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Thermal Properties of Cross-Linked Poly(*N*-isopropylacrylamide) [P(*N*-iPAAm)], Poly(methacrylic acid) [P(MAA)], Their Random Copolymers [P(*N*-iPAAm-*co*-MAA)], and Sequential Interpenetrating Polymer Networks (IPNs)

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ABSTRACT: The thermal behavior of cross-linked poly(*N*-isopropylacrylamide) [P(*N*-iPAAm)], poly(methacrylic acid) [P(MAA)], their random copolymers and their sequential interpenetrating polymer networks (IPNs) has been investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The state of the water has been studied on the basis of DSC traces of swollen samples. Several types of water have been found depending on water concentration and polymer structure. The lower critical solution temperature (LCST) as studied by DSC only occurs in the high *N*-iPAAm containing hydrogels. For the low water concentration regime, LCST seems to depend on the T_g value. TGA analysis of the dry samples indicates that the copolymers having higher content in *N*-iPAAm monomer have a lower thermal stability than that of the component homopolymers. On the contrary, sequential IPN samples degrade at higher temperature than their component homopolymers and copolymers with similar composition, indicating that interchain interactions improve thermal stability. The T_g of the same series of materials has been also measured. A T_g vs composition plot of P(*N*-iPAAm-*co*-MAA) copolymers presents a S-shaped curve indicating that structural units interact among them through strong specific interactions. For interpenetrating networks, it seems that only one T_g occurs, indicating a good compatibility and interpenetration.

Introduction

Cross-linked polymers able to swell in water are interesting kinds of materials from a technological point of view.[1−4] Materials combining the property to react to changes of temperature and pH have been introduced because of their interesting applications in the biomedical field.[5−7] Very recently, systems have been worked out to combine the pH and temperature sensitivities by copolymerizing two monomers[8−14] or by forming interpenetrating polymer networks (IPNs)[15−19] of the pH- and temperature-sensitive materials. The changes in the swelling behavior of polymer gels based in *N*-isopropylacrylamide (*N*-iPAAm) and methacrylic acid (MAA) has been reported.[9,10,15] P(*N*-iPAAm) exhibits[3,20,21] a sharp phase transition in water (lower critical solution temperature, LCST) at 32 °C. It is a temperature-induced collapse from a perturbed coil into a globule structure (coil-to-globule transition) which is macroscopically revealed as a sudden decrease of the degree of swelling (swelled to shrunk state). In some instances, it has been also defined as a Θ temperature[20] or demixing transition.[21] We have investigated the cross-linked P(*N*-iPAAm), P(MAA) homopolymers, several of their copolymers, and sequential interpenetrating networks of both homopolymers.[22,23] The gels present differences in their swelling behavior depending on temperature, pH and a combination of both.[22] The use of different NMR techniques provided insight into the dynamic and structure of these xerogels and hydrogels.[23] Magic-angle spinning ^{1}H-MAS NMR measurements of 50 wt % water-swollen gels revealed that, for the same amount of cross-linking agent, gels having a higher ratio in MAA present lower mobility than high *N*-iPAAm content hydrogels. The mobility of the water inside of the gels can be tailored by means of DSC. DSCgram traces of hydrogels show multiple endotherms, which can be explained in terms of free or unbounded water, intermediate water or freezing bound water, and non-freezable or bound water. More refined[24] studies found as many as four distinguishable different types of water ranging from the most tightly bound to free, bulklike water.

IPNs ideally, are a mixture of two or more cross-linked polymers, which are dispersed or mixed at the segmental level. The degree of interpenetration in IPNs depends on the degree of cross-linking. IPNs having a high cross-linking ratio show a good compatibility.[25] Furthermore, it is also known that in systems having groups, which can act as hydrogen donor and hydrogen acceptor, reversible complexes through hydrogen bonding can be formed. Interpolymer complexation in systems including polyacids and poly(acrylamide) derivatives is found in the literature.[26−29] This seems to be the case of IPNs based on *N*-iPAAm and MAA. This physical interlocking among the component polymers, from the practical point of view, may be considered as a physical cross-linking. These IPNs changed dramatically their swelling properties compared with their component homopolymers. The peculiar swelling behavior of the present system may be explained by the formation of hydrogen bonds between the carboxylic groups of the MAA units (proton donors) and the amide groups of the *N*-iPAAm units (proton acceptors) and

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their self-associated species.[22] From the line width and chemical shift of the pulse saturation transfer ^{13}C PST-MAS NMR spectra of IPNs, some interaction at a molecular level between P(MAA) and P(*N*-iPAAm) networks has been detected,[23] suggesting the presence of complexes.

The interactions and compatibility of a multicomponent system can be also studied by measuring the glass transition temperature, T_g. Random copolymers and compatible blends show a single T_g. The compatibility of a two components system can be improved through hydrogen bonding. Nevertheless, hydrogen bonding in mixtures and copolymers has been found responsible of large deviations of T_g vs composition from the classical models.[30,31]

In the present paper, we are reporting the thermal properties of a series of dried and swollen cross-linked polymers, copolymers and IPNs in order to obtain a more deep insight into the different hydrophilic and hydrophobic polymer−polymer and polymer−solvent interactions. There exits many works dedicated to the study of swelling properties and applications of smart gels. However, their thermal stability and the glass transition behavior have not been so deeply studied. The study of these characteristics, as function of polymer structure, is particularly interesting since they are related to the interaction properties of the system.

Experimental Section

Materials. *N*-Isopropylacrylamide (*N*-iPAAm) (Acros Organics, Morris Plains, NJ) 99% purity, methacrylic acid (MAA) 98% purity, tetraethylene glycol dimethyl acrylate (TEGDMA), ammonium persulfate (APS), *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED), benzoyl peroxide (BP), *N*,*N*-dimethyl-*p*-toluidine (DMPT) and 2,2-dimethoxy-2-benzophenone (DPMA) (Fluka-Chemie, A.G., Buchs, Switzerland), ethylene glycol (EG) (Riedel-de Haën, Seelze, Germany), ethanol and methanol, (Panreac Monplet&Esteban, S.A., Barcelona, Spain) were used. Deionized water from a Millipore Milli-U10 water purification facility was used where appropriate.

Synthesis of Copolymer Hydrogels. Poly(*N*-isopropylacrylamide-*co*-methacrylic acid) hydrogels were synthesized by free radical polymerization in solution using a mixture of water and ethanol (50/50 wt %) as solvent and initial monomer molar ratios *N*-iPAAm/MAA of 0, 0.15, 0.30, 0.5, 0.70, 0.85 and 1.0. A 0.25 mol % of cross-linking agent tetraethylene glycol dimethyl acrylate (TEGDMA) as received, was added. Ammonium persulfate (APS) (0.5 wt %) activated by TEMED (0.5 wt %) was used as initiator system. The reaction was carried out at 308 K in a temperature-regulated water bath.

Synthesis of the Sequential P(MAA)/P(*N*-iPAAm) IPNs. To synthesize IPNs, the sequential method was used. Methacrylic acid (MAA) cross-linked with a 0.25 mol % of TEGDMA was previously polymerized by free radical solution polymerization using 0.25 wt % of BP as initiator and 0.06% of DMPT as accelerator. The vacuum-dried P(MAA) network was swollen in a methanol solution of *N*-iPAAm with the same molar concentration of cross-linking agent and an UV-sensitive initiator, 2,2-dimethoxy-2-benzophenone (DMPA). When the swelling equilibrium was reached, the swollen gel was placed under an UV source for 10 min. IPNs of different compositions were prepared.

Elemental Analysis. The chemical compositions of copolymers and IPNs were estimated by organic elemental analysis. They are given in Table 1.

Thermogravimetric Analysis (TGA). TGA analysis was carried out with a Perkin-Elmer TGA 7 with a TAC 7/DX under an oxygen free nitrogen atmosphere. Dry samples of 5−8 mg weight were used. A linear temperature heating rate of 10 K·min.$^{-1}$ was maintained from 323 to 873 K. TGA weight loss curves and their derivative curves were recorded.

Table 1. Molar Composition of Cross-Linked Samples As Determined by Elemental Analysis

sample	P(*N*-iPAAm) (% mol)	P(MAA) (% mol)
P(*N*-iPAAm-*co* -MAA) 85/15	82.6	17.4
P(*N*-iPAAm-*co* -MAA) 70/30	66.7	33.3
P(*N*-iPAAm-*co* -MAA) 50/50	50.5	49.5
P(*N*-iPAAm-*co* -MAA) 30/70	32.4	67.6
P(*N*-iPAAm-*co*-MAA) 15/85	15.4	84.6
IPN5	30.2	69.8
IPN4	28.3	71.7
IPN3	15.4	84.6
IPN2	1.7	98.3

Differential Scanning Calorimetry (DSC). DSC measurements were carried out under a blanket of N_2 with a Mettler-Toledo TA8000 connected to a cooling system. DSC was used in order to determine the LCSTs of the gels with higher *N*-iPAAm contents and also to investigate the state of the water in the swollen networks as well as to determine glass transition temperatures of the higher *N*-iPAAm content copolymers and for the plasticized higher MAA content samples. To investigate the swollen samples, they were submitted to the following thermal history. Samples of known water content were prepared by weighting amounts of the dry sample and water in open aluminum pans. Weights of 5−10 mg depending on sample composition were employed. After being sealed off, they were left to stand at room temperature for 24 h. For DSC experiments, the samples were submitted to the following ramps. The sample was cooled from 303 to 173 K at a rate of cooling of 10 K·min^{-1}. Subsequently the sample was heated from 173 to 343 K at a rate of heating of 10 K·min^{-1}. Thermal traces of the first and second runs were recorded. Glass transition temperatures T_gs of the dried homopolymers, copolymer gels, IPNs and plasticized systems were also investigated by DSC. The samples were prepared according to the following procedure. Polymer disks of preestablished dimensions were cut from water-swelled gel. These disks were vacuum-dried (10^{-3} mmHg) at 333 K for 12 h. They were used for T_g determination as described below. However, for the preparation of samples of plasticized systems, a mixture of EG + H_2O of known concentration was added to the dried sample in open aluminum pans in order to attain a more rapid swelling of the sample by EG. The sample was left to stand overnight to be swelled by the EG + H_2O mixture. Subsequently, the specimen in the open pan was vacuum-dried (10^{-3} mmHg) at 333 K for 12 h. The ratio of the EG in the samples was estimated by weighing before and after the water removal. Then the pans were sealed off.

The sealed pans were submitted to the following thermal history. In a first run the sample was heated from room temperature to 453 K at $R_H = 20$ K·min^{-1}. Then the sample was immediately cooled to 233 K at $R_C = 30$ K·min^{-1}, and as in the second run the sample was heated from 233 to 473 K. The glass transition was estimated from the trace of this second run. In both cases to determine the glass transition temperature T_g of samples the criterion of T_g at $\Delta C_p/2$ was adopted.

Results and Discussion

Interaction between Hydrogels and Water. The State of Water in the Hydrogels. In parts a and b of Figure 1, the cooling and heating DSCgrams of a series of water-swollen P(*N*-iPAAm) gels are presented. These traces are quite complex. In the water melting region, multiple endotherms appear. Similar behavior has been reported for some other polymeric hydrogels.[32−37] Stillinger[38] pointed out that the modifications in phase transitions of water result from finite size effects where the presence of boundaries and interfaces reduces the number of freedom degrees and disrupts the natural order in the bulk phase of water. Moreover, Rault et al.[39,40] have studied the thermal behavior of a series of

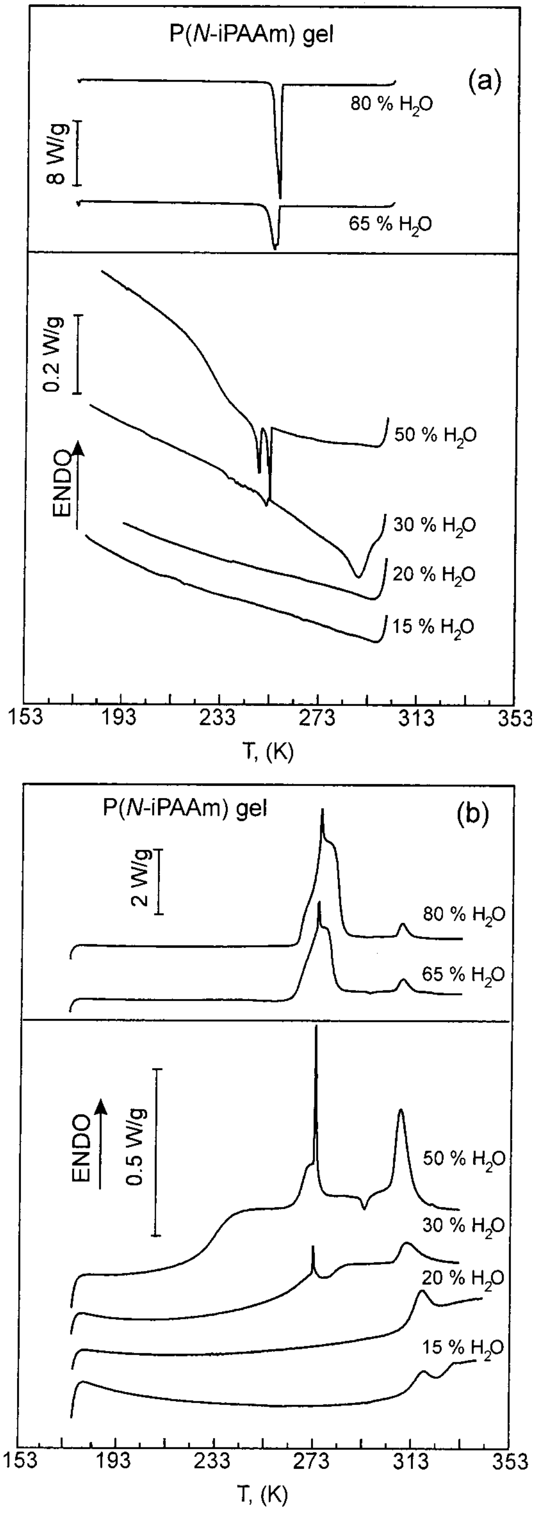

Figure 1. DSCgram traces of a P(*N*-iPAAm) with different water contents as a function of temperature: (a) recorded at a rate of cooling of 10 K·min^{-1} and (b) recorded at a rate of heating of 10 K·min^{-1}.

hydrogels interpreting their thermal transitions by means of a simple thermodynamic framework based on the phase diagram. Three water concentration regimes have been established:[39,40] (i) the melting temperature depression of water; (ii) the occurrence of crystallization on heating (even when it was absent upon cooling); (iii) the existence of an amount of noncrystallizable water. We can also find these three regimes proposed by Rault et al.[39,40] In the first region, water does not crystallize and a diminution in the T_g value is observed. This regime corresponds to the 15, 20, and 30 wt % H_2O swollen P(*N*-iPAAm). Rault el al.[39,40] postulated that the origin of the unfreezable water is not the bounding of the water to the polymer but is the glassy state of the polymer–water system that is reached before the crystallization temperature of water. As far we are concerned, this argument is not totally correct because the decreasing of the T_g is caused by the water plasticization effect, and the plasticization needs some specific interactions among the polymer and the plasticizer leading to the so-called "bound water". However, we have also observed that the nonfreezing or bound water decreases with increasing the swelling degree of the gel. For instance, the relation $m_{\text{bound water}}/m_{\text{polymer}}$, decreases from 0.96 for a 50 wt % H_2O swollen sample to 0.55 for a sample with a 80 wt % H_2O, suggesting that in this regime not all the unfreezable water is bound, as has been postulated by Rault et al.[39,40] In the second regime, only a very slight lowering of the crystallization temperature is observed. For the second regime, we have not observed any melting point T_m dependence on H_2O concentration in opposite to that suggested by Rault et al.[39,40] In the third regime, a regularization of the T_g occurs, the glass transition does not depend on the composition. This means that T_g, for high amounts of crystallizable water, is not detected and only a change on the baseline after the water melting point is observed. To analyze the nature of water, i.e., its plasticization effect, the Gordon–Taylor–Wood[41,42] (GTW) equation has been applied. A value of 136 K for the glass transition of water has been used.[43] From this analysis, it can be conclude that for the low concentration regime, water behaves as a typical plasticizer.

Parts a and b of Figure 2 display DSCgram traces of 50 wt % H_2O swollen samples of P(*N*-iPAAm), P(MAA), and some of their copolymers in the region from 173 to 333 K, recorded at a rate of 10 K·min^{-1}, for the cooling and heating cycles, respectively.

The sharp peak appearing in all thermograms around 273 K, should correspond to water segregated off the gel in the cooling process, since this peak increases in subsequent cooling and heating cycles. Rault et al.[39] also observed this endotherm independent of the water content, and they attributed to the melting of a small fraction of water in form of aggregates in the larger spaces left by heterogeneities in the network.

In the trace corresponding to pure P(*N*-iPAAm) gel, an endotherm at a temperature well below the melting point of pure water appears, which may correspond to the called intermediate water. This peak clearly appears in copolymers with *N*-iPAAm molar contents of 85 and 70%. For the 50% *N*-iPAAm copolymer gel, the endotherm becomes broader and splits clearly in two for the 30% *N*-iPAAm one. Decreasing the *N*-iPAAm content, the left-hand peak decreases, and the highest temperature peak, becomes the main endotherm for the 15% *N*-iPAAm gel. The left-hand peak does not appear for the pure P(MAA) gel. This fact may suggest either that there is not an intermediate water for this gel and/or that this peak is related to the presence of *N*-iPAAm structural units in the gel. The amount of bound water on the hydrogels can be estimated from the difference between the whole amount of water in the sample and the freezable water measured on the area of the peak by using the heat of melting of pure water (79.6 cal·g^{-1}). As Quinn et al.[34] pointed out, this method is not totally

Table 2. Relation of $m_{\text{bound water}}$ to m_{polymer} for 50 and 65 wt % H_2O Content of a Series of P(*N*-iPAAM), P(MAA), Their Copolymers, and One of Their Interpenetrating Networks at 298 K

	$m_{\text{bound water}}/m_{\text{polymer}}$	
sample	50 wt % H_2O	65 wt % H_2O
P(*N*-iPAAm)	0.96	0.77
P(*N*-iPAAm-*co*-MAA) 85/15	0.94	
P(*N*-iPAAm-*co*-MAA) 70/30	0.74	0.64
P(*N*-iPAAm-*co*-MAA) 50/50	0.79	
P(*N*-iPAAm-*co*-MAA) 30/70	0.70	0.72
P(*N*-iPAAm-*co*-MAA) 15/85	0.93	
P(MAA)	0.84	0.52
IPN4	0.45	

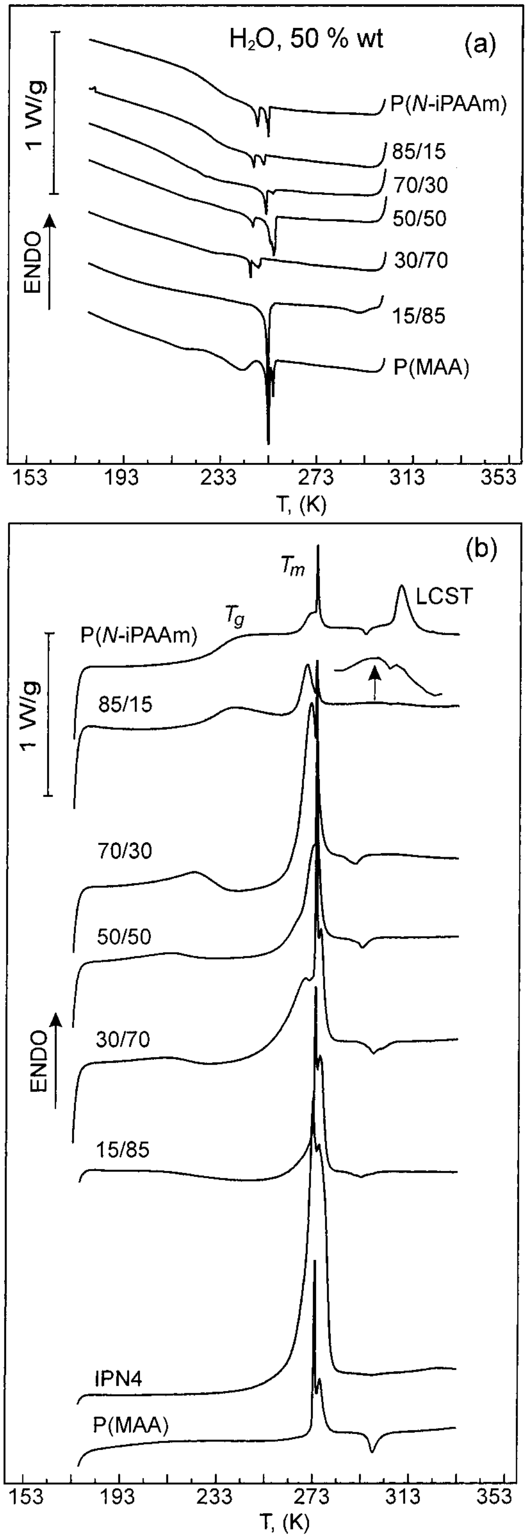

Figure 2. DSCgram traces of P(*N*-iPAAm), P(MAA), and some of their copolymer hydrogels with a 50 wt % H_2O content as a function of temperature: (a) Recorded at a rate of cooling of 10 K·min^{-1} and (b) recorded at a rate of heating of 10 K·min^{-1}

correct since the heat of melting of freezable water is not constant. This melting enthalpy represents an upper limit that leads to an overestimation of the amount of nonfreezable water in the hydrogel. Table 2 displays the percentage of bound water with respect to the polymer amount, for a series of 50 and 65 wt % H_2O content swollen gels. It seems that the bound water also depends on the swelling ratio of the hydrogels. Bound water corresponds approximately to 40–50% of the dried polymer. In Figure 2b, the DSCgram corresponding to the 50 wt % H_2O IPN4 sample is also shown. The amount of bound water for this sample is lower than for the copolymer of the same composition, as can be seen in Table 2. Similar to the gels with a higher MAA content, IPN4 has a considerable amount of free water. Free water, therefore the freezing water, increases as the hydrogel approaches the swelling equilibrium.

In DSCgram traces displayed in Figure 2b, the glass transition (T_g) can be distinguished for some of the gels. In particular, for P(*N*-iPAAm), T_g clearly occurs around 230–235 K. It also appears in copolymers around this temperature as it can be better appreciated in the cooling traces showed in Figure 2a. On heating, a cold crystallization occurs after the T_g that obscures the process. The crystallization enthalpy is considerable lower than the melting enthalpy. This fact also indicates that the decreasing of the baseline before the melting endotherm is due to the water crystallization on heating. Similar undercooling effects have been reported in the literature.[39,40]

Mobile enriched *N*-iPAAm copolymers displayed a low-temperature endotherm corresponding to the intermediate water, whereas enriched MAA copolymers exhibit higher amount of free water for similar water concentration. The change in the baseline after the T_g is more visible for flexible gels based mainly in *N*-iPAAm. For more rigid gels, the regime where free water dominates is reached at lower water concentration.

Lower Critical Solution Temperature Transition (LCST). To study the influence of the water concentration on the LCST of pure P(*N*-iPAAm) gels, in Figure 3a a magnification of the LCST region of the DSCgram traces displayed in Figure 1b is given. The LCST of the P(*N*-iPAAm) hydrogel is in agreement with those found by some other authors.[3,44–46] The onset of the DSCgrams corresponds to the temperature collapse.[47] According to Shibayama et al.[48] the dissociation enthalpy of the hydrophobic interaction depends on polymer concentration, but as we are aware, a dependence of the LCST temperature on the polymer concentration has not been reported. In the same Figure 3a, it is very clearly seen that the temperature of the LCST maximum remains constant for high swelling ratios and shifts toward higher temperatures, when the water concentration in the P(*N*-iPAAm) gel is below 50 wt % For the gel with a 20 wt % H_2O content, the glass transition temperature T_g overlaps practically with the LCST transition. If the water content decreases still more, namely to a 15%, T_g appears even at a higher temperature. At this point it should be noted, as it has been mentioned above, that the samples were aged, i.e.,

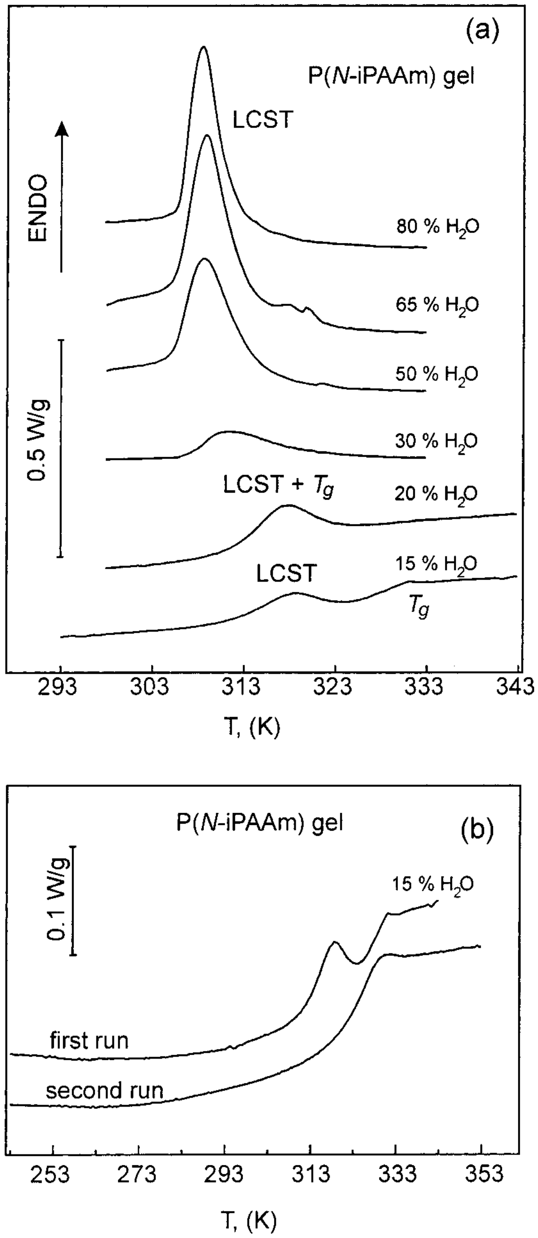

Figure 3. DSCgram traces of a series of poly(*N*-isopropylacrylamide) [P(*N*-iPAAm)] hydrogels with different water contents: (a) Effect of the water content on the LCST transition and glass transition temperature. (b) Effect of the thermal history on a P(*N*-iPAAm) with a 15 wt % water content as a function of temperature obtained at a rate of heating of 10 K·min^{-1}.

left to stand for 24 h at room temperature before the DSCgram traces were recorded. Nevertheless, in Figure 3b, it is seen that if the 15% H_2O content gel is immediately submitted to a second heating run, the LCST no longer appears. It is obvious that the sample in the vitreous state needs long time to return to the original conformation. These features indicate that for the low water concentration regime, where the T_g is not constant, the LCST value also depends on the water concentration because the gel needs of some mobility in order that such event may take place.

In Figure 4, DSCgram traces of P(*N*-iPAAm) and a series of P(*N*-iPAAm-*co*-MAA) copolymers with a 20% H_2O content are shown. In this Figure 4, the change of the T_g with gel composition may be observed. The T_g of the copolymer gels lies between those of the homopolymers, however for those water plasticized samples, T_g is not strongly dependent on composition. Associated to the T_g, an endothermic peak appears, which in the case of pure P(*N*-iPAAm) we have attributed to the LCST. These peak decreases in intensity with increasing MAA comonomeric unit content. This means that it is related to the presence of *N*-iPAAm and probably to the LCST itself.

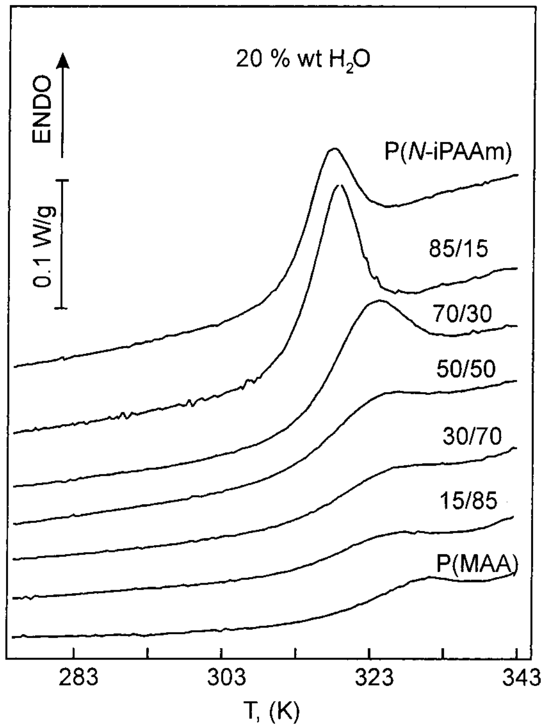

Figure 4. DSCgram traces of a series of hydrogels with a 20 wt % water content of P(*N*-iPAAm) and P(MAA) and some of their P(*N*-iPAAm-*co*-MAA) copolymers as a function of temperature obtained at a rate of heating of 10 K·min^{-1}.

In general, the addition of more hydrophilic monomers to P(*N*-iPAAm) hydrogel should increase the LCST value because the monomer hinders the dehydration of the polymer chains and acts to expand the collapsed structure.[9,20,45−47,49] Whereas the addition of hydrophobic comonomer decreases the LCST.[20,44,47−49] Specifically, the hydrophilic acrylic acid (AAc) units tend to increase the LCST of P(*N*-iPAAm-*co*-AAc) copolymers because the ionized $-COO^-$ groups are sufficiently soluble to counteract the aggregation of the hydrophobic temperature sensitive units.[12] Also, the repulsion of the $-COO^-$ groups or the formation of hydrogen bonds between the amide groups in P(*N*-iPAAm) and the carboxyl groups in MAA may hinder the collapse induced by the *N*-iPAAm units, increasing the LCST. In general thermosensitivity does not remain for the whole range of composition. P(*N*-iPAAm) gel loses this characteristic with small increment of the hydrophilic balance.

The swelling behavior of copolymers is also depending on the pH because they contain carboxyl groups. In the case of IPNs, the association between the complementary binding sites produces complexes that decrease the ability of the hydrogel to swell in water. The complexes through hydrogen bond are disrupted when the pH of the medium is increased.

To investigate the pH influence on the LCST by DSC, dry samples were immersed in buffer solutions of pH = 4, 5, and 9 and in a strong basic media of pH = 11. These

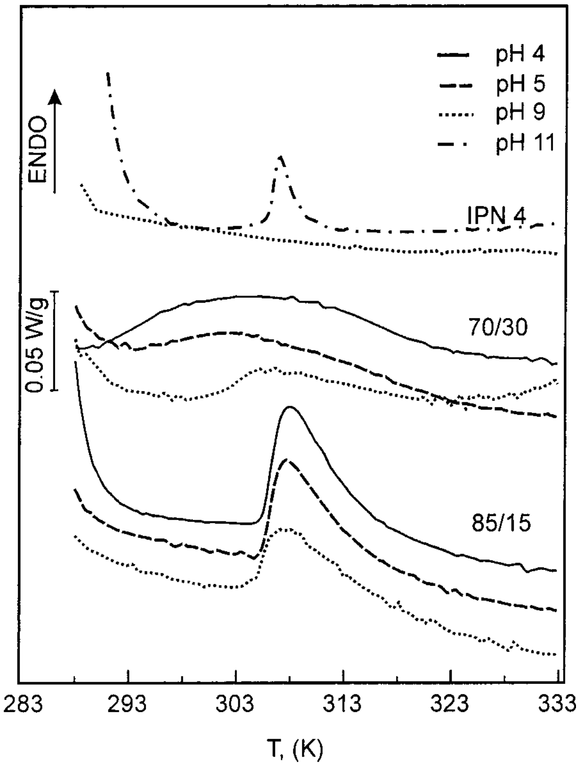

Figure 5. Magnified DSC traces for swollen interpenetrating network INP4 and 70/30 and 85/15 P(*N*-iPAAm-*co*-MAA) copolymers equilibrated in a series of buffer solutions at a swelling ratio of Q=10 at room temperature. Scanning rate: 10 K·min^{-1}. The swollen sample weight was ca. 7 mg.

samples were swelled to a swelling ratio of $Q = 10$ (Q = dry weight/swelled weight) and subsequently submitted to the same thermal history than that of the samples swelled in distilled water studied before. The results for swollen interpenetrating network INP4 and 70/30 and 85/15 P(*N*-iPAAm-*co*-MAA) copolymers at room temperature are shown in Figure 5. As can be seen, the endotherms appear at the same temperature of pure P(*N*-iPAAm) gel. Endotherms corresponding to LCST in the DSC traces were only shown by P(*N*-iPAAm-*co*-MAA) copolymers with a high *N*-iPAAm content, namely, 70/30 and 85/15 at pH = 4, 5, and 9, and for IPN4 at pH = 11. The transition enthalpy is smaller than that corresponding to P(*N*-iPAAm) homopolymer gel. The shape of the endotherm of the 85/15 copolymer is quite similar to that of the homopolymer. However, for the 70/30 copolymer, the endotherm is considerably broader. When the pH is increased, neither the disappearance of the transition nor a change in its temperature is observed, but a reduction of the endotherm area. In swelling experiments, the LCST did not appear at high pHs where MAA carboxylic groups are ionized, but at acid conditions below the pK_a of MAA, shrinking of the 70/30 and 85/15 copolymers occur. These discrepancies between DSC and swelling experiments indicate the existence of a macro- and a microtransition as Shibayama et al.[20] suggested for P(*N*-iPAAm-*co*-AAc).

Thermal Stability of the Copolymers and IPNs Xerogels. The thermal stability of a xerogel may be interesting not only because it represents a characteristic of the materials but also because it can act as a datum to keep in mind to determine the glass transition under safe conditions. Schild[50] has observed that P(*N*-iPAAm) is more thermally stable than poly(acrylamide) P(AAm), it degrades in an unique step starting around 673 K and it does not leave any appreciable residue.

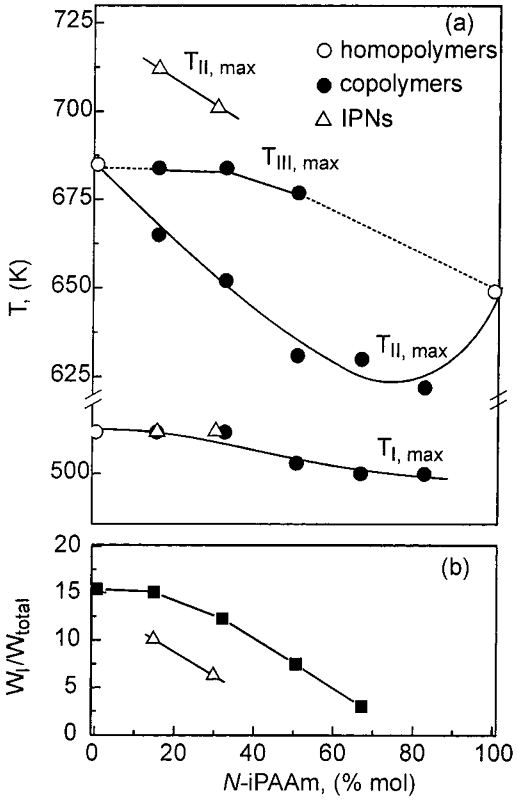

Figure 6. Characteristic parameters of the thermal stability obtained from the first derivative of the TGA curve of a series of P(*N*-iPAAm-*co*-MAA) copolymers, their homopolymers, and some of their polymer sequential interpenetrating networks IPNs.

The thermal stability of P(MAA) has also been studied by some authors.[51−53] A two-step mechanism was proposed: on heating P(MAA) is converted into poly(methacrylic anhydride) [P(MAN)] comprising six-membered glutaric anhydride-type rings. The derivative maxima for the two-step degradation occur at 513 and 743 K, respectively. Monomer is being released at low temperature with water and carbon dioxide.

The maxima of the TGA first derivative of a series of P(*N*-iPAAm), P(MAA), and a series of copolymer and IPNs have been plotted in Figure 6a as function of composition. As it can be appreciate, some of the gels present up to three degradation steps, their maxima are designed as $T_{I,max}$, $T_{II,max}$, and $T_{III,max}$. P(MAA) degrades in a two-step process. In Figure 6a, it is seen that, excluding the P(*N*-iPAAm) homopolymer, all the other specimens show the maximum located around 523 K characteristic of the first step of degradation of MAA structural units. For copolymers with MAA content below 50%, the first loss step of MAA units is very hardly detected. This parameter is quite similar for copolymers and their respective IPNs and it only depends very slightly on composition.

The plot of the maxima of the second peak from the first derivative, namely, $T_{II,max}$ shows a well defined dependence on composition. This maximum is present in copolymer as well as in their homopolymers and decreases with increasing *N*-iPAAm content, taking a minimum value around 70−85% *N*-iPAAm. High MAA content samples, as can be seen in Figure 6a, also present a splitting appearing as a third maxima $T_{III,max}$, this temperature remains almost constant and close to

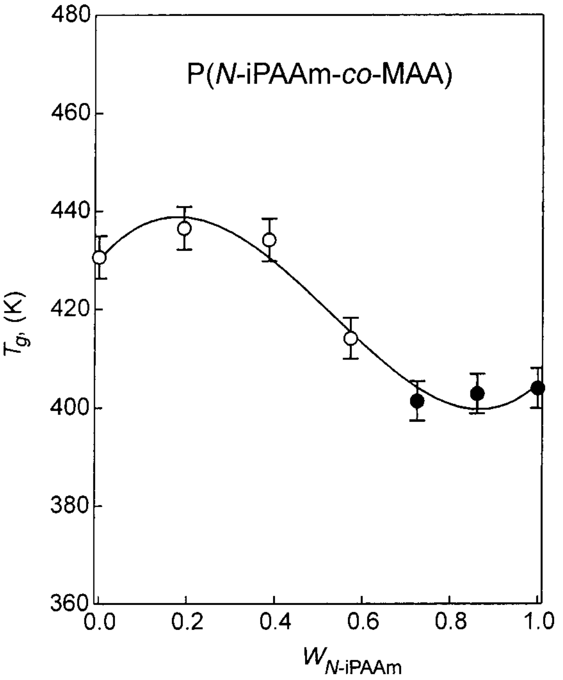

Figure 7. Plot of the glass transition temperatures of P(MAA) and P(*N*-iPAAm) and their copolymers as a function of composition.

the value found for pure P(MAA). When copolymers and IPNs are compared, it is seen that samples with similar composition present different thermal stabilities. In Figure 6b, the ratio between the weight loss of the first degradation process and the whole weight loss expressed as W_I/W_{total} is presented. The first step of degradation is lower for IPNs compared to copolymers and pure P(MAA). The main degradation process shifts also to higher temperature and occurs in only one well-defined step, in opposite that occurs in copolymer with the same composition. This higher thermal stability points out that the IPNs possess a good degree of interpenetration due to specific interactions through amide and carboxyl groups.

Glass Transition of the Xerogels. As we have seen above, P(MAA) is a very labile polymer to temperature from the structural point of view. Because its glass transition temperature lies closely to the first stage of its degradation, it was necessary to use an indirect procedure such as the plasticization method to estimate its glass transition temperature and also those of P(*N*-iPAAm-*co*-MAA) copolymers with a high MAA content. Ethylene glycol (EG) has been used as an excellent plasticizer due to the strong solvating effect on these hydrophilic copolymers For the estimation of T_g from this analysis, a value of 154 K for the T_g of ethylene glycol has been assumed.[54] The cross-linked copolymers show a single T_g indicating the formation of random copolymers, the T_g of P(*N*-iPAAm) is around 404 K according to the value found by Sousa et al.[55] of 408 K; however, Kuckling et al.[56,57] gave a slightly higher value.

A useful method to understand the interactions of these copolymers is the determination of T_g as a function of composition. In general, for polymers blends, deviations from linear dependence have to be considered as a measure of the strength of the interactions.[58,59] The T_g values have been plotted together in Figure 7 as a function of *N*-iPAAm content. As we can see, the experimental results show S-shaped T_g−composition curve. This unexpected S-shaped curve, in our case, for instance, could be interpreted in term of the hydrophilic and hydrophobic interactions. Thus, in the case of miscible polymer blends, S-shaped behavior has been interpreted in terms of different types of polar interactions.[60,61] Similar effects on glass transition temperature vs composition have been also observed not only in blend of polymers, but also in acrylic copolymers with electron acceptor and electron donor groups interactions.[62,63] In these systems, the T_g behavior has been explained because an inversion from reduced to increased mobility of the copolymeric chain as the composition of the interacting groups (donor/acceptor ratio) is changed.

From the qualitative point of view, having a look in Figure 7, the introduction of increasing amounts of the hydrogen bond (*N*-iPAAm) acceptor moiety in the copolymer results, first, in a soft increase in the stiffness and therefore in the glass transition. Second, an accentuated diminution of the T_g, reflected in the shape of the T_g vs composition and, a third range in which the glass transition shows only a smoothed dependence on composition. This suggests an inversion of the hydrogen bond interactions in the copolymers. In fact this effect must be due not only to the change of composition but to a change of the hydrogen bond interactions.

The composition dependence of the glass transition temperature of random copolymers can be described according to the Gordon−Taylor−Wood equation.[41,42] Kwei[64] modified the former GTW equation in order to interpret the T_g behavior when specific interactions such as hydrogen bonding exists.

$$T_g = \frac{(W_1 T_{g1} + kW_2 T_{g2})}{W_1 + kW_2} + qW_1W_2 \tag{1}$$

The first term on the right-hand side is identical to the Gordon−Taylor−Wood equation. The quadratic term qW_1W_2 should be proportional to the number of specific interactions existing in a mixture and can be interpreted as the contribution of the hydrogen bonding. However, this equation is not able to reproduce the trend of our data.

More recently, Painter et al.[30] presented a classical thermodynamic theory for the composition dependence of the glass transition temperature for miscible polymer blends that involve strong specific interactions such as hydrogen bonds. They have separated the derived T_g equation into three terms: (i) a nonspecific interaction component and (ii) a heat of mixing in the liquid-state term (iii) that accounts for that part of the temperature dependence of the specific heat that is due to self-association. Following these authors,[30] a more general form of the Kwei[64] equation can be written as

$$T_g = \frac{W_1 T_{g1} + kW_2 T_{g2}}{W_1 + kW_2} + q'(W)W_1W_2 + q'_2(T)W_1W_2 \tag{2}$$

where $q'(W)$ is a composition-dependent term that depends on the balance of interactions (self-association vs interassociation) in the system while $q'_2(T)$ represents the contribution from the temperature dependence of the specific heat of the self-associating component (or components). Painter et al.[30] pointed out that when the enthalpic terms are of opposite sign and asymmetric in their composition dependence, it would be possible to

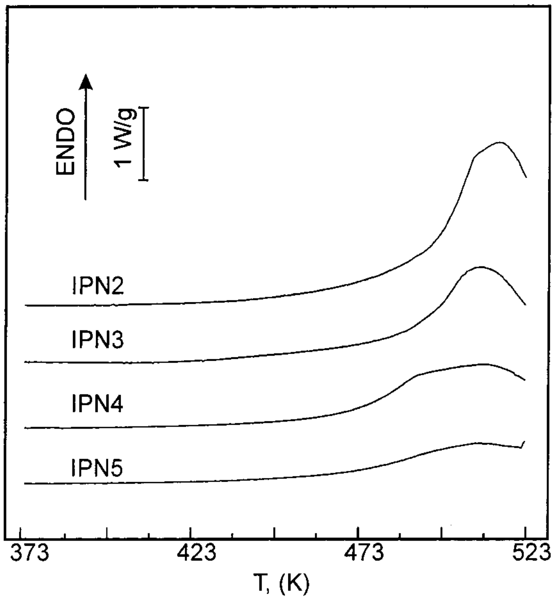

Figure 8. DSCgram traces in the region from 373 to 523 K of a series of P(MAA)/P(*N*-iPAAm) sequential IPNs.

obtain unusual S-shaped T_g curves. We do believe that the same approach may be used for glass transition temperatures of slightly cross-linked P(*N*-iPAAm-*co*-MAA) copolymers in which the interacting groups may be located in the same or different backbone. Unfortunately, we do not know the values of equilibrium constants and some other parameters needed to make these predictions for the present system.

Schneider et al.[31] have proposed an extension of the Gordon−Taylor−Wood equation for asymmetric T_g vs composition curves:

$$T_g = \frac{(W_1 T_{g1} + kW_2 T_{g2})}{W_1 + kW_2} + \frac{k(k_1 + k_2)W_1 W_2}{(W_1 + kW_2)^2} + \frac{k^2(k_2 - k_3)W_1 {W_2}^2}{(W_1 + kW_2)^3} \quad (3)$$

The first term of the right-hand side represents the contribution due to the Gordon−Taylor−Wood equation,[41,42] it represents the mixing term derived from the additive rule of entropy and/or of the volume of the copolymer. The second and third terms represent the extension for contributions of diads and triads, where k_1 characterizes the contributions of the heterodiad sequences to T_{g1} whereas k_2 and k_3 of the respective different heterotriad sequences containing either two repeating units of the first, or of the second component, respectively. However the physical characteristics of our system are not available, this equation may be useful to fit the parameters by an adjustable method. From the best fitting procedure of the experimental data to eq 3 the following values for the adjustable parameters have been obtained: $T_{g1} = 405$ K; $T_{g2} = 430$ K; $k = 1.1$; $k_1 + k_2 = -101.1$; $k_2 - k_3 = 203.9$. The full line in Figure 7 has been drawn using these parameters.

Glass Transition of Interpenetrating Networks. Figure 8 shows a series of DSCgram traces in the region from 373 to 523 K of a series of IPNs. In these DSCgrams, any traces of a glass transition temperature can be detected. Furthermore at the temperature range corresponding to the glass transition of pure cross-linked P(*N*-iPAAm) does appear any transition. At much higher temperature an endothermic peak occurs. It is related to the amount of MAA in the sample. The enthalpy involved in the process increases with increasing the MAA content in the IPNs. The lack of detection of the T_g must be due to the fact that, in general, the first degradation stage of the networks lies at temperatures below their T_gs.

It was assumed that the polymer starts to decarboxylate prior to the T_g. This fact indicates that the T_g of the IPN is higher than that of the copolymers with similar composition. It has been observed that for polymer complexes the T_g values are much higher than those of the blends. These high values of T_g have been attributed to interchain hydrogen bonds acting as promoters of physical cross-linking. Undoubtedly, the interchain amide-carboxyl interactions are less favorable in copolymers than IPN because of symmetry factors.

Conclusions

•Different types of water have been found depending on water concentration and polymer structure. For low water concentrations, the maximum temperature of the LCST depends on T_g value and consequently on the water concentration. Only the copolymer gels with a predominant *N*-iPAAm content show a calorimetric LCST transition. The temperature of the LCST maximum does not depend appreciably on the copolymer composition but a broadening is observed, specifically for the 70 mol % *N*-iPAAm gel. This is indicative of a decreasing of the swelling thermosensitivity. The enthalpy of the transition depends on the pH and increases with decreasing pH because the carboxyl groups of the MAA are not ionized. On the other hand, IPN shows temperature sensitivity under basic conditions where the hydrogen bonding between the amide from *N*-iPAAm and carboxyl from MAA structural units is broken.

•P(MAA) and their P(*N*-iPAAm-*co*-MAA) cross-linked copolymers degrade by a two-step mechanism. However, the P(*N*-iPAAm) homopolymer is more thermally stable; it degrades at higher temperatures and by an unique stage mechanism because its pendant *N*-isopropyl group minimizes side group elimination reactions. IPNs show higher thermal stability than the parent homopolymers and copolymers with similar compositions, which indicates a good degree of interpenetration.

•The T_g behavior of the P(*N*-iPAAm-*co*-MAA) copolymers as a function of composition cannot be described by simple additive models. It is much more complex showing an inversion from reduced to increased mobility of the copolymeric chain as the hydrophobic (*N*-iPAAm) content is increased. It shows a S-shaped T_g curve behavior on composition.

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