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# Structural characterization of poly(*N*-isopropylacrylamide) gels and some of their copolymers with acrylamide through positron annihilation lifetime spectroscopy

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In this work, poly(*N*-isopropylacrylamide) (NIPAAm), poly(acrylamide) (AAm) and poly(*N*-isopropylacrylamide)-*co*-acrylamide (NIPAAm/AAm) gels were characterized through positron annihilation lifetime spectroscopy (PALS). PALS was used to determine the average free volume radii of NIPAAm and NIPAAm/AAm gels, through the measurement of the *ortho*-positronium (*o-Ps*) lifetime. NIPAAm gel 10 × 1 showed a radius of approximately 2.9 Å. The copolymers with acrylamide, NIPAAm/AAm 10 × 1, with the acrylamide composition varying from 2 to 100 wt%, showed a decreased radius down to 2.1 Å in AAm 10 × 1 gel. The free volume estimated for the gels decreases with increasing acrylamide concentration. The results are discussed in terms of the changes in the gels' structure due to different polymer–polymer interactions. © 1998 Published by Elsevier Science Ltd. All rights reserved.

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## INTRODUCTION

A gel can be defined as a polymer network which possesses the ability to swell in the presence of a compatible solvent and can undergo a phase transition with changes in the surrounding conditions such as pH, temperature, solvent composition and electric field[1,2].

Due to such behaviour, many different applications have been suggested for polymer gels, such as their use for concentration of macromolecular solutions[3–5], purification of residue waters[6], immobilization of enzymes[7,8], sensors[9–11], drug delivery systems[12–15] and various biomedical uses[16].

One of these gels, poly(*N*-isopropylacrylamide) (NIPAAm), swells to a large extent in water, at low temperature, and shrinks with increasing temperature, showing a first-order phase transition around 34°C, behaving as a polymer solution with a lower critical solution temperature (LCST)[17]. This interesting phase behaviour—a dramatic dependence of the swelling volume on temperature and a discontinuous transition—has attracted, in the past years, the interest of many researchers all over the world. Studies on the thermodynamic behaviour of this system[18–24], different potential applications[25,26] and permeability to small solutes[27–29] have been reported.

The thermodynamics of polymer gels describes the swelling equilibrium as a result of two opposite contributions: the change in the free energy of mixing as the gel is contacted with solvent and the change in the elastic free energy due to the elongation of the network as the gel swells absorbing solvent[30]. The understanding of their elastic structure is, therefore, fundamental. This structure is directly related with the cross-linking density and polymer–polymer interactions. The voids present in the gels' structure are a direct function of the cross-linking density and polymer–polymer interactions.

The positron has been recently used as a nanoprobe '*in situ*' through positron annihilation lifetime spectroscopy (PALS) for determination of the free volume size distribution and microstructure characterization in various materials like polymers, zeolites, metal alloys and others[31–34]. The great advantage of this technique is its enormous sensibility for the free volume ($V_f$) determination with dimensions up to some tens of angstroms. Due to its short lifetime ($10^{-10}$ to $10^{-9}$ s) and the low activity of the positron source, the PALS technique, different from other methods, does not change the material properties[35].

According to the free volume model for positronium (*Ps*) formation, the *Ps* lifetime should increase with increasing volume of voids and the *Ps* intensity should increase with increasing number and volume of the voids[36]. In the free volume model, the *ortho*-positronium (*o-Ps*) is confined in the spherical potential well (free volume) and the lifetime of this specie ($\tau_3$) is directly related to the free volume radius ($R$). Assuming that the annihilation rate of the *o-Ps* inside the electron layer of width $\Delta R$ at the internal surface of $V_f$ is 2 ns$^{-1}$ [37], the size of the $V_f$ can be estimated by making use of the following equations, which have been proven to be

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applicable to a large variety of molecular solids[38]:

$$1/\tau_3 = 2[1 - r + 1/(2\pi)\sin(2\pi r)] \quad (1)$$

$$V_f = (4\pi R^3)/3 \quad (2)$$

with $r = R/R_0$, where $R$ is the radius of the voids in which the *o-Ps* survives and $\Delta R = R_0 - R = 0.166$ nm is the width of the electron layer where the *o-Ps* annihilates, by pick-off.

In this paper, we report the structural characterization of poly(*N*-isopropylacrylamide) (NIPAAm) and copolymer *N*-isopropylacrylamide/acrylamide (NIPAAm/AAm) gels through PALS. The average free volume radii of the gels were determined, as well as their free volume sizes. The free volumes of the gels were analysed and all the results are discussed in terms of the changes in the gels' structure as a consequence of different polymer–polymer interactions due to the presence of acrylamide with different compositions.

## EXPERIMENTAL

Poly(*N*-isopropylacrylamide) gels were synthesized by free-radical solution polymerization/cross-linking of *N*-isopropylacrylamide monomer. The monomer (Eastman Kodak) was purified and recrystallized to yield 100% NIPAAm, as determined by HPLC. The cross-linker, *N*,*N*′-methylenebisacrylamide (Polysciences) was electrophoresis grade and the initiators, ammonium persulfate (Merck) and sodium metabisulfite (Reagen), were reagent grade, and were all used as received. The polymerization was carried out under a nitrogen atmosphere, at 8°C for 24 h, in cylindrical glass tubes. The gel composition used in this study (10 × 1 gel) was 10 g of monomer (*N*-isopropylacrylamide plus *N*,*N*′-methylenebisacrylamide) per 100 g of milli-Q water, with 1 g of cross-linker (*N*,*N*′ -methylenebisacrylamide) per 100 g of NIPAAm plus cross-linker. Details of the monomer purification and gel synthesis are reported elsewhere[39,40].

Poly(*N*-isopropylacrylamide)-*co*-acrylamide gels were synthesized following the same procedure, the acrylamide monomer (Eastman Kodak) being used as received. The gels were also 10 × 1, with respect to the total monomer concentration and the cross-linker concentration. Eight different copolymer compositions were obtained by using 2, 5, 10, 20, 50, 70, 90 and 100 g of acrylamide monomer per 100 g of NIPAAm plus AAm. These gels are represented by 10 × 1 × 2, 10 × 1 × 5, 10 × 1 × 10, 10 × 1 × 20, 10 × 1 × 50, 10 × 1 × 70, 10 × 1 × 90 and AAm 10 × 1, respectively.

After polymerization, the gels were thoroughly washed with milli-Q water, dried at 60°C for 48 h, and cut into small pieces with a granulometry ranging from 48 to 74 mesh.

The lifetime spectra were obtained using an ORTEC fast–fast coincidence circuit, with 280 ps of time resolution, from the $^{60}$Co prompt curve. Carrier-free $^{22}$NaCl, of approximately $4 \times 10^5$ Bq activity, sandwiched between two 3.5 $\mu$m thick foils of Mylar, was used as the positron source. The source correction amounted to 10%. The samples of poly(*N*-isopropylacrylamide) (NIPAAm), poly(acrylamide) (AAm) and poly(*N*-isopropylacrylamide)-*co*-acrylamide (NIPAAm/AAm) gels were put in two acrylic supports and, between them, the foils of Mylar, containing the $^{22}$NaCl, were introduced. The measurements were carried out at 294.2 ± 1.5 K.

The lifetime spectra were satisfactorily analysed in three components using the POSITRONFIT-EXTENDED program[41], leading to the intensities ($I_i$) and lifetimes ($\tau_i$) of the various positron states: subscripts 1, 2 and 3 refer to *para*-positronium (*p-Ps*), free positron and *ortho*-positronium (*o-Ps*), respectively. The *o-Ps* lifetimes ($\tau_3$) and intensities ($I_3$) were determined from the spectral analysis with all $\tau_i$ free and with $\tau_2$ fixed at 400 ps.

## RESULTS

The positron lifetime spectra for NIPAAm 10 × 1, NIPAAm/AAm 10 × 1 × 50 and AAm 10 × 1 gels are shown in *Figure 1*.

The PALS parameters for NIPAAm, NIPAAm/AAm and AAm gels are shown in *Tables 1* and *2*. With an increase of the acrylamide concentration, a reduction in the *Ps* intensity and lifetime is observed. The reduction of $I_3$ and $\tau_3$ for gels with increasing acrylamide composition can be better visualized by *Figures 2* and *3*, respectively.

The average free volume radii ($R$) and free volume sizes ($V_f$), estimated by use of equation (2), for NIPAAm 10 × 1, NIPAAm/AAm 10 × 1 and AAm 10 × 1 gels are shown in *Figure 4*.

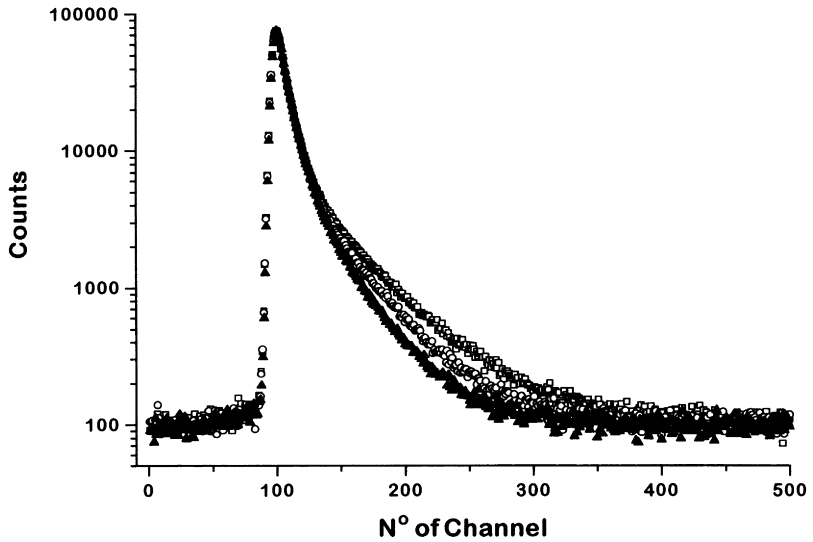


**Figure 1** Positron annihilation lifetime spectra for NIPAAm 10 × 1 (□), NIPAAm/AAm 10 × 1 × 50 (○) and AAm 10 × 1 (▲) gels

**Table 1** PALS parameters for the gels with values obtained from the spectra analysis with all $\tau_i$ free, and free volume radii and volume

| Gel | | $\tau_3$ (ps) | $I_3$ (%) | $R$ (Å) | $V_f$ (Å$^3$) |
|---|---|---|---|---|---|
| NIPAAm 10 × 1 | | 2016 ± 50 | 29.1 ± 0.7 | 2.863 | 98.30 |
| NIPAAm/AAm | 10 × 1 × 2 | 1995 ± 50 | 28.8 ± 0.7 | 2.844 | 96.36 |
| | 10 × 1 × 5 | 1906 ± 50 | 28.2 ± 0.7 | 2.761 | 88.16 |
| | 10 × 1 × 10 | 1891 ± 50 | 28.2 ± 0.7 | 2.747 | 86.83 |
| | 10 × 1 × 20 | 1872 ± 50 | 28.2 ± 0.7 | 2.728 | 85.04 |
| | 10 × 1 × 50 | 1627 ± 50 | 27.1 ± 0.7 | 2.479 | 63.81 |
| | 10 × 1 × 70 | 1518 ± 50 | 26.2 ± 0.7 | 2.358 | 54.92 |
| | 10 × 1 × 90 | 1350 ± 50 | 26.5 ± 0.7 | 2.157 | 42.04 |
| AAm 10 × 1 | | 1322 ± 50 | 24.9 ± 0.7 | 2.122 | 40.02 |

**Table 2** PALS parameters for the gels with values obtained from the spectral analysis fixing $\tau_2 = 400$ ps, and free volume radii and volume

| Gel | | $\tau_3$ (ps) | $I_3$ (%) | $R$ (Å) | $V_f$ (Å$^3$) |
|---|---|---|---|---|---|
| NIPAAm 10 × 1 | | 2067 ± 50 | 28.1 ± 0.7 | 2.909 | 103.11 |
| NIPAAm/AAm | 10 × 1 × 2 | 2049 ± 50 | 27.8 ± 0.7 | 2.893 | 101.42 |
| | 10 × 1 × 5 | 1949 ± 50 | 27.3 ± 0.7 | 2.801 | 92.05 |
| | 10 × 1 × 10 | 1943 ± 50 | 27.1 ± 0.7 | 2.796 | 91.56 |
| | 10 × 1 × 20 | 1933 ± 50 | 27.0 ± 0.7 | 2.786 | 90.58 |
| | 10 × 1 × 50 | 1680 ± 50 | 25.7 ± 0.7 | 2.535 | 68.24 |
| | 10 × 1 × 70 | 1575 ± 50 | 24.5 ± 0.7 | 2.422 | 59.51 |
| | 10 × 1 × 90 | 1436 ± 50 | 23.7 ± 0.7 | 2.263 | 48.54 |
| AAm 10 × 1 | | 1402 ± 50 | 22.3 ± 0.7 | 2.222 | 45.95 |

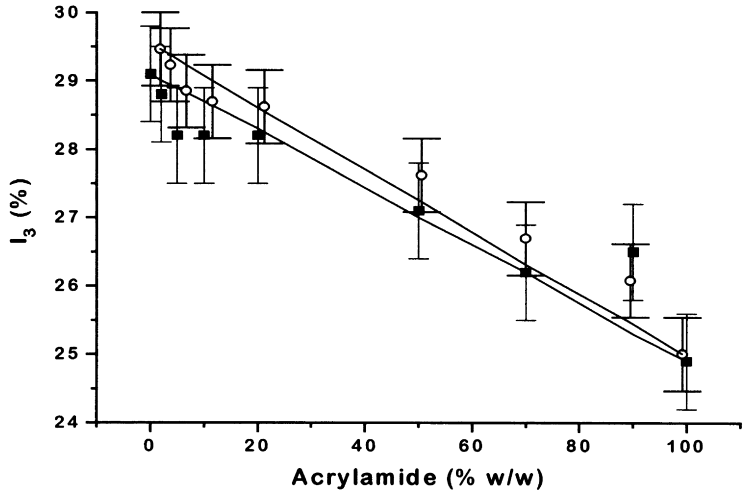


**Figure 2** Variation of *o-Ps* intensity as a function of acrylamide concentration: (■) $\tau_i$ free and (○) $\tau_2$ fixed

## DISCUSSION

The results obtained for the *o-Ps* intensity are shown in *Figure 2* and *Tables 1* and *2*. There is a significant linear decrease of $I_3$ with the increasing concentration of acrylamide, indicating a kind of ideal solution behaviour for the *Ps* formation in the gels. As already observed[42], in these cases the variation in the *o-Ps* yield obeys the following equation:

$$I_3 = c_{\mathrm{AAm}} I^0_{3,\,\mathrm{AAm}} + (100 - c_{\mathrm{AAm}}) I^0_{3,\,\mathrm{NIPAAm}} \qquad (3)$$

where $c_{\mathrm{AAAm}}$ is the concentration in weight per cent of the acrylamide monomer and $I^0_{3,\,\mathrm{AAm}}$ and $I^0_{3,\,\mathrm{NIPAAm}}$ are, respectively, the intensity of *o-Ps* formed in the AAm 10 × 1 and NIPAAm 10 × 1 gels. The straight lines in *Figure 2* were calculated using the values of $I^0_{3,\,\mathrm{AAm}}$ and $I^0_{3,\,\mathrm{NIPAAm}}$ from *Tables 1 and 2* into equation (3). The good agreement between calculated and experimental *o-Ps* intensities shows that acrylamide present in the NIPAAm/AAm copolymers is unable to inhibit the *Ps* formation. This behaviour can be expected considering the high *Ps* formation in both AAm 10 × 1 and NIPAAm 10 × 1 gels (see *Tables 1 and 2*). This is corroborated by the significant $I_3$ observed in the AAm and NIPAAm monomers, 46.2 ± 0.7% and 48.5 ± 0.7%, respectively, for values obtained from the spectra analysis with all $\tau_i$ free, and 43.2 ± 0.7% and 46.6 ± 0.7%, respectively, for values obtained from the spectra analysis with $\tau_2$ fixed and equal to 400 ps. This suggests that the observed decrease in the positronium yield is not due to chemical reactions with the *Ps* formation precursors inside the spur. According to the spur model[43] the *Ps* is formed from the combination of free positrons and electrons inside the terminal spur created during the positron thermalization. Any substance reacting with these *Ps* precursors inhibits their formation and, in the majority of the cases, the $I_3$ quickly and non-linearly decreases with the increasing inhibitor concentration, $c$, according to the Stern–Volmer equation[38], normally reaching total inhibition at $c$ high enough:

$$I_3 = I^0_3 (1 + kc)^{-1} \qquad (4)$$

where $k$ is a total inhibition constant, which is related to the

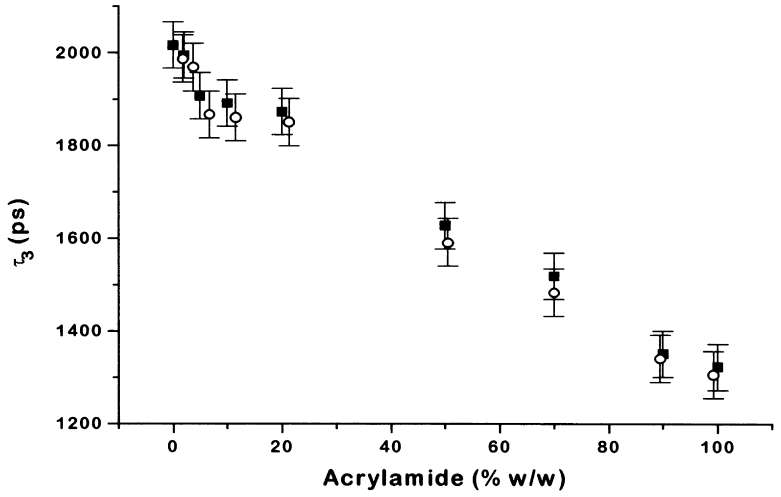


**Figure 3** Variation of *o-Ps* lifetime as a function of acrylamide concentration: (■) $\tau_i$ free and (○) $\tau_2$ fixed

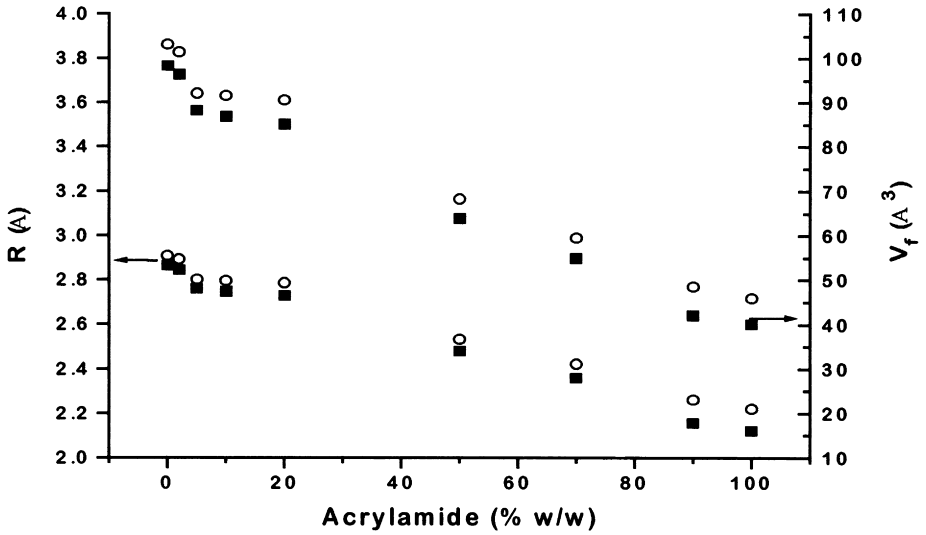


**Figure 4** Variation of free volume radius and size as a function of acrylamide concentration: (■) $\tau_i$ free and (○) $\tau_2$ fixed

inhibitor chemical efficiency. As the observed results cannot be adjusted to equation (4), this $I_3$ decrease cannot be explained as a result of chemical effects on the *Ps* formation. This behaviour could only be understood on the basis of the structural changes in the gels promoted by the increasing acrylamide concentration.

By analysing the results shown in *Figure 3* and summarized in *Tables 1 and 2*, it is observed that the copolymer NIPAAm/AAm gels exhibit smaller $\tau_3$ than the NIPAAm gel, and, while the amount of acrylamide increases continuously, from 2 to 100%, the $\tau_3$ decreases from 2016 to 1322 ps, considering the analysis with all the lifetimes free. The same behaviour is verified when the positron lifetime is fixed to 400 ps. The $\tau_3$ decrease is generally associated with a chemical quenching due to a solute and this decrease is not linear. However, no quencher is known that is unable to promote inhibition. As we have shown that the acrylamide is not an inhibitor we can conclude that the decrease in $\tau_3$ is not due to chemical reaction between *Ps* and acrylamide. Hence, the decrease in both $I_3$ and $\tau_3$ results from structural changes in the gels promoted by the increasing acrylamide concentration, leading to a decrease both in the free volume radii of the gels and in the average free volume size, as shown in *Figure 4*.

These results can be explained considering polymer–polymer interactions, which play an important role when one considers the swelling of the gels in the presence of a compatible solvent. The swelling equilibrium can be described as a result of two opposite contributions: the change in the free energy of mixing as the gel is contacted with solvent and the change in the elastic free energy due to the elongation of the network as the gel swells absorbing solvent. Polymer–polymer interactions are important not only for the understanding of the mixing term, but, principally, for the understanding of the elastic nature of the gels. This nature is directly related to the cross-linking density and polymer–polymer interactions.

Considering that the systems studied in this work were synthesized under the same conditions, that is, the synthesis temperature, the amount of initiator, the total monomer concentration and the cross-linker concentration were all kept the same, it can be assumed that the cross-linking density is about the same for all gels. Hence, any observed change in the elasticity of the gels should be associated with changes in polymer–polymer interactions.

Due to the fact that the acrylamide groups are much smaller than the *N*-isopropylacrylamide ones, it is expected that the copolymer NIPAAm/AAm gels show higher

polymer–polymer interactions, increasing with the acrylamide concentration. That is, the lower steric hindrance of the acrylamide groups when compared to the *N*-isopropylacrylamide ones allows a more effective interaction among the segments in the polymer network. The chemical structure of the *mers* suggests the some of these interactions could be through the formation of dimers by hydrogen bonding, the dimerization being more effective the smaller the substituent. This larger polymer–polymer interaction implies a lower free volume in the polymer network structure, as well as a lower average free volume radius and size, when compared to the poly(*N*-isopropylacrylamide) gel.

## CONCLUSIONS

By using positron annihilation lifetime spectroscopy we have determined the free volume sizes and the average free volume radii of NIPAAm 10 × 1, NIPAAm/AAm 10 × 1 with varying compositions and AAm 10 × 1 gels. We have shown that the decrease in these two parameters, from NIPAAm gel to copolymers with increasing acrylamide concentration up to the AAm gel, is due to structural changes in the gels. When one uses the positron as a probe for structural analysis, it is important to rule out the possibility of chemical effects, which could shadow structural changes. This was demonstrated in this work.

These structural changes were correlated in terms of increasing polymer–polymer interactions due to the presence of the acrylamide groups, which exhibit a lower steric hindrance, probably allowing a more effective dimerization through hydrogen bonding, in the dry state.

These results are important in describing the swelling equilibrium of gels, considering that they represent evidence that polymer–polymer interactions play an important role not only in the mixing free energy term, but also in the elastic free energy contribution. Also, they indicate the possibility of controlling the porosity of NIPAAm gels by making copolymers in such a way that the elasticity of the systems is dramatically changed by modifying polymer–polymer interactions. Such control is especially important when one considers the recent potential applications suggested for these gels, such as drug delivery systems and separation of macromolecular solutions, among others.

## ACKNOWLEDGEMENTS

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