

# Synthesis and Swelling Characteristics of Poly(4-vinylpyridine) Gels Crosslinked by Irradiation

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**ABSTRACT:** The effect of irradiation under vacuum on thermal properties and swelling behavior on poly(4-vinylpyridine) (P4VP) was investigated. The gel percentage in the irradiated P4VP films was determined by Soxhlet extraction. UV spectroscopy was also used to determine sol percentage, which decreased as the radiation dose increased. The changes in thermal properties, such as glass-transition temperature ( $T_g$ ), were followed by differential scanning calorimetry before and after Soxhlet extraction. The gels prepared after irradiation were characterized with respect to their swelling properties and network structures. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2609–2614, 2001

**Key words:** irradiation; poly(4-vinylpyridine); gel; characterization

## INTRODUCTION

Crosslinked polymers capable of assimilating large volumes of solvent are termed gels. Interest in the preparation of gels with various properties has increased considerably in recent years because of their applications in many fields. Crosslinked gels are generally prepared either from monomers, with or without some comonomers, in the presence of crosslinking agents, or by treating the polymer with radiation ( $\gamma$  rays). Because of its advantages, radiation-induced crosslinking is prominent among most of the methods. This technique is generally termed a clean technique, neither requiring any extra chemicals nor leaving some unwanted residues. It can be applied at any temperature and dose rate. In many instances, radiation induces simultaneous crosslinking and scission reactions. A moderate number of crosslinks change the physical properties of polymers so that the irradiated materials have enhanced industrial performance.<sup>1</sup> A

polymer with a rigid chain, such as poly(4-vinylpyridine) (P4VP), crosslinks on irradiation below its glass-transition temperature ( $T_g$ ), which is a very interesting phenomenon, as shown by methods such as thermal analysis. Knowledge of the changes in thermal properties of the polymer on irradiation is important for its application in many fields such as advanced composites and as insulating materials for wire and cables in nuclear power plants.

In the present work P4VP films were irradiated and their thermal properties were determined after irradiation. The gels prepared were characterized with respect to their swelling properties and network structures.

## EXPERIMENTAL

### Materials

P4VP was obtained from Reilly Inc. as a 25% w/w solution in methanol, from which the solid was obtained by evaporation of solvent. The measured value of limiting viscosity number in ethanol at 298 K ( $82.6 \text{ dm}^3/\text{kg}$ ), in conjunction with the

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Mark–Houwink constants, yielded a molecular weight of  $14.9 \times 10^4$  g/mol.<sup>2</sup> P4VP was dissolved in ethanol and the solvent was then cast in a petri dish, to give a thin film of P4VP. The films were then dried *in vacuo* at 343 K before irradiation.

### Irradiation

P4VP films were cut into strips, suitable for placing into glass ampoules, for six different doses (0.20, 0.61, 1.03, 1.43, 1.84, and 2.19 MGy). The glass ampoules, which contained P4VP films, were put on a vacuum rig and evacuated for 4 h, after which they were sealed. Glass ampoules were subjected to irradiation doses by Isotron plc. The dosimetry system was cellulose triacetate (CTA) film (Nissin Electric) and radiosensitive dye-impregnated nylon (Far West Technology). The former was used for validation purposes and the latter for routine monitoring. A 4.5-MeV Dynamitron (LINAC) accelerator was used. There was no discernible increase in temperature during the process, in which each of the samples received a target dose per pass. The ampoules were at ambient temperature before entering the irradiation cell for each pass.

### Gel Determination

Each irradiated sample was weighed into a Soxhlet thimble and extracted with ethanol for 15 h to determine the insoluble part in the samples gravimetrically and spectrometrically. This procedure was also used for the nonirradiated samples. After extraction, the amount of polymer dissolved in ethanol was determined spectrometrically by using a Hewlett–Packard 8452 A UV spectrometer (Hewlett–Packard, Palo Alto, CA). P4VP had an absorbance peak at 264 nm. The absorbance of a series of standard solutions of P4VP was measured at this wavelength and found to obey the Lambert–Beer law, the extinction coefficients of which had derived values of 472.8 m<sup>2</sup>/mol. After extraction, the gel percentages in the irradiated samples were calculated as follows:

$$\text{Gel \%} = \frac{w_I}{w_0} 100 \quad (1)$$

where  $w_0$  and  $w_I$  represent the initial weights of irradiated samples (before Soxhlet extraction) and the insoluble part (after Soxhlet extraction),

respectively. Swelling measurements were done with the insoluble part (gel) of P4VP samples.

### Swelling Measurements

Clean, dried irradiated P4VP films of known weights, after removal of the sol fraction, were immersed in ethanol at 25°C until equilibrium was reached (24 h). The films were removed and blotted quickly with absorbent paper, to remove the liquid attached to the surface, and weighed.

$$\text{Ethanol uptake \%} = \frac{(w_s - w_d)}{w_d} 100 \quad (2)$$

where  $w_d$  and  $w_s$  represent the weights of dry and swollen irradiated samples, respectively.

For a P4VP gel, swelling data from the gravimetric analysis were used to calculate the volume fraction  $V_{2m}$  and equilibrium degree of swelling  $q_v$  of polymer in a given gel sample swollen to equilibrium in ethanol.

$$q_v = \left( 1 + \frac{\rho(q_w - 1)}{d} \right) \quad (3)$$

where  $q_w$  is the ratio of the weights of the network in the swollen state and dry state, and  $\rho$  and  $d$  are the densities of P4VP and ethanol, respectively. The equilibrium degree of swelling  $q_v$  was defined as  $q_v = 1/V_{2m}$ . Using the values of  $\rho = 0.95$  g/mL and  $d = 0.786$  g/mL,  $q_v$  values were calculated.

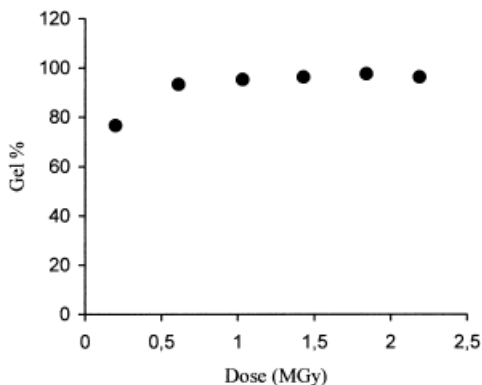
### Measurements of Thermal Properties

DSC measurements were carried out using a DSC Mettler TA 3000. Samples ( $\sim 20$  mg) of the irradiated P4VP were used for measurements. Indium, zinc, and nickel standards were utilized to calibrate the temperature and thermal scales. The measurements were carried out in N<sub>2</sub> atmosphere at a heating rate of 10°/min. The  $T_g$ 's of irradiated and nonirradiated films were determined. After Soxhlet extraction all films were dried under vacuum at 318 K and  $T_g$ 's were determined in the gel part.

## RESULTS AND DISCUSSION

### Gel Determination

The formation of intermolecular crosslinks is one of the most important changes brought about by



**Figure 1** Gel percentage of P4VP with irradiation dose.

radiation because crosslinking of polymers leads to beneficial changes in some of their properties, such as heat resistance and so forth. Therefore, the gelled part (i.e., the insoluble part) was determined in the samples with varying degrees of crosslinking. Results, given in Figure 1, show the relation between the gel percentage and irradiation dose for P4VP samples. Initially, the gel percentage increases with increasing irradiation dose up to 0.61 MGy; at higher doses the increase in gel percentage is small. The P4VP film, which was subjected to irradiation with a dose rate of 1.84 MGy, was broken during the irradiation process. The irradiation environment, in the presence of oxygen during radiation, markedly affected radiation resistance. When irradiation is carried out in the presence of oxygen, additional chemical reactions can occur.<sup>3</sup> Thus, the gel percentage of P4VP film subjected to irradiation at a dose of 1.84 MGy was greater than that of the film that was subjected to irradiation with a dose rate of 2.19 MGy.

Generally, the chemical change occurring in the polymeric substance is directly proportional to the active sites formed. The efficiency of such sites to initiate a crosslinking process is higher in the amorphous region than that in the crystalline region because of the higher mobility of the active sites in the amorphous region. Therefore, the number of radicals formed by irradiation at first increases as the dose increases. At higher doses, no more active sites are formed and the constant concentration of radicals also gives a curvature relationship for degree of crosslinking with dose.<sup>4,5</sup>

Much effort is expended on measuring the relationship between radiation dose and gel fraction because this determines the efficiency of

crosslinking, the  $G$  value of crosslinking  $G_x$ , and the  $G$  value of scission  $G_s$ . In many instances, radiation induces simultaneous crosslinking and scission reactions. In these cases, the yields for each reaction can be determined by the Charlesby–Pinner relationship<sup>6</sup>:

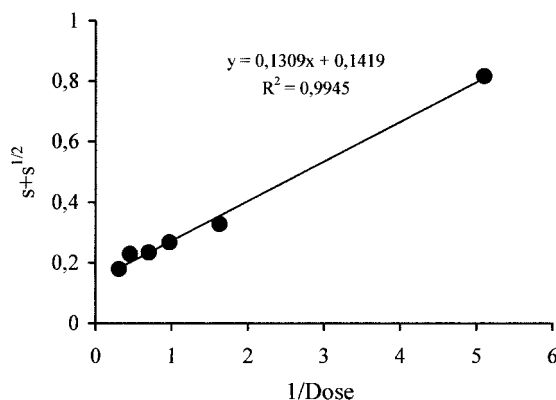
$$s + s^{1/2} = \frac{50N}{M_n} G_x \frac{1}{D} + \frac{G_s}{G_x} \quad (4)$$

where  $s$  is the sol fraction of the irradiated polymer,  $M_n$  is the number-average molecular weight of the polymer prior to irradiation,  $D$  is the absorbed dose,  $G_s$  is the scission yield, and  $G_x$  is the crosslinking yield. As proposed by Charlesby and Pinner, the plot of  $s + s^{1/2}$  against  $1/D$  makes it possible to obtain the ratio  $G_s/G_x$  from the intercept. Results are shown in Figure 2 and Table I. As shown in Figure 2,  $s + s^{1/2}$  versus  $1/D$  gives a linear plot and from the intercept, the value of  $G_s/G_x$  is 0.14. The value of  $G_s/G_x$  for polystyrene (PS) is 0.2.<sup>3</sup>

Extrapolation to complete solubility ( $s + s^{1/2} = 2$ ) allows estimation of the gel points. For a calculation of both crosslinking and scission yields, the gel point dose  $r_g$  and the scission to crosslinking ratios may be substituted in eq. (5).<sup>7</sup>

$$\frac{w}{M_w} = r_g \left( G_x - \frac{G_s}{2} \right) \quad (5)$$

in which  $w$  is the molecular weight of the repeating unit,  $r_g = 7.05 \times 10^{-2}$  MGy, and  $M_w = 14.9 \times 10^4$  g/mol. Substituting  $G_s/G_x = 0.14$  gives  $w/M_w = r_g(0.93G_x)$  and  $G_x$  is found to be 0.011. The scission yield is  $G_s = 1.54 \times 10^{-3}$ , which



**Figure 2** Sol–dose plot consistent with eq. (4).

**Table I** Determination of Sol-Gel Fractions of Irradiated Samples by UV Spectroscopy

Sample	Dose (MGy)	1/Dose	$w_{\text{sol}}$ (g)	$w_{\text{gel}}$ (g)	$w_{\text{sol}} + w_{\text{gel}}$	$s_{\text{sol}}$ fraction	$s^{1/2}$	$s + s^{1/2}$	$g_{\text{gel}}$ fraction
1	0.196	5.102	0.285	0.932	1.217	0.284	0.533	0.817	0.766
2	0.614	1.629	0.078	1.076	1.154	0.068	0.260	0.328	0.932
3	1.027	0.973	0.045	0.904	0.950	0.048	0.218	0.266	0.952
4	1.432	0.698	0.026	0.661	0.687	0.038	0.195	0.233	0.962
5	1.841	0.543	0.020	0.798	0.818	0.024	0.155	0.179	0.976
6	2.188	0.457	0.035	0.900	0.935	0.037	0.192	0.229	0.963

means that crosslinking occurs more easily than does chain scission.

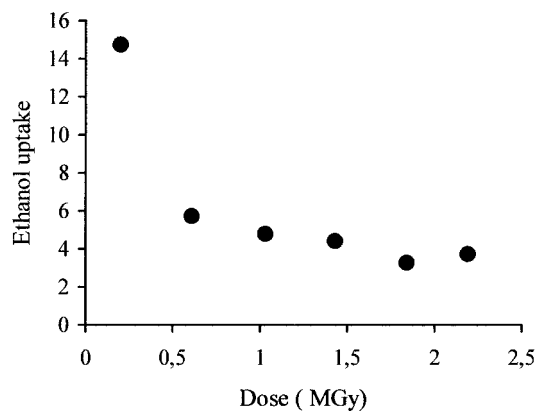
The vinylpyridine monomers are similar to styrene, except for the presence of a nitrogen atom on the pyridyl ring. The vinylpyridine monomers are somewhat more reactive than styrene, an observation that is consistent with the methyl affinities (relative reactivity of monomer toward the methyl radical) of the respective monomers. The methyl affinities of styrene and 4VP are 792 and 1360, respectively, which can explain why PS is more resistant than P4VP to irradiation, although they have similar chemical structures.<sup>8,9</sup>

### Swelling Measurements

Figure 3 represents the ethanol uptake of P4VP as a function of irradiation dose. It can be seen that the ethanol uptake decreases with increasing irradiation dose because the gel percentage increases with increasing dose.

### Determination of $M_c$ Values of Gels

The gels thus prepared were characterized with respect to their swelling properties and network



**Figure 3** Ethanol uptake of P4VP as a function of irradiation dose.

structures. One of the basic parameters that describes the structure of a gel network is the molecular weight between crosslinks ( $M_c$ ) for swollen networks. This describes the average molecular weight of polymer chains between two consecutive junctions. These junctions may be chemical crosslinks, physical entanglements, crystalline regions, or even polymer complexes.<sup>10</sup> Several theories have been proposed to calculate the molecular weight between crosslinks in a gel. Probably the most widely used of these theories is that of Flory and Rehner.<sup>11,12</sup> This earliest theory describes the equilibrium swelling characteristics of a crosslinked polymer system, in which the polymer chains are reacted in a solid state. This theory deals with neutral polymer chains within the polymer gel. From the swelling expression the average molecular weight between consecutive crosslinks  $M_c$  can be expressed by eq. (6). This equation, widely used to characterize a variety of networks, was used when the network was prepared from polymer.

$$\frac{1}{M_c} = \frac{2}{M_n} - \bar{v}/V_1 \frac{[\ln(1 - V_{2m}) + V_{2m} + \chi V_{2m}^2]}{[V_{2m}^{1/3} - V_{2m}/2]} \quad (6)$$

Here  $M_c$  is the number-average molecular weight of starting polymer,  $\bar{v}$  is the specific volume of polymer,  $V_1$  is the molar volume of the swelling agent,  $V_{2m}$  is the polymer volume fraction in the equilibrium-swollen system, and  $\chi$  is the Flory polymer-solvent interaction parameter.  $\chi$  is 0.49 for the P4VP-ethanol system<sup>13</sup> and  $V_1$  is 58.3 g cm<sup>-3</sup> for ethanol. The  $M_c$  values, thus determined from eq. (5), are given in Table II. The results obtained show that the average molecular weight between crosslinks is affected by the irradiation dose.

When a nonionic polymeric network is placed in a swelling agent, there are two contributions to

**Table II** Values of  $M_c$  for Gel Systems

Dose (MGy)	$M_c$ (g/mol)	$q_v$
0.20	107,269	19.7
0.61	49,965	7.0
1.03	38,441	5.8
1.43	34,859	5.3
1.84	20,127	3.9
2.19	26,470	4.5

the free energy of the system, mixing and elastic-retractive free energies, as expressed by  $\Delta G_{\text{mix}}$  and  $\Delta G_{\text{el}}$ , respectively. It is assumed that the change in total free energy is the sum of  $\Delta G_{\text{mix}}$  and  $\Delta G_{\text{el}}$ .<sup>14</sup> Thus,

$$\Delta G = \Delta G_{\text{mix}} + \Delta G_{\text{el}} \quad (7)$$

The state of equilibrium is obtained when the two changes balance each other. Mathematically, this state is expressed as

$$\left(\frac{\partial \Delta G}{\partial n_1}\right)_{T,P} = \left(\frac{\partial \Delta G_{\text{mix}}}{\partial n_1}\right)_{T,P} + \left(\frac{\partial \Delta G_{\text{el}}}{\partial n_1}\right)_{T,P} = 0 \quad (8)$$

where  $n_1$  is the number of molecules of swelling agent and subscripts  $T$  and  $P$  indicate that the differentiations were made at constant temperature and pressure, respectively.

Performing the differentiations indicated in eq. (8),

$$\ln(1 - V_{2m}) + V_{2m} + \chi V_{2m}^2 + \frac{V_1 \rho}{M_c} (V_{2m}^{1/3} - V_{2m}/2) = 0 \quad (9)$$

or, adopting the terminology

$$\frac{V_1 \rho}{M_c} = N^{-1} \quad (10)$$

where  $N$  is the number of segments in a network chain and  $\rho$  is the density of the polymer network.

$$\ln(1 - V_{2m}) + V_{2m} + \chi V_{2m}^2 = -N^{-1} (V_{2m}^{1/3} - V_{2m}/2) \quad (11)$$

The left-hand member in this equation represents the lowering of the chemical potential resulting from the mixing of polymer and swelling agent;

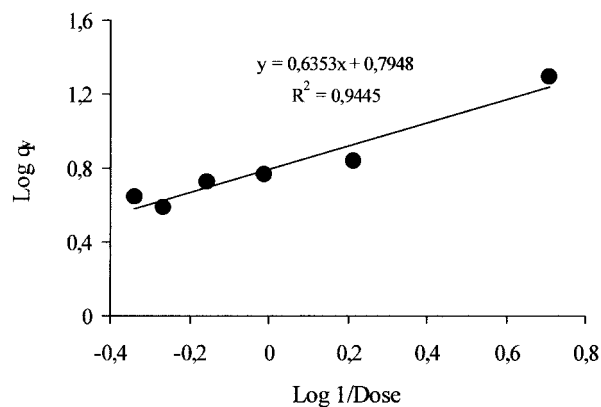
the right-hand member gives the increase from the elastic region of the network. As expressed earlier, at swelling equilibrium,  $1/V_{2m}$  may be replaced by  $q_v$ . At  $M_c$  values of 10,000 or more,  $q_v$  in a good solvent will exceed 10; then  $V_{2m}/2$  is considerably smaller than  $V_{2m}^{1/3}$  and can be neglected. The higher terms in the series of expansion of the first term member of eq. (9) may also be neglected. The swelling equilibrium equation may then be solved for  $V_{2m} = 1/q_v$ , with the following result<sup>12</sup>:

$$q_v^{5/3} = N^{-1}(0.5 - \chi) \quad \text{or} \quad q_v = \left(\frac{0.5 - \chi}{N}\right)^{3/5} \quad (12)$$

Theoretically, a plot of  $\ln q_v$  versus  $\ln N$  should give a straight line, with 0.6 as the slope. Figure 4 shows the logarithmic relation between  $q_v$  and  $1/\text{dose}$ . The slope (0.64), obtained from Figure 4, is very similar to the theoretical value.

### Measurement of Thermal Properties

Glass-transition temperatures of P4VP films were measured before and after Soxhlet extraction. The results of measurements are given in Table III. As shown in Table III, the  $T_g$  for P4VP shifts to a higher temperature with dose. On irradiation new radicals are created, which are the precursors of crosslink formation. The  $T_g$  is governed by the chemical structure of repeating units of polymer, bulkiness, interaction of chains, and the presence and the absence of crosslinks. In this case, it is reasonable to consider that the shift in  $T_g$  to higher temperature by irradiation is the result of restriction of chain mobility caused by network structure formed on irradiation.<sup>15</sup> Radi-



**Figure 4** Plot of  $\log q_v$  versus  $\log 1/\text{dose}$  for P4VP gels.

**Table III** Changes in  $T_g$  of Irradiated Samples with Gel Percentage, Before and After Soxhlet Extraction

Dose (MGy)	Gel %	$T_{gm}$ (°C)	$T_{g1}$ (°C)	$T_{g1}$ (calcd) <sup>a</sup> (°C)	$\Delta T_{g1}$ <sup>b</sup> (°C)
0	0	139.6	—	—	—
0.20	76.7	141.9	152.4	142.7	8.7
0.61	93.3	144.1	152.1	144.4	7.6
1.03	95.2	148.9	152.5	149.4	3.0
1.43	96.2	151.9	157.6	153.1	4.5
2.19	96.3	152.7	161.9	153.3	8.7

<sup>a</sup> Calculated by Fox's equation.

<sup>b</sup>  $\Delta T_{g1} = T_{g1} - T_{g1}$  (calcd).

ation has a significant effect on the amorphous region rather than on the crystalline region. Although the radicals form uniformly throughout the whole polymer, they cannot form crosslinks in the rigid lattice, but do so in the amorphous polymer or amorphous regions of the semicrystalline polymer.<sup>15</sup> Changes in the amorphous regions are indicated by an increase in the  $T_g$  with dose, suggesting that crosslinking is an important mechanism in P4VP.

$T_g$  is an important property of polymeric systems, determining their range of applicability. Fox's equation, proposed for predicting  $T_g$  dependence on composition for polymer blends,<sup>16</sup> was used to calculate  $T_g$  values of samples after Soxhlet extraction:

$$\frac{1}{T_{gm}} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (13)$$

where  $T_{gm}$  is the  $T_g$  of the irradiated sample before separation of gel and sol parts;  $T_{g1}$  is the  $T_g$  of the irradiated P4VP sample after Soxhlet extraction (contains only the gel part);  $T_{g2}$  is the  $T_g$  of the original P4VP sample before irradiation (139.6°C); and  $w_1$  and  $w_2$  refer to the weight fraction of the gel and sol parts, respectively. Results are shown in Table III, and as shown from the table, the observed  $T_{g1}$  values for all samples were 3–9°C higher than the calculated  $T_{g1}$  values.

## CONCLUSIONS

The principal structural change that occurs on irradiation of solid P4VP is crosslinking with very little chain scission, although the sol fraction still contains branched and degraded chains. The  $T_g$  of

the sol fraction is not the same as that of the nonirradiated P4VP. In this study, the amount of P4VP in the sol fraction is too low to precipitate with ethyl acetate. Because of the colloidal solution formation, complete separation was not achieved by centrifugation, so  $T_g$  of nonirradiated P4VP was used as the  $T_g$  of the sol fraction.

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