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Effect of copolymerization and semi-interpenetration with conducting polyanilines on the physicochemical properties of poly(*N*-isopropylacrylamide) based thermosensitive hydrogels

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ABSTRACT

Thermosensitive hydrogels are made by radical homopolymerization of *N*-isopropylacrylamide (NIPAAM) or copolymerization of NIPAAM with 2-acrylamido-2-methyl-propane sulfonic acid (AMPS). The networks are semi-interpenetrated (s-IPN) with linear conducting polymers: polyaniline (PANI) or poly(*N*-methylaniline) (PNMANI). The semi-interpenetration affect slightly the phase transition temperature (measured by DSC) of the hydrogels, while water uptake capacity is strongly affected and depends on the relative hydrophobicity of the conducting polymer. Since polyanilines can be protonated in aqueous media, the swelling capacity of the s-IPN hydrogel depends strongly on pH unlike the unmodified hydrogel. The release of a model compound (tris(2,2′-bipyridine)ruthenium (II), $Ru(bpy)_3^{+2}$), driven by swelling or temperature, is also strongly affected both by the introduction of sulfonic groups, by copolymerization of NIPAAM with AMPS, semi-interpenetration and on the hydrophobicity of the conducting polymer. In that way, composite materials with quite different ion exchange behavior can be made by copolymerization and conducting polymer interpenetration.

1. Introduction

Polymeric hydrogels are crosslinked networks which does not dissolve in water but swell considerably in aqueous media [1]. Smart hydrogels are stimuli responsive materials which suffer a phase transition, with volume change, in response to changing environmental conditions such as temperature, pH, solvent composition or electrical stimuli [2]. Hydrogels have been used in the medical device industry as contact lenses, artificial muscles, controlled cell adhesion, sensors, etc. [3–9]. Besides simple hydrogels, novel materials can be made using interpenetrating polymer networks (IPN), where two crosslinked networks interpenetrated among themselves, or semi-interpenetrating (s-IPN) ones, where a linear polymer interpenetrates a network [10]. The incorporation of the second polymer allows improving the mechanical properties of the material without affecting significantly the thermal sensitivity of the hydrogel. Poly(*N*-isopropylacrylamide) (PNIPAAM) is one of the most studied thermosensitive hydrogels [11], and several s-IPN or IPN networks have been made using PNIPAAM [12]. Muniz and Geuskens [13] prepared a s-IPN hydrogel based on crosslinked polyacrylamide and PNIPAAM to increase the elastic modulus and mechanical properties of the hydrogel. Dhara et al. [14] synthesized gelatine/PNIPAAM IPN hydrogels, and then the volume phase transition in aqueous medium was investigated to understand the role of inter molecular interactions and molecular structure.

We have recently shown that insertion of conducting nanoparticles into a macroporous PNIPAAM based hydrogel makes the material sensitive to microwave and light (near infrared) irradiation, due to the strong absorption by the conducting particles 15], which drives the thermal

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transition of the hydrogel. However, the nanoparticle insertion was not effective in micro or mesoporous hydrogels, therefore a method was needed to produce such material. While light absorption can be introduced by s-IPN of a colored polymer, strong absorption of radiation in the microwave range requires a conducting material. Conducting polymers can be used for that purpose and can be interpenetrated by in situ polymerization [16,17]. Indeed, there have been reports of s-IPN of conducting polymers, such as polypyrrole, into PNIPAAM [18].

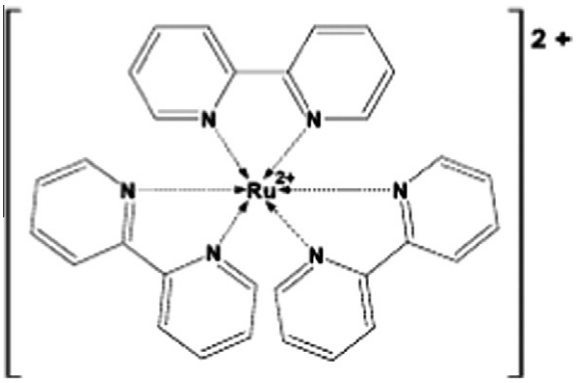
While the presence of the conducting polymer clearly adds bulk electronic conductivity and electroactivity, this is out of the scope of this work. Since we want to drive the phase transition of the hydrogel, it is necessary to know the effect the presence of the semi-interpenetrated polymer on physicochemical properties like swelling capacity, ion exchange or phase transition temperature.

In this work, we study the synthesis of PNIPAAM based hydrogels semi-interpenetrated with polyanilines and the effect of copolymerization with AMPS and semi-interpenetration on swelling capacity and phase transition temperatures. Besides that, the ion exchange capabilities of the hydrogels can also be affected by interpenetration. To test that, we use an inorganic complex (tris(2,2′-bipyridine)ruthenium (II)) as model exchanged compound. The ion has shown to be useful to study the microenvironments present inside acrylamide based hydrogels [19], it is thermally stable and has a strong absorption in the UV–visible range [20]. The study of ion exchange was carried out at physiological pH to provide useful data towards the design of drug delivery systems in biologic media.

2. Experimental

2.1. Materials

N-isopropylacrylamide (NIPAAM), 2-acrylamido-2-methyl propane sulfonic acid (AMPS) (Scheme 1) and *N*,*N*′-methylenebisacrylamide (MBAAm) (Scheme 1) were used as received. Aniline (ANI) and *N*-methylaniline (NMANI) (Fluka) (Scheme 1) were vacuum-distilled. *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) was purchased from Aldrich. Ammonium peroxidisulfate (APS) (Cicarelli) and $Ru(bpy)_3Cl_3{\cdot}6H_2O$ (Aldrich)



Tris(2,2`-bipyridine)ruthenium (II) - ($Ru(bpy)_3^{+2}$)

Scheme 2. Chemical structure of the model compound.

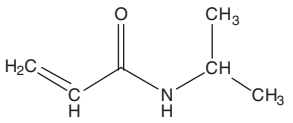
(Scheme 2) were used as received. Water was triply distilled. Solutions were deoxygenated by bubbling of nitrogen.

2.2. Synthesis of hydrogels

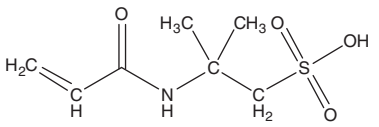
NIPAAM monomer (1.5 mmol) and MBAAm (as crosslinking agent at 2.0% mole ratio based on NIPAAM) (0.03 mmol) were dissolved in distilled water (3 mL) to form a 0.5 M monomer solution. Copolymerization was effected adding AMPS monomer at 2% (0.03 mmol) or 20% (0.3 mmol) mole ratio based on NIPAAM. The free radical polymerization of the hydrogels was carried out in a glass tube at room temperature (22 °C) for 3 h, using APS (0.01 mmol) and TEMED (0.03 mL) as redox initiator. After the polymerization, the hydrogel pieces were immersed in distilled water at room temperature for 48 h. The water was renewed every other hour in order to remove soluble by-products.

2.3. Semi-interpenetration of polyanilines into the hydrogels

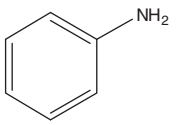
Small discs of dry (ca. 0.1 g) of crosslinked PNIPAAM (homopolymer or copolymers with AMPS) hydrogel were immersed in a monomer solution of aniline (ANI) or *N*-



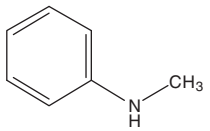
N-isopropylacrylamide



2-acrylamido-2-methyl propane sulfonic acid

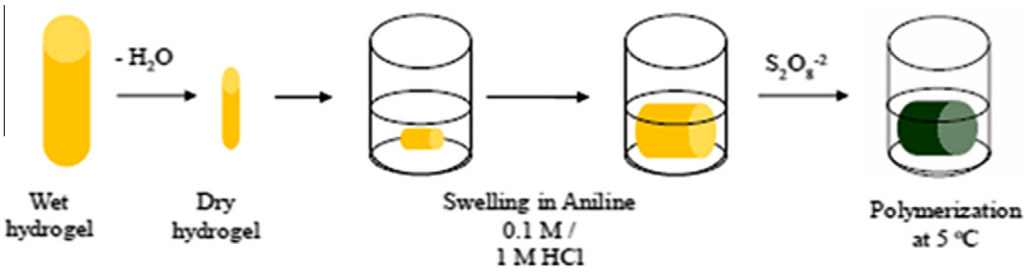


Aniline



N-methylaniline

Scheme 1. Chemical structure of the monomers used.



Scheme 3. Sequence of steps used to semi-interpenetrate a polyaniline into the hydrogel.

methylaniline (0.3 mmol) in aqueous 1 M HCl (3 mL), until all the solution was absorbed into the hydrogel (taking 3 h at least). To the clean disc, an equimolar amount of APS (0.3 mmol) (dissolved in 1 mL of 1 M HCl) is added as oxidant to produce PANI or PNMANI inside the gel. In that way the linear conducting polymer is formed and remains interpenetrated into the gel (Scheme 3).

The polymerization was carried out for 12 h inside an ice bath (ca. 5 °C). All semi-interpenetrating hydrogels obtained were then immersed in flushing stirred distilled water (>1 L) at room temperature for at least 48 h in order to extract unreacted chemicals and side products. The successful semi-interpenetration of the colorless hydrogel with the deep green–blue PANI or PNMAN) can be easily detected after the polymerization (Fig. 1).

The material becomes green in acid solution and blue in basic solution, following the color changes of the conducting polymer. The optimum order of the impregnation steps depends on the gel and it is optimized to obtain a homogenous interpenetrated material. The amount of conductive polymer incorporation was measured by weighting the dry hydrogel before interpenetration and comparing with the weight of the interpenetrated material, dried under vacuum.

2.4. Calorimetric measurements

The DSC measurements were conducted using TA Instruments DSC 2010 under N_2 flow. The samples were previously wetted in buffer solution at different pH. The sealed pan with the sample (ca. 100 mg) was quickly cooled inside the differential scanning calorimeter (DSC) chamber at −25° by filling the outer reservoir with a frozen solution of 80% w/w $CaCl_2$ (16 g) in water (20 mL). Several minutes were allowed for the system to attain thermal equilibrium. The sample holder assembly was then heated at a rate of 10°/min from −25° to 60° (after of phase transition). The temperature is kept below 100 °C to avoid decomposition of the sample and evaporation of water.

2.5. Dynamic swelling measurements

The swelling ratio was measured in various buffer solutions. Pre-weighted dry hydrogels samples (ca. 0.2 g) were immersed in solutions with various pHs until they swelled to equilibrium. By different measurement, it was confirmed that 10 h immersion was enough to reach equilibrium swelling of the samples. After excessive water was removed with filter paper, the fully swollen samples were weighed. The swelling ratio can be calculated as a function of time:

$$\%\text{Swelling} = ((Ws - Wd)/Wd) \times 100 \quad (1)$$

where *Ws* represents the weight of the swollen state of the sample at a given time and *Wd* is the weight of dry sample. The swelling experiments were repeated five times until there was no further weight increase.

2.6. Study of model compound release by diffusion at 20 °C

The dry hydrogels were impregnated with $Ru(bpy)_3^{+2}$ solution inside a bath for 24 h. Then, the hydrogel were gently washed and put back in clean buffer solution. The absorbance of the released compound was measured at 450 nm, as a function of time. A Hewlett–Packard-8453 UV–visible spectrophotometer and quartz cells (Helma) were used for the measurement. The data were reported

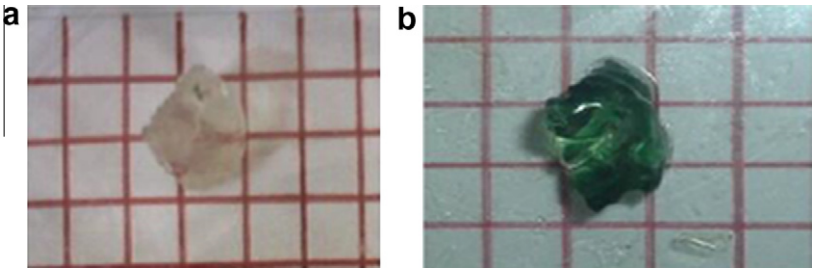


Fig. 1. Steps of semi-interpenetration of hydrogel (up). Photograph of a hydrogel before (a) and after (b) of semi-interpenetration with PANI in acid solution (bottom).

as absorbance (Abs_{450nm}) of $Ru(bpy)_3^{+2}$ per gram of hydrogel.

2.7. Equilibrium delivery driven by temperature

The amount of metal complex $Ru(bpy)_3^{+2}$ released from the gel is measured by UV–visible spectrophotometry in the solution outside the gel. Pre-weighted dry hydrogels (W) samples were immersed in $Ru(bpy)_3^{+2}$ buffer solution (0.1 mM) until equilibrium swelling. So, we want to avoid model compound release by diffusion and detect the delivery driven by temperature effect. The data of initial absorption (Abs_0) at 20° and after each temperature (Abs_T) were registered. Percentage of $Ru(bpy)_3^{+2}$ delivered from gel is calculated as the difference between Abs_0 and Abs_T at 450 nm, relative to initial absorbance (Abs_0) per gram of hydrogel, according to the following equation:

$$\%Abs_{450\,nm} = (100 \times (Abs_0 - Abs_T)/Abs_0)/W_{hydrogel} \quad (2)$$

The spectra of $Ru(bpy)_3^{+2}$ solutions freshly prepared and those released from the gels are identical, indicating that the complex is released as one unit and is not affected by the temperature changes.

3. Results and discussion

First we investigate the effect of material composition on thermosensitivity.

3.1. Effect of copolymerization on the phase transition temperature (Tp)

In Table 1 are shown the results of phase transition temperature for different hydrogel systems, stabilized at pH 7, measured by DSC.

As it can be see, the phase transition temperature of PNIPAAM increases when charged monomer units ($-SO_3^-$ of AMPS) are incorporated in the chain. It seems that the charged groups increase the hydrophilicity of the material, through ion–water interactions, and the transition to a hydrophobic state is shifted to higher temperatures. In fact poly(NIPAAM-*co*-20%AMPS) did not show a phase transition below the water boiling temperature.

3.2. Effect of conducting polymer interpenetration on the phase transition temperature (Tp)

The presence of the conducting polymer (PANI) has little effect on the *Tp* of plain PNIPAAM s-IPN hydrogel. However, when PANI is interpenetrated into a PNIPAAM-*co*-2%AMPS, the transition temperature increases. On the other hand, negligible effect is observed when PNMANI is intercalated.

Table 1
Relative amount of semi-interpenetrated polymer (w/w) inside different hydrogels.

Materials	w/w
PNIPAM/PANI	0.94
PNIPAM/PNMANI	0.99
PNIPAM-*co*-2%AMPS/PANI	0.56
PNIPAM-*co*-2%AMPS/PNMANI	0.52

3.3. Effect of pH on the phase transition temperature (Tp)

In addition, we could observe that the effect of pH on *Tp* both in PNIPAAM or poly(NIPAAM-*co*-2%AMPS) are negligible (Table 1). On the other hand, when PANI or PNMANI are interpenetrated into the hydrogel, clear effect of pH on *Tp* are observed. This is likely to be due to the fact that both conducting polymers have a protonation/deprotonation equilibrium in aqueous media [21]. Since the phase transition in thermosensitive hydrogels involves a change in the hydrophobic/hydrophilic equilibria in the material, it is affected by the charges (fixed positive charges and attached counterions) present in protonated polyanilines. Accordingly, in Fig. 2 are shown the DSC thermogram of poly(NIPAAM-*co*-2%AMPS) s-IPN with PANI, with two peaks at 37.8° and 48.8°. This means that there are two zones with different phase transition temperature. It is noteworthy that a double peak is detected when the hydrogel was interpenetrated in the external parts of hydrogel (not homogenously). Such behavior is observed when the reaction time is too short for the aniline to diffuse on the whole gel volume. Whereas, when the system was fully interpenetrated, the DSC curves showed one intermediate peak at 40.4°. However, shifting of *Tp* ($\Delta Tp = 3.6$ °C) regarded to poly(NIPAAM-*co*-2%AMPS) could be related to amount of PANI interpenetrated (see Table 2). Therefore, we consider that the system could have different microenvironments with different degree of interpenetration. Most likely the AMPS rich domains are interpenetrated with PANI while PNIPAAM remains unchanged for lower degree of interpenetration.

3.4. Dynamic swelling of the hydrogels

In Fig. 3 are shows the measurement of swelling percentage as a function of time for PNIPAAM and copolymers with different amount of AMPS. The results indicate that the swelling rate and water uptake capability increase when the relative amount of AMPS increased. The

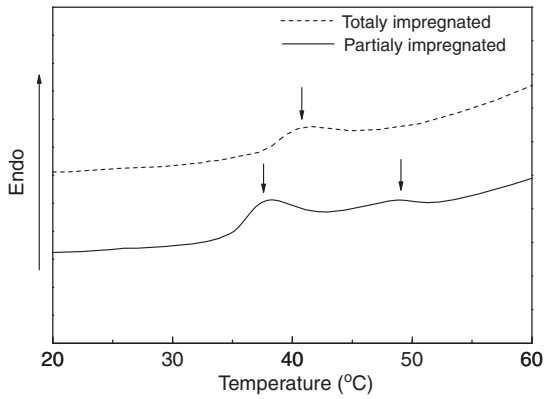


Fig. 2. DSC thermograms of the poly(NIPAAM-*co*-2%AMPS) s-IPN with PANI and swollen in solution at pH 7.

Table 2
Phase transition temperatures (*Tp*) of different materials, at different pH, measured by DSC.

Hydrogel	Interpenetrated conducting polymer	*Tp*/°C[a]		
		pH 4	pH 7	pH 10
Poly(NIPAAM)	None	33.0	32.6	32.7
Poly(NIPAAM)	PANI	32.9	33.4	34.2
Poly(NIPAAM)	PNMANI	33.2	33.8	
Poly(NIPAAM-*co*-2%AMPS)	None	38.8	36.8	37.7
Poly(NIPAAM-*co*-2%AMPS)	PANI	36.2	35.7	36.0
Poly(NIPAAM-*co*-2%AMPS)	PNMANI	35.4	36.5	37.2

[a] Average error: ±0.2 °C.

measurements with hydrogels interpenetrated with PANI show also a large water uptake capability and fast swelling.

When PNIPAAM–20%AMPS is swelled, we observed that the hydrogel breaks after 2 h (% of swelling ca. 2000). But when the same gel is interpenetrated with PANI, the gel does not break up to ca. 4000%, because the mechanical resistance had been increased by the effect of the interpenetrated polymer.

PNIPAAM hydrogel is only slightly affected by pH, probably due to ionic force effects. On the other hand, the hydrogel semi-interpenetrated with PANI shows a clear pH effect (Fig. 3A). This is likely to be due to the charging of the PANI chains related to the protonation of polyaniline [22]. The swelling capacity is higher at pH 10, because of the electrostatic repulsion of sulfonic groups. At pH 4, these groups are likely to be compensated by the positive charges present in protonated PANI. So, the swelling capacity is lower.

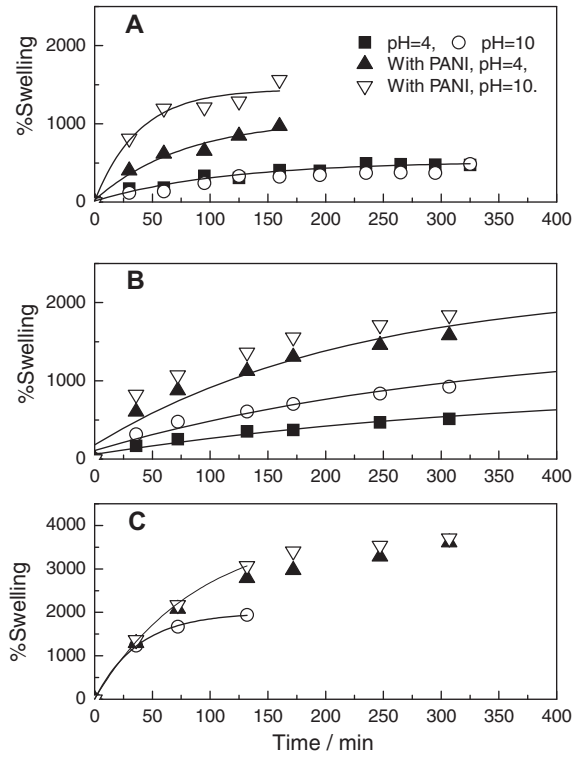


Fig. 3. Swelling dynamics of the hydrogels at different pH. (A) PNIPAAM, (B) PNIPAAM-*co*-2%AMPS and (C) PNIPAAM-*co*-20%AMPS.

In Fig. 4 are shown the maximum equilibrium swelling of different hydrogels, based on poly(NIPAAM-*co*-2% AMPS). The swelling capacity of the hydrogel with PANI is higher both than of the plain hydrogel and of the hydrogel interpenetrated with PNMANI, throughout the whole pH range. The effect of pH on the hydrogel s-IPN with PANI and PNMANI are also different. At pH 4, the swelling capacity of the hydrogel with PNMANI is larger, at pH 7 these are similar, and at pH 10 the swelling capacity of the hydrogel with PNMANI is lower than of plain hydrogel. This result may be related to the fact that PNMANI is more hydrophobic, due to the methyl groups in the backbone [23]. At pH 4, PNMANI is protonated and water molecules swell the gel due to ion–dipole interactions. At pH 10, PNMANI is deprotonated and its capacity to interact with water, shown in the swelling capacity, is diminished.

3.5. Delivery of a model compound by diffusion

Since hydrogels can be used for drug release, we measure the effect of copolymerizaton and semi-interpenetration on the release of a model compound: $Ru(bpy)_3^{+2}$. In Fig. 5 are shown the profiles of $Ru(bpy)_3^{+2}$ absorbance when it is released from an hydrogel into a buffer solution of pH 7. The delivery rate of compound from the hydrogel decreases when the percent of AMPS increases. It seems that the positively charged compound is preferentially retained when negatively charged sulfonic groups (AMPS monomer units) are present.

On the other hand, the interpenetration of a conducting polymer (PANI or PNMANI) increases the amount $Ru(bpy)_3^{+2}$ (Table 2) released from the material. The amount released is also larger when the conducting polymer is semi-interpenetrated in neutral PNIPAAM, therefore

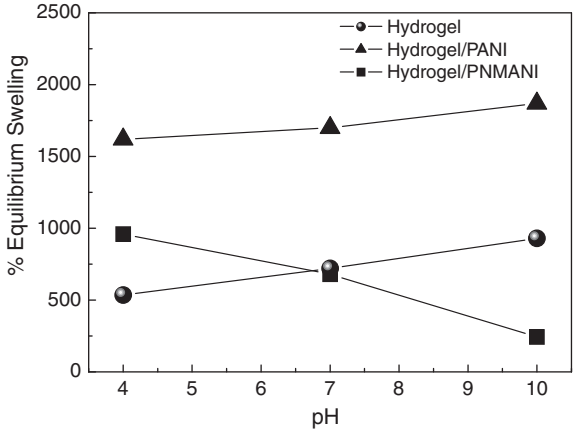


Fig. 4. Maximum swelling percentage of poly(NIPAAM-*co*-2% AMPS), and its s-IPN hydrogels with PANI and PNMANI, at different pH. Equilibrium swelling taken after 300 min.

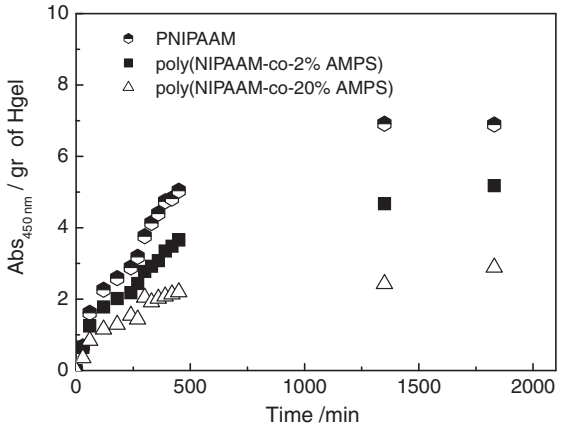


Fig. 5. Delivery of $Ru(bpy)_3^{+2}$ in buffer solution at pH 7 and 20 °C. The drug was impregnated in each hydrogel, previously.

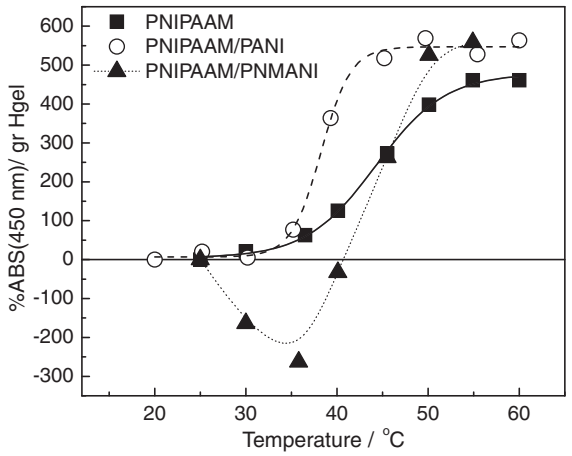


Fig. 6. Temperature driven exchange of $Ru(bpy)_3^{+2}$ to PNIPAAM based hydrogels and s-IPN with PANI or PNMANI, at pH 7.

electrostatic attraction with the sulfonate group could not be responsible. It seems that the presence of the conducting polymer in the s-IPN materials have an additional hydrophobic effect which help increasing $Ru(bpy)_3^{+2}$ loading. In that way, PNIPAAM-*co*-20%AMPS/PANI has six times more $Ru(bpy)_3^{+2}$ than PNIPAAM-*co*-20%AMPS. The effect is stronger when PNMANI (more hydrophobic) is interpenetrated instead of PANI (less hydrophobic), giving support to the mechanism. Similar results had been observed when poly-(acrylic acid-*co*-acrylamide) was used as delivery system of $Ru(bpy)_3^{+2}$. It was found that both electrostatic and hydrophobic interactions have to be taken into account to explain the exchange [24].

3.6. Ion exchange driven by temperature

Since PNIPAAM suffers a phase transition with temperature, we studied the exchange of $Ru(bpy)_3^{+2}$ between the hydrogel and its bathing solution during transition at pH 7. The pH was chosen to simulate a physiological environment. If the temperature driven ion exchange is made into clean solution, a contribution of concentration driven exchange could not be avoided and will make the interpretation impossible. Therefore, we measure the exchange of the compound into the equilibrated solution at the initial temperature. At the phase transition temperature, entropic effects make the polyacrylamide backbone more hydrophobic and the gel volume collapse, releasing water to the surrounding media. A simple model would indicate that soluble compounds (like $Ru(bpy)_3^{+2}$) would be released along with water. However, the actual situation is more complex.

In Fig. 6, it could be observed the exchange of $Ru(bpy)_3^{+2}$ from PNIPAAM gels, untreated or semi-interpenetrated with PANI or PNMANI. As it can be seen, the compound is released from the gels at temperatures higher than the phase transition temperature (*Tp*). The amount of compound released is not significantly affected by the interpenetration with PNMANI and diminishes somewhat when PANI is interpenetrated into the gel. On the other hand, while PNIPAAM/PANI releases the compound monotonically, the intake of $Ru(bpy)_3^{+2}$ is observed at intermediate temperatures in the case of PNIPAAM/PNMANI. It is likely that the changes of hydrophobic nature in PNIPAAM, carried out by the temperature changes, are coupled differently with the hydrophilic PANI than with the more hydrophobic PNMANI.

A different situation is observed when the exchange of $Ru(bpy)_3^{+2}$ is measured in gels based on PNIPAAM-*co*-2%AMPS (Fig. 7).

The presence of negative sulfonic groups in the hydrogel makes that the gel intake $Ru(bpy)_3^{+2}$ instead of releasing it at higher temperatures, likely due to a combination of coulombic attraction with the cation and hydrophobic interactions. In the non interpenetrated gel, the release of $Ru(bpy)_3^{+2}$ is observed at intermediate temperatures followed by an intake. It is likely that domains rich in PNIPAAM or PAMPS are present, having different transition temperatures. The interpenetration of a positively charged conducting polymer eliminates such intermediate state. This is probably due to the fact that the conducting

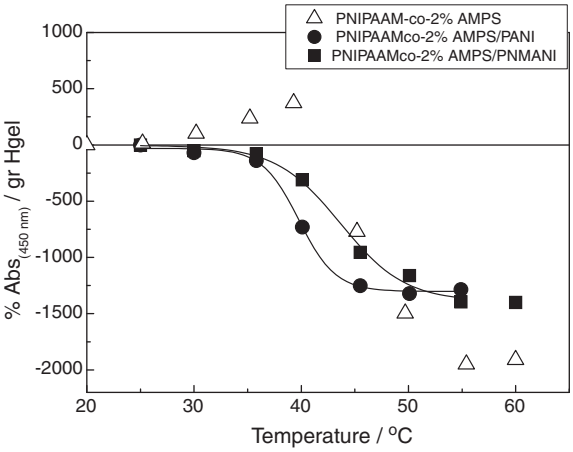


Fig. 7. Temperature driven exchange of $Ru(bpy)_3^{+2}$ to PNIPAAM-*co*-2%AMPS based hydrogels and s-IPN with PANI or PNMANI, at pH 7.

Table 3
Maximum absorbance change (ΔAbs) per gram of hydrogel due to released $Ru(bpy)_3^{+2}$ (20 °C and pH = 7).

Materials	ΔAbs[a]/g hydrogel
PNIPAAM	6.9
PNIPAAM-*co*-2%AMPS	5.2
PNIPAAM-*co*-20%AMPS	2.9
PNIPAAM/PANI	20.5
PNIPAAM-*co*-2%AMPS/PANI	13.2
PNIPAAM-*co*-20%AMPS/PANI	8.7
PNIPAAM/PMANI	24.6
PNIPAAM-*co*-2%AMPS/PMANI	21.9
PNIPAAM-*co*-20%AMPS/PMANI	18.1

[a] Equilibrium absorbance at 450 nm due to free $Ru(bpy)_3^{+2}$ in the surrounding solution.

polymer presence increases the transition temperature of PNIPAAM making it to switch at the same temperature than domains rich in PAMPS.

These results could be quantified through the calculation of a partition coefficient (*Cp*), defined as:

$$Cp = [C]_{hydrogel}/[C]_{water} \quad (3)$$

where [*C*] is the molar concentration of the compound in the hydrogel ($C_{hydrogel}$) and bathing solution (C_{water}), when the system is at thermal equilibrium. The *Cp* indicates the amount of drug that can enter to hydrogel. $Cp = 1$ indicates that the drug is equally partitioned, while a $Cp > 1$ indicates that the drug is preferentially located inside to hydrogel.

The values of *Cp* for $Ru(bpy)_3^{+2}$ in PNIPAAM and PNIPAAM-*co*-2%AMPS at 20 and 60 °C are shown in Tables 3 and 4. It is clear that $Ru(bpy)_3^{+2}$ is equally partitioned ($Cp \approx 1$) at room temperature and is released ($Cp < 1$) along with the water expelled when the transition temperature of NIPAAM units is reached.

On the other hand, $Ru(bpy)_3^{+2}$ is retained ($Cp > 1$) in PNIPAAM-*co*-2%AMPS, likely due to coulombic attraction between the cation and sulfonate groups, at both temperatures. When the temperature is increased, $Ru(bpy)_3^{+2}$ is inserted, instead of released from the gel which confirm the results observed of Fig. 7. Therefore, a small change of structure inverts the sense of model compound flux. A device which releases $Ru(bpy)_3^{+2}$ upon heating or cooling can be built using the same base hydrogel and similar synthetic procedure, only changing the composition.

The semi-interpenetration of PNIPAAM-*co*-2%AMPS with PANI increases strongly the retention of $Ru(bpy)_3^{+2}$ at each temperature and also increases the ratio between *Cp* at each temperature. The semi-interpenetration of PNIPAAM-*co*-2%AMPS with PNMANI increases less significantly $Ru(bpy)_3^{+2}$ retention but makes the *Cp* more sensitive to the temperature, since the ratio between temperatures is bigger for this material than for any other (Table 4). Such property could be used to reversibly absorb contaminant from aqueous solutions.

Table 4
Partition coefficients (*Cp*) of $Ru(bpy)_3^{+2}$ in smart hydrogels before and after of phase transition temperature, at pH 7.

Materials	*Cp*[a] (20 °C)	*Cp*[a] (60 °C)	Ratio[b]
PNIPAAM	1.4	0.4	0.3
PNIPAAM/PANI	1.2	-	-
PNIPAAM/PNMANI	1.4	7.6	5.4
PNIPAAM-*co*-2%AMPS	4.9	20.9	4.23
PNIPAAM-*co*-2%AMPS/PANI	24.0	240.0	10.0
PNIPAAM-*co*-2%AMPS/PNMANI	2.4	40.1	16.7

[a] Average error: ±0.5.
[b] Ratio: *Cp* (60 °C)/*Cp* (20 °C).

4. Conclusions

The properties of poly(NIPAAM) can be easily tailored by copolymerization with AMPS and/or conducting polymer interpenetration inside the network. The presence of AMPS in the hydrogels increases the phase transition temperature and the swelling capacity. On the other hand, the interpenetration with PANI does not change significantly the transition temperature but increases the water swelling capacity and makes the composite pH dependent. In addition, it seems that the mechanic properties are improved by interpenetration, without changing significantly the thermal sensitivity of the hydrogels. In that way, nanocomposites based on s-IPN hydrogels, which are sensitive to pH and temperature could be easily built. The exchange of a model compound ($Ru(bpy)_3^{+2}$) is strongly affected by the incorporation of negative groups (AMPS) in the hydrogel network and by conducting polymer semi-interpenetration. The presence of the conducting polymer affects the ion exchange mainly by changing the hydrophobicity of the composite material. Since temperature driven phase transition changes the hydrophobicity of PNIPAAM, the in exchange at different temperatures is also affected. An additional factor is the relative hydrophobicity of the conducting polymer. Using the same synthetic procedure, it is possible to semi-interpenetrate polyaniline (PANI) or poly(*N*-methylaniline) (PNMANI) into thermosensitive hydrogels giving materials with different properties. Both the swelling and the compound release are strongly affected by the nature of the conducting polymer. The properties of these systems can be used to design a material which release or retain a drug with similar characteristic to $Ru(bpy)_3^{+2}$, depending on the application requirements. On the other hand the reversible changes in the ionic concentration inside a film could be used to absorb contaminants from aqueous solutions.

A simple model which does not take into account the interaction of the exchanged compound with the complete composite matrix is unable to explain the actual exchange of $Ru(bpy)_3^{+2}$ from PNIPAAM based gels.

The effect of conducting polymer interpenetration on the thermosensitivity, swelling and ion exchange has to be taken into account when interpenetrated materials are used as electrochemical or radiation absorbing materials. The results also show that polyanilines are organic polymers which can be used to easily change the properties of hydrogels, disregarding their conducting properties.

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