Study of polymer–polymer complexes and blends of poly(*N*-isopropylacrylamide) with poly(carboxylic acid). 2. Poly(acrylic acid) and poly(methacrylic acid) partially neutralized

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Abstract

Polymer complexes of poly(*N*-isopropylacrylamide) with poly(acrylic acid) and poly(methacrylic acid) partially neutralized have been isolated, for degrees of neutralization up to 15%, as a consequence of their mutual precipitation in aqueous solution. Blends of these polymers have been prepared for higher degrees of neutralization of the polyacids, where no insolubilization is observed in their aqueous mixtures. The obtained samples have been calorimetrically studied. All complexes present a single high T_g, while the blends present two T_gs, one of them also very high. Thermal behavior of complexes and blends have also been studied. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Miscibility in polymer mixtures is not a common trend. Due to the high molecular weight of both components, the entropy contribution though favorable is very small, so miscibility is controlled by the enthalpy term [1]. Therefore, polymers which are capable of establishing specific interactions ($\Delta H < 0$) form an important part of the miscible polymer blends. When these specific interactions occur at frequent intervals along the chain, macromolecular aggregates called polymer–polymer complexes may result. These complexes usually exhibit a well-defined stoichiometry, independent of the starting polymer mixture composition, and have their own identity and properties [2,3].

An important number of interpolymer complexes result from a cooperative interaction involving hydrogen bonding between long sequences of the chains. When formed in aqueous media, hydrophobic interactions are considered to play an important role in the stabilization of their structures. These interactions are also responsible for the insolubilization of the complexes, which is of great importance as it makes possible their isolation and study [4–6].

Interpolymer complexation in systems including polyacids and polyacrylamide derivatives have been reported [7–11]. In a previous paper [12], the complexation and blending of Poly(*N*-isopropylacrylamide)(PNIPAAM) with Poly(acrylic acid)(PAA) and Poly(methacrylic acid) (PMAA) has been studied. As it was expected, PNIPAAM, with a strong tendency for H-bonding, contributes to important hydrophobic interactions as a consequence of isopropyl side groups leading to an additional stabilization of the complex [13–15]. This paper presents a study on the complexation and blending of PNIPAAM with PAA and PMAA for various degrees of neutralization of the polyacid. It is to be noted that the neutralization of the polyacid will result in a decrease of the number of hydrogen bonds as the acrylates are non-active groups and will also make more difficult the hydrophobic interactions in the system and therefore the insolubilization of the complex. The influence of parameters, such as the initial polymer mixture composition and the degree of neutralization of the polyacid, have been studied.

Blends obtained by evaporation of the solvent and complexes isolated by centrifugation have been characterized by Differential Scanning Calorimetry (DSC). A thermogravimetric study of these samples allows us to compare the thermal stability of the complexes and blends with respect to that of the original polymers.

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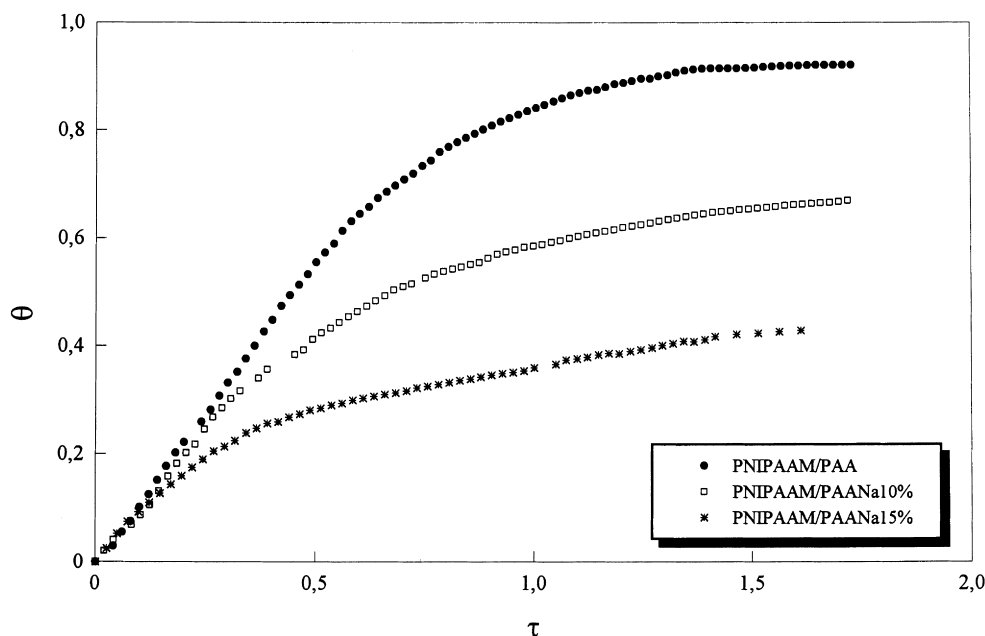*E-mail address:* qfpgapem@lg.ehu.es (M.T. Garay).

Fig. 1. Variation of the complexation degree θ with τ for the systems presenting complexation.

2. Experimental

The PAA sample used, from Polysciences, was purified by freeze-drying from a previously filtered water solution. The reference molecular weight was 150,000. The PMAA sample, supplied by Polysciences, was purified by dissolution in methanol and further precipitation in an excess of diethyl ether. Its molecular weight, determined by viscometry [16] in methanol at 25°C was 2.3×10^4.

The PNIPAAM sample was obtained by redox polymerization of NIPAAM in water according to a previously reported method [12]. The selected fraction was purified in the system chloroform/hexane and its molecular weight, measured by GPC, was 8.20×10^4.

All samples were dried under vacuum at 60°C for 48 h. The solvent used for complexation and blending, water, was Milli-Q grade.

Polymer mixtures were prepared by mixing separate water solutions, of polymer concentration 0.2 mol monomeric unit per liter, for different unit molar ratios of the polymer components. Partially neutralized polyacid samples were prepared by addition of adequate amounts of a previously titrated NaOH aqueous solution to the original polyacid solution. Those mixtures leading to a precipitate, as a consequence of the insolubilization of the formed complex, were left for 3 days and after that they were separated from the solution by centrifugation. The obtained complexes were washed twice with water, again centrifuged, and they were dried under vacuum at 60°C for 72 h. The mixtures, which remain transparent, were cast from solvent and dried under vacuum at 60°C during 72 h.

2.1. Instrumentation

The molecular weights of the polymers were measured either using an Ubbelhode automatic viscometer or by Gel Permeation Chromatography (GPC), using a WATERS chromatograph equipped with two μ-styragel columns with an exclusion limit of 10^7, using THF as the solvent at 25°C. Potentiometric measurements were performed in a METROHM 691 pH-meter, equipped with a glass electrode.

The glass transition temperatures (T_gs) of the complexes and blends were determined using a PERKIN–ELMER differential scanning calorimeter, model DSC-4, and their thermal stability in a Perkin–Elmer thermogravimetric analyzer, model TGS-2. The T_g values are reproducible to about ± 1°C. The composition of the complexes were determined using a Perkin–Elmer 2400 CHN Elemental Analyzer.

3. Results and discussion

The formation of complexes between a poly(carboxylic acid) and a polyamide occurs mainly through hydrogen bond formation between the carboxylic group of the polyacid and the amide group of the polyamide [12,15,17]. When complexation in aqueous solution progresses, by adding successive amounts of polyamide to the polyacid solution, the concentration of free carboxylic groups decrease, and according to the dissociation equilibrium of the polyacid, $[H^+]$ decreases, that is, pH increases until complexation is complete.

Table 1
Yield of complexes PNIPAAM/PAANaX%

X% neutralization	0	5	10	15
Yield (wt.%)	19.8	17.4	4.40	0

In this work, potentiometric measurements have been made as a previous study to check the existence or not of complexation between PNIPAAM and PAA in water, for different degrees of neutralization of the polyacid. Besides, from these data it has been possible to quantify the complexation through the determination of the degree of complexation, θ, according to the equations given by Iliopoulos et Audebert [18] and considering the progressive dilution of the polyacid original solution when adding the polyamide solution to it. The equation used was

$$\theta = (1 - \alpha - \delta') - \left[(1 - \alpha - \delta) \frac{(\alpha + \delta')\delta'}{(\alpha + \delta)\delta} \frac{[PAA]}{[PAA]_0} \right]$$

where α is the degree of neutralization

$$\alpha = \frac{[NaOH]}{[PAA]_0} = \frac{[-COO^-]_{neutr}}{[PAA]_0}$$

δ and δ' are the fractions of acrylate groups resulting from the polyacid dissociation before and after the successive polyamide additions. $[PAA]_0$ and $[PAA]$ are the total concentration of PAA, expressed in monomer units per liter, in the absence and in the presence of polyamide, respectively.

At low pH

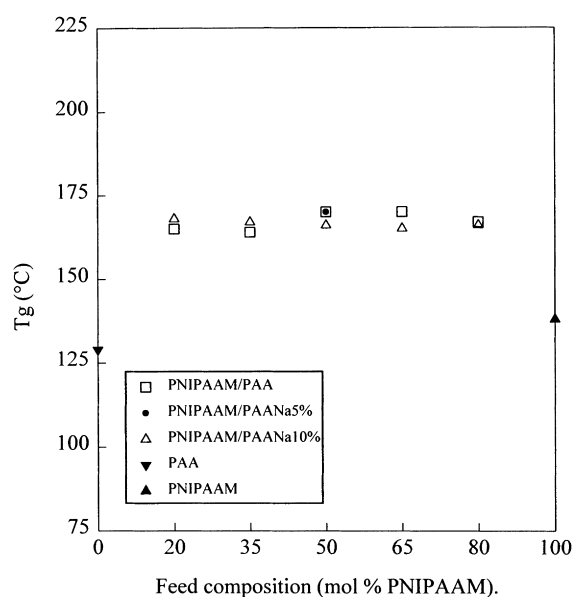$$\delta = \frac{[-COO^-]}{[PAA]_0} = \frac{[H^+]_0}{[PAA]_0} \qquad \delta' = \frac{[H^+]}{[PAA]}$$

Fig. 2. Glass transition temperatures for PNIPAAM/PAA complexes vs. composition of the original mixture.

where $[H^+]_0$ and $[H^+]$ are the proton concentrations for the initial polyacid solution and for this solution after each addition, in the presence and absence of the polyamide, respectively.

In Fig. 1 a plot of the degree of complexation, θ, versus $\tau = [PNIPAAM]/[PAA]$ can be seen for those systems in which complexation exists, that is, PNIPAAM/PAA10% and PNIPAAM/PAA15%, along with that for the system PNIPAAM/PAA non-neutralized for comparison. As can be seen, the degree of complexation is strongly impeded when increasing the degree of neutralization of the polyacid—being negligible for a 20% of neutralization of the polyacid—which means that the presence of low contents of acrylate groups (<20%) in the polyacid make impossible the necessary interactions for complex formation, confirming that hydrogen bonding is responsible for the complex formation and that a minimum sequence length of interactions is necessary for complexation. A similar behavior has been observed for other systems in which complexation occurs through hydrogen bond formation [18].

3.1. PNIPAAM/PAA complexes: effect of the degree of neutralization

Although potentiometric measurements indicate the existence of complexation between PNIPAAM and PAA up to 15% of neutralization of the polyacid, the isolation of an appreciable quantity of complex by insolubilization has been possible only for the systems PNIPAAM/PAA5% and PNIPAAM/PAA10%; not for the system PNIPAAM/PAA15% where some turbidity appears but no complex was isolated, even by centrifugation.

Yields of polymer complexes for all systems obtained starting from an equimolar mixture are shown in Table 1. As can be seen, the complex yield rapidly decreases when increasing the degree of neutralization of the polyacid, as expected, if we consider that the progressive neutralization of the polyacid results in the reduction of the number of hydrogen bond interactions, responsible for the complex formation, and simultaneously the appearance of hydrophilic carboxylate groups, which make more difficult the hydrophobic interactions to be established, which are responsible for the insolubilization of the complex. This seems to be the reason why complex yield is so low for the system 10% neutralized and negligible for the system 15% neutralized.

All complexes, studied by DSC, exhibit a single glass transition higher than that of the component polymers as expected for complexes obtained through hydrogen bond formation between their chains, leading to a flexibility reduction and therefore to higher values of T_g [19–28]. The T_g values obtained for all complexes of the system PNIPAAM/PAA for different neutralization degrees of the polyacid and for various compositions of the initial mixture are shown in Fig. 2, along with the T_g values obtained for the

Table 2
Glass transitions for PNIPAAM/PAANa10% blends after complex extraction

Initial mixture composition	20/80	35/65	50/50	65/35	80/20
T_g (°C)	–	158	169	153	139

Table 4
Glass transitions for the 50/50 mixtures of PNIPAAM/PAANaX% neutralized

X% neutralization	15	20	40	100
T_g (°C)	164	155–182	137–189	135–240

system PNIPAAM/PAA [12] non-neutralized. As can be seen, all T_g values obtained are very similar, which seems to indicate that complex composition does not appreciably change with the initial mixture composition, nor with the neutralization degree of the polyacid up to 10%. The composition of the complexes, obtained by elemental analysis confirm these results, being in all cases simple relations (PNIPAAM/PAA) of approximately 1:1.

The supernatant solution left for the system PNIPAAM/PAA10% after the complexes were separated was examined. The solvent was evaporated and the residue had been studied calorimetrically. A unique T_g has been found in all cases higher than those of the components (Table 2), which seems to indicate that in this mixtures, either by solvent evaporation or due to the thermal treatment given to the samples in the calorimeter, complexation occurs. This behavior has been observed in other systems [20,29–31] and is explained as a rearrangement of the interacting groups when heating the sample above their T_g so that additional hydrogen bonds can be formed, resulting in complex formation. The fact that for the 50/50 initial composition evaporated mixture, the obtained T_g is coincident with that of the complex confirms the 1:1 stoichiometry of the previously obtained complex, and suggests that the materials obtained from these solution mixtures are blends of the complex plus excess polymer, resulting in lower T_g values than that of the complex.

3.2. PNIPAAM/PAA blends: effect of the degree of neutralization

Several mixtures have been prepared for the systems PNIPAAM/PAA15%, PNIPAAM/PAA20%, PNIPAAM/PAA40% and PNIPAAM/PAA100% in water. As expected, no precipitation is observed and the blends obtained, after solvent removal, have been studied calorimetrically.

In Table 3 can be seen the calorimetric results obtained for the system PNIPAAM/PAA20% at different mixture compositions. As can be seen, the mixture 25/75 presents a single T_g higher than those of the components. However, mixtures of higher PNIPAAM initial composition, 50/50 and 75/25 present phase separation as shown by the appearance of two different T_gs. It is to be noted that in both cases,

an identical T_g is observed at 182°C, higher than those of the components, which suggests, once more, complex formation but now immiscible with the excess material.

In Table 4 are shown the calorimetric results obtained for a 50/50 initial mixture composition for all the systems PNIPAAM/PAA partially neutralized studied, 15, 20, 40 and 100% of neutralization. As can be seen, only the 50/50 mixture for the system 15% neutralized presents a single T_g; the other systems studied present phase separation as shown by the existence of two T_gs. Once more, an unusually high T_g is observed in all cases indicating complex formation, but immiscible with the excess material.

From these results it can be concluded that the mixtures PNIPAAM/PAA partially neutralized present phase separation for a degree of neutralization higher than 15%, being more evident as the degree of neutralization increases and for a determined degree of neutralization as PNIPAAM content in the mixture increases.

Finally, it is to be noted that those blends presenting a single T_g phase separate when heated up to 215°C. This is not the case for the isolated complexes as they present a reproducible T_g when heated up to 310°C, indicating a higher phase separation stability of the isolated complexes with respect to blends.

3.3. PNIPAAM/PMAA complexes: effect of the degree of neutralization

Several mixtures for the systems PNIPAAM/PMAA10% and PNIPAAM/PMAA20% in water have been prepared. The isolation of complex was possible only for all compositions of the system PNIPAAM/PMAA10%.

The obtained complexes were calorimetrically studied and they all exhibited a single glass transition. T_g values obtained (Table 5), very similar for the different compositions, indicate that the complex nature does not depend on the initial mixture composition. Their composition, obtained by elemental analysis is approximately 1:1.

It is to be noted, however, that these complexes phase separate when heated above 210°C, leading to a phase separated material as shown by the existence of two T_gs, at 139 and 210°C, respectively, obtained after successive runs.

Table 3
Glass transitions for PNIPAAM/PAANa20% blends

Blends composition	25/75	50/50	75/25
T_g (°C)	168	155–182	140–182

Table 5
Glass transitions for PNIPAAM/PMAANa10% complexes

Initial mixture composition	25/75	50/50	75/25
T_g (°C)	199	197	196

Table 6
Glass transitions for all complexes studied

Systems	T_g (°C)	Systems	T_g (°C)
PNIPAAM/PAA	170	PNIPAAM/PMAA	186
PNIPAAM/PAANa5%	170	–	–
PNIPAAM/PAANa10%	166	PNIPAAM/PMAANa10%	197

Finally, in Table 6 are summarized the T_g values for all complexes obtained for the systems PNIPAAM/PAA and PNIPAAM/PMAA for comparison. From these results, we can conclude that though PNIPAAM/PAA complexes nature are not affected by partial neutralization of the polyacid, at least up to 10%, it is not the same for PNIPAAM/PMAA complexes, for which partial neutralization results in an increase in T_g. According to previous results [12] we concluded that the introduction of an α-methyl group in the polyacid results in a small increase in the rigidity of the formed complex. From the results presented in this work we can also conclude that a 10% neutralization of PMAA results in an additional rigidity and compaction of the complex formed with PNIPAAM.

3.4. Thermogravimetric behavior

A thermogravimetric study of these materials gives us information on their thermal stability compared to that of the polymer components.

Thermograms for pure and partially neutralized PAA for different neutralization degrees are shown in Fig. 3. Pure PAA has a poor thermal stability [32–34], with anhydride formation accompanied by loss of water in first stage, between 180 and 220°C, and anhydride decomposition

with loss of CO_2 in second stage, at 270–300°C. Finally, from 350 to ~500°C there is an important weight loss with a nearly complete sample degradation. The partially neutralized PAA samples present different behavior depending on the degree of neutralization. Thus, for the 10% and 20% partially neutralized PAA samples a two stage degradation is observed, one very broad located between 170 and 300°C accompanied with a weight loss of approximately 25%. For PAA partially neutralized (40% and higher), an improvement is observed in their thermal stabilities at low temperatures, being more important as neutralization degree increases. Thus, PAANa100% presents a weight loss of only approximately 10% between 170 and 455°C. Therefore, we can conclude that for low neutralization degrees (10 and 20%) the thermal stability of PAA is lower and increases for higher neutralization degrees reaching the maximum stability for the sample 100% neutralized.

The PNIPAAM thermogram [12,35] presents a single degradative step between 350 and 450°C with a nearly complete loss of mass.

All complexes, PNIPAAM/PAA10%, obtained for different compositions of the initial mixture have been thermogravimetrically studied and no significant differences are observed in their thermal behavior, which confirms that polymer complexes have a definite composition irrespective of the starting polymer mixture. Thermograms of the PNIPAAM/PAANa10% complex along with those of the component polymers are shown in Fig. 4. The complex presents a two stage degradative process; first step, between 240 and 365°C, with a mass loss of approximately 20% and a second one, between 365 and 400°C, reaching a total mass loss of 90%. An improvement in the thermal stability of PAANa10% is observed after complexation with
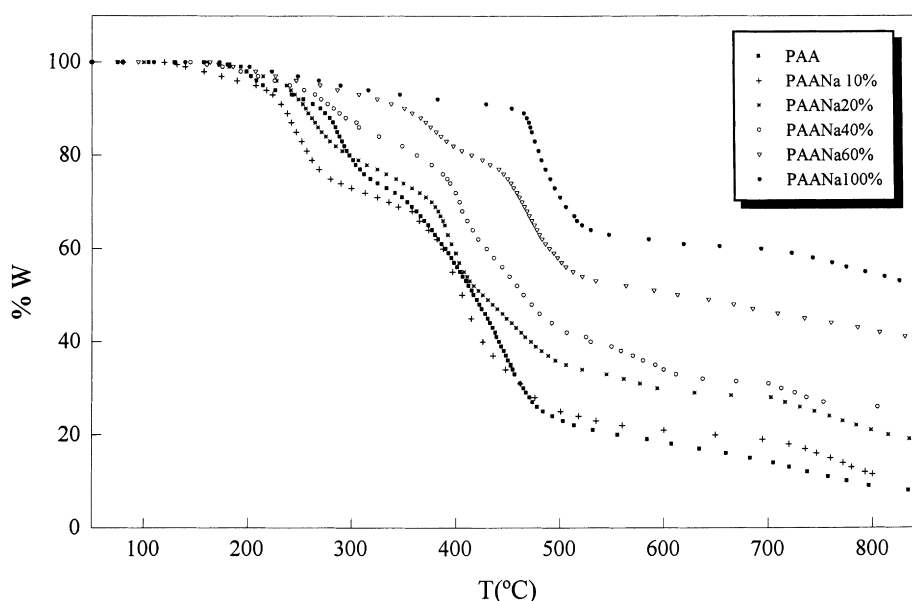

Fig. 3. TGA weight loss curve for PAA at different neutralization degrees.
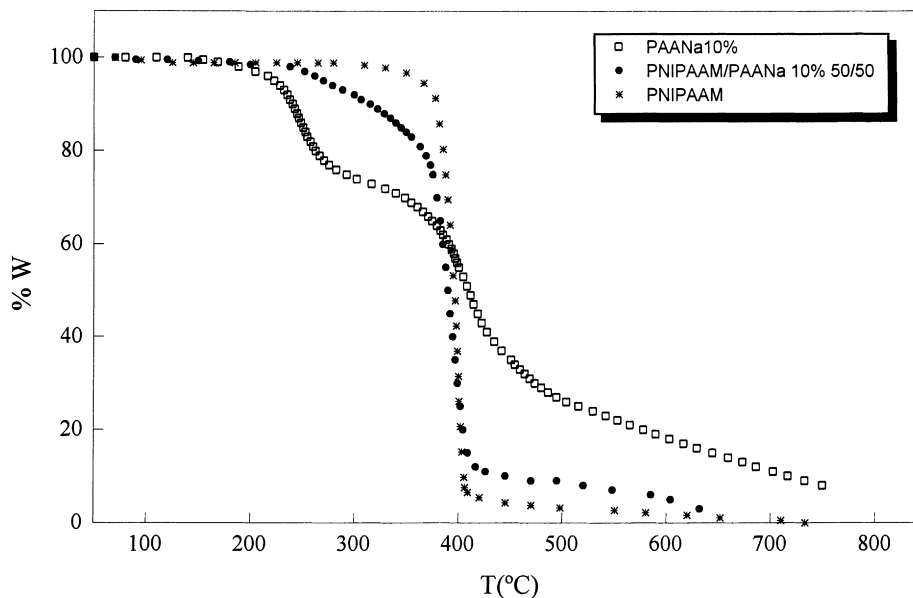
Fig. 4. TGA weight loss curve for polymers and 50/50 complex.

PNIPAAM, similar to what happens to PAA, as a result of a reduction in the anhydride formation and later decarboxylation.

Besides, no significant differences are observed when comparing the thermograms of the complexes PNIPAAM/ PAA, PNIPAAM/PAA5% and PNIPAAM/PAA10% (Fig. 5), indicating that the neutralization degree of the polyacid up to 10%, do not influence appreciably the thermal behavior of the resulting complexes, in agreement with calorimetric results.

Blends obtained for the system PNIPAAM/PAA20% have been also thermogravimetrically studied (Fig. 6).

The consideration that blends are mixtures of the complex and excess polymer inferred from calorimetric results is now reinforced according to the obtained thermograms. Thus, the presence of free, non-complexed PAANa20% is evident in the thermograms of those blends obtained starting from a high content in PAANa20% as shown by the presence of the polyacid characteristic degradation step.

Thermograms obtained for the 50/50 blends for the systems PNIPAAM/PAANa40% and PNIPAAM/ PAANa100%, along with those of their components polymers, are shown in Figs. 7 and 8. As can be seen, the thermal
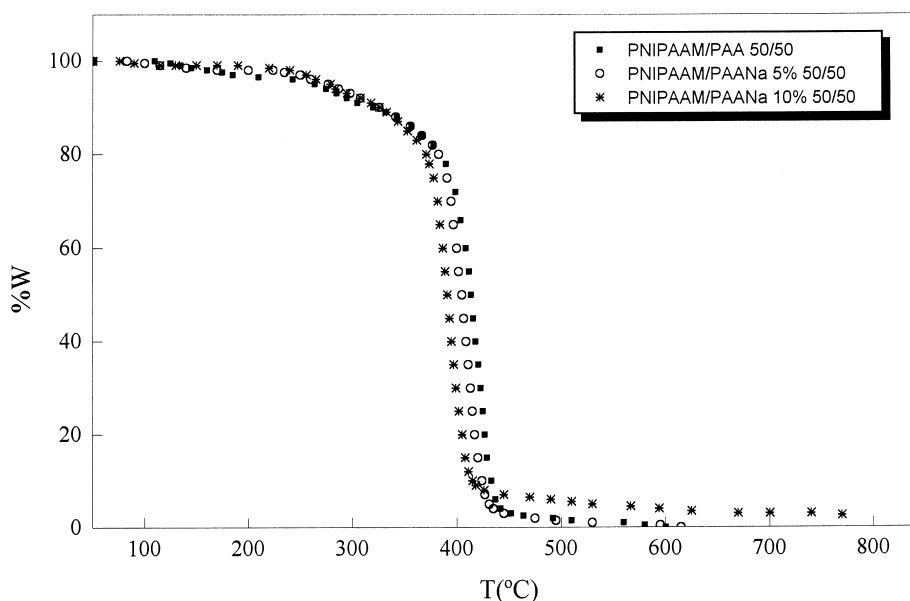

Fig. 5. TGA weight loss curve for complexes at different PAA neutralization degrees.
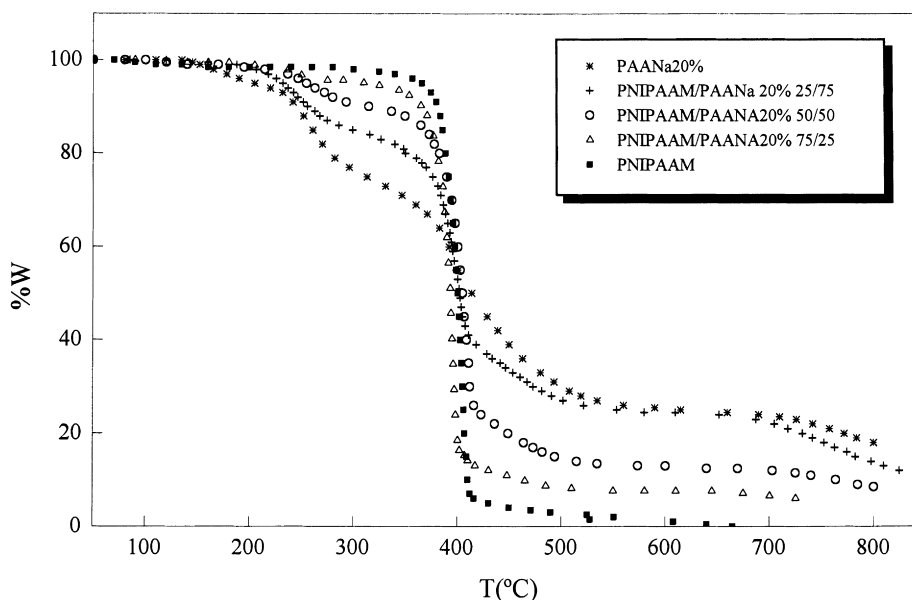
Fig. 6. TGA weight loss curve for polymers and PNIPAAM/PAANa20% blends.

stability of the blends increase when increasing the neutralization degree of the polyacid as expected. It is to be noted that PNIPAAM/PAANa100% blend presents a very good thermal stability, better than the complexes studied, though it presents phase separation as shown by calorimetric results.

The thermogram obtained for the PNIPAAM/PMAANa10% complex, along with that obtained for the PNIPAAM/PMAA for comparison [12] are shown in Fig. 9. As can be seen, the neutralization of PMAA to 10% leads to a slightly higher thermal stability of the resulting complex.

4. Conclusions

The complexation between PNIPAAM and PAA is strongly impeded when the neutralization degree of the polyacid increases, being inexistent for a 20% neutralization as shown by potentiometry.

The isolation of complexes by insolubilization is possible for the systems PNIPAAM/PAANa5%, 10% and PNIPAAM/PMAANa10%. All these complexes present a single glass transition, independent of the composition of the starting mixture. The high T_g values observed can be attributed to hydrogen bond formation. The compositions
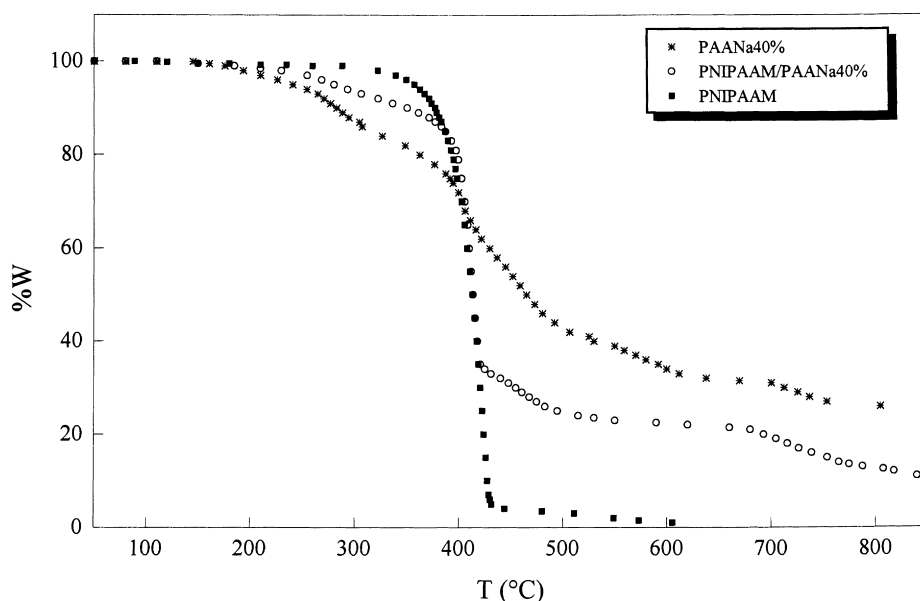

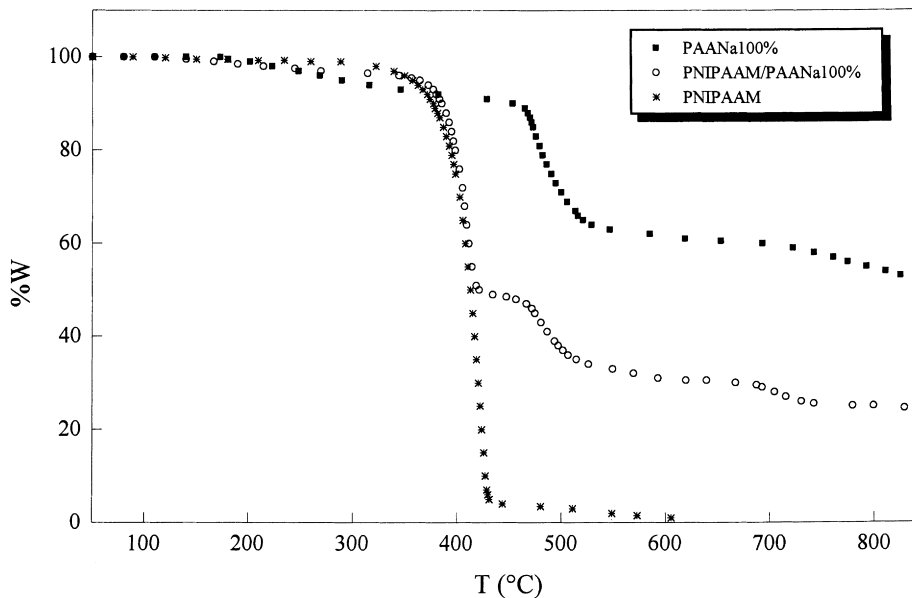Fig. 7. TGA weight loss curve for polymers and PNIPAAM/PAANa40% blend.

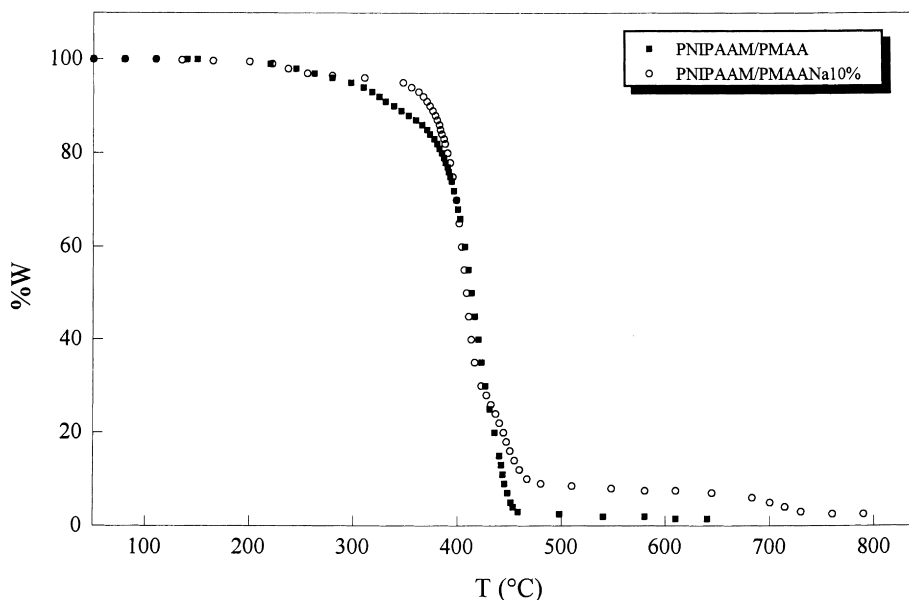Fig. 8. TGA weight loss curve for polymers and PNIPAAM/PAANa100% blend.

Fig. 9. TGA weight loss curve for PMAA complexes.

of the complexes can be represented by simple molar ratios of the interacting groups.

Blends between PNIPAAM and PAA for higher neutralization degrees have been obtained and they present phase separation as shown by the presence of two T_gs, one of them unusually high, indicating that there is complex formation, but immiscible with the excess polymer.

According to thermogravimetric measurements we can conclude that both, complexation of the polyacid with PNIPAAM as well as neutralization of the polyacid, result in an important improvement of its thermal stability. It is

also the case for phase separated blends, unless the sample includes free, non-complexed polyacid.

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