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Importance of Postgel Reactions in Determining the Polymer Network Structure and Properties. Poly(*N*-vinylimidazole) Hydrogels

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ABSTRACT: We compare the characteristics of polymer networks synthesized in the same or in different times of reaction, always after gelation. Several poly(*N*-vinylimidazole) hydrogel samples labeled with fluorescein (PVI) were synthesized by radical copolymerization in aqueous solution with *N*,*N*′-methylenebis(acrylamide) (BA) as cross-linker, with different times of polymerization, and with different concentrations of VI and BA in the polymerization feeding mixture. The glass transitions of samples synthesized with larger BA concentration were broader and shifted to larger T_g and with smaller heat capacity jump. Throughout postgel reactions, T_g decreases from a value typical of rigid domains enriched in BA to values closer to that of linear PVI, and the average density of permanent cross-links (obtained with the DiMarzio equation) decreases. In apparent contradiction with these facts, the equilibrium swelling degree in water and methanol, gravimetrically determined, decreases significantly upon increasing the time of polymerization. The effective cross-linking density, obtained from swelling measurements, increases throughout postgel reactions, contrary to permanent cross-links. It was concluded that spatial inhomogeneities give a porous structure characterized by high swelling and large T_g which during postgel reactions evolves to a less porous and less rigid material. The characteristics of the fluorescence spectra of labeled samples report on the access of water to polymer material and support that conclusion.

Introduction

The structure at different length scales of polymer networks and, in particular, of hydrogels is the matter of abundant current and past research.[1] The most basic parameter in the description of the polymer network structure is the cross-linking density ν_e, characterized also by N, the number of monomeric units in elastically effective chains between adjacent cross-linking points. A more detailed description includes the size of different type of domains in heterogeneous samples[2] or the proportion of network defects such as dangling chains, unreacted pendant double bonds, intramolecular cyclizations, and multifunctional knots formed by sequences of cross-linker or entanglements.[2,3]

The structure of cross-linked polymers is the consequence of several synthetic variables.[4−15] Very often hydrogels are synthesized by radical cross-linking copolymerization, and in such a case, the structure of hydrogels depends on the nature of the mold,[4] the monomer, and the solvent employed in the reaction of polymerization[5,6] as much as on the hydrophobicity of the cross-linker.[7] The usual chosen solvent for hydrogels is water, and once the mold, the nature of monomer and cross-linker, the temperature of the reaction, and the initiator concentration are fixed, the most important variables controlling the polymer network structure are the compositional data of the comonomers reacting mixture.[8−10]

Another important aspect that should be taken into account in studying the structure of polymer networks is the time of polymerization. Polymer networks are built in three steps: pregelation, gelation, and postgel reactions.[15] The structure of the polymer portion formed in the two first steps was broadly studied,[13] and it is generally admitted that during gelation isolated soluble particles formed by microgels and ramified chains interconnect with each other[6,11−15] to form a giant macromolecule which extends to the whole reacting mass or, at least, to macroscopic distances. Structural changes of the polymer network during postgel reactions are less known. In that stage, just after gelation, monomer molecules and unconnected polymer chains remain trapped, swelling the recently formed gel, and the gel itself contains potentially reacting pendant vinyl groups. In postgel reactions pendant vinyl groups and trapped monomer molecules continue the polymerization, although much more slowly, due to high local viscosity which makes the necessary diffusion difficult. Postgel reactions take a number of days to complete, and they increase the gel compactness and modify other gel properties.[12,15] Nevertheless, sets of polymer samples synthesized to evaluate the influence of any variable in polymer network properties are usually synthesized in standard conditions without paying much attention to the extent of postgel reactions. In this work, we place the focus on the importance of the latter variable.

Many studies on the building of polymer networks are related with poly(acrylamide),[11,14−16] the prototype of heterogeneous cross-linked polymer whose structure is important to know because of implications in electrophoresis uses. The formation of spatial heterogeneity in many other cross-linked polymers as polystyrene was also broadly studied.[17] The aim of this work is to study how postgel reactions modify the structure of poly(*N*-vinylimidazole) hydrogels (PVI). We are interested in PVI hydrogels because of their remarkable properties: they are quite effective in uptaking metal cations[18,19] or in regulating the pH of aqueous media without dissolving.[20] Besides, they are neutral or ionic, depending on the swelling medium,[21,22] thus making them very useful in studying typical hydrogel effects such as thermo- or pH-responsiveness.[23−25] From the commercial point of view, they are also important in the construction of enzyme electrodes for the determination of sugars[26] or as supports for solid-phase extraction.[27]

Experimental Section

Preparation of Hydrogels. Poly(*N*-vinylimidazole) hydrogel samples (PVI) were synthesized by radical cross-linking copolym-

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Table 1. Characteristics of PVI Hydrogel Samples Synthesized at 70 °C with [AIBN] = 1.0 × 10^{-2} M and Variable Feeding Concentrations of VI and BA, in 1.5 h (Except PVI-2.38, Synthesized in 1.25 h)[a]

sample	[VI] (mol/L)	[BA] (mol/L)	C_T[BA] (mol/L)^2	α (%)	T_g (°C)	ΔT (°C)	S, g(H_2O)/g(dry gel)
PVI-6.21	6.17	0.0379	0.235	13.1	187	50	21.2
PVI-4.22	4.16	0.0564	0.238	26.2	194	66	11.0
PVI-3.69	3.62	0.0712	0.263	28.7	202	66	9.7
PVI-2.38	2.28	0.1023	0.243	42.8	227	68	14.5
PVI-1.78	1.64	0.1364	0.243	50.5	216	64	12.9

[a] Yield of the polymerization, α; glass transition temperature, T_g; difference of the onset and end temperatures of the glass transition, ΔT; and equilibrium swelling degree in deionized water, S, in grams of water per gram of dry gel.

erization of *N*-vinylimidazole (VI), fluorescein−methacrylate (FlMA), and *N,N′*-methylenebis(acrylamide) (BA) in aqueous solution, with AIBN (1.0 × 10^{-2} M) as initiator. *N*-Vinylimidazole (Aldrich) was distilled under reduced pressure, just prior use. Water was distilled and deionized by a Milli-Q system from Millipore. BA (Aldrich), FlMA (Aldrich), and AIBN (Fluka) were high-quality products, used as received. FlMA concentration was 1.5 × 10^{-5} M in all cases whereas the concentration of VI and BA was different in the feeding of each sample (see Table 1) with total comonomer concentrations, C_T, ranging from 1.8 to 6.2 M and [BA] from 0.14 to 0.04 M in such way that their product was within 0.245 ± 0.02. Samples will be denoted as PVI-C_T. Glass tubes of internal diameter 12.85 mm were employed as molds. Once the reaction mixtures were in their tubes, they were sonicated for 15 min, bubbled with argon for 10 min, and introduced in a thermostatic bath at 70 °C during a given time of polymerization. Ten minutes after being introduced in the bath, tubes were inverted to check movement of its content, and in all cases it was found that samples did not flow, indicating that gelation did already take place.

A poly(*N,N′*-methylenebis(acrylamide)) (PBA) sample was prepared in 2-propanol with [BA] = 0.229 M and [AIBN] = 6.0 × 10^{-3} M. After 15 min sonication and 10 min of argon bubbling, it was introduced in the thermostatic bath at 70 °C for 1.5 h. The precipitate formed during polymerization was isolated by centrifugation and dried in open air.

After synthesis, the hydrogels were taken out of molds and cut in disklike pieces of 12.8 mm diameter and less than 1 mm thick. Two samples 1 cm thick from top and bottom of the cylinder were disregarded, and only the central part was employed. Samples were then washed exhaustively with an excess of methanol (better solvent than water) for 15 days with daily change of solvent to extract monomer and soluble polymer trapped in the polymer network. Clean hydrogels were used without drying to avoid the influence of thermal history on samples behavior.

Measurements. The swelling degree of these samples in methanol and in deionized water was measured gravimetrically. Clean samples swollen in washing methanol were immersed in the swelling solvent that was replaced frequently. From time to time, samples were removed from the bath, blotted with tissue paper to dry the surface fluid, and weighed. In about 30 days, once they reached a constant weight (m_h), they were measured in their diameter (D) and left to dry slowly for 13 days, at open air, to prevent deformations. The final drying step was in an oven at 70 °C, for 15 days in a dry atmosphere and 3 more days under vacuum just prior determining the weight of dry samples, to avoid retention of water vapor from the air. The specific swelling degree, S, was determined as the ratio of the weight of swelling solvent ($m_h - m_0$), to the weight of dry gel (m_0)

$$S = (m_h - m_0)/m_0 \qquad (1)$$

The swelling degree, S, and polymer volume fraction, υ_2, are related by xerogel (i.e., dry gel) (ρ_2) and swelling solvent (ρ_1) densities:

$$\upsilon_2 = (1 + \rho_2 S/\rho_1)^{-1} \qquad (2)$$

The thermal analysis was carried out by means of a Mettler Toledo 12E differential scanning calorimeter provided with a DSC822 oven and a subambient cooling unit. The temperature response of the calorimeter was calibrated with the melting points of high purity samples of zinc and indium. Reproducibility of temperature readings, from single thermograms of any calibrating sample, was below ±0.2%.

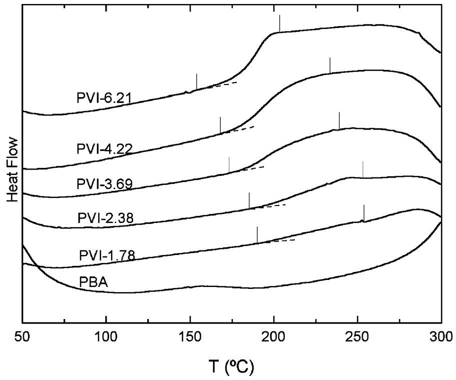


Figure 1. Second run DSC profile of several PVI samples synthesized in 1.5 h (except PVI-2.38, synthesized in 1.25 h) with several feeding compositions summarized in Table 1.

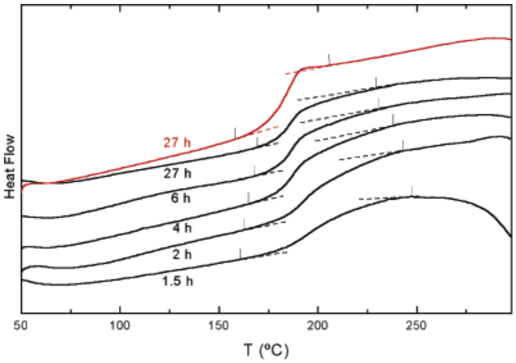


Figure 2. Second run DSC profile of PVI-3.69 samples synthesized in different time of polymerization (overimposed). The red line corresponds to sample PVI-6.21 synthesized in 27 h and represents the transition with the smaller T_g and ΔT of those observed in this work.

DSC experiments were made with specimens of 8 mg, determined within ±0.02 mg by means of a Mettler Toledo AG285 electrobalance. Two runs were performed with each specimen, in a nitrogen atmosphere, using an empty aluminum cell as a reference. First run was scanned at 5 °C/min and was extended to 240 °C, a temperature well below the beginning of thermal instability of PVI xerogels (loss weight is significant[18,21] only above 400 °C) and just below the endothermic upturn of PBA. A fast cooling at 40 °C/min followed it, and second run was scanned at 10 °C/min in the range 30−300 °C. Only second run results were presented.

The observed glass transitions were, in some cases, very broad and not completely sigmoid. Among the several criteria proposed for the determination of T_g, we take the midpoint of the heat flow jump. The width of the transition ΔT was taken as the difference of the end and onset temperatures, marked by sticks in Figures 1 and 2, to help in visualizing it. Glass transition temperatures from independent thermograms were reproducible to better than 1 °C.

Steady-state fluorescence spectra of labeled PVI with fluorescein moieties were measured in an SLM-Aminco Bowman AB2 spectrometer with front-face excitation. The hydrogel, swollen or dry, was placed in the sample holder covered by a quartz plate, forming an angle with the incident beam equal to 30°, to avoid overlapping of emission (observed at 60° of the polymer surface) with reflection. The excitation wavelength was set at 488 nm, and both the excitation and emission band-passes were kept in 4 nm. The very low degree of labeling guarantees that the basic properties of the hydrogel were not modified by the cromophore and that it is randomly distributed in the polymer network.

Results and Discussion

Three sets of PVI hydrogel samples were synthesized (i) with different concentrations of VI and cross-linker (Table 1) such that the product C_T[BA] was the same (within 0.245 ± 0.02) in a short time of polymerization (1.25 or 1.5 h) and (ii) with the same feeding composition and different times of polymerization (1.5−27 h) for $C_T = 6.21$ and 3.69 M. The reason for the particular selection of C_T and [BA] of any sample, such that the product C_T[BA] will be the same for all them, is that after some previous theoretical model[10] and experimental results[10,22] they are expected to have the same swelling degree. We intend to investigate whether it is true or not in the first stages of postgel reactions and whether it changes throughout them.

In the conditions here employed, gelation takes place in less than 10 min, and therefore the employed times of polymerization, ranging from 1.25 to 27 h, cover the influence of postgel reactions and represent commonly used conditions of synthesis. Polymer networks contain a fraction of linear or branched polymer chains unconnected to the main macroscopic network which have an important influence on swelling.[28] In-situ measurements relative to the polymer network may be partially interfered by trapped unconnected chains into the network, and to avoid such interference, samples here employed were exhaustively extracted before measurements. The yield of the reaction, determined after extraction, ranges from 13 to 70%, and for samples synthesized in 1.5 h (Table 1), it is larger for the feeding with larger [BA], despite having a smaller total comonomer concentration. This suggests a much larger reactivity of BA with respect to VI that will be confirmed below in the analysis of DSC results and already reported for similar systems.[29,30]

Samples prepared with $C_T = 6.21$ and 4.22 mol/L were translucent when swollen in water or methanol, but those prepared with $C_T = 3.69{-}1.78$ mol/L (see Table 1 for feeding composition) became totally opaque and white when swollen in both solvents. Lower C_T is accompanied by larger [BA], and thus, this comonomer must be responsible for the formation of spatial inhomogeneities, leading to an increase in turbidity.[9,12,31,32]

Glass Transition Temperatures. DSC profiles of PVI xerogels synthesized in 1.25 or 1.5 h show the pattern depicted in Figure 1, a glass transition whose T_g and width (ΔT) depend on the feeding composition employed for each sample (Table 1). Samples with larger [BA] (lower C_T) show a much broader transition shifted to higher temperatures with a smaller jump of heat capacity. In the limit, for sample PVI-1.78, it is difficult to detect the transition. In poly(*N*,*N*′-methylenebis(acrylamide)) (PBA) segmental motions are suppressed, and as for other densely cross-linked networks,[33] no transition was observed (Figure 1) over the entire temperature range studied, 30−300 °C. The broadness of the transition is typical[17,34] of cross-linked polymers made by free radical polymerization and corresponds to superposed transitions of domains with a large disparity of rigidity and T_g's too close to be resolved in separated transitions. Different types of domains with rigidity into a range limited by linear PVI and highly cross-linked PBA must therefore coexist in PVI xerogels.

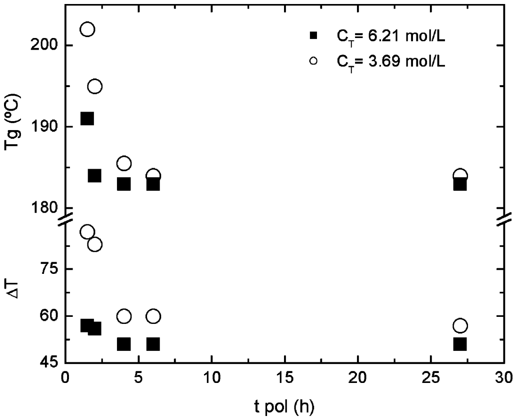


Figure 3. T_g and width of the glass transition of PVI samples as a function of the time employed in their synthesis.

There are several proposals on how cross-links contribute to T_g. It was argued that infrequent chemical cross-links lower T_g[33] either because they create locally an increase of free volume or by copolymer effect,[34−36] but these contributions coexist with the limitation of chain mobility by permanent cross-links that increase T_g and is the dominant effect above a certain degree of cross-linking.[37,38] PVI samples synthesized with high [BA] are highly cross-linked; T_g must be intimately related to the rigidity induced by chemical cross-links, but some other contributions, positive and negative, to T_g may not be totally disregarded. For example, the most densely cross-linked domains should show a very large T_g, but in accordance with the complete suppression of mobility in PBA, they do not contribute to the total jump of specific heat capacity ΔC_p and may not be observed. Pendant unreacted vinyl groups of BA would be likely to decrease T_g because they are rather flexible and not too bulky, and the same effect must be expected for flexible dangling chains.[37] Intramolecular cyclizations[11,13] are rigid structures whose T_g's rise with decreasing size[39] and may enhance the cross-linking effect if they are in a significant proportion. Entanglements are not expected to influence T_g since in the solid state, with nonextended chains, they do not modify rigidity. The influence on T_g of these network defects can be neglected, to a first approximation, to consider only the cross-linking effect.

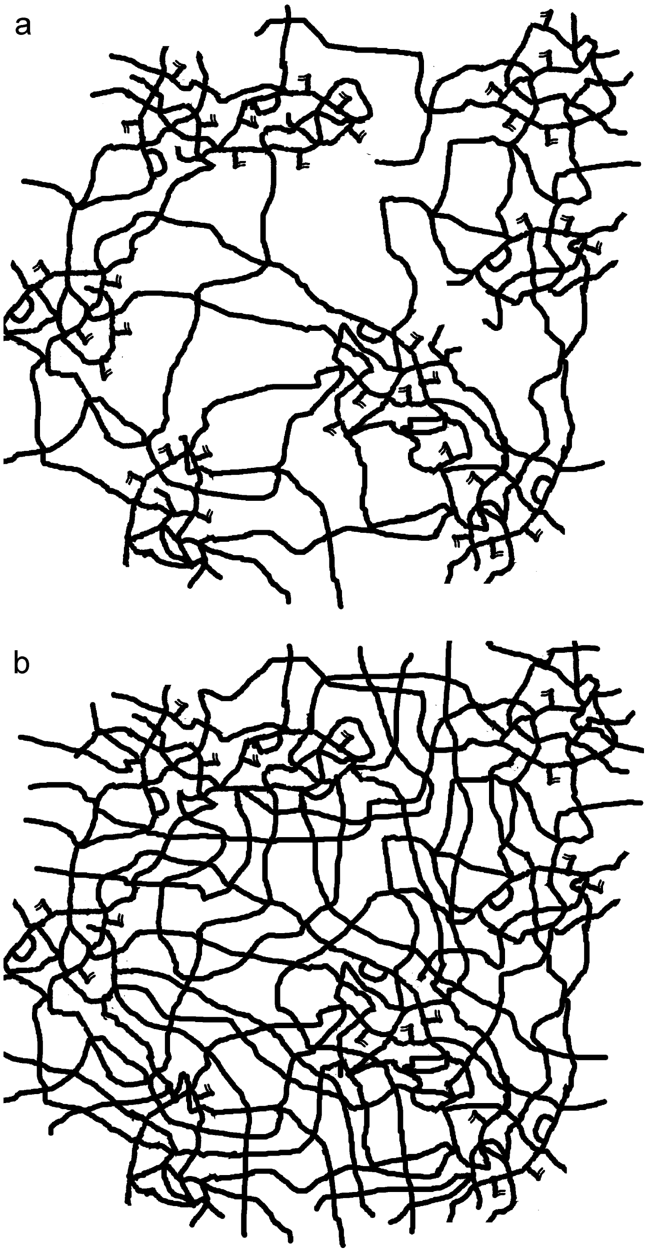
Throughout postgel reactions the glass transition becomes slightly narrower and T_g decreases, as shown in Figures 2 and 3. T_g values in the early stages of postgel reactions correspond to rigid domains enriched in BA, but they evolve to values closer to that of linear PVI, about 182 °C,[40,41] The descent is more pronounced for samples with larger BA concentration in the feeding. This indicates that in early stages of postgel reactions samples depart from a structure mostly formed by rigid and compact domains rich in BA (Scheme 1a), and during postgel reactions loosely cross-linked domains are formed between them, in such way that the average density of permanent cross-links decreases throughout polymerization (Scheme 1b).

In the frame of the Gibbs−DiMarzio theory of glass transitions, the following expression was derived[42] for cross-linked polymers

$$T_g - T_g^{\,L} = T_g^{\,L}\,\frac{kM_0\nu_e/\rho_2\gamma}{1 - kM_0\nu_e/\rho_2\gamma} \qquad (3)$$

where $T_g^{\,L}$ is the glass transition temperature of un-cross-linked

Scheme 1



polymer (here 453 K),[40,41] k is a parameter independent of the polymer and equal to 1.3×10^{-23} in molecular units, M_0 is the molecular weight of the polymer repeating unit (here 94.12 g/mol), ν_e is the permanent cross-linking density or number of cross-links per unit volume of xerogel, ρ_2 is the xerogel density (here 1.225 g/cm^3), and γ is the number of flexible bonds per monomeric unit (2 for polystyrene and similar polymers such as PVI).

Figures 4 and 5 show the dependence on the time course of polymerization of the permanent cross-linking density, $\nu_e(T_g)$, determined through T_g measurements and eq 3. The most rigid domains contribute to a very large ν_e in the early stages of the reaction while in later stages linear chains grow between compact domains and the average $\nu_e(T_g)$ decreases. As shown below, this dependence of ν_e on the time of reaction is the opposite to that observed through swelling measurements.

Swelling in Water and Methanol. Figure 6 shows how the equilibrium degree of swelling in water or in methanol decreases upon increasing the time of polymerization, for the set of samples synthesized both with $C_T = 6.21$ and with $C_T = 3.69$ mol/L. Changes of S with the time of polymerization (Figure 6) indicate a significant modification of the gel structure during postgel reactions. This result is supported by the opposite trend of υ_2, independently determined through size measurements, because S and υ_2 are inversely dependent (eq 2).

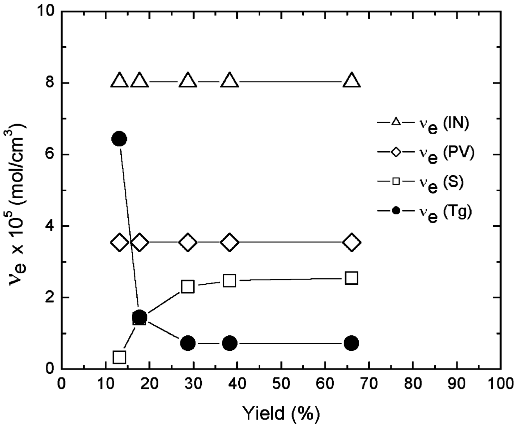


Figure 4. Cross-linking density determined through T_g and swelling measurements and calculated with the models of ideal network and polymer network with pendant vinyl groups for samples synthesized with $C_T = 6.21$ M in different times of polymerization, plotted vs the yield of the reaction.

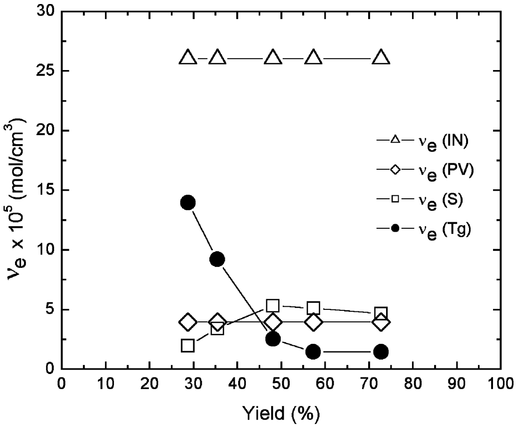


Figure 5. Cross-linking density determined through T_g and swelling measurements and calculated with the models of ideal network and polymer network with pendant vinyl groups for samples synthesized with $C_T = 3.69$ M in different times of polymerization, plotted vs the yield of the reaction.

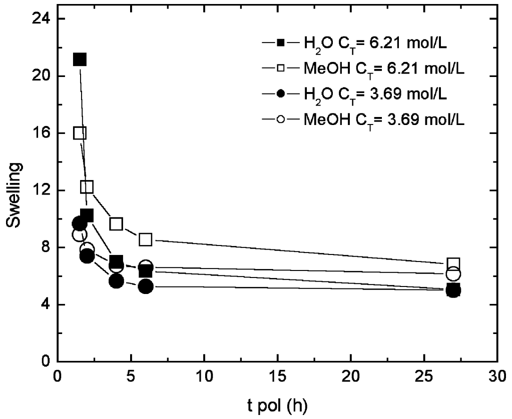


Figure 6. Equilibrium degree of swelling in methanol or water of PVI samples synthesized in different times of polymerization and with two different total comonomer concentrations.

For neutral hydrogels, the Flory−Rehner equation,[43] modified to take into account υ_{2r}, the polymer volume fraction just after polymerization,[44] and particularized to tetrafunctional knots

$$\ln(1 - \upsilon_2) + \upsilon_2 + \chi \upsilon_2^{\,2} + \frac{V_1 \rho_2}{M_c}(\upsilon_{2r}^{\,2/3} \upsilon_2^{\,1/3} - \upsilon_2/2) = 0 \qquad (4)$$

affords M_c, the molecular weight of chains between cross-links or $\nu_e(S)$, the effective cross-linking density, i.e., half the number of chains per unit volume of dry gel

$$\nu_e(S) = \rho_2/2M_c \qquad (5)$$

V_1 is the solvent molar volume. υ_2 values determined with eq 2 for PVI samples swollen at equilibrium in water were employed in eqs 4 and 5 in order to determine $\nu_e(S)$. The polymer−solvent interaction parameter is greater in gels than in solutions of the corresponding soluble polymer,[45] and it seems to be well represented by a linear function of the polymer concentration in the swollen network. It was previously found[22] that for PVI hydrogels swollen in water at room temperature $\chi = 0.496 + 0.308\upsilon_2$, in good accordance with the general expression proposed by Huglin.[46] Another crucial magnitude in eq 4 is υ_{2r}. It was determined with eqs 2 and 1 but using the polymer mass just after polymerization instead of m_h in eq 1. Xerogel densities were pycnometrically determined with acetone, a precipitant of PVI, and it was concluded that they were about the same for all the samples, $\rho_2 = 1.225$ g/mL.

Figures 4 and 5 show that the habit of the elastically effective cross-linking density determined with S measurements $\nu_e(S)$ is opposite to that shown by the permanent cross-linking density ν_e determined with T_g's. These two acceptations of the cross-linking density have different physical meaning.

Density of Permanent and Effective Cross-Links. These results indicate deep changes of the most basic structure of the polymer network, the reason for which is not evident. We first consider permanent cross-links, that is to say, those constraining mobility in the solid state. In this system, they may be identified with chemical cross-links, points of the network in which at least one BA unit (it might also be a sequence of BA units)[3] was incorporated by reaction of its two vinyl groups. Assuming that only one BA unit forms knots and that the network is ideal, without defects, the number of monomeric units in chains between cross-links is

$$N_{IN} = [VI]/2[BA] \qquad (6)$$

with N_{IN} being constant throughout polymerization. The corresponding cross-linking density $\nu_e(IN)$ may be calculated as half the chain density

$$\nu_e(IN) = \rho_2/2M_0N_{IN} \qquad (7)$$

For real networks, the cross-linking efficiency, determined as the ratio of the experimental ν_e and $\nu_e(IN)$, is usually very low[2,3,47] due to the consumption of BA in network defects. In the case of polyacrylamide hydrogels, a similar system to PVI, the cross-linker, BA, shows higher reactivity than the comonomer,[29,30,48] and this has two important consequences: (i) The most reactive comonomer is preferentially consumed in the first stages of the polymerization, and it causes a drift of the composition of the reacting mixture throughout polymerization in such way that the composition of the network portion formed at any moment of the reaction, changes.[30] (ii) It gives place to cross-linker sequences which act as the nuclei of compact domains.[49] Four chains depart from a knot formed by a single BA unit, but if the knot is formed by a BA sequence, it behaves as multifunctional and much less than four chains per BA unit depart from the knot, the efficiency of BA as cross-linker diminishes.

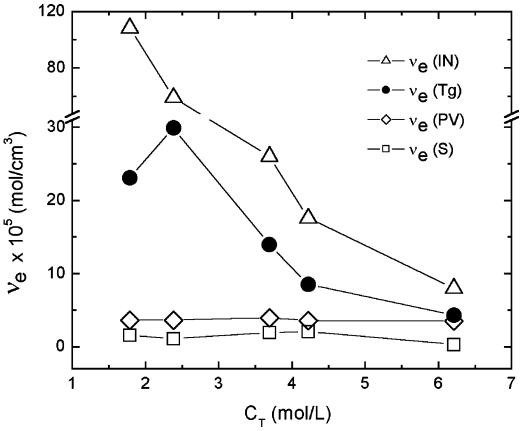


Figure 7. Cross-linking density determined through T_g and swelling measurements and calculated with the models of ideal network and polymer network with pendant vinyl groups for samples synthesized in 1.5 h (except PVI-2.38, synthesized in 1.25 h), with different total comonomer concentrations, C_T.

On the basis of the above, it may be understood how $\nu_e(T_g)$ decreases throughout polymerization (Figures 4 and 5). The network portion formed in the first stages is enriched in BA with respect to the feeding composition, which decreases the cross-linker ratio, and the subsequent network portions have less and less BA. The preferential incorporation of BA in the first stages should make $\nu_e(T_g)$ larger than $\nu_e(IN)$, but it is not observed in the whole range of feeding compositions here considered, as shown in Figure 7. It could be argued that, as mentioned before, some highly cross-linked domains may be opaque to DSC measurement; thus, $\nu_e(T_g)$ could underestimate the real permanent cross-linking density, but it may not be the explanation of $\nu_e(T_g)/\nu_e(IN)$ being less than one because such opaque domains are not expected in samples with the largest C_T (see Figure 1) whose ratio $\nu_e(T_g)/\nu_e(IN)$ equals 0.8, also below 1. It must therefore be admitted that the early incorporation of BA is quite inefficient as a cross-linker and much more inefficient as C_T decreases and [BA] increases (Table 1), which is consistent with the formation of intramolecular cycles[13] and BA sequences larger than single BA units.[3]

In addition to the formation of BA sequences and intramolecular cycles, other network defects consume BA without forming permanent cross-links. There exists no theory which accounts for the contribution of all the different types of network defects to swelling, but the existence of pendant vinyl groups in a polymer network was taken into account in the polymer network model by Bromberg et al.[10] The equilibrium swelling of PVI hydrogels depends inversely on both the total comonomer concentration and the cross-linker ratio in the feeding mixture. This dependency was explained by considering that S of neutral hydrogels, according to the Flory−Huggins theory, depends on $N^{0.6}$. Assuming that some of the cross-linker molecules, while incorporated to the polymer network, do not form knots but pendant vinyl groups, N is[10]

$$N_{PV} = 1/2a^6C_T[BA] \qquad (8)$$

with a^6 equal to 0.0116, the product of BA and VI molar volumes[22] in L/mol. Then, $S \sim ([BA]C_T)^{-0.6}$. Experimentally, it was found that for PVI hydrogels[22] S scales with $([BA]C_T)^{-0.37}$ in water (a good solvent for PVI) and with $([BA]C_T)^{-0.46}$ in methanol (a better solvent than water), and similar relationships were found for other polymers.[10,50] These scaling laws are slightly different than those theoretically predicted and the model has been criticized,[51] but while both C_T and [BA] vary greatly, all the data fall onto a single curve.[10,22,50] This confirms that a single compositional value, the product [BA]C_T, is enough to determine the corresponding swelling of hydrogels and suggests that samples synthesized with feeding mixtures having different C_T and [BA] but the same product [BA]C_T, as those employed here (Table 1) are expected to have the same cross-linking density (same N_{PV}, same $\nu_e(PV) = \rho_2/2M_0N_{PV}$) and consequently the same swelling capacity. Figures 4, 5, and 7 show that ν_e(PV) values are closer to the experimental ones, particularly to $\nu_e(S)$, than values predicted for an ideal network, ν_e(IN). But the model of polymer network with pendant vinyl's fails in that the swelling degree of samples synthesized with constant [BA]C_T, in 1.25−1.5 h, is not the same (Table 1), and $\nu_e(S)$ is not constant but increases with the time of polymerization. For samples synthesized in the longer time of polymerization, ν_e(PV) approaches ν_e(S), but the model of pendant vinyl groups does not explain swelling at short reaction times or the time evolution of the effective cross-linking density. Other effects must be considered.

The gel formed in first stages tends to be biphasic since it is formed by highly cross-linked nuclei, joined to each other by loosely cross-linked domains (Scheme 1a). Such biphasic structures behave as porous and retain much more swelling solvent than the equivalent homogeneous sample.[51,52] Equation 4 results in the equilibrium between polymer−solvent mixing and elastic contributions to the swelling osmotic pressure and applies rigorously only to homogeneous networks, but real networks are heterogeneous. For porous gels it yields apparent or effective ν_e(S) values much smaller than permanent cross-linking densities because external-like solvent, trapped in pores above a certain size, and noninteracting with polymer, increases swelling without contributing to the osmotic swelling pressure.[51] In this way, large swelling degrees caused by external solvent are attributed in eq 4 to a cross-linking density much lower than the real one. Figure 7 shows how ν_e(S) in samples synthesized in first stages of postgel reactions takes very small values.

Throughout polymerization, the almost empty regions in between the original compact nuclei are filled with loosely cross-linked material, and the polymer distribution becomes more uniform;[13,53] the highly cross-linked domains dilute in the whole network and porous diminish to eventually disappear (Scheme 1b). The volume fraction of pores in the swollen gels at equilibrium, ϕ, may be determined[54] as

$$\phi = \frac{(S - S_{ref})/\rho_1}{1/\rho_2 + S/\rho_1} \tag{9}$$

taking as reference for nonporous hidrogel, S_{ref}, the degree of swelling of the sample obtained with the same feeding and the longest time of polymerization. Figure 8 shows that in samples synthesized in only 1.5 h (lowest yields) more than 50% of swollen gels at equilibrium is occupied by pores filled with swelling solvent and that increasing conversion the volume of pores decreases and swelling levels off.

The consequence of this structural change is that swelling decreases and the effective cross-linking density ν_e(S) increases, as observed in Figures 4 and 5. Cross-linked polymers synthesized with and without porogen have[54] the same T_g, and therefore, the variation of T_g throughout postgel reactions may not be ascribed to the descent of porosity. Swelling depends not only on permanent cross-links but also on entanglements,[8,50] and that could explain that at the end of polymerization the density of effective cross-links is slightly larger than for permanent cross-links due to the additional contribution of entanglements.

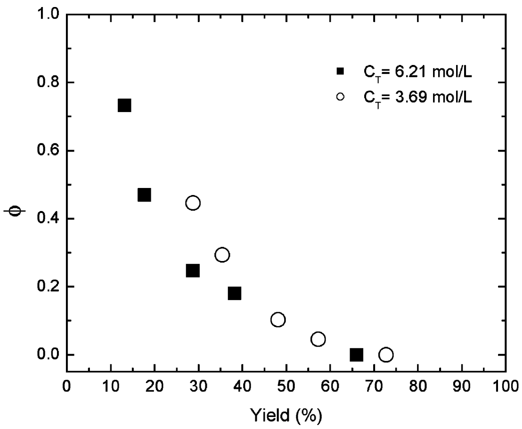


Figure 8. Volume fraction of pores of PVI samples swollen in deionized water at equilibrium as a function of the yield of polymerization.

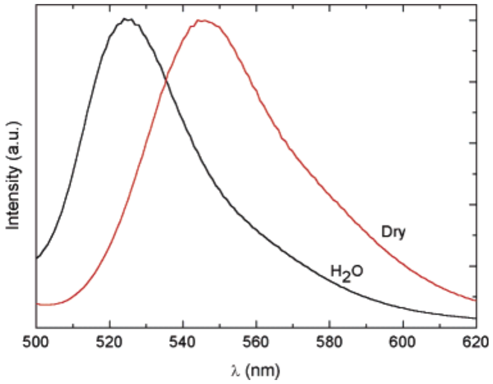


Figure 9. Fluorescence spectra of labeled PVI-6.21 dry and swollen in water, normalized to the maximum.

PVI samples here employed were labeled with fluorescein (see the Experimental Section), and hence, the characteristics of their fluorescence spectra inform on the average environment inside the network, either dry or swollen. Fluorescein exists in a complex equilibrium of several neutral and ionic forms whose relative concentrations depend on the dielectric constant of the environment so that spectral changes represent changes in the equilibrium population of those forms.[55] Figure 9 illustrates how the fluorescence spectrum of fluorescein in dry PVI (around 550 nm) is red-shifted with respect to PVI samples swollen in water (520 nm). The wavelength of the maximum and the width of the band at half-maximum inform on the average dielectric constant and the variety of local environments, respectively. This type of labeling with solvatochromic chromophores provides useful information in nanometer scale on polymer networks features, namely, the mechanism of formation[15,56] or swelling−shrinking.[57]

When water does not have access to the label, for example, because it is placed in compact domains (Scheme 1a) of swollen samples, the fluorescence spectrum is red-shifted with respect to the emission of labels placed in pores and surrounded by solvent. Figure 10 shows that, on average, samples swollen in water and synthesized in short times have emissions peaking between 525 and 535 nm, which represents restricted accessibility of water to the label in samples synthesized with larger [BA] (smaller C_T). This supports the view of these samples

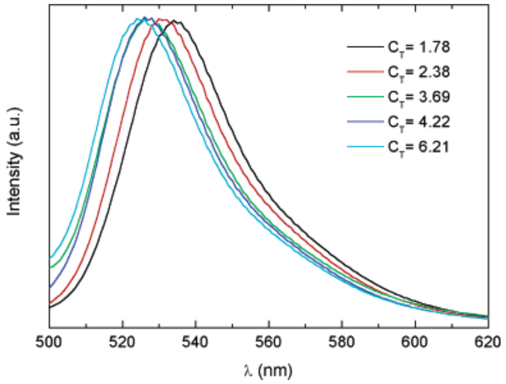


Figure 10. Fluorescence spectra of labeled PVI samples synthesized in 1.5 h (except for PVI-2.38, synthesized in 1.25 h) and swollen in water, normalized to the maximum.

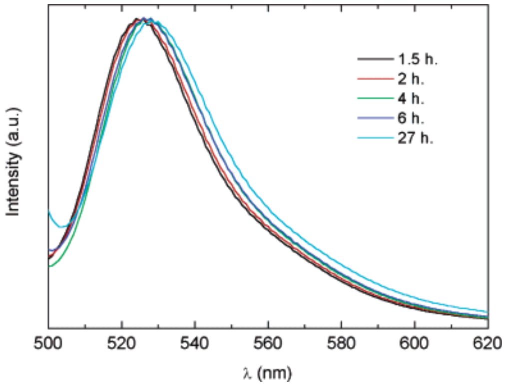


Figure 11. Fluorescence spectra normalized to the maximum of labeled PVI-6.21 samples synthesized in different times of polymerization and swollen in water.

sketched in Scheme 1a with larger volume fraction of compact domains as [BA] increases. By comparing the spectra of samples swollen in water and synthesized in increasing times of polymerization, depicted in Figure 11, it can be said that, on average, labels become less accessible to water, in accordance with the disappearance of pores (Scheme 1b) and the descent of swelling.

Finally, it must be noticed that in early stages of postgel reactions only one-quarter hour of difference in the time of reaction (1.25−1.5 h) causes significant changes of the conversion and the effective or permanent degree of cross-linking as well as of the polymer network properties. Even more, the structures of samples synthesized with the same time of polymerization are not comparable because the evolution of network defects and polymer heterogeneity interfere in the experimental ν_e values, and such evolution is different in samples synthesized with different feeding compositions, despite the fact that the time of reaction would be the same. Only very long times of polymerization, in forced conditions, guarantee that postgel reactions were completed and that comparable structures were obtained. Other networks, even if they were synthesized in the same time, are likely nonequivalent in terms of topology and heterogeneity.

Conclusions

In early stages of postgel reactions of PVI in aqueous medium, the spatial distribution of polymer material is not uniform: sequences of BA conform compact domains joined to each other by linear and loosely cross-linked polymer chains. Such structure is porous and although the permanent cross-linking density (in compact domains and therefore in average) is large, the solvent fills the pores and the swelling degree results to be large, as for very small effective cross-linking density. Compact domains must be small in samples synthesized with larger C_T and smaller [BA], since they are translucent when swollen, whereas samples made with C_T above 3.69 M are opaque, thus revealing large domains (with respect to the wavelength of visible light) of high refractive index. Fluorescein, covalently attached to the polymer network and randomly distributed inside compact domains and in chains delimiting pores, informs, through the characteristics of the fluorescence spectra, on the access of solvent to polymer, and in accordance with previous results, in samples synthesized with larger C_T and smaller [BA], the access is almost complete (small compact domains) while it is restricted for samples made with larger [BA].

Throughout postgel reactions, the space between compact nuclei is filled with polymer material loosely cross-linked, which progressively makes the swollen sample less porous. The disappearance of pores decreases swelling, and the access of solvent to polymer, as revealed by the fluorescence spectra of the label, and dilution of the more rigid and compact domains in a network with lower average density of permanent cross-links decreases T_g.

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