

Synthesis and characterization of poly N-isopropylacrylamide-co-acrylic acid and their binary blend films properties

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Abstract

In past decades, the combination of polymers to obtain blends in film shapes has been a very effective strategy to meet the needs of the increasingly demanding market. In this sense, pH- and thermo-sensitive (PHT) polymers have recently drawn the attention of researchers for their countless applications. However, binary mixtures of typical PHTs like polyacrylic acid (p-AAc) and poly-N-isopropylacrylamide (p-NIPAm) were unable to form films. In this sense, it was hypothesized that NIPAm copolymerized with AAc monomers can yield blends with virtually the same functional group composition of binary mixtures of p-NIPAm and p-AAc homopolymers but with different properties of film formation. For this, a copolymeric radical synthesis and the subsequent analytical studies were complemented to get a broad description of these materials. P-NIPAm and p-AAc homopolymers and different proportions of copolymers p-NIPAm-co-AAc were obtained and thoroughly characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Size Exclusion Chromatography (SEC), acid-basic titration, and rotational rheology. Among the samples, the solutions of p-AAc with p-NIPAm and p-NIPAm-co-AAc copolymers with a higher proportion of NIPAm units (0.8 and 0.6 NIPAm/AAc) precipitated as interpolymer complexes. Since it was expected, the combination with p-NIPAm-co-AAc 40/60 copolymer, which has a higher proportion of AAc groups and pH sensitivity, allowed obtaining blends suitable for the preparation of films. Furthermore, despite the fact that the combinations of p-NIPAm-co-AAc 40/60 with p-NIPAm-co-AAc 80/20 or p-NIPAm were successful, the mechanical properties of the films are worse compared to the other blends, leaving this issue open for subsequent studies.

Keyword

p-NIPAm, p-AAc, p-NIPAm-co-AAc, pH-sensitive polymers, polymer blends materials, polymer films.

1. Introduction

In past decades, the combination of polymers to obtain blends has been a very effective strategy to meet the needs of the increasingly demanding market. Usually, polymeric blend materials (PBM) are prepared in compositions that make them superior to individual components [1]. Relevant studies have been carried out searching PBM and particularly to describe the miscibility of the polymers on the mixtures [2,3]. This characteristic is fundamental because it accounts for the mechanical properties of the PBM as a product of the interactions present between the functional groups of the polymer chains [3-5]. Furthermore, a PBM needs stability in a homogeneous phase that underlies the compatibility between the components, such property being indispensable for technological applications.

One of the most studied thermo-sensitive polymeric materials is poly (N-isopropyl acrylamide) (p-NIPAm) which presents reversible phase transitions close to the human body temperature [6], and it becomes an ideal material for biomedical applications [7]. P-NIPAm shows a lower critical solution temperature (LCST) in the aqueous medium at around 32°C [8] produced by a change in hydrophilic-hydrophobic behavior. Below LCST, H-bonds of water with polymer chains form a solvation layer surrounding the chains [9], providing stability to the structure. Increasing the temperature above LCST induces the breaking of H-bonds by collapsing the chain structure due to the generation of intra- and inter-chain hydrophobic bonds [10]. As a result, the conformation changes from a random coil to a globular shape expelling water molecules from the solvation layer. Thus, the hydration-dehydration process plays a fundamental role in the demixing transition behavior and the structure of the polymer backbone [6]. These p-NIPAM properties have been exploited for the development of chemical actuators [11], controlled drug release [12], etc. It should be noted that most studies have been performed with p-NIPAm in solutions, while there are a few references in solid materials. However, it is remarkable that the amide group can act as a proton scavenger in H-bridge interactions and interact with functional groups capable of donating protons such as carboxyl. In comparison with the other studies found that poly (N, N-dimethyl acrylamide) acceptor amide group shows miscibility with polyvinyl alcohol and poly-2-hydroxypropyl methacrylate. Also, polyethylene oxide exhibits adequate characteristics when mixed with poly tert butylamine and p-NIPAM. Furthermore, the compatibility of p-NIPAm with carbonyls and the formation of complexes with polyacrylic acid (p-AAc) was described by Staikos et al [13].

P-AAc is a hydrophilic molecule that collapses and swells at lower and higher pH values around its polymer pK_a (generally close to pK_a of the acrylic acid monomer) [10,14]. Although, the solvation level is not strongly affected by the number of repetitive units [15]; conversely, the transition process is dependent on the length of the polymer chain [16]. The combination of p-NIPAm and p-AAc is relevant since both polymers have high affinity and are compatible with the formation of blends. However, Mano et al. [3] found that mixtures of these two polymers were unable to form solids, particularly film formation was impossible under the conditions studied. They also found a decrease in T_g of this blend concerning the individual components due to the intense interactions that decrease the interchain free volume [3]. From a synthetic point of view, the impossibility of obtaining films from the homopolymers p-NIPAm and p-AAc leaves open the possibility and the question regarding that what would be the behavior of mixtures of copolymers that contain different proportions of monomers N-isopropylacrylamide (NIPAm) and acrylic acid (AAc). The inability to form stable solutions is probably not only a consequence of the strong interactions between amide and carbonyl moieties. But also, an effect of the cooperative bonds produced when long chains (containing these functional groups) interact between them.

This scenario suggests that the development of poly (N-isopropyl acrylamide-co-acrylic acid) (p-NIPAm-co-AAc) could provide valuable clues. Usually, p-NIPAm-co-AAc shows a weak thermo-sensitive property, and it is also possible to establish on/off states for one of the sensitive responses [17-20]. In this regard, Zhan et al. [10] suggested that the copolymerization process produces variations on the properties of the final product related to LCST variation. Furthermore, Fundueanu et al. [18] studied thermo- and pH-sensitive properties of poly (N-isopropylacrylamide-co-maleic acid) and found a response when maleic acid was in the neutral form. In this sense, a fraction of monomers controls the sensitivity response against external stimuli [21]. Therefore, the evidence indicates that monomer distribution in copolymers produces variations about homopolymers and likely that the amide and carbonyl groups function as spacers between them to control the excessive interaction that induces the p-NIPAm-p-AAc precipitation.

Consistent with the above information in this work, it was hypothesized that NIPAm copolymerized with AAc can yield blends with virtually the same functional group composition of binary mixtures of p-NIPAm and p-AAc but with different properties of film formation. For this, a copolymeric radical synthesis and the subsequent analytical studies were complemented to get a broad description of these materials. P-NIPAm and p-AAc homopolymers and different proportions of copolymers p-NIPAm-co-AAc were obtained. All purified products are aqueous solutions with different concentrations thoroughly characterized by Fourier Transform Infrared Spectroscopy (FT-IR), Size Exclusion Chromatography (SEC), acid-basic titration, and rotational rheology. Finally, different copolymer mixtures were assayed to identify the combination with

better compatibility. The films proposed were studied by strain-stress tests and thoroughly analyzed to discover the PBM with better mechanical performance.

2. Materials and methods

2.1. Materials

The following chemicals were purchased: N-isopropyl acrylamide (NIPAm), acrylic acid (AAc), N, N, N', N'-tetramethyl ethylenediamine (TEMED); ammonium peroxydisulfate (APS), sodium hydroxide, sodium phosphate dibasic and sodium phosphate monobasic from Anedra (Buenos Aires, Argentina); potassium acid phthalate analytical reagent from Mallinckrodt chemical works (Dublin, Ireland). The poly (acrylic acid) sodium salt calibration standards were obtained from Polymer Standards Service (PSS GmbH) (Mainz, Germany). All solutions were prepared with ultra-pure water ($18 \text{ M}\Omega \cdot \text{cm}^{-1}$) from a Millipore Milli-Q ® system (Germany). All reagents were used as received.

2.2. Synthesis

P-NIPAm, p-AAc, and copolymers p-NIPAm-co-AAc with proposed structure of repetitive units (Fig. 1) were synthesized by free radical polymerization. The amounts of reagents used in each sample are detailed in Table 1. An aqueous solution with monomers and APS was prepared. The solution contained in a vial with a cap was deoxygenated with N_2 for 6 min and then a TEMED solution with a concentration of 0.1 M was injected to initiate the polymerization. The reagents were kept at 37°C for 30 min and then in a thermostatic bath at 24°C for 16 h. To purify each synthesis product a dialysis method was performed. A dialysis tube (D7884 SIGMA - 2000~NMWCO) was filled with the sample and submerged in 500 mL of distilled water under stirring, for 7 days with several changes of solvent. The purified product was dried at 40°C in an oven, and then it was powdered with mortar by using liquid air. After that, it was dried again at 40°C until it reached a constant weight.

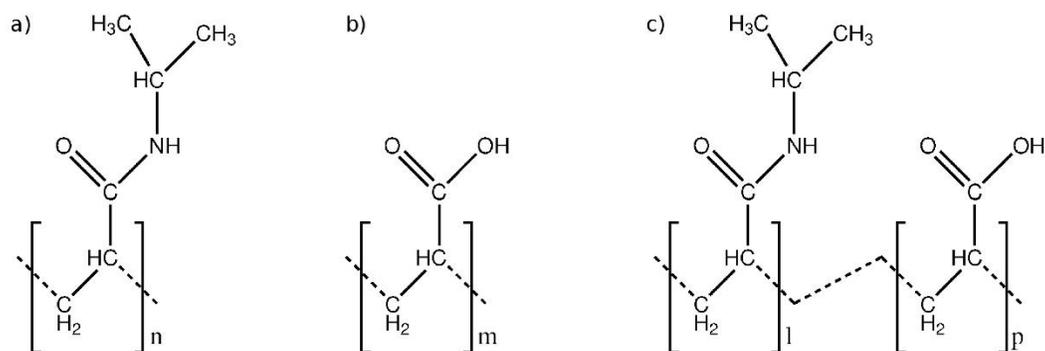


Fig. 1 Molecular structures of polymers obtained from radical synthesis. a) p-NIPAm, b) p-AAc and c) p-NIPAm-co-AAc.

Table 1 Composition of synthesized polymers.

Sample	NIPAm (mg)	AAc (μ L)	APS (mg)	Mili-Q (mL)	TEMED (mL)
p-AAc	-	600	61.6	4.80	0.60
p-NIPAm-co-AAc 40	424.5	374	61.5	5.00	0.60
p-NIPAm-co-AAc 60	610.7	250	61.3	5.20	0.60
p-NIPAm-co-AAc 80	826.5	125	61.4	5.30	0.60
p-NIPAm	901.1	-	61.9	5.40	0.60

2.3. Acid groups quantification in p-AAc and p-NIPAm-co-AAc copolymers

The acid constant (K_a) of p-AAc was determined by using acid-basic titration. The equilibrium pH of 1 wt.% p-AAc solution was measured with a pHmeter Sartorius PB11 P20 (Germany). Then, a 50 mL sodium hydroxide solution, around 0.6 M, was prepared. After that, NaOH solution was titrated with a potassium acid phthalate solution (0.2 M) obtaining a concentration of 0.64 M. A burette was filled with the standardized NaOH solution and it was added drop by drop to 1:4 p-AAc solution: distilled water dilution contained in an Erlenmeyer flask. One drop of phenolphthalein was used as an indicator.

The acid groups present in p-NIPAm-co-AAc copolymers were determined by a similar method. Due to the acid group concentration in copolymers is lower than in p-AAc, a 0.39 M NaOH standardized solution was prepared for the titration.

2.4. Fourier transform infrared spectroscopy (FTIR)

FTIR spectrum of the dry samples was determined using an infrared microscope Nicolet iN10. Specular reflectance and transmittance methods were used to quantify infrared absorbance of the samples in wavelengths between 400 and 4000 cm^{-1} , with a resolution of 0.4 cm^{-1} , 16 scans, and step size of 0.482 cm^{-1} .

2.5. Size exclusion chromatography (SEC)

The chromatographic system consisted of a separation module with a vacuum degasser, a quaternary pump, an autosampler, a thermostatted column device 2695 Alliance Series and a refractive index detector (RID) 2414 Series (Waters Alliance, Milford, MA, USA). The separation was performed using guard column and three analytical SEC columns TSKgel Guard PW_{XL} (40 x 6 mm², 12 μ m), TSKgel G4000PW_{XL} (300 x 8 mm², 10 μ m), TSKgel G5000PW_{XL} (300 x 8 mm², 10 μ m) and TSKgel G6000PW_{XL} (300 x 8 mm², 13 μ m) (TOSOH Biosciences, Tokyo, Japan).

Flow rate was 1.00 mL·min⁻¹ in all analysis. The column temperature was set at 19°C. Detector temperatures were maintained at 30.0°C and the injection volume was 100 µL.

Aqueous-phase SEC analysis was carried out as described elsewhere [22] samples and calibration standards were dissolved and analyzed in an aqueous solution of 0.1 mol·L⁻¹ Na₂HPO₄ adjusted to pH= 9.05, under which conditions the carboxylic groups of p-AAc and p-NIPAm-co-AAc are ionized to eliminate hydrogen-bonded interactions. Moreover, the polyelectrolyte effect is circumvented. Often interactions other than size exclusion effects are observed for the SEC analysis of ionic polymers. When such interactions are present, the elution of the polymer may not be solely based on its molecular size. Therefore, it may interfere with an accurate molecular weight determination calculation of the polymer. At this pH, no adsorption and delay in elution is observed since hydrophobic interaction is well suppressed as the polymer is in fully dissociated form. Then poly (acrylic acid) sodium salt standards (PAANa) with molecular masses ranging from 1250 to 1.39 × 10⁶ g·mol⁻¹ were prepared at a concentration of 1 mg·mL⁻¹ at least 24 h prior to SEC analysis and used to construct the calibration curve.

2.6. Rheology

The mechanical properties of the samples were determined by using a rheometer Anton Paar (MCR 301). About ~0.5 mL of polymeric solutions was added between the parallel plate geometry of 25 mm in diameter (PP25). The viscosity of each sample was measured with the rotational method at different share rates using a scan between 1 s⁻¹ and 100 s⁻¹. A Peltier module was used to control the temperature with a precision of 0.01°C.

Water solutions and a pH 7.2 phosphate buffer with 1 wt.% of p-NIPAm, p-AAc and p-NIPAm-co-AAc copolymers were prepared. All samples were measured in duplicate.

2.7. Casting blends

Blends films were prepared following the procedure described by Mano et al. [3]. Aqueous solutions of the individual polymers (2 wt.%) were mixed in equal proportions and stirred for 30 min at room temperature. Then, the films were cast on silicone molds by water evaporations and stored in a desiccator.

2.8. Mechanical tests

Tensile tests are performed using a 23-5S Instron-Emic (Brazil) mechanical analyzer connected to a 5 N load cell and according to ASTM D 638-10. Films are cut with average dimensions of 4 cm in length, 1 cm in width, and 50 µm in thickness. For all determinations, the displacement speed is adjusted to 10 mm/min and at a constant temperature of 25 °C. The

deformation is calculated as the ratio between the length of the sample during the test with respect to the initial.

3. Results

P-NIPAm, p-AAc and p-NIPAm-co-AAc copolymers were successfully obtained by free radical polymerization. The reaction yield was determined by weighing the purified materials and comparing them with the reagent mass as shown in Table 2. These results indicated reaction yields higher than 90% in most of the cases. The observed differences cannot be associated with any reaction condition and could only be related to the radical reaction variability.

Table 2 Reaction yields.

Sample	Reaction yields
p-AAc	96.5 %
p-NIPAm-co-AAc 40	76.1 %
p-NIPAm-co-AAc 60	98.7 %
p-NIPAm-co-AAc 80	92.8 %
p-NIPAm	98.7 %

3.1. FTIR spectroscopy analysis

To determine the presence of functional groups of NIPAm and AAc in the p-NIPAm-co-AAc structure and to estimate the relative proportion of repetitive (thermo- and pH-sensitive) units, FTIR was performed. Fig. 2 shows the FTIR spectra of p-NIPAm, p-AAc and copolymers.

All analyzed samples show strong absorption in the regions between 2000 and 4000 cm^{-1} , with an exception of p-NIPAm. In this case, the absorption is narrowed to the region between 3000 and 4000 cm^{-1} , and associated with the stretching of the N-H bond from the amide functional group, with the peak centered at $\sim 3441 \text{ cm}^{-1}$. In this sense, p-AAc presents a broad and diffuse band belonging to O-H stretching from the carboxylic acid functional group with the highest absorption at $\sim 3450 \text{ cm}^{-1}$. The presence of this bond is the reason for the described broad strong absorption. In the case of p-NIPAm-co-AAc copolymers, both absorption bands are overlapped. However, each contribution can be clearly identified for their gradual change related to the different proportions of N-H and O-H bonds. In the region between 2800 and 3000 cm^{-1} , the stretching of C-H sp^2 and sp^3 bond absorption can be observed.

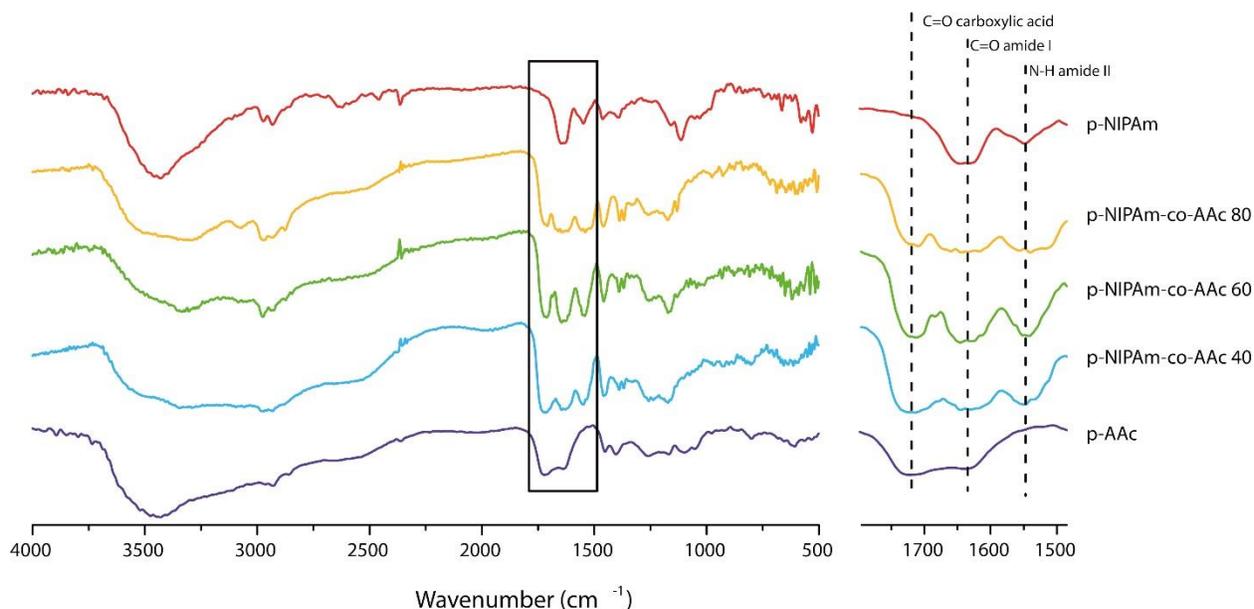


Fig. 2 FTIR spectra of homopolymers (p-NIPAm and p-AAc) and copolymers (p-NIPAm-co-AAc). Box: region of interest.

In the fingerprint region, specifically at the interval $800\text{-}1800\text{ cm}^{-1}$, there are five significant peaks present. In p-NIPAm, the stretching of C=O bond, from the amide group, is assigned to a peak at 1635 cm^{-1} ; whereas, for N-H bending, the absorption presents a maximum at 1549 cm^{-1} . On the other hand, p-AAc presents an absorption at 1720 cm^{-1} from the stretching of C=O bond in the acid group, at $\sim 1645\text{ cm}^{-1}$ of C=O from carboxylate and at 1258 cm^{-1} from C-O stretching.

To quantify the proportion of repetitive (thermo- and pH-sensitive) units in the different copolymers, the region between 795 cm^{-1} and 1485 cm^{-1} was selected. Then, the region of interest (ROI) was deconvoluted in three main peaks: P_1 centered at 1720 cm^{-1} belongs to C=O stretching, P_2 centered at 1633 cm^{-1} and P_3 centered at 1544 cm^{-1} both from C=O and N-H, respectively. The molar fractions of repetitive units were estimated from relations between peak areas (A) or intensities (I) assigned to AAc (P_1) and NIPAm (P_2 and P_3) units. These estimated relations were determined from the ratio of A_{P_1}/A_{P_2} , I_{P_1}/I_{P_2} , A_{P_1}/A_{P_3} and I_{P_1}/I_{P_3} . The calculated average ratio for each copolymer and the determined extrapolated value for p-NIPAm are represented in Fig. 3. Also, a linear regression was made to fit the obtained data, and then a correction of theoretically expected compositions was made taking into account the values predicted by the fit.

Moreover, the repetitive units composition in the copolymers was determined by using a second methodology based on a different physicochemical property. The acidic groups from AAc repetitive units were quantified by the acid-base titration method.

Table 3 shows initial NIPAm molar fraction as a reagent, and the values obtained through both methodologies. Tendency values arise from the linear regression of data points, which is a

good estimation for data sets. The results for the different copolymers are 0.42 ± 0.07 for p-NIPAm-co-AAc 40, 0.59 ± 0.05 for p-NIPAm-co-AAc 60 and 0.77 ± 0.08 for p-NIPAm-co-AAc 80.

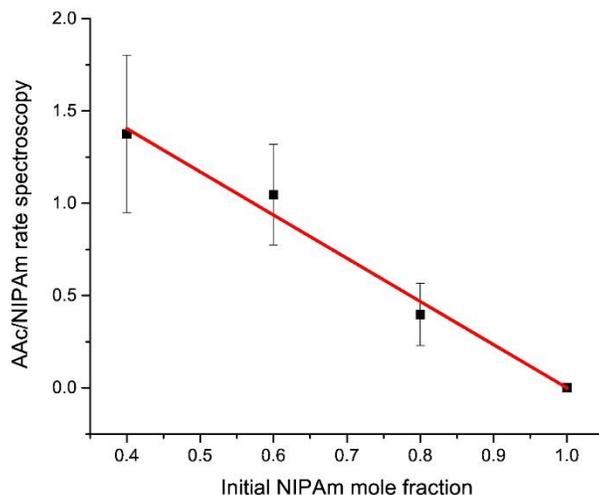


Fig. 3 AAC/NIPAm ratios by spectroscopy.

Table 3 NIPAm mole fraction.

Sample	Reagents	Titration	Spectroscopy	Tendency
p-NIPAm-co-AAc 40	0.40	0.43	0.41	0.42
p-NIPAm-co-AAc 60	0.60	0.48	0.57	0.59
p-NIPAm-co-AAc 80	0.80	0.75	0.83	0.77

3.2. SEC studies

With aqueous-phase SEC, the presence of hydrogen bonding as well as hydrophobic and ionic interactions needs to be minimized to avoid non-size-exclusion phenomena. In the case of p-AAc and copolymers analysis, suitable conditions for SEC separation require: i) hydrophilic column packing together with an eluent of $\text{pH} \approx 9$ to provide complete ionization of p-AAc and thus avoid hydrogen bonding interactions, ii) an inorganic salt to suppress the polyelectrolyte effect and, optionally, iii) an increased temperature in order to lower the eluent viscosity. There are two types of molecular weight distribution (MWD): a differential MWD and a cumulative (or an integral) MWD. A differential MWD is illustrated by plotting the weight w_i or the weight fraction W_i of a polymer of a given MW M_i against M_i or $\log M_i$. When the ordinate is expressed as $dW/d(\log M)$ and the abscissa as $\log M$, then the total area of the differential MWD is normalized to unity as $\int W_{\log M} d(\log M) = 1$, where $W_{\log M}$ is the weight fraction of molecules with molecular weight M . A cumulative MWD is illustrated by plotting the cumulative weight fraction or the % cumulative weight fraction on the ordinate and $\log M$ on the abscissa [23]. Fig. 4 shows

chromatograms, cumulative and differential MWD, respectively, for the polymers studied under the experimental conditions stated in section 2.5.

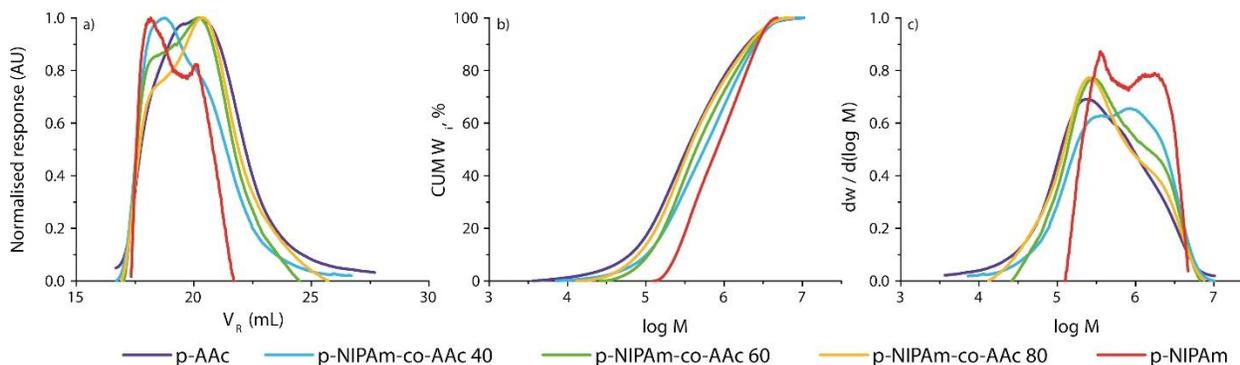


Fig. 4 a) typical RI detector response vs. V_R (mL); b) cumulative MWD; c) molecular weight distribution for the polymers studied.

Table 4 contained the polymer properties measured with SEC studies, where the agreement between the three data sets is satisfactory as well. The aqueous-phase SEC data reflect the quality of the 3rd polynomial fit used as a calibration curve with PAANA. All samples presented an average molecular weight (M_n) with a global average in order to 10^5 (and slightly higher for p-NIPAm). However, if the mass average molar mass (M_w) is considered as a quantification criterion, the polymer chains showed lower dispersions for the different compositions. Particularly, for each molecular distribution p-NIPAm presented an elevated M_n and M_w in contrast with p-AAc, which showed the lowest M_w and M_n of the data series. These results indicate, as expected, more reactivity of NIPAm monomer over acrylic acid monomer at the selected experimental conditions. In addition, the polydispersity index (PDI) indicates that these chains have a broad distribution typical of the radical free synthesis. Also, copolymers showed intermediate molecular distributions with respect to homopolymers.

Table 4 Molecular weight of NIPAm, AAc and copolymers

Sample	M_w (g mol ⁻¹)	M_n (g mol ⁻¹)	PDI
p-AAc	7.54×10^5	1.17×10^5	6.43
p-NIPAm-co-AAc 40	9.90×10^5	2.11×10^5	4.70
p-NIPAm-co-AAc 60	8.64×10^5	2.58×10^5	3.35
p-NIPAm-co-AAc 80	7.68×10^5	1.90×10^5	4.04
p-NIPAm	1.16×10^6	5.55×10^5	2.08

3.3. Rheological analysis

The polymeric samples were analyzed considering the model developed by of Ostwald - de Waele since is an accepted way which relates η with $\dot{\gamma}$, in a power-law function as below:

$$\eta = K\dot{\gamma}^{n-1} \quad (2)$$

where K and n are the flow consistency and behavior indexes, respectively [24,25]. When $n < 1$, η decreases at higher values of $\dot{\gamma}$ and the behavior is called pseudoplastic; when $n > 1$, η increases together with $\dot{\gamma}$, in this case the behavior is named dilatant; and when $n = 1$ the Newtonian law of viscosity is recovered (with $\eta = K$). Fig. 5 shows the viscosity (η) vs. shear rate ($\dot{\gamma}$) for p-NIPAm, p-AAc and copolymers measured at $\phi = 1$ wt.% at different experimental conditions and the straight line represents the adjustment with the Ostwald-de Waele model (Table S.1 exhibits the fitting parameter values).

The results indicate that n strongly depends on the temperature for polymer solutions with higher proportion of NIPAm units (1, 0.8 and 0.6 NIPAm molar fractions). In this sense, these variations could indicate viscoelastic changes of these solutions from almost Newtonian behavior at 20°C (with a flow index of $n \approx 0.9$) to pseudoplastic viscoelasticity with $n \approx 0.2$ at 40°C, being η practically inversely proportional to $\dot{\gamma}$ in a clear distance from the Newtonian behavior [26,27]. The molecular effects for this dependency could be related to the manifestation of hydrophobic interactions at 40°C. Furthermore, at 20°C, the value of n remains almost constant for the three samples, whereas, at 40°C, increases for copolymers; the presence of AAc units in the copolymer chains tends to raise the transition temperature relative to the p-NIPAm homopolymer reducing the hydrophobic effect. This is mainly due to the electrostatic repulsive forces between groups -COO⁻ which prevents the coil-to-globe transition [28,29]. Moreover, viscosity above LCST is higher as a consequence of strong association and network formation followed by contraction between polymer chains [30,31]. However, as $\dot{\gamma}$ increase, the η decrease as the thermal gelation process becomes more difficult [32]. On the other hand, p-AAc and p-NIPAm-co-AAc 40 exhibit minimal variations in the flow behavior index when the temperature is varied. In addition, the viscosity decreases proportionally over the whole range of shear rate, a change associated with the proper decrease in water viscosity with increasing temperature.

Conversely, the pH modifications on the solution (above and below pK_a of p-AAc) cause a slight variation in the value of n , in p-AAc and copolymers (p-NIPAm could not be well diluted in this buffer). In all cases, $n < 1$ indicates that under these conditions the samples have a pseudoplastic behavior. In addition, the viscosity values in buffer solutions are greater than those in aqueous solutions with an acidic dissociation. It is known that the viscosity of p-AAc solutions increases the value with the pH until reaching a critical pH above its pK_a [33,34,35]. The effect of the increase in viscosity with pH could be related to the ionization process of the carboxylic groups [34,35]. The electrostatic force of repulsion between the ionized COO⁻ groups expands the p-AAc

chains. The uncoiled chain takes a rod shape causing an increase of viscosity [34,36]. At the same time, this effect in copolymer is reduced due to the lower presence of AAc units in their chains. Furthermore, in p-NIPAm-AAc 80, which has an AAc molar fraction of 0.2, the difference between viscosities values is minimal.

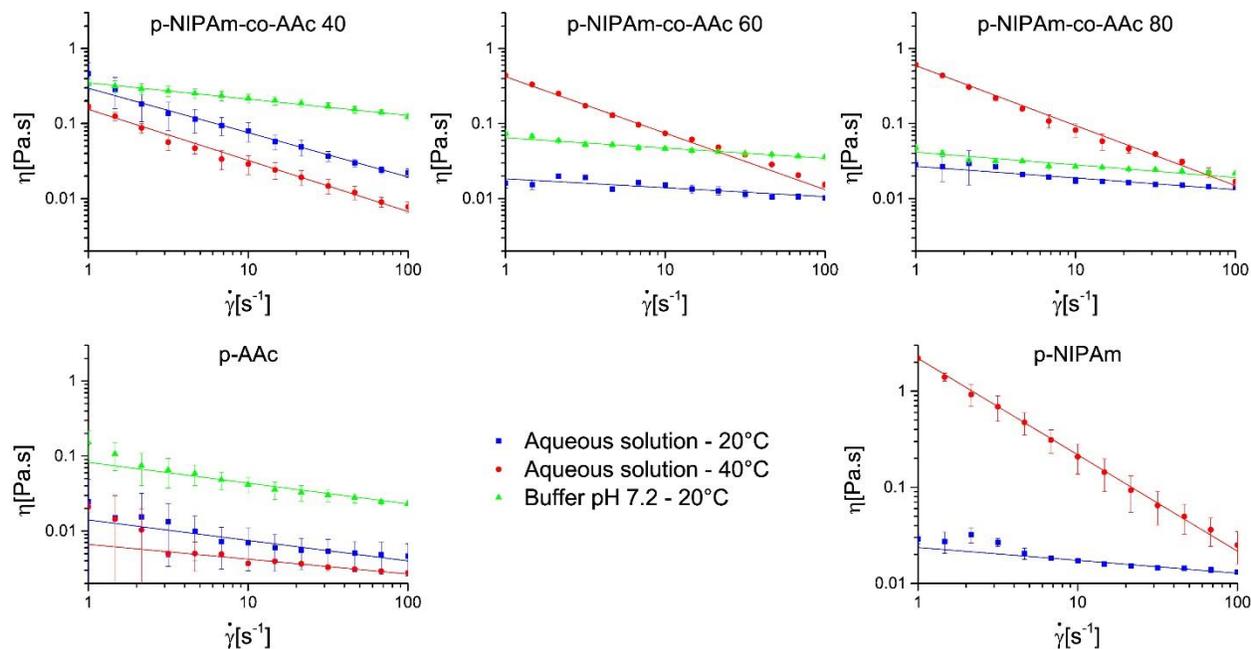


Fig. 5 Viscosity (η) vs. shear rate ($\dot{\gamma}$) measured at $\varphi = 1\text{wt.}\%$, of homopolymers (p-NIPAm and p-AAc) and copolymers (p-NIPAm-co-AAc).

Through the rheological study it was possible to establish the sensitivity of the copolymers to thermal and pH stimuli. On the one hand, the thermal response is only seen in the copolymers with a higher proportion of NIPAm units. On the other hand, the response to pH variations can be appreciated even in p-NIPAm-co-AAc 80 although in a very slight way.

3.4 Preparation of binary mixtures and obtention of films by casting

Following the procedure described in section 2.4, binary mixtures were made between the aqueous solutions of the p-NIPAm and p-AAc homopolymers and the three copolymers, resulting in 10 possible combinations. As previously reported by other authors [3, 13] the p-NIPAm/p-AAc combination does not produce a homogeneous solution but forms a compact structure between polymer chains called interpolymer complexes that precipitates in aqueous solutions. Furthermore, the mixture of p-AAc with p-NIPAm-co-AAc copolymers with a higher proportion of NIPAm units (0.8 and 0.6 NIPAm molar fraction) also forms an interpolymer complex. The presence of large amounts of isopropyl side groups of NIPAm from the copolymers promotes hydrophobic interactions with the p-AAc chains and contributes to the formation of the complex

[13]. In contrast, the p-AAc/p-NIPAm-co-AAc 40 blend did not produce complexes, forming a homogeneous solution. On the other hand, the binary blends between the combinations between p-NIPAm with the copolymers, and between copolymers produced homogeneous solutions after stirring for 30 min. The combinations are outlined in Fig. 6.

By casting from homogeneous aqueous solutions, films with very similar macroscopic characteristics were formed. In general, they show transparent and colorless films with little opacity in the mixtures p-NIPAm / p-NIPAm-co-AAc 80, p-NIPAm / p-NIPAm-co-AAc 60, and p-NIPAm-co-AAc 80 / p-NIPAm-co-AAc 60 All the films exhibited some degree of flexibility. The p-AAc / p-NIPAm-co-AAc mixture shows brittleness in a region where the film was thinner.

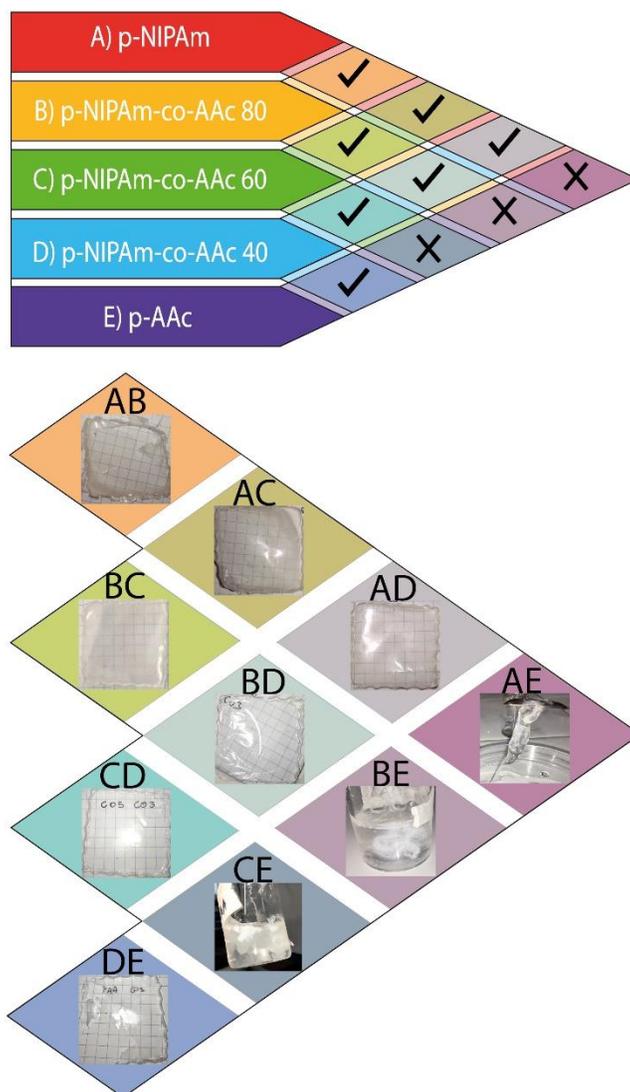


Fig. 6 Binary mixtures between p-NIPAm, p-AAc and their copolymers. a) Cross (X): represents intercomplex polymer and checkmark (✓): homogeneous solution. b) Photographs of the interpolymer complexes and the films obtained by casting.

3.5 Elongation at break tests

Fig. 7 shows a representative curve of the stress-strain measurements for mixtures that were able to achieve blended films (according to results in Fig 6). In this sense, Table 5 exhibits a summary of the average values of tensile strength, Young's modulus, elongation at break, over all the repetitions of each sample. It should be noted that binary films studied present a fragile behavior, with a low elongation at break (<5%). This characteristic could be related with the H-bonds between the AAc and NIPAm groups, resulting in compact networks with low chain mobility and free volume that improves their molecular rigidity [4,37]. Furthermore, sample with NIPAm/AAc ratio close to 1 presents the lowest elongation, since the functional groups that accept and donate H bonds are in similar proportions, a large number of interpolymeric H bonds can be achieved, with a uniform and homogeneous distribution of H bonds [38]. Particularly, Mano et al. observed [3] that p-NIPAm films are brittle too, and this brittleness also affected binary blends of p-NIPAm and poly (vinyl alcohol) (PVA). In addition, it has also been studied that higher amount of p-AAc provide low elongation at break in blends of p-AAc/PVA [4] and p-AAc with methylcellulose [39].

Similarly, the values of the tensile strength and Young's modulus are within the estimated ones for analogous samples. However, the visual inspection indicates the relationship between the diminution of the tension strength and Young's modulus when one of the components of the blend has a high molar fraction of NIPAm and the other of AAc (AD and BD). This tendency could be associated with a lower miscibility of the components, which prevents intertwine at molecular level, deteriorating the mechanical properties [38, 40].

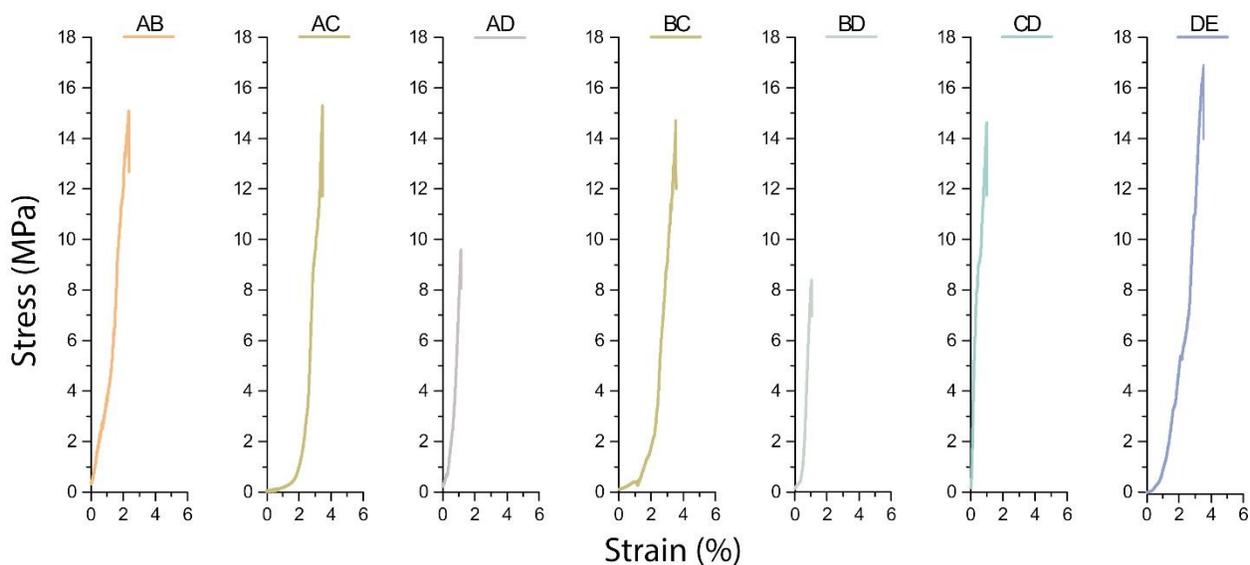


Fig. 7 Stress-strain curves for binary blend films.

Table 5 Mechanical properties of films.

Code	NIPAm/ AAc ratio	Tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
AB	7.33	12	1070	3
AC	3.51	16	1105	3
AD	2.08	9	691	2
BC	2.09	16	825	3
BD	1.39	9	740	2
CD	1.01	12	1064	1
DE	0.23	17	682	4

4. Conclusion

In this work, thermo-sensitive p-NIPAm, pH-sensitive p-AAc and different proportions of their copolymers (p-NIPAm-co-AAc) were obtained by radical synthesis and subsequently purified. The molar fractions of each repeating unit present in the copolymers were quantified by FTIR spectroscopy and acid-base titration, getting a good correlation between both methods. Additionally, SEC studies were carried out to know the average molecular weight (M_n), with a global average in order to 10^5 (and slightly higher for p-NIPAm), and the mass average molar mass (M_w). Based on rotational rheological studies, thermo and pH sensitivity in viscosity measurement was determined. Thermo sensitivity could be only observed in samples with a major molar fraction of NIPAm. On the other hand, pH sensitivity was well observed in copolymers with a NIPAm/AAc proportion of 0.4 and 0.6, and very slight in the copolymer with a higher NIPAm/AAc ratio.

Water solutions binary blend films and interpolymer complexes of NIPAm and AAc based polymer were obtained by casting. Among the samples, the mixture of p-AAc with p-NIPAm and p-NIPAm-co-AAc copolymers with a higher proportion of NIPAm units (0.8 and 0.6 NIPAm/AAc) formed interpolymer complexes. The presence of large amounts of isopropyl side groups of NIPAm promotes hydrophobic interactions with the p-AAc chains and contributes to the formation of the complex. However, the combination with p-NIPAm-co-AAc 40 copolymer, which has a higher proportion of AAc groups and pH sensitivity, allows obtaining blends suitable for the preparation of films. Thus, an effective method for obtaining film from binary blends of polymers based on NIPAm and AAc with thermal and pH response is established.

On the other hand, the mechanical properties of the films are affected by the NIPAm / AAc ratios. When both functional groups are in similar proportions, the possibility of H-bond formation increases, resulting in higher molecular rigidity and lower elongation at break. Furthermore, despite the fact that the combinations of p-NIPAm-co-AAc 40 with p-NIPAm-co-AAc 80 or p-NIPAm were successful, the mechanical properties of the films are worse compared to the other blends. This phenomenon could be due to a lower degree of miscibility between the components of the blend, and subsequent studies will be necessary to discover how to improve the mechanical properties of these promising blends.

Supplementary material

See the supplementary material for a more detailed analysis of the rheological study.

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