

Polyvinylpyridine–Ethanol Systems

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SYNOPSIS

Polymeric matrices of poly(2-vinylpyridine) were prepared with application of gamma irradiation to its ethanolic solutions. The interaction parameter (χ) between the polymer and the solvent, and the average molecular weight between the crosslinks (M_c) were calculated from the swelling properties. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Three-dimensional network structure of polymers can be obtained either by using monomers with a functionality higher than 2 or by forming crosslinks between polymer chains by application of irradiation, vulcanization, or various other chemical reactions. Hydrogels are 3-dimensional network structures made of hydrophilic homo- or copolymers and have gained a lot of attention, especially in the biomedical field, as materials for contact lenses, soft tissue implants, drug depots, etc. The hydrophilicity and the resultant softness of the implant materials enhances biocompatibility by achieving permeation of the body fluid through the implant structure. The permeation of chemicals through the polymer network structure depends on its swelling ability, which in return is highly influenced by factors such as crosslink density, crystallinity, porosity, tortuosity, and hydrophilicity as well as the chemical structure of the polymer.

Flory and Rehner¹ studied the theory of the crosslinking process and the resultant networks assuming that the crosslinks are tetrafunctional and length of the chains between the crosslinks (M_c) have a Gaussian distribution. The midportion of the chains is free to take many configurations while each end is constrained to join the ends of three other chains at the crosslinkage. Therefore, in its relaxed state the network takes the most probable config-

uration. Application of any force alters this and causes a decrease in entropy.

Absorption of a solvent by the network structure creates such a force, and the chains between the crosslinks get elongated. As swelling proceeds, elastic retracting force of the chains develop and at equilibrium becomes equal to the thermodynamic dilution force. The polymer–solvent interaction parameter, χ , is quite influential on the free energy change involved in dilution. It is the sum of two terms where the first term is a function of the polymer–solvent system and independent of polymer concentration and the second term contains polymer concentration as a factor. With some modifications and simplifications, it can be expressed as²

$$\chi = [(1/2) - (V_1q)] + \lambda\nu_{2s}$$

where V_1 is the molar volume of solvent, ν_{2s} is the volume fraction of polymer in the swollen state, q is the term which express deviations from ideal behavior, and λ gives the relation with polymer concentration.

On the other hand, M_c is calculated according to Bray–Merril³ modification of Flory's derivations:

$$\frac{1}{M_c} = \frac{2}{M_n} - \frac{v/V_1 [\ln(1 - \nu_{2s}) + \nu_{2s} + \chi\nu_{2s}^2]}{\nu_{2r} [(\nu_{2s}/\nu_{2r})^{1/3} - (\nu_{2s}/2\nu_{2r})]} \quad (1)$$

Here ν_{2r} and ν_{2s} are volume fractions of the gel samples in the relaxed and swollen states, respectively, M_n is the number average molecular weight of the uncrosslinked polymer, χ is the Flory polymer–solvent thermodynamic interaction parameter, v is the specific volume of the polymer, and V_1 is

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the molar volume of solvent. This equation is shown to be valid for loosely crosslinked networks in which the chains between the crosslinks demonstrate a Gaussian distribution. Lucht and Peppas⁴ modified this equation further for isotropic, highly crosslinked networks and obtained the following equation:

$$\frac{1}{\bar{M}_c} = \frac{2}{\bar{M}_n} - \frac{v/V_1[\ln(1 - \nu_{2s}) + \nu_{2s} + \chi\nu_{2s}^2][1 - (\nu_{sr}^{2/3}/N)]^3}{\nu_{2r}[\nu_{sr}^{1/3} - (\nu_{sr}/2)][1 + (\nu_{sr}^{1/3}/N)]^2} \quad (2)$$

where, ν_{sr} denotes the ratio ν_{2s}/ν_{2r} , N = number of links of the chains = $2M_c/M_r$, and M_r = molecular weight of the PVN repeating unit.

In this study, poly(2-vinylpyridine), a hydrophobic polymer, was crosslinked with gamma irradiation in ethanol. The resultant network structure was converted to hydrophilic poly(2-vinyl-*N*-methylpyridinium iodide salt) by quaternizing with methyl iodide.⁵ It is assumed that quaternization does not affect the crosslinks, and thus the average molecular weights between the crosslinks (M_c) would not be altered. By using the data from the swelling properties of poly(2-vinylpyridine) in ethanol, and using both the equations, χ and M_c values were calculated.

EXPERIMENTAL

Poly(2-vinylpyridine) (PVN), a thermally polymerized and purified sample (monomer purchased from Sigma, Co., USA) that has an average molecular weight of 4.33×10^5 g mol⁻¹ was used in the preparation of the network structures.⁵ PVN solutions (5% w/v) were prepared in extra pure ethanol (ethanol was obtained by removing the trace water by metallic magnesium followed by distillation and

stored over molecular sieve), placed into irradiation tubes under nitrogen atmosphere, heat-sealed, and irradiated with gamma rays by using a ⁶⁰Co source.

The volumes of relaxed, swollen, and dry polymers were found by using the pycnometric method. For this purpose, the crosslinked structures were taken out by breaking the tubes, and immediately weighed in air and in *n*-decane to find the relaxed volume (V_r). Later, the samples were put into ethanol until they reached equilibrium swelling, and the swollen volume (V_s) was determined. The samples were then dried under vacuum to the constant weight before finding the dry volume of the polymer (V_p). These measurements were repeated at least five times for each sample and the values were averaged.

The polymer volume fractions in both relaxed (ν_{2r}) and swollen (ν_{2s}) states were calculated as

$$\nu_{2r} = V_p/V_r$$

$$\nu_{2s} = V_p/V_s$$

Solvent content (W %), weight swelling ratio (Q), and the volume of adsorbed solvent (VAS) were calculated according to the following equations⁶:

$$W \% = 100(w_{as} - w_{ad})/(w_{as})$$

$$Q = w_{as}/w_{ad}$$

$$VAS = (w_{as} - w_{ad})/(d_{so}w_{ad})$$

where w_{as} and w_{ad} are the weights of the swollen and dry samples, respectively, and d_{so} is the density of solvent.

The thermodynamic interaction parameter χ is calculated from the previously given equation: $\chi = [(1/2) - (V_1q)] + \lambda\nu_{2s}$, where q can be found using the equilibrium data of a measurable property, such as osmotic pressure, vapor pressure, or swelling data. The q from the swelling data can be presented

Table I Applied Radiation Dose and Swelling Properties of the Network Polymers

Sample	Dose (kGy)	Solvent Content (W %)	Weight Swelling Ratio (Q)	Volume of Adsorbed Solvent (VAS)
1	182	85.76 \pm 0.005	7.03 \pm 0.004	7.675 \pm 0.0001
2	210	84.00 \pm 0.036	6.26 \pm 0.004	6.706 \pm 0.0004
3	245	81.90 \pm 0.001	5.52 \pm 0.005	5.764 \pm 0.0001
4	280	80.27 \pm 0.003	5.07 \pm 0.002	5.182 \pm 0.0003
5	315	78.71 \pm 0.002	4.70 \pm 0.002	4.710 \pm 0.0003

Table II Structural Characteristics of PVN Networks in Ethanol

Gamma (kGy)	ν_{2r} (∓ 0.0005)	ν_{2s} (∓ 0.0001)	q_v	q_w	χ
182	0.083	0.070	14.286 \mp 0.007	15.23 \mp 0.005	0.499 \mp 0.0002
210	0.072	0.070	14.286 \mp 0.024	13.31 \mp 0.003	0.499 \mp 0.0002
245	0.081	0.080	12.500 \mp 0.015	11.44 \mp 0.002	0.499 \mp 0.0003
280	0.082	0.081	12.346 \mp 0.004	10.29 \mp 0.004	0.499 \mp 0.0003
315	0.092	0.093	10.753 \mp 0.008	9.35 \mp 0.001	0.499 \mp 0.0004

as a change in volume (q_v), or a change in weight (q_w):

$$q_v = V_s/V_p$$

$$q_w = (w_{as} - w_{ad})d_p/(w_{ad}d_{so})$$

For some systems, polymer-solvent interaction parameter χ is found as a nearly linear function of ν_{2s} , indicating that λ must be constant or nearly constant. The term $[(1/2) - (V_1q)]$ is a function of polymer-solvent system but is independent of the polymer concentration. The value of χ at zero, ν_{2s} (very highly swollen, lightly crosslinked gel) can be calculated from the following equation:

$$\chi = (1/2) - (V_1q_v)$$

In the calculation of M_c , it has been assumed that M_n is large enough that the term $2/M_n$ in the equations is neglected. Constants used are

$$v = 0.504 \text{ cm}^3/\text{g}, \quad V_1 = 58.68 \times 10^{-6} \text{ m}^3/\text{mol}, \\ d_{so} = 0.785 \text{ g/cm}^3$$

RESULTS AND DISCUSSION

The gel samples irradiated with application of different doses achieved different swelling properties.

Table III M_c Values of PVN Network Structures

Sample	M_c [Eq. (1)]	M_c [Eq. (2)]
1	37,337 \mp 2594	37,522 \mp 3011
2	31,239 \mp 2320	31,488 \mp 2300
3	23,578 \mp 1545	23,835 \mp 1552
4	23,005 \mp 1618	23,262 \mp 1628
5	16,979 \mp 1054	17,242 \mp 1053

The values of solvent content, weight swelling ratio, and volume of adsorbed solvent for these samples are listed in Table I. It is observed that solvent content, swelling ratio, and volume of adsorbed solvent decreases from 85.76 to 78.71%, from 7.03 to 4.70, and from 7.675 to 4.710, respectively, with an increase in the applied irradiation dose from 182 to 315 kGy. The decrease in these properties demonstrates an increase in the crosslink density, while causing a decrease in M_c values. The values of ν_{2r} , ν_{2s} , q_v , q_w , and χ calculated from the previously given equations are listed below in Table II.

The volume fractions of the polymer series varies in between 0.072 and 0.092 for the relaxed state and in between 0.070 and 0.093 for swollen state. The calculated χ value is found as 0.499 for all cases. Although it is known that χ value increases with an increase in the polymer volume fraction, it has not been observed here since the polymer volume fraction itself is very small. In the literature there is no data about the χ value of polyvinylpyridine-ethanol systems. However, for a polymer-good solvent system, such as poly(vinyl alcohol)-water,⁷ polystyrene-tetralin,⁸ poly(*N*-vinylpyrrolidone)-water,⁹ poly(methacrylic acid)-water,¹⁰ χ values were found, by using swelling data, to be in the range 0.40-0.59. Therefore, the calculated value of χ for polyvinylpyridine and ethanol system is quite expected.

The average molecular weight between the crosslinks was calculated by using two different versions of the same theoretical approaches for loosely crosslinked structures [eq. (1)] and for tightly crosslinked structures [eq. (2)]. The results are presented in Table III.

As seen from the table, both approaches give approximately the same M_c values. The similarity of the results shows that if the interaction between polymer and solvent is high and components are compatible, then both approaches will be applicable in the calculation of M_c values. Also, as expected from the action of radiation on polymers the degree

of crosslinking increased as the applied dose increased leading to lower M_c values for the latter samples.

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