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Study of polymer–polymer complexes and blends of poly(*N*-isopropylacrylamide) with poly(carboxylic acid): 1. Poly(acrylic acid) and poly(methacrylic acid)

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Polymer complexes of poly(*N*-isopropylacrylamide) with poly(acrylic acid) and poly(methacrylic acid) have been isolated as a consequence of their mutual precipitation in aqueous solution. Their composition can be represented, in most cases, by simple molar ratios of the interacting groups. The glass transition temperature (T_g) of the complexes is higher than that of their components. Blends of these polymers cast from clear methanol solutions have also been prepared. Again, T_g values of the blends are higher than the component ones, but now a dependence on the composition of the mixture is observed. The thermal behaviour of complexes and blends has also been studied. © 1997 Elsevier Science Ltd.

(Keywords: complex; blend; glass transition)

INTRODUCTION

Many investigations have been devoted to study polymer–polymer complexation through cooperative specific interactions[1–6]. Electrostatic, hydrogen bonds and hydrophobic interactions are the main driving forces for complexation.

Several studies in systems including polyacids and polyacrylamide derivatives as simple blends, complexes, copolymers and even IPNs have been reported[7–21] and they have found increasing use in a great variety of applications.

This paper presents a study on the complexation and blending of poly(*N*-isopropylacrylamide) (PNIPAAM) with poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA). The effect of solvent and molecular weight on complex formation has been studied. In aqueous solution, the strong hydrophobic interactions in the system lead to their mutual precipitation, which allows the isolation of the complex. However, when using methanol as solvent, a solvent-cast blend is obtained from the resulting transparent solution.

A comparative study of the glass transition temperature (T_g) of the obtained complexes and blends, as well as their thermal behaviour, is also presented.

EXPERIMENTAL

Materials

PAA samples used were supplied by Polysciences as aqueous solutions and, after being filtered, they were freeze-dried. Their reference molecular weights were 5.000 (PAA5), 50.000 (PAA50) and 150.000 (PAA150). The PMAA sample, supplied by Polysciences, was purified by dissolution in methanol and precipitation in diethyl ether. Its molecular weight, determined by viscometry in methanol at 25°C[22], was 2.3×10^4 (PMAA23).

The *N*-isopropylacrylamide monomer (NIPAAM), from Polysciences, was purified by crystallization in the mixture benzene/hexane (35/65) at room temperature. A second crystallization in the system acetone/heptane at 0°C led to an improved purity of the sample[23,24].

Ammonium peroxodisulfate and sodium disulfite, from Merck, were used without any further purification.

The solvent used for complexation, water, was Milli-Q grade, and methanol used for blending was purified by distillation after being refluxed with calcium hydride.

*Synthesis of poly(*N*-isopropylacrylamide)*

Several PNIPAAM samples were obtained by redox polymerization of NIPAAM in water at room temperature, under nitrogen atmosphere, using ammonium peroxodisulfate as initiator and sodium disulfite as accelerator, both in 0.5wt% of monomer. The obtained polymer was precipitated by addition of an equal amount of methanol due to the cononsolvent character of the methanol/water (50/50) mixture[23,25]. The fractions obtained, separated at different temperatures, once dried, were purified in the system chloroform/hexane and vacuum dried at 60°C during 48 h. Three samples were used in this work; their molecular weights measured by gel permeation chromatography (g.p.c.) were 76.1×10^3 (PNIPAAM76), 52.8×10^3 (PNIPAAM52) and 9.10×10^3 (PNIPAAM9) respectively.

Preparation of complexes and blends

All complexes were prepared by mixing separate water

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Table 1 Glass transition temperatures of the PNIPAAM/PAA complexes

PNIPAAM/PAA	T_g (°C)						
(feed comp.)	0/100	20/80	35/65	50/50	65/35	80/20	100/0
PNIPAAM76/PAA50	124	164	167	166	164	168	132
PNIPAAM76/PAA150	129	165	164	170	170	166	132
PNIPAAM52/PAA5	95	171	170	167	164	161	128
PNIPAAM52/PAA50	124	162	161	159	171	170	128

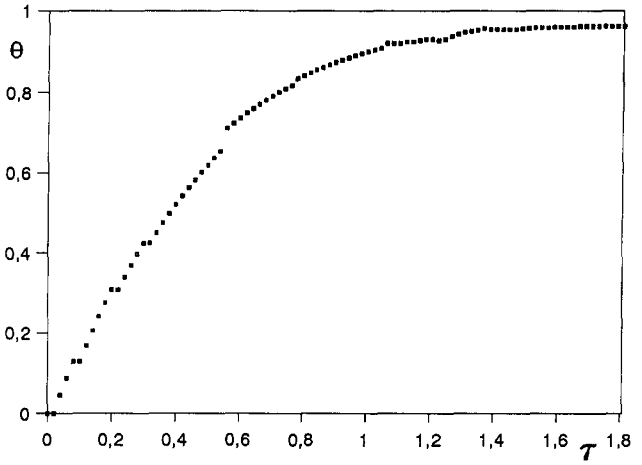

Figure 1 Variation of the complexation degree, θ, with τ for the system PNIPAAM52/PAA50 in water

solutions of polymer, concentration 0.2 mol monomeric unit l^{-1}. Solutions were mixed to give different unit molar ratios of polymer components. The precipitates formed when mixing were left for 3 days, and after that they were separated from the solution by centrifugation at 3.800 rpm during $\frac{1}{2}$h. The obtained complexes were washed twice with water and again centrifuged. After that, they were dried under vacuum at 50°C for 72 h.

Blends were prepared at the same compositions and polymer concentration, but now using dry methanol as solvent and under a nitrogen atmosphere to avoid the presence of water in the system. When mixing both polymer methanolic solutions, the mixture remained transparent, and solvent was immediately eliminated by vacuum drying at room temperature.

Instrumentation

The molecular weights of the polymers were measured either using an Ubbelhode automatic viscometer or by g.p.c., using a Waters chromatograph equipped with two μ-styragel columns with an exclusion limit of 10^7, using the THF as solvent at 298 K.

Potentiometric measurements were performed in a METROHM 691 pH-meter, equipped with a glass electrode.

The T_gs of the complexes and blends were determined using a Perkin-Elmer differential scanning calorimeter (d.s.c.), model DSC-4, and their thermal stability in a Perkin-Elmer thermogravimetric analyser (t.g.a.), model TGS-2. The T_g values are reproducible to about ±1°C.

The compositions of the complexes were determined using a Perkin-Elmer 2400 CHN Elemental Analyser.

RESULTS AND DISCUSSION

The complexation between PNIPAAM and poly(carboxylic acid) is expected to occur mainly through hydrogen bonding formation between the carboxylic group of the polyacid and the amide group of the PNIPAAM. Potentiometry is a useful technique to show the existence of complexation in protic solvents. The addition of increasing amounts of PNIPAAM solution to a polyacid solution will lead to an increase in pH for those solvents where complexation exists, and pH will stabilize when complexation is complete. In other words, as complexation progresses, the concentration of free carboxylic groups will decrease and, according to the dissociation equilibrium of the polyacid, the dissociated acid groups will also decrease, increasing the pH of the medium.

Potentiometric titration for the system PNIPAAM52/PAA50 indicated that complexation exists when using water as solvent, but not when using methanol, in which the pH of the solution remained constant. Therefore, water was used as solvent for complex formation and methanol for the preparation of blends.

From data obtained in water we can calculate the degree of complexation θ[26,27]

$$\theta = 1 - \frac{[\mathrm{H}^+]^2}{[\mathrm{H}^+]_0^2}$$

where $[\mathrm{H}^+]$ and $[\mathrm{H}^+]_0$ are the proton concentration in the polyacid solution in the presence and absence of PNIPAAM.

A plot of θ *versus* $\tau = [\mathrm{PNIPAAM}]/[\mathrm{PAA}]$, *Figure 1*, indicates a high degree of complexation, and also that complexation is complete at $\tau \simeq 1$.

PNIPAAM/PAA complexes

Several mixtures for the system PNIPAAM/PAA in water for different molecular weights of both components and for different compositions of the initial mixture have been prepared. All mixtures result in turbidity but, in some of them, the isolation of the precipitated complex was not possible even by centrifugation. It is to be noted that the existence of a precipitate indicates insoluble complex formation, but no appearance of a precipitate does not necessarily indicate that there is no complex formation, since the complex may be soluble in the medium. In this work we will use the term complex for the precipitate once isolated.

Yields of polymer complexes are negligible for the systems including the low molecular weight PNIPAAM sample, that is PNIPAAM9/PAA5 and PNIPAAM9/PAA50. For systems including PNIPAAM76 and PNIPAAM52, PNIPAAM76/PAA50, PNIPAAM76/PAA150, PNIPAAM52/PAA5, PNIPAAM52/PAA50 yields were the more significant, but lower yields were obtained for the system PNIPAAM52/PAA150, i.e. dependence on the relative molecular weights of the component polymers and on the composition of the initial mixture was observed. These results seem to indicate that PNIPAAM molecular weight is decisive in

Table 2 Glass transition temperatures of PNIPAAM/PMAA complexes

PNIPAAM/PMAA (feed comp.)	T_g (°C) 0/100	20/80	35/65	50/50	65/35	80/20	100/0
PNIPAAM76/PMAA23	[a]	157	179	186	186	172	132

[a] Reported value 228°C[22]

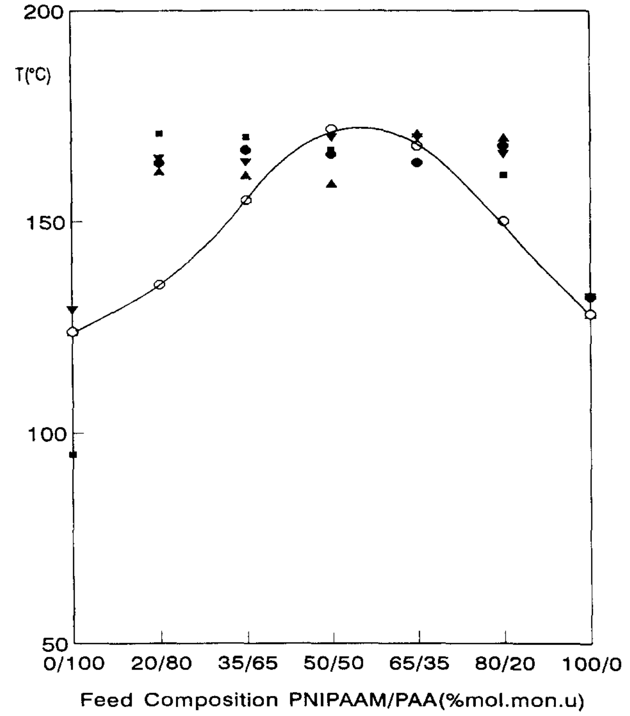

Figure 2 Glass transition temperatures for PNIPAAM52/PAA50 blends (○) and complexes: PNIPAAM52/PAA5 (■), PNIPAAM52/PAA50 (▲), PNIPAAM76/PAA50 (●) and PNIPAAM76/PAA150 (▼) vs composition of the original mixture

the stabilization and insolubilization of the complex, that is, there is a minimum PNIPAAM chain length under which the isolation of the complex is not possible and this minimum chain length increases when the molecular weight of the polyacid is increased. If we consider that the precipitation of the complex requires a high hydrophobicity of the system, the results are expected due to the strong hydrophobic character of PNIPAAM.

The composition of the complexes determined by elemental analysis were, in most cases, simple relations, PNIPAAM/PAA approx. 1/1.

The complexes obtained for the different systems and compositions were studied by d.s.c. All complexes exhibited a single glass transition, much higher than the T_gs of both component polymers; their values and those of their polymer components are shown in *Table 1*. This behaviour is often seen in systems capable of forming hydrogen bonds between their chains, which act as physical crosslinks, leading to a decrease in chain flexibility[28–35]. As can be seen, all T_g values obtained are very similar, which seems to indicate that complex composition does not appreciably change with molecular weight, nor with mixture composition.

PNIPAAM/PAA blends

Several blends were prepared for the system PNIPAAM52/PAA50, at the same compositions and for the same polymer concentration as in the complex preparation, but now using methanol as solvent.

The materials obtained after solvent removal were calorimetrically studied. All samples had single T_gs, higher than those of the pure components, and which varied with the composition mixture. The T_g values obtained for PNIPAAM52/PAA50 blends, as well as those for all the complexes studied, are shown in *Figure 2*. The fact that blends obtained for compositions 50/50 and 65/35 give T_g values which were coincident with that of the stable complex led us to think that though the original mixtures do not exhibit any apparent complexation, there is complex formation during the thermal treatment in the calorimeter. Several authors have found a similar behaviour[5,29,36,37], and it is explained as being due to a rearrangement of the interacting groups when heating the sample above their T_g, so that additional hydrogen bonds are formed leading to complexation. This is confirmed by the fact that some of the samples have a reproducible T_g value only after several consecutive scans in the calorimeter. The results can be explained, therefore, if one considers the samples not as polymer mixtures but mixtures of complex and excess polymer, leading to a decrease in T_g with respect to the T_g of the complex.

PNIPAAM/PMAA complexes

Several mixtures for the system PNIPAAM76/PMAA23 were prepared in water in order to elucidate the effect of the introduction of an α-methyl group in the polyacid on its complexation with PNIPAAM.

All mixtures result in phase separation, and significant complex yields were obtained in most cases as expected due to the hydrophobic character of the α-methyl group in the polyacid. The composition of the complexes obtained were, in most cases, simple relations, PNIPAAM/PMAA approx. 1/1.

All complexes obtained were studied by d.s.c., and they exhibited a single glass transition. T_g data for this system are shown in *Table 2*. With the exception of the 20/80 mixture whose yield of complex was very low (unstable complex), the T_g values obtained were all very similar, indicating that the complex composition does not depend on the composition of the original mixture. The PNIPAAM/PMAA complexes had T_g values slightly higher than those of PNIPAAM/PAA, that is, the introduction of an α-methyl group in the polyacid does not result in an important change in the complex nature, just a small increase in their rigidity, as shown by the small increase in T_g. Similar results have been obtained in other systems[38,39].

Thermogravimetric behaviour

Thermogravimetric analyses of pure polymers, complexes and blends show interesting thermal behaviours of these materials.

The samples of the polyacids (PAA and PMAA) had poor thermal stability. Their thermograms exhibited a two-stage degradation mechanism[40–42]. The first stage,

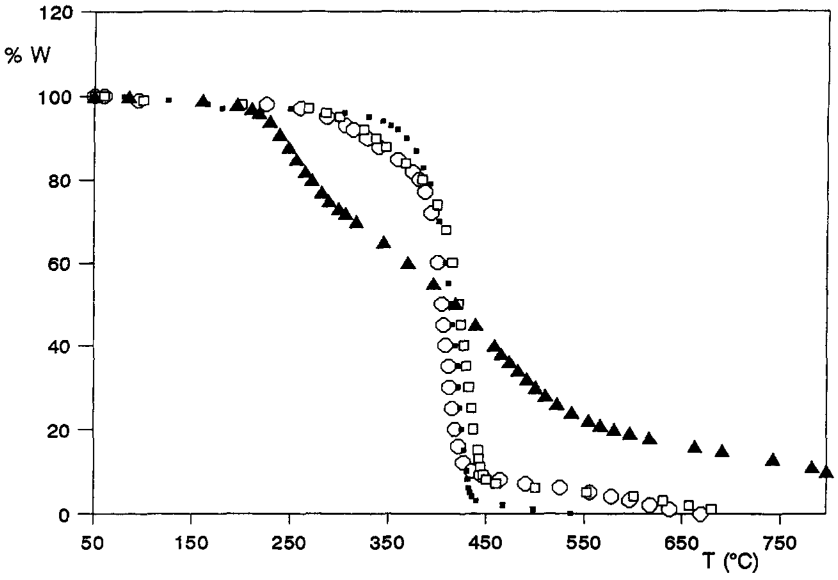

Figure 3 T.g.a. weight loss curve for polymers and complexes: ■, PNIPAAM52; ▲, PAA5; □, PNIPAAM/PAA 65/35; ○, PNIPAAM/PAA 35/65

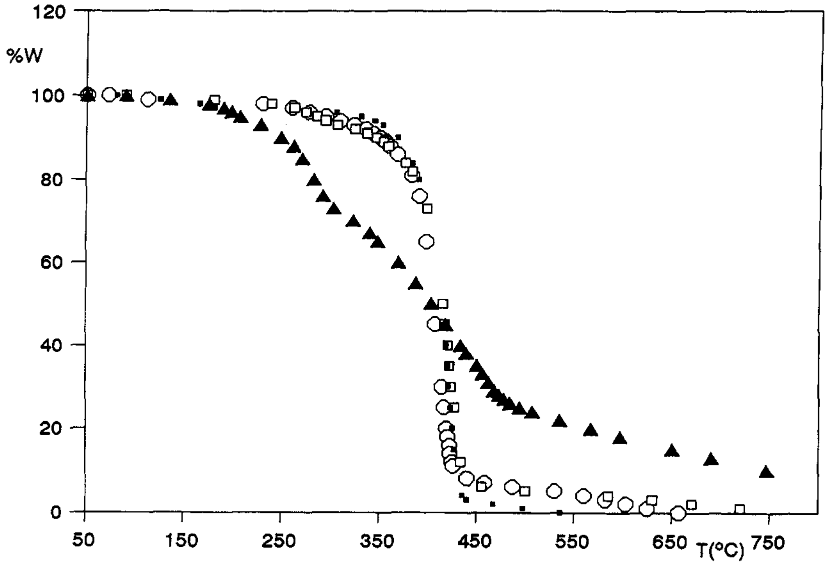

Figure 4 T.g.a. weight loss curve for polymers and complexes: ■, PNIPAAM52; ▲, PAA50; □, PNIPAAM/PAA 65/35; ○, PNIPAAM/PAA 35/65

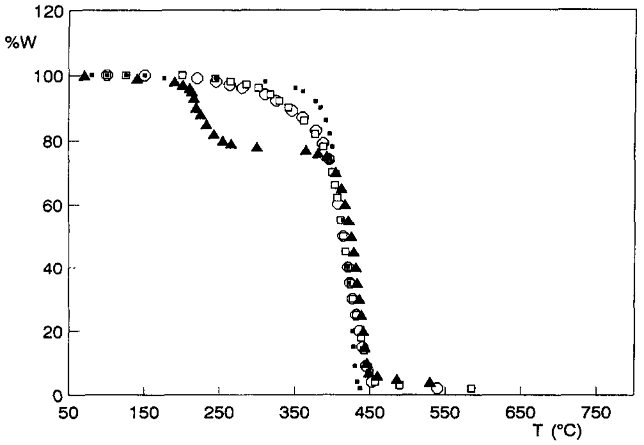

Figure 5 T.g.a. weight loss curve for polymers and complexes: ■, PNIPAAM52; ▲, PMAA23; □, PNIPAAM/PMAA 65/35; ○, PNIPAAM/PMAA 35/65

which is a consequence of anhydride formation, with loss of water, occurs between 180 and 220°C for PAA, and between 200 and 260°C for PMAA. The second step, caused by anhydride decomposition, with loss of CO_2, occurs between 270 and 300°C for PAA and between 380 and 450°C for PMAA. Both PAA and PMAA begin their degradation at lower temperatures, around 130–140°C. Although at this temperature this is a slow process, it is important to take it into account when drying the samples.

The samples of PNIPAAM were thermally stable with a single degradative step between 350 and 450°C, slightly lower for the low molecular weight sample.

Thermograms for the complexes PNIPAAM/PAA at two feed compositions, 35/65 and 65/35, are shown in *Figures 3* and *4*, along with those of the pure components in each case. As can be seen, all the complexes have a degradative process similar to that of PNIPAAM. It can be considered as a two stage process. The first stage occurs in the range 250–350°C, with a mass loss up to

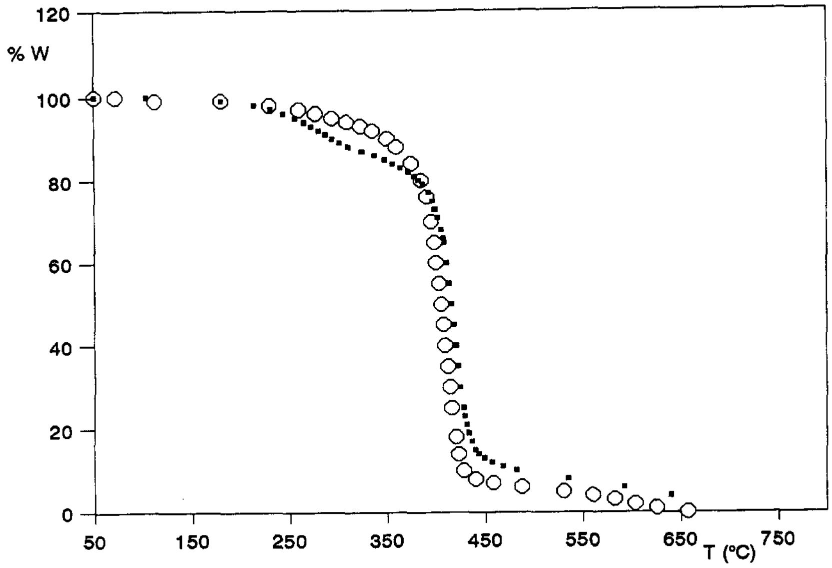

Figure 6 T.g.a. weight loss curve for PNIPAAM52/PAA50 complex (○) and blend (■), both obtained from a 35/65 original mixture

20%, being less important as the molecular weight of the polyacid is increased; the second one, between 350 and 450°C, results in a nearly complete loss of mass.

The results obtained indicate that complexation of PAA with PNIPAAM result in an important improvement in the thermal stability of the polyacid, probably due to an inhibition in the formation of anhydride and later decarboxylation. Evidence on thermal stability alteration for blends showing interpolymer hydrogen bonding has been reported[43]. Also, no significant differences are observed in the thermal behaviour of complexes obtained for different initial compositions, which confirms the idea that polymer complexes have a definite composition irrespective of the starting polymer mixture.

Similar results were obtained for complexes PNIPAAM/PMAA, as shown in *Figure 5*.

Considering the observed T_g behaviour of PNIPAAM/PAA blends, remembering that after heating the samples there is a complex formation, it seemed to be of great interest to make a comparative study of the thermal behaviour of the PNIPAAM/PAA blend and complex for the same composition, especially for those cases with a great excess of PAA. In *Figure 6* are shown the results obtained for samples of PNIPAAM/PAA blend and complex, both for a 35/65 feed composition. As can be seen, the blend shows a mass loss starting from 200°C, characteristic of free PAA degradation, as expected if we consider that this sample should have an amount of PAA not complexed.

According to these results we can conclude that complexation of PAA with PNIPAAM results in an important improvement of its thermal stability, but this is not the case for the blends when they include an amount of free PAA, that is, PAA not complexed.

CONCLUSIONS

Blends and complexes can be formed between PNIPAAM and polyacid (PAA or PMAA) depending on the solvent used for their preparation, as shown by potentiometry.

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

Polymer complexes have a T_g much higher than those of the polymer components, and no dependence is observed on the composition of the initial mixture. The high T_g values can be attributed to hydrogen bonds which act as physical crosslinks.

Blends show a single T_g, also higher than those of the polymer components, but which varies with the composition of the mixture. These results are explained, considering that there is complex formation during the thermal treatment of the samples in the calorimeter, which result in mixtures of complex and excess polymer.

According to thermogravimetric measurements we can conclude that complexation of PAA with PNIPAAM results in an important improvement of its thermal stability, but this is not the case for the blends when they include an amount of PAA not complexed.

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