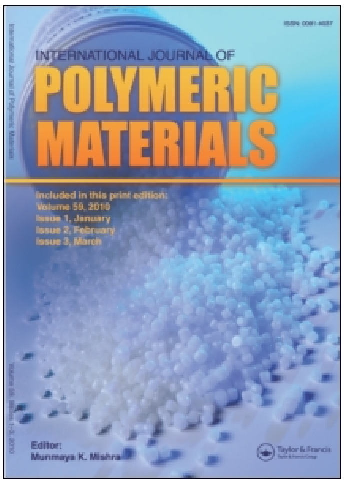

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SWELLING PROPERTIES OF POLY(N-VINYLIMIDAZOLE) HYDROGELS

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The swelling capacity of poly(N-vinylimidazole) hydrogels in aqueous solutions and organic solvents was measured as a function of polymer network structure. In pure water, the swelling capacity decreases monotonously upon increasing the crosslinker ratio and the total comonomers concentration in the polymerization feed mixture. In methanol a similar behaviour was observed while in ethanol, the swelling capacity shows an abrupt change from large values to 0.01 grams of water per gram of dry gel, that is to say, PVI experience swollen-collapsed transitions with small changes of the gel crosslinking degree. Molecular weight of chains between crosslinks, determined from swelling measurements in methanol, scales with the product of the crosslinker and total comonomers concentrations in the feed mixture to -1.14 ± 0.05. *The dependence of the polymer solvent interaction parameter on the polymer concentration inside the swollen gel was also determined for water and ethanol.*

Keywords: poly(N-vinylimidazole), hydrogels, swelling

INTRODUCTION

The equilibrium water content of a hydrogel is its more interesting property, since it affects any relevant property of these materials such as permeability, mechanical, optic and surface properties or biocompatibility. Besides, most applications of the hydrogels are related to their capacity of retaining water or other solvents. The degree of swelling of a network depends on the chemical nature of the polymer, on its composition and degree of

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crosslinking [1–4], and on external effects such as the nature and composition of the solvent, the temperature, pressure, ionic strength and pH of the solution [5–7].

This paper presents some studies on the swelling capacity of poly(N-vinylimidazole) (PVI). This hydrogel has interest because it is able to regulate, without dissolving, the pH of an aqueous solution [8] and to uptake heavy metal cations [9, 10]. The aim of the work is to analyze the dependence of swelling properties on the gel structure and composition. It would be extremely useful to be able to quantitatively predict the properties of a hydrogel from feed compositional data. Bromberg *et al.* [1] have recently proposed a scaling law relating the length of chains between crosslinks with comonomer concentrations in the feed, which will be checked for the PVI-methanol system. The molecular weight of chains between crosslinks, measures the network degree of crosslinking and, for neutral gels as PVI, it is related to the swelling degree through well established theories [11, 12]. Scaling concepts have been proved to be very useful tools in studying polymer systems [13] and, in particular, hydrogels [1, 14, 15].

EXPERIMENTAL PART

Preparation of Hydrogels

Poly(N-vinylimidazole) hydrogels were synthesised by radical crosslinking polymerization of N-vinylimidazole (VI) and N,N′-methylene-bis-acrylamide (BA) in aqueous solution, with AIBN (6×10^{-3} M) as initiator. N-vinylimidazole purchased from Aldrich, was distilled under reduced pressure at 55°C just prior use. Water was distilled and deionized by a Milli-Q system from Millipore. BA (from Aldrich) and AIBN (from Fluka) were high quality products, used as received. The aqueous solution of VI, BA and AIBN was sonicated at 60°C for 10 minutes and then it was immersed in a bath at 90°C for 2 hours. The hydrogels were taken out of moulds and they were cut into circular pellets of about 1 cm diameter and 1 mm thick. The hydrogel was then washed repeatedly with Milli-Q water during about one month; water was spectrophotometrically analysed to detect the end of the extraction of soluble material, in particular, of residual VI. Clean hydrogels were dried in oven at 80°C during 24 hours.

The composition of the monomers feed mixture is specified by C_T, total monomers concentration in g/100 mL or % w/v and C, the crosslinker ratio in w/w % of BA. In the following, any sample will be denoted by the symbol $GC_T(C)$; for example, G40(2) represents a hydrogel obtained with a feed mixture composition of 40 g/100 mL total monomers concentration and 2% w/w BA in the mixture of BA and VI.

Characterisation of Hydrogels

Characterisation of hydrogels was performed by DSC (Mettler DSC 30 at $10\,\mathrm{K\,min^{-1}}$ heating rate in nitrogen atmosphere) and swelling measurements. Table 1 shows the glass transition temperature T_g, the swelling degree, S, in pure water and the mole fraction of elastically effective knots, F_C, determined through swelling measurements in methanol.

Swelling measurements were carried out gravimetrically. PVI dry pellets were immersed in the swelling solvent (water, ethanol or methanol) for about one week. Once they have reached a constant weight, (m_h), S is calculated as

$$S = \frac{m_h - m_o}{m_o} \tag{1}$$

where m_o is the weight of the dry pellet. The Flory-Rehner equation [11] modified by Peppas and Merrill [12], allows calculation of molecular weight between crosslinks, M_c, for systems with known V_1 (solvent molar volume), χ (polymer-solvent interaction parameter), ρ_2 (xerogel density) and v_{2r} (polymer volume fraction in the network relaxed state):

$$\ln(1 - v_2) + v_2 + \chi v_2^2 + \frac{V_1 \rho_2}{M_c}\left(v_2^{1/3} v_{2r}^{2/3} - v_2/2\right) = 0 \tag{2}$$

with v_2, the polymer volume fraction in the equilibrium swollen gel,

$$v_2 = \frac{m_o/\rho_2}{(m_o/\rho_2) + (m_h - m_o)/\rho_1} \tag{3}$$

and where ρ_1 represents solvent density. The following parameters were taken for the methanol-PVI system: $\chi = 0.472$ (calculated from the second virial coefficient given in Ref. [16]), $V_1 = 40.45\,\mathrm{cm^3/mol}$ [17], $\rho_2 = 1.156$ $\mathrm{g/cm^3}$ [17] and $v_{2r} = [1 + (100 - C_T)\rho_2/C_T]^{-1}$. Once M_c was known, F_c was calculated as

$$F_c = \frac{1}{2(M_c/M_0) + 1} \tag{4}$$

where M_0 represents the molecular weight of VI.

TABLE 1 Characteristics of some representative PVI samples

Sample	*Tg (°C)*	*S (gH_2O/gdg)*	*F_c (%)*
G40(2)	186.7	4.32	0.14
G40(10)	185.7	2.03	1.62
G40(15)	181.7	1.68	3.04
G20(2)	187.3	9.14	0.05
G20(10)	188.0	5.24	0.49
G20(15)	188.9	4.43	0.81

RESULTS AND DISCUSSION

The equilibrium swelling of PVI in water, methanol and ethanol depends inversely on the crosslinker ratio and total comonomers concentration in the polymerization feeding mixture. Figures 1(a) to (c) show such results. Samples with low C and C_T show *S* values not very different for methanol and ethanol and about twice for water. Nevertheless, for large C and C_T, *S* is very much solvent dependent. In water and methanol, swelling changes a tenfold over the whole range of feed mixture compositions employed here but in ethanol, swelling changes are more drastic. Namely, sample G20(10) collapses in ethanol whereas another sample with very close composition, G20(6), is highly swollen.

From the qualitative point of view it can be easily understood. Increasing C and C_T, the effective degree of crosslinking increases by formation of covalent crosslinks and chain entanglements and by decreasing network defects such as elastically inactive intramolecular cycles. From the quantitative point of view, results shown in Figure 1 can be analysed in light

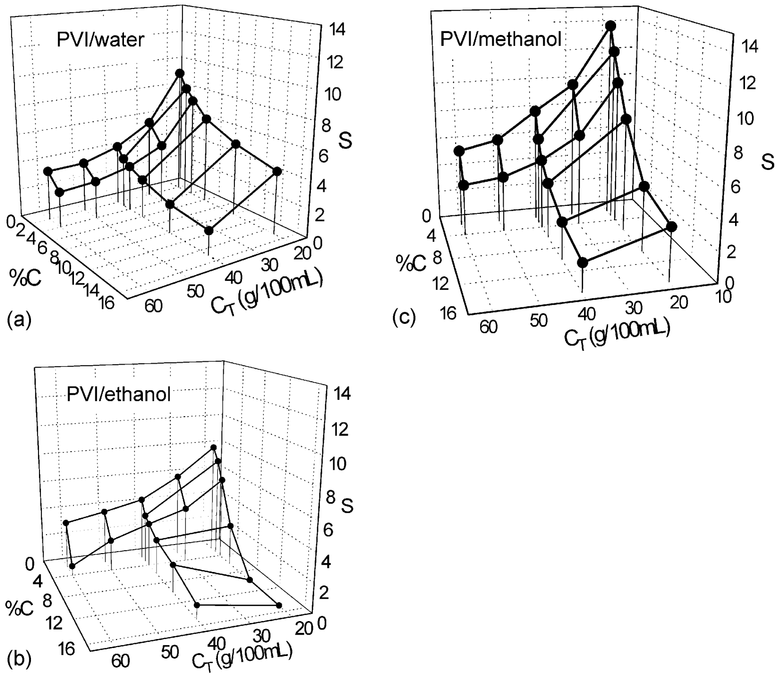

FIGURE 1 Equilibrium swelling degree of PVI in (a) deionized water, (b) ethanol and (c) methanol, as a function of total comonomers concentration and crosslinker ratio in the feed.

of the scaling law proposed by Bromberg *et al.* [1], which predicts proportionality of the number of bonds in the skeleton of chains between crosslinks (N) and the concentrations of crosslinker (c_{xl}) and total comonomers concentration in the feed ($c_{xl} + c_m$):

$$N \approx 1/\left[a^6 c_{xl}(c_m + c_{xl})\right] \tag{5}$$

where a represents the length of a monomeric unit. This law was deduced on the basis of a random walk view of the polymerization and assuming 100% degree of conversion and Gaussian or non-correlated segments in the network. N may be calculated as $2M_c/M_o$ and M_c was determined from swelling measurements in methanol, through the Flory-Rehner equation (Eq. (2)).

Figure 2 shows the double logarithmic plots of N *versus* c_{xl} ($c_{xl}+c_m$) with c_{xl} and c_m expressed in mol/L. Linear regression of the whole set of data yield an slope equal to -0.95 ± 0.13. Assuming $v_{2r} = 1$, which is reasonable taking into account that samples were synthetised in water instead of methanol, the correlation improves and the slope becomes -1.14 ± 0.05. We may therefore conclude that N scales with $[c_{xl}(c_{xl}+c_m)]^{-1}$ as proposed in Ref. [1]. From the intercept of Figure 2 it was inferred that $a = 1.52$ and 1.31 Å, respectively, in very good accordance with expectation for flexible hydrocarbon polymers.

The Flory-Rehner equation may also be applied to determine the polymer-solvent interaction parameter as a function of v_2 for water and ethanol, making use of M_c values determined from results in methanol. As shown in Figure 3, χ increases with polymer concentration in the gel except for samples G20(C) with large C values, swollen in water. This indicates that not only v_2, but also gel microstructure depends on the average solvent quality expressed in χ values. Fitting of all results in Figure 3(a) except those

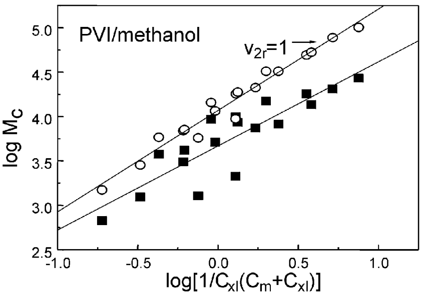

FIGURE 2 Molecular weight between crosslinks as a function of comonomer concentration in the feed. Empty points represent M_c values calculated with $v_{2r} = 1$ and filled points those calculated with v_{2r} as a function of C_T.

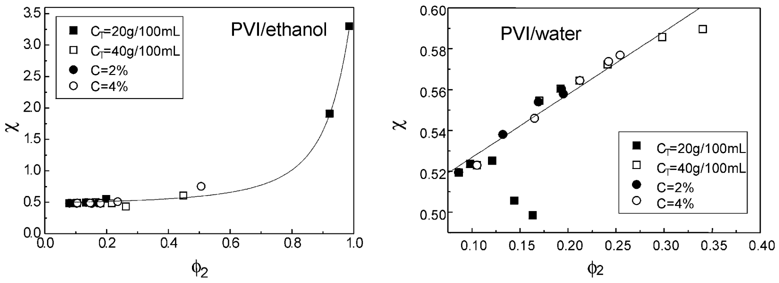

FIGURE 3 Flory-Huggins polymer-solvent interaction parameter plotted as a function of the polymer volume fraction in the hydrogel swollen in (a) deionized water and (b) ethanol.

of samples G20(10) and G20(15), yield the relationship:

$$\chi = 0.496 + 0.308 v_2 \tag{6}$$

The χ extrapolated value at infinite dilution (0.496) agrees well with reported results on the θ nature of the system PVI-water at 25°C [18]. An abrupt rise of χ can be observed in Figure 3 for ethanol-swollen samples, in accordance with gel collapse experienced by PVI in this solvent.

It would be interesting to know whether phase separation (gel collapse) takes place by specific polymer-solvent interactions or by changes of the gel microstructure developed during polymerization for certain feeding conditions. The first effect would be revealed by anomalous dependence of the enthalpic and entropic components [14] of χ on v_2. The second one would correspond to two different laws scaling v_2 with feeding compositions, for the same range of $[c_{xl}(c_{xl}+c_m)]$. Figure 4 shows the plots necessary to find the scaling laws. It can be clearly observed that, for ethanol, a set of samples

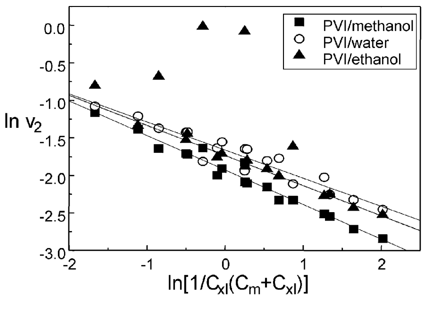

FIGURE 4 Double logarithmic plot of PVI volume fraction *versus* concentration of monomers in the feed for the three swelling solvents here studied.

do not follow the scaling law operative for most of them: $v_2 \approx [c_{xl}(c_{xl}+c_m)]^{-0.40}$. The negative exponent (-0.40 ± 0.01) is very close to that observed for a similar system [1] in a good solvent (-0.377). The Flory-Huggins theory [11] for good solvents predicts $v_2 \approx N^{-0.60}$ and according with previous results $v_2 \approx [c_{xl}(c_{xl}+c_m)]^{-0.60}$, but v_2 was determined from S gravimetric measurements assuming that ρ_2 is equal to the density of the linear polymer [17]. Nevertheless, it has recently been found that the density of PVI modified xerogels depends on C_T [19] and it could explain the difference of the experimental exponent (-0.41) and the theoretical one (-0.60).

On the other hand, only one scaling law (Fig. 4) was observed for water and methanol with exponents equal to -0.37 ± 0.03 and -0.46 ± 0.02, respectively. This result suggests specific interactions for the system PVI-ethanol, non observed for the other two solvents. In order to elucidate this point, more research is being done.

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