

Hydrogels based on *N*-isopropylacrylamide and methacrylic acid: thermal stability and glass transition behaviour

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Summary

The thermal stability and glass transition behaviour of crosslinked poly(*N*-isopropylacrylamide) [P(*N*-iPAAm)], poly(methacrylic acid) [P(MAA)], their random copolymers and sequential interpenetrating polymer networks (IPNs) have been investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). P(MAA) shows a two-step process of degradation. P(*N*-iPAAm) shows an unique process of degradation at higher temperature. Copolymers having higher content in *N*-iPAAm units have a lower thermal stability than their component homopolymers and show an unique degradation process at high temperature. On the contrary, enriched MAA copolymers show better stability but they exhibit two degradation steps at the main degradation region. Sequential IPN samples exhibit a better stability than their component homopolymers and copolymers. The high temperature backbone degradation occurs in only one step, which indicates the formation of a true interpenetrating network. 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 polymer networks, it seems that only one T_g occurs indicating a good compatibility and interpenetration.

Introduction

Blends or interpenetrating networks of polymers having in their structure proton donor and proton acceptor groups can interact through strong specific interactions forming interpolymer complexes in aqueous solutions. The formation of these complexes is due to a large number of hydrogen bond leading to very compact structures. Complexes between poly(acrylamide) [P(AAm)], poly(ethylen glycol) [P(EG)] and poly(acrylic acid) [P(AA)] or poly(methacrylic acid) [P(MAA)] have been widely explored [1-6]. Complexation by inter- and intra-chain interactions has been also found in the case of copolymers containing both proton donor and proton acceptor comonomers [7]

Complexes involving P(*N*-iPAAm) have been found interesting [8]. It has been pointed out that P(*N*-iPAAm)/P(AA) form very strong complexes with a very hydrophobic character strengthened by increasing temperature [8].

Very recently, complexes between *N*-isopropylacrylamide and methacrylic acid based polymers have been studied and molecular interaction between amide and carboxyl groups has been shown by means of ATR-FTIR [9] and NMR techniques [10]. Some special features due to this kind of interactions have arised great interest on these polymers and a potential use as drug delivery systems has been proposed [11].

Interactions between functional groups will exert a great influence on the thermal properties of the system. Abnormal T_g behaviour have been reported for systems interacting through strong specific interactions [12-15]. In the composition region where this type of complexes is formed, an increase of the T_g has been found [16-18]. In the same way it is expected some effect on the degradation temperature of the system. Improvement of the thermal stability has been noted [16]. In this contribution the thermal stability and glass transition behaviour of copolymers and IPNs based on *N*-iPAAm and MAA are studied and related to the hydrogen bonding between the amide group of the *N*-iPAAm and the carboxyl group of the MAA.

Materials and Methods

Materials

N-isopropylacrylamide (*N*-iPAAm) (Acros Organics, New Jersey, USA) 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). Deionized water from a Millipore Milli-U10 water purification facility was used where appropriate.

Synthesis

Synthesis of P(MAA), P(*N*-iPAAm) homopolymers, P(*N*-iPAAm-*co*-MAA) copolymers and [P(*N*-iPAAm)]/[P(MAA)] IPNs with a 0.25 % mol of cross-linking agent TEGDMA has been described in detail elsewhere [10]. Polymer composition is displayed 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 5-8 mg weight being 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.

Differential scanning calorimetry (DSC)

DSC measurements were carried out under a blanket of N₂ with a Mettler-Toledo TA8000 connected to a cooling system. Glass transition temperatures T_g s of the dried homopolymers, copolymer gels, IPNs and their plasticized systems were investigated by DSC. The samples were prepared according to the following procedure. Polymer disks of pre-established dimensions were cut from water swelled gel. These disks were vacuum dried (10⁻³ mm Hg) at 333 K for 12 hours. They were used for T_g determination as described below. However, for the preparation of samples of plasticized systems, a mixture of EG + H₂O of known concentration was added to the dried sample in open aluminium 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 + H₂O mixture. Subsequently, the specimen in the open pan was vacuum dried (10⁻³ mm Hg) at 333 K for 12 hours. The ratio of the EG in the samples was estimated by weighting before swelling 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 up from room temperature to 453 K at a $R_H = 20 \text{ K.min}^{-1}$. Then the sample was immediately cooled down to 233 K at a $R_C = 30 \text{ K.min}^{-1}$ and as in the second run the sample was heated up 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 criterium of T_g at $\Delta C_p/2$ was adopted.

¹H-NMR measurements

Solution ¹H spectra were recorded in a Varian INOVA 400 MHz spectrometer using a solution of NaOH in D₂O. Chemical shift was assigned using the solvent signal as internal standard.

Result and discussion

Thermogravimetric analysis

The TGA first derivative of P(*N*-iPAAm), P(MAA) homopolymers and their copolymers has been plotted in Figure 1 and parameters derived from them are collected in Table 1. The P(MAA) synthesised in this study by radical polymerization, is mostly syndiotactic with a 73 % of rr and a 27 % of mr triads content [10]. Its degradation behavior is in agreement with that of a syndiotactic P(MAA) reported by Lazzari et al. [19] As shown in Figure 1, P(MAA) degrades in a two-step process. After the first elimination of water between pairs of carboxylic groups to form anhydride structures, the resulting material has a higher thermal stability. Nevertheless, P(*N*-iPAAm) is only relatively more thermally stable than P(MAA) if

the first loss step of P(MAA) is not taken into account. In this Figure 1, it is seen that if we exclude the P(*N*-iPAAm) homopolymer, all the other specimens show the wide peak 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. The second peak at higher temperature, corresponding to the backbone decomposition, starts to resolve into two peaks for 50/50 sample, increases for 30/70 and for 15/85, the left side peak moves toward the other. It is noteworthy to mention that the thermal stability of copolymers with less MAA content is lower than those of the component homopolymers.

A physical mixture of P(*N*-iPAAm) and P(MAA) has been prepared for comparative purposes. Figure 2 illustrates the thermal degradation of a copolymer, IPN5 and the physical mixture having 30 % wt of P(*N*-iPAAm).

The samples with similar composition present different thermal stabilities. As it is very easily seen in the case of the physical mixture, the degradation takes place in three very well defined steps. We assumed that the first one is due to anhydride formation, the second one to the P(*N*-iPAAm) degradation and the third and also the highest to the degradation of the poly methacrylic anhydride [P(MAN)]. These two peaks appearing at higher temperature were assigned by taking into account the fact that the MAA is the major component in the mixture. The IPN has a higher thermal stability than the copolymer and also higher than the homopolymers. Its high temperature backbone degradation occurs only in one step, which indicates the formation of a true interpenetrating network between both polymers.

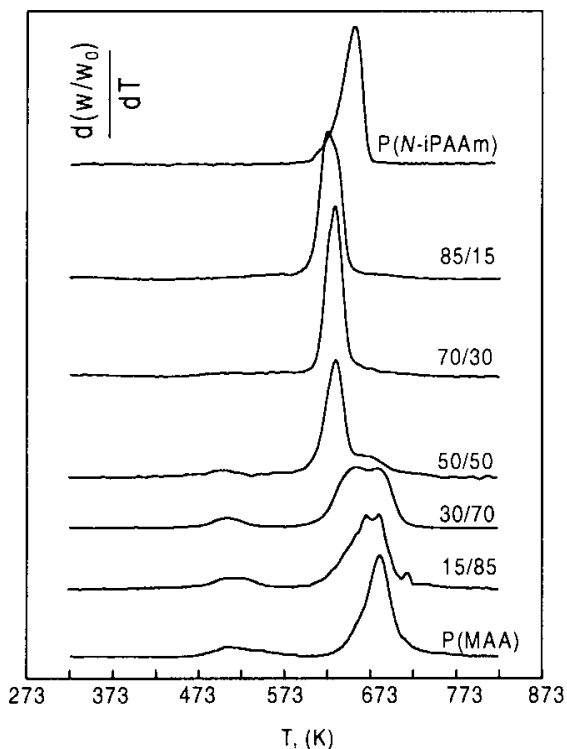


Figure 1. TGA first derivative as a function of temperature of a series of P(*N*-iPAAm-co-MAA) copolymers and their homopolymers P(MAA) and P(*N*-iPAAm)

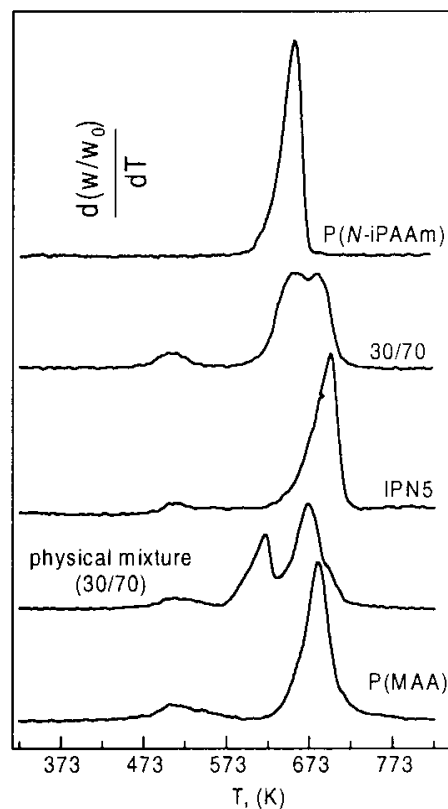


Figure 2. TGA first derivative as a function of temperature of poly(methacrylic acid) [P(MAA)]; a physical mixture (30/70) of P(MAA) and P(*N*-isopropylacrylamide) [P(*N*-iPAAm)]; a sequential interpenetrating polymer network of P(MAA) and P(*N*-iPAAm); a 30/70 P(*N*-iPAAm-co-MAA) copolymer and a P(*N*-iPAAm) homopolymer. Physical mixture, IPN and copolymer have the same molar composition.

Table 1. Thermogravimetric Analysis Parameters of the Xerogels: T_{in} , temperature of initial degradation, T_I , T_{II} , $T_{III,max}$, maxima temperature of the first, second and third step of degradation. $[W_I/(W_{total})] \cdot 100$, relation between the first weight loss (W_I), and the whole weight loss (W_{total})

Sample	P(<i>N</i> -iPAAm) (%mol)	T_{in} (K)	$T_{I,max}$ (K)	$T_{II,max}$ (K)	$T_{III,max}$ (K)	$(W_I/W_{total})100$
P(<i>N</i> -iPAAm)	100	-	-	649	-	-
P(<i>N</i> -iPAAm- <i>co</i> -MAA) 85/15	82.6	-	500	622	-	-
P(<i>N</i> -iPAAm- <i>co</i> -MAA) 70/30	66.7	468	500	630	-	3.0
P(<i>N</i> -iPAAm- <i>co</i> -MAA) 50/50	50.5	472	503	631	677	7.5
P(<i>N</i> -iPAAm- <i>co</i> -MAA) 30/70	32.4	479	512	652	684	12.3
P(<i>N</i> -iPAAm- <i>co</i> -MAA) 15/85	15.4	482	509-513	665	684	15.1
P(MAA)	0	473	512	685	-	15.4
IPN5	30.2	488	512	701	-	6.3
IPN3	15.4	481	512	712	-	10.1

¹H spectra of IPN under strong basic conditions

An important thermal characteristic of pure P(*N*-iPAAm) is its Lower Critical Solution Temperature (LCST) in water solutions. That 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 [20] or demixing transition [21]. The LCST is mainly due to the rupture of an ordered structure of water molecules surrounding hydrophobic *N*-isopropyl groups. It has been explained by the hydrophobic/hydrophilic balance of the side groups on the polymer chains, which leads to rapid dehydration of the polymer as the temperature is increased above the LCST.

Copolymers with high *N*-iPAAm content preserve the LCST transition and the magnitude of the process increases in acidic medium. However IPNs display a very low swelling degree in water and loose the LCST transition. These characteristics have been attributed to the association between the complementary binding sites of P(MAA) and P(*N*-iPAAm) leading to hydrophobic complexes.

If the suppression of the LCST is due to the hydrogen bond formation, the disruption of the complexes when the pH of the medium is increased, will produce the recovering of the original LCST character to the P(*N*-iPAAm). In strongly basic media, hydrogen bonds are broken and the P(*N*-iPAAm) network recovers their primitive thermosensitivity. LCST is shown by NMR as a sudden decrease in the mobility of the polymer chains, leading to a less resolved spectrum with weaker and broader signals [10]. Figure 3 displays ¹H-NMR spectra recorded in the swollen state of the P(MAA)/P(*N*-iPAAm) IPN5 in a deuterated aqueous solution of pH = 11 at 293 and 310 K, respectively. At 293 K the proton signals corresponding to both homopolymers can be observed. On the contrary, at 310 K, a temperature above the LCST transition, the proton signals from the P(*N*-iPAAm) disappear due to an abrupt fall of the mobility. However, P(MAA) signals do not seem to be affected by the transition, as at this high pH P(MAA) is released from its hydrogen bond interaction with P(*N*-iPAAm).

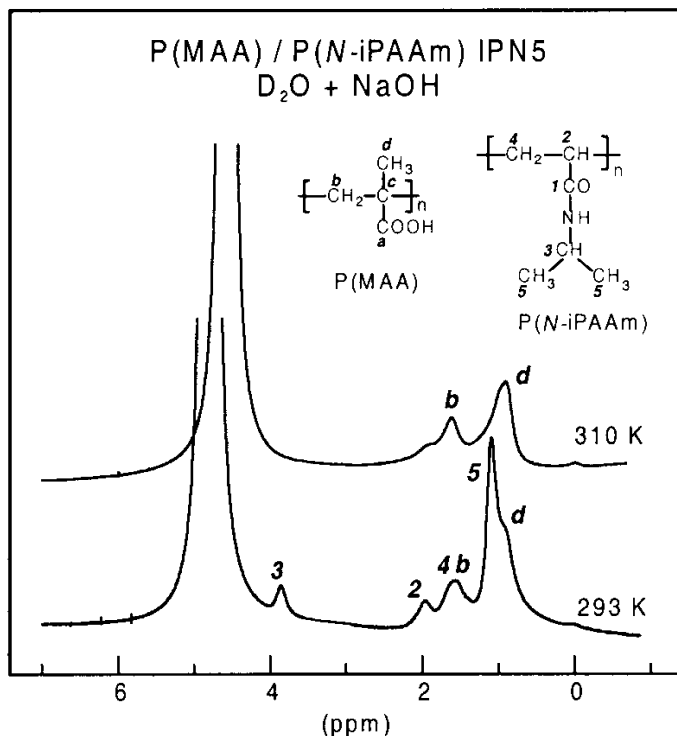


Figure 3. $^1\text{H-NMR}$ spectrum of a sequential poly(methacrylic acid)/poly(*N*-isopropylacrylamide) P(MAA)/P(*N*-iPAAm) IPN in a deuterated solution of pH = 11, at 293 and 310 K.

Glass Transition

A useful method to understand the interactions of these copolymers is the determination of T_g as a function of composition. 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 the glass transition temperatures of P(MAA) and some of its MAA high content P(*N*-iPAAm-*co*-MAA) copolymers. Ethylene glycol (EG) has been used as an excellent plasticizer because it has an elevated vapour pressure and because of its solvating effect on these hydrophilic copolymers. The relationship between the EG concentration and the T_g of the plasticized polymer may be described very simply by the well-known Gordon-Taylor-Wood's equation [22,23]:

$$T_g = \frac{(W_1 T_{g1} + k W_2 T_{g2})}{W_1 + k W_2} \quad (1)$$

where T_{g1} and T_{g2} are the glass transitions of the plasticizer and the polymer, respectively; k is a constant which is a function of the thermal expansion coefficients, namely, $k = (\alpha_2' - \alpha_2^s) / (\alpha_1' - \alpha_1^s)$, W_1 and W_2 are weight fractions of plasticizer and polymer, respectively. This equation may be arranged to an alternative form as,

$$T_g = T_{g2} - (1/k) \cdot (T_g - T_{g2}) \cdot (W_1/W_2) \quad (2)$$

Therefore, it should give the value for T_{g2} when the weight fraction of the plasticizer falls to zero. In Figure 4 a series of values of T_g against $(T_g - T_{gEG}) \cdot (W_{EG} / W_{polymer})$ for the P(*N*-iPAAm-*co*-MAA)/EG system have been plotted according to the Gordon-Taylor-Wood's equation [22,23]. From such a plot and assuming a value of 154 K for the glass transition temperature of the ethylene glycol [24], values of T_{g2} and k have been obtained.

The glass transition values of copolymer xerogels measured directly and extrapolated, both determined by DSC are presented in Figure 5 as a function of *N*-iPAAm content. The T_g of P(*N*-iPAAm) is around 404 K according to the value found by Sousa et al. [25] of 408 K, however Kuckling et al. [26,27] gave a slightly higher value.

The crosslinked copolymers show a single T_g indicating the formation of random copolymers. A great deviation from the linear dependence of the T_g with the composition can be appreciated for all the copolymers. Keeping in mind that the samples were synthesised in the same conditions, namely, temperature, solvent and crosslinker concentration, the changes in the T_g s must be attributed to polymer-polymer interactions. In general, for polymer blends, deviations from linear dependence have to be considered as a measure of the strength of the interactions [28,29]. In our case, the unexpected S-shaped T_g -composition curve, for instance, could be interpreted in term of the hydrophilic and hydrophobic interactions. Thus in the case of miscible polymer blends S-shaped behaviour has been interpreted in terms of different types of polar interactions [12,13]. Similar effects on glass transition temperature vs composition have been also observed not only in blends of polymers but also in acrylic copolymers with electron acceptor and electron donor groups interactions [14,15].

From the qualitative point of view, having a look at Figure 5, 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. Secondly, 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 smooth dependence on composition. In fact, this effect must be due not only to the change in composition but to a change in the hydrogen bond interactions. This suggests an inversion of the hydrogen bond interactions in the copolymers.

In random copolymers it is observed that the glass transition depends on the microstructure, so on the overall composition of the copolymer. Schneider et al. [30] have proposed an extension of the Gordon-Taylor-Wood's 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 [22,23], 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 characterises the contributions of the hetero-diad sequences to T_{g1} whereas k_2 and k_3 of the respective different hetero-triad sequences containing either two repeating units of the first, or of the second component, respectively. Although 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 and taking $T_{g1} = 404$ K; $T_{g2} = 431$ K from the experimental T_g s of P(*N*-iPAAm) and P(MAA), the following values for the adjustable parameters have been obtained: $k = 1.1$; $k_1 + k_2 = -103.5$; $k_2 - k_3 = 228.6$. However these values should be considered as orientative, due to small number of points employed in the fitting procedure. But it should be considered the difficulty of the T_g measurement for these copolymers. The full line in Figure 5 has been drawn using these parameters.

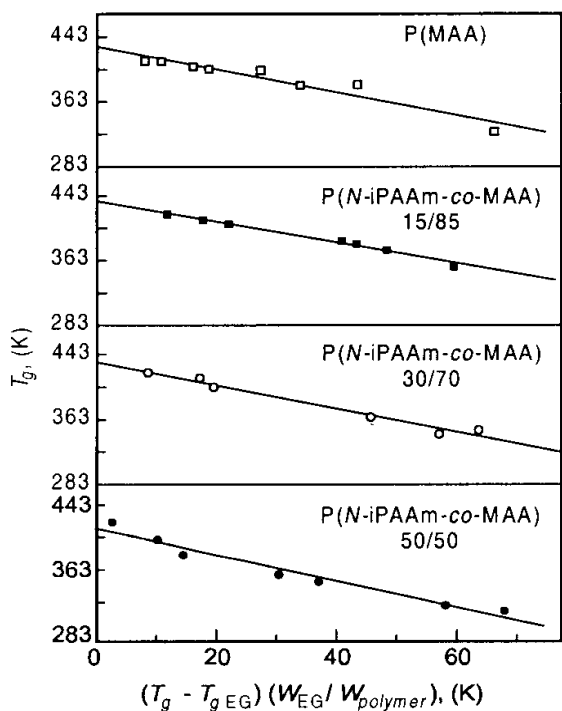


Figure 4. The effect of ethylene glycol (EG) on the T_g . Plots of the glass transition temperatures for the plasticized P(MAA) and a series P(*N*-iPAAm-*co*-MAA) copolymers according to the Gordon-Taylor-Wood's equation.

Conclusions

Hydrogen bonding between amide and carboxyl groups exerts strong influence on the thermal properties of the P(*N*-iPAAm-*co*-MAA) and [P(MAA)]/[P(*N*-iPAAm)] IPNs. Copolymers with higher MAA content exhibit relative higher thermal stability than enriched *N*-iPAAm copolymers, if the low degradation temperature is not taken into account. However IPNs exhibit the highest thermal stability interpreted on the bases of the formation of inter-polymer complexes between complementary chains. These complexes may present higher thermal stability than a simple mixture of both polymers.

The behaviour of the glass transition temperature as function of composition for copolymers can not be explained from the additive model. It presents a S-shape characteristic of systems with strong specific interactions

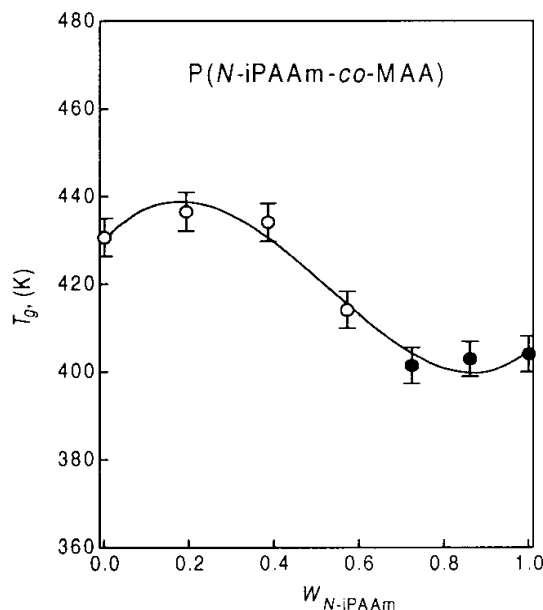


Figure 5. Plot of the glass transition temperatures of P(MAA), P(*N*-iPAAm) and their copolymers as a function of composition.

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