average molecular weight between crosslinks were calculated by considering the chain-end effects. Diffusion and partition coefficients of rhodamine dye were calculated by following the diffusion of the solute out of PVP gel cylinders into water at 30°. The effect of gel structure on diffusion was studied by preparing gels with various radiation doses and PVP molecular weights.  $V_e$  increased with rise in radiation dose, indicating clearly that hydrogels of controlled structure can be prepared. The molecular weight of the polymer altered the gel structure, but these effects were more pronounced at lower absorbed radiation doses. Diffusion coefficient decreased with increase in radiation dose showing the influence of gel structure on solute diffusion.

### INTRODUCTION

Polyvinylpyrrolidone (PVP) is a polyamide that has unusual complexing and colloidal properties and is physiologically inert. Aqueous solutions of PVP when heated with strong bases such as sodium metasilicate or trisodium phosphate form a precipitate [1] but, when PVP aqueous solutions are submitted to high energy radiation, hydrogels with high water absorption are obtained [2]. The water absorption capacity is directly related to the degree of crosslinking which depends to a great extent on the radiation dose, the type of high-energy radiation (electron-beams,  $\gamma$ -rays, fast protons, X-rays, etc.), and to a smaller extent on the dose rate and temperature [2–4].

The excellent biocompatibility, the high water permeability, the controlled release of drugs, etc. of hydrogels have caused increasing interest in these materials for biomedical applications. For this particular purpose, the high energy radiation process offers a special advantage since no additives are necessary in the aqueous solution; moreover the availability of reliable and powerful radiation sources has increased and their costs have diminished as compared with chemical treatment [5, 6].

The most important characteristic of an elastomeric network is unquestionably its degree of crosslinking. It is of great importance in the design of materials having specified properties for a wide range of applications. The measurement of solvent swelling is a convenient means for determining this variable if the appropriate solvent-polymer interaction parameters are known [7, 8]. Diffusion coefficient is important to quantify solute diffusion through hydrogels, and partition coefficient characterizes the equilibrium distribution of the diffusing substance between the gel phase and the solution, a quantity which reflects the relative strengths of the attractive and repulsive interactions in the system [9, 10].

Although there are many publications concerning the direct or indirect effects of ionizing radiation on PVP aqueous solutions [11], very little has been published on transport phenomena for these gels.

The objective of this work is to prepare hydrogels from PVP aqueous solutions and gamma radiation, to calculate the network crosslinking density, and to study the influence of the molecular weight of the polymer and gel structure on the diffusion and partition coefficients of low molecular weight solutes.

### EXPERIMENTAL PROCEDURES

#### 1. Hydrogel preparation

The PVP samples used in this study were commercial products of Sigma Chemical Co. references K24 ( $\bar{M}_n = 24,000$ ), K40 ( $\bar{M}_n = 40,000$ ), and K90 ( $\bar{M}_n = 360,000$ ). Air was removed from PVP aqueous solutions by placing them in small Petri dishes (4 cm dia by 2 cm height) with moulds (rings of 0.7 cm dia by 1.0 cm height). The Petri dishes were placed in vessels which were submitted to a vacuum of 15 mmHg for 2 hr and then saturated with  $N_2$  for 15 min. Under this  $N_2$  atmosphere, the vessels were sealed and then irradiated. Irradiations of aqueous solutions at a concentration of 10% w/w were carried out in a Cobalt-60  $\gamma$ -ray irradiator at 40°. The dose rate was 0.13 Mrads/hr as determined by a conventional Fricke dosimeter and the total dose ranged from 10 to 30 Mrads.

#### 2. Swelling measurement

The hydrogels were removed from the moulds and immersed in distilled water for extraction of the sol fraction for 2–3 days, the water being occasionally changed. The water of the gels was removed first by placing them for a day in an oven at 30° and then at 40° until constant weight was attained. The final specimen weight was taken as the unswollen weight. The hydrogel unswollen volume was calculated by using the polymer density (1.2 g/cm<sup>3</sup>) [12]. The specimen was then immersed in distilled water at 30° and allowed to swell until no further sorption was detected. The difference between the swollen and unswollen specimen weights was taken as the amount of solvent sorbed by the

specimen. The corresponding water volume was calculated by using the density of water at 30°.

The swelling ratio ( $q$ ) of the polymer network was calculated as the (specimen swollen volume)/(specimen unswollen volume).

### 3. Diffusion experiment

The swollen cylindrical specimens were prepared by filling glass capillaries (25 mm length by 1.1 mm dia) with PVP solution and then irradiating. After reaction, the gel cylinders were pushed out of the moulds and immersed in distilled water to extract the sol and to reach equilibrium swelling. Each swollen cylindrical specimen measuring 1.1 mm dia and about 20 mm length (evaluated with calipers) was immersed in 50 ml of rhodamine dye solution of known concentration at 30° for four days. The concentration of the diffusing solute in this solution was then measured. For the diffusion experiment, the gel cylinders were suspended in 10 ml of distilled water at 30° with constant agitation. At intervals of 2 min, the concentration of the extracting solution was measured by taking about 1.5 ml with a syringe and a long needle and reading the absorbance in a calibrated spectrophotometer. From the absorbance data and a calibrated curve of the diffusing dye, the concentration of the solute released from the gel was calculated. The rhodamine dye level slowly approached equilibrium after about 40 min.

## RESULTS AND DISCUSSION

### 1. Determination of the concentration of effective chains

A crosslinked hydrogel swells by absorption of solvent to an extent depending on the concentration of effective chains ( $V_e$ ) which is related to the average molecular weight between crosslinks and the measurable variables  $\rho$  (density of the polymer),  $V_1$  (molar volume of water),  $v_1$  and  $v_2$  (volume fractions of the polymer in both relaxed and swollen states) and  $\chi_1$  (interaction parameter) by the following equations:

$$V_e = -\frac{[\chi_1 \times v_2^2 + \ln(1 - v_2) + v_2]}{V_1 \times \rho \times (v_1^{2/3} \times v_2^{1/3} - V_2/2)} \quad (1)$$

and

$$V_e = \frac{1}{\bar{M}_c} - \frac{2}{\bar{M}_n} \quad (2)$$

when chain-end effects are considered.

For an aqueous solution with a polymer concentration of 10% w/w, the interaction parameter obtained from osmotic pressure data [13] and Flory's

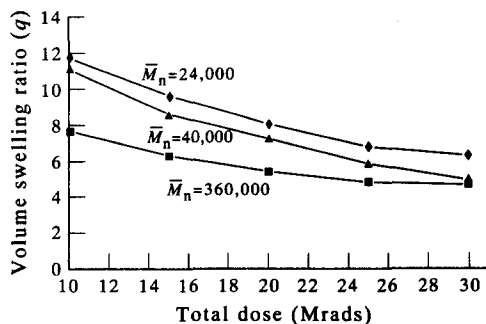


Fig. 1. Dependence of the volume swelling ratio on the absorbed dose for PVP solutions at concentration of 10% w/w.

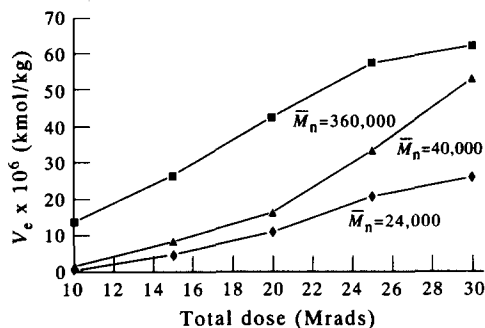


Fig. 2. Dependence of the concentration of effective chains ( $V_e$ ) of PVP gels on the absorbed dose in PVP aqueous solutions at 30°.

equation [7] and used in this work was 0.5296. For the unswollen state,  $v_1$  was taken as unity and for the swollen state  $v_2$  was calculated from the volume swelling ratios ( $q$ ).

From equations (1) and (2), the values of  $\bar{M}_c$  and  $V_e$  were calculated, with results shown in Figs 2 and 3.

Figure 1 shows the changes in the volume swelling ratio  $q$  deduced from swelling as a function of absorbed radiation dose. There is an approximately linear dependence of  $q$  on the absorbed dose, as well as changes in the swelling ratio as a function of the average molecular weight of the polymer.

Figure 2 shows the dependence of the concentration of effective chains on the absorbed radiation dose. Increase in the absorbed dose is accompanied by a rise in the concentration of effective chains, which in turn is accompanied by a decrease of the average molecular weight between crosslinks ( $\bar{M}_c$ ), as shown in Fig. 3. It is observed in Figs 2 and 3 that the values of  $V_e$  and  $\bar{M}_c$  for a given absorbed dose are higher for hydrogels obtained from solutions of polymers of higher molecular weight.

The effects of the absorbed radiation dose on the hydrogel structure, i.e. changes in  $q$ ,  $V_e$  and  $\bar{M}_c$ , are due to the direct effects of the radiation on the water and indirect effects on the polymer (PVP), leading to a denser and more rigid network as the absorbed radiation dose increases [3, 4, 14].

### 2. Determination of the diffusion coefficient

When the gel cylinder initially loaded uniformly with solute is suspended in a well-stirred solution, the

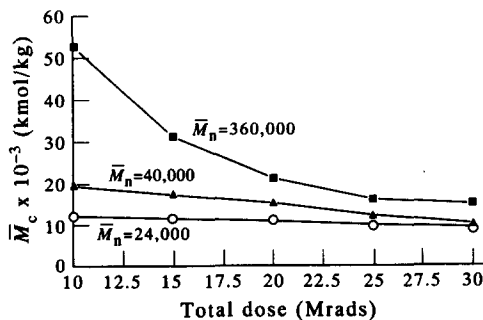


Fig. 3. Dependence of the average molecular weight between crosslinks ( $\bar{M}_c$ ) on the absorbed dose for PVP solutions at concentration of 10% w/w.

solute diffuses out of the gel until equilibrium is established. If the diffusion coefficient ( $D$ ) and partition coefficient ( $K$ ) are both assumed to be constant, the variation of concentration of the solute in the solution is given by [15]:

$$1 - \frac{C(t)}{C_e} = \sum_{n=1}^{\infty} \frac{4 \times \lambda \times (1 + \lambda)}{4 \times (1 + \lambda) \times \lambda^2 q_n^2} \times \exp\left(-\frac{q_n^2 \times D \times t}{a^2}\right) \quad (3)$$

where  $\lambda$  called "effective volume-ratio", is given by:  $\lambda = (C_i - C_e)/C_e = (V_1/V_2) \times K$ .  $C(t)$  is the concentration of the extracting solution at time  $t$ ,  $C_e$  is the equilibrium concentration,  $a$  is the radius of the cylindrical gel, and  $q_n$  are non-zero, positive roots of the equation:

$$2J_1(q) + \lambda q J_0(q) = 0 \quad (4)$$

$J_n$  being a Bessel function of  $n$ th order.

The values of  $\lambda$  are fixed by experimental conditions and  $q$ -values may be determined for as many terms as desired. Carman and Haul [15] have tabulated roots of equation (4) as a function of  $\lambda$ . By interpolation, one obtains  $q$  for a given value of  $\lambda$  characterizing a particular experiment. In a given experiment, the value of  $\lambda$  was calculated and two roots ( $q_1$  and  $q_2$ ) were used. During an experiment, several values of  $C(t)$  were obtained, and from equation (3) several values of diffusion coefficient were calculated; an average value was obtained and is reported in Table 1.

The partition coefficient of solute between the solution and the gel was calculated by using the expression:

$$K = V_2 \times (C_i - C_e)/V_1 \times C_e \quad (5)$$

where:  $V_1$  is the volume of equilibrated solution,  $V_2$  is the volume of hydrogel cylinder,  $C_i$  is the concentration of dye soaking solution,  $C_e$  is the equilibrium conc. of extracting solution.

For each total dose, the value of  $K$  was calculated by using equation (5); results are shown in Table 1.

The equilibrium concentrations inside and outside the gel are unequal because of attractive interactions between the solute and the gel and "repulsive" interactions due to pore size exclusion of large molecules; therefore the partition coefficients are dependent on the natures of solvent, solute and hydrogel network [11]. For rhodamine dye, the values of  $K$  in all the gels are less than unity, showing its affinity for the gel matrix. That conclusion is reasonable because the dye is an organic compound.

Table 1. Equilibrium partition coefficient ( $K$ ) and diffusion coefficient [ $D$  (cm<sup>2</sup>/sec)] for rhodamine dye in PVP hydrogels as a function of total absorbed dose (Mrads) at 30°

Total dose	$\bar{M}_n = 24,000$		$\bar{M}_n = 40,000$		$\bar{M}_n = 360,000$	
	$K$	$D \times 10^7$	$K$	$D \times 10^7$	$K$	$D \times 10^7$
10	—	—	—	—	0.5146	9.9906
15	0.6255	14.2556	0.5834	9.0704	0.5063	7.3090
20	0.6579	12.4777	0.6141	8.0888	0.5611	6.6194
25	0.7524	10.5474	0.5816	6.1523	0.5725	5.8872
30	0.6434	9.4684	0.6693	5.6181	0.6568	5.2666

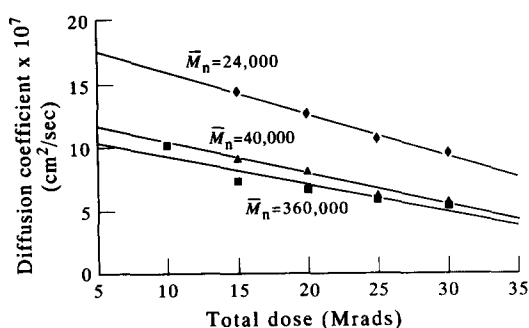


Fig. 4. Dependence of the diffusion coefficient on the absorbed dose for rhodamine dye in PVP hydrogels obtained by gamma radiation at 30°.

Figure 4 shows the dependence of the diffusion coefficient on the absorbed radiation dose for rhodamine dye in PVP hydrogels at 30°. The diffusion coefficient ( $D$ ) decreases as the absorbed dose increases; for a given absorbed dose,  $D$  is higher for lower  $\bar{M}_n$  values. Describing the functional dependence of the solute diffusion coefficient on the swelling and the size of the solute, Yasuda *et al.* [16] applied free-volume considerations and visualized the free volume as a "hole" opened up by thermal fluctuations of molecules or present because of geometrical requirements of random chain packing; the hole serves as the passage for diffusing penetrant molecules, meaning that the concentration of effective chains directly affects the solute diffusion through the polymer network because of change in the number of junctions [17], which affect the structural screening effects of the gel for solute diffusion. The results presented in Figs 4 and 5 are therefore as expected because, the higher the number of junction points, the more difficult is it for solute to diffuse through the gel structure and so the  $D$  values are lower.

## CONCLUSIONS

1. The changes with radiation dose of the parameters that characterize the gel network (concentration of effective chains, volume swelling ratio and average molecular weight between crosslinks) indicate clearly that radiation polymerization can be used to prepare PVP hydrogels of controlled structure from PVP aqueous solutions.

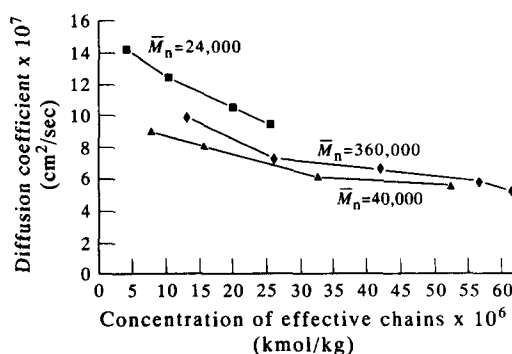


Fig. 5. Dependence of the diffusion coefficient of the rhodamine dye on the concentration of effective chains of PVP hydrogels at 30°.

2. The average molecular weight of the polymer (PVP) alters the hydrogel structure, but these effects are more pronounced at lower absorbed radiation doses.

3. The choice of the hydrogel structure determines its permeability and therefore diffusion rate of the solute. The diffusive conditions can be optimized by controlling the degree of swelling and the concentration of effective chains.

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