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Radiation synthesis of a thermo-pH responsive binary graft copolymer (PP-g-DMAEMA)-g-NIPAAm by a two step method

H. Iván Meléndez-Ortiz, Emilio Bucio (✉)

Departamento de Química de Radiaciones y Radioquímica, Instituto de Ciencias Nucleares,
Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria,
04510 México D.F.
E-mail: ebucio@nucleares.unam.mx

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Summary

(PP-g-DMAEMA)-g-NIPAAm was synthesized using gamma radiation from a ^{60}Co source. Graft polymerization of N,N'-dimethylaminoethylmethacrylate (DMAEMA) onto polypropylene (PP) was accomplished in about 100 percent yield by the mutual irradiation technique at a dose of 10 kGy. Grafting of N-isopropylacrylamide (NIPAAm) onto PP-g-DMAEMA was carried out by the pre-irradiation method with doses from 20 to 100 kGy. The influence of temperature, reaction time, and monomer concentration on grafting yield was studied. Grafting processes were confirmed by infrared spectroscopy (FTIR-ATR). (PP-g-DMAEMA)-g-NIPAAm films were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The lower critical solution temperature (LCST) and critical pH point of the films were obtained by water contact angle and percent swelling measurements. The LCST was also determined by DSC. We report here hare a new binary graft copolymer which shows two LCST values, synthesized in two steps.

Introduction

A material is classified as "smart" if it possesses an intrinsic ability to sense and respond to external stimuli in a predictable fashion. This response typically manifests itself as an abrupt and pronounced change in the physical properties of the materials. The ability to control the structure and hence the function of materials by application of an external stimulus forms the technological basis of pharmaceutical and biotechnological applications [1-3]. Temperature and pH stimuli have been considerably investigated because they are relatively convenient and effective in many applications [4-7]. One property of temperature-responsive polymers is the presence of a lower critical solution temperature (LCST), at which the polymer undergoes a sharp phase transition due to aggregation of hydrophobic groups to give a turbid solution [8]. To date, most effort toward the development of such "smart" materials has focused on stimulus-responsive copolymers [9-15]. They have potential to obtain sensitive materials which are required for advanced applications such controlled drug release [16-18], immobilization of enzymes [19], in separation processes [20-21], sensitive coatings [22-23], catalysis [24], controlled cell detachment [25], etc. On the one hand, it is well-known that poly(N,N’-dimethylaminoethylmethacrylate), P(DMAEMA) is a cationic polyelectrolyte, and it has been shown to be both temperature and pH sensitive [26-28]. Previous studies have shown that the critical pH point is close to the pKa [29]. P(DMAEMA) has a pKa of about 7.0 in pure water which is close to the physiological pH [30]. Also, it has a LCST in water. Various values have been reported for the phase transition temperature of P(DMAEMA) in aqueous media, and they fall in the wide range of 38-50 ºC depending on the molecular weight, pH, and salt concentration [31-32]. Below pH 7.0, P(DMAEMA) is soluble over a wide range of temperatures as a cationic polyelectrolyte because of the protonation of the tertiary amine group. These special properties of P(DMAEMA) based copolymers have been extensively used in the fields of biomaterials and gene delivery systems [33-35]. On the other hand, poly(N-isopropylacrylamide), P(NIPAAm) is a thermoresponsive polymer which shows a LCST at around 32°C [36-38]. Hence, this polymer has a potential application as a sensor in humans, as well as in size-selective separation processes involving materials which can be denatured at high temperatures [39]. Finally, it is noted that radiation graft copolymerization is a well established technique for the modification of polymers [40]. Polypropylene, (PP) is a hydrophobic polymer which has good thermal stability and shows good mechanical properties [41]. P(DMAEMA) and P(NIPAAm) do not show these properties, so preliminary graft of these polymers onto PP is of interest [23, 42].

Experimental

Synthesis of (PP-g-DMAEMA)-g-NIPAAm.

Isotactic PP films (from PEMEX, Mexico), 60 μm thickness and 1 x 5 cm in size were previously washed with methanol for 24 h and then dried under reduced pressure. DMAEMA and NIPAAm were purchased from Aldrich Co, USA. DMAEMA was distilled under reduced pressure; NIPAAm was recrystallized from a solution of hexane/ toluene (1/1, v/v).

PP-g-DMAEMA was synthesized placing a PP film in a glass ampoule (previously weighed) in a solution of DMAEMA/toluene (1/1, v/v). The ampoule was degassed by repeated freeze-thaw cycles, sealed and then irradiated with a ^{60}Co γ source (Gamma Beam 651 PT, Nordion International) at an irradiation dose of 10 kGy and a dose rate of 12 kGyh^{-1}. The grafted film was extracted with toluene and then dried under reduced pressure. Grafting yield (Y_g) was calculated by the equation:

Y_g (%) = $100[(W_g - W_0)/W_0]$ (Equation 1), where W_g and W_0 are the weights of the grafted and initial films, respectively.

Grafting of NIPAAm onto PP-g-DMAEMA was carried out by the two step pre-irradiation method. PP-g-DMAEMA films (previously weighed) were placed individually in glass ampoules and then were irradiated in the presence of air at an irradiation dose between 20 and 100 kGy, and at dose rate of 12 kGyh^{-1}. A NIPAAm 1 molL^{-1} aqueous solution was added, and then the solution was deaerated by bubbling argon during 15 min, and the ampoules were sealed. Then they were heated in a water bath at 60°C for 5 hours. After heating the grafted films were washed with water for 24 h to extract the residual monomer and P(NIPAAm) formed. Grafting yield (Y_g) was calculated by the equation 1.

Characterization

FTIR-ATR (attenuated total reflection) spectra were obtained using a Perkin-Elmer Paragon 500 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT).

For determination of equilibrium water absorbency, the graft copolymers were immersed into distilled water for various periods of time. It was found that equilibrium water absorbency is achieved after 2 h. The critical pH point was found by measurement of percent swelling for the copolymer films. Weighted film samples were placed in citric acid/Na_2HPO_4buffer solutions of pH values from 2 to 9 for 2 h, and the percent weight increase was determined and is reported as percent swelling. The LCST was determined by placing copolymer films into a vial containing distillated water in a temperature controlled bath in a range from 25 to 50 ºC for 2 h. To determinate gravimetrically the equilibrium water absorbency, the surface of the copolymer film was wiped with filter paper in order to remove the free water and then the swollen samples were weighed. Swelling percent was determined by the equation:

Swelling (%) = $100[(W_s - W_d) / W_d]$ (Equation 2), where W_s and W_d are weights of the swollen and initial films respectively.

Contact angles were measured with a Contact Angle Measuring System DSA 100. Decomposition temperatures were determined under nitrogen using a TGA Q50 (TA Instruments, New Castle, DE). Differential Scanning Calorimetry results were obtained under nitrogen using a DSC 2010 calorimeter (TA Instruments, USA) at heating range of 10 ºCmin^{-1} with sample weights of about 5 mg. In order to examine temperature-sensitive behavior, LCST was determined by DSC. Equilibrium swollen graft copolymer samples with weights of 20-30 mg were sealed in hermetic sample pans. The analysis was performed in the temperature range between -10 and 50 ºC with a heating rate of 1 ºC min $^{-1}$ and nitrogen flow rate of 60 mLmin^{-1}.

Results and Discussions

Synthesis of (PP-g-DMAEMA)-g-NIPAAm.

PP-g-DMAEMA was first synthesized at an irradiation dose of 10 kGy and a DMAEMA/ toluene ratio of (1/1, v/v) [10]. A grafting yield around 100 % was obtained. Figure 1 shows the effect of irradiation dose on grafting yield of NIPAAm onto PP-g-DMAEMA. The graph shows that as irradiation dose rises the grafting yield increases. It also indicates that there is no a significant dependence on grafting yield when the content of DMAEMA is decreased on PP-g-DMAEMA.

The grafting yield as a function of reaction time and temperature for PP-g-DMAEMA pre-irradiated samples at 100 kGy and reacted in a 1 molL^{-1} NIPAAm aqueous solution is shown in Fig. 2. An increase of temperature results in decomposition of peroxides and hydroperoxides formed in PP-g-DMAEMA during irradiation and also results in an increase of monomer diffusion in the film; therefore grafting yield increases would be expected when the temperature is raised. However, Fig. 2 clearly shows that grafting is more effective at 60 than at 70°C. Above 60 ºC the radicals formed in the bulk could have decayed due to mutual recombination before grafting took place. This would explain a grafting rate decrease at the higher temperature. Also, when the reaction temperature is increased from 60 to 70 ºC the grafting yield might have decreased because of a stronger homopolymerization of NIPAAm.

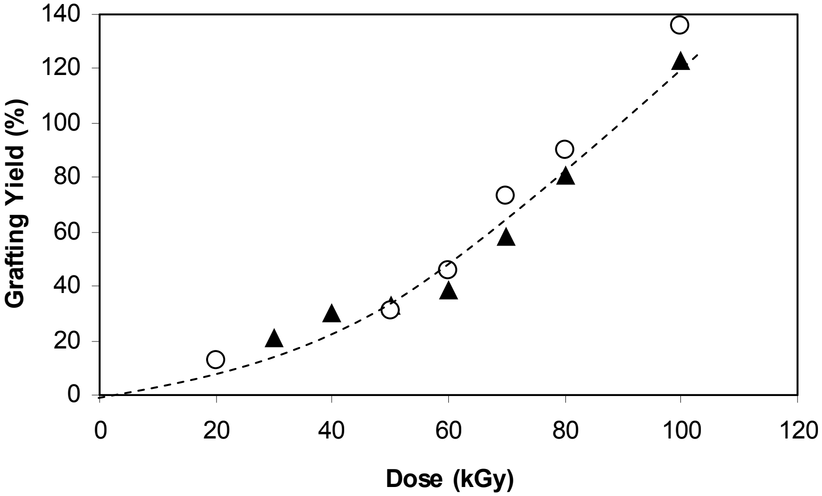

Figure 1. Effect of irradiation dose on the grafting yield of NIPAAm onto pre-irradiated PP-g-DMAEMA 50 % graft (○), and PP-g-DMAEMA 100% graft (▲). Reaction time 5h, graft temperature 60°C, and NIPAAm concentration 1 molL^{-1}.

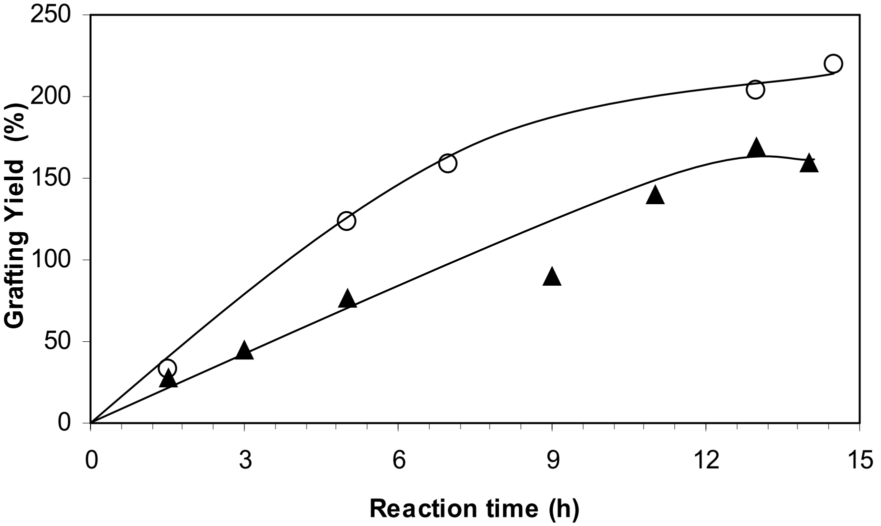

Figure 2. Evolution of the grafting yield of P(NIPAAm) onto pre-irradiated PP-g-DMAEMA 100% graft for increasing reaction times at 60 ºC (○) and 70 ºC (▲); pre-irradiation dose 100 kGy and NIPAAm concentration 1 molL^{-1}.

The effect of NIPAAm concentration on the grafting yield at 60 ºC and reaction time of 5 h was examined. The data plotted in Figure 3 showed that grafting yield rises dramatically when NIPAAm concentration is increased at 1 molL^{-1}.

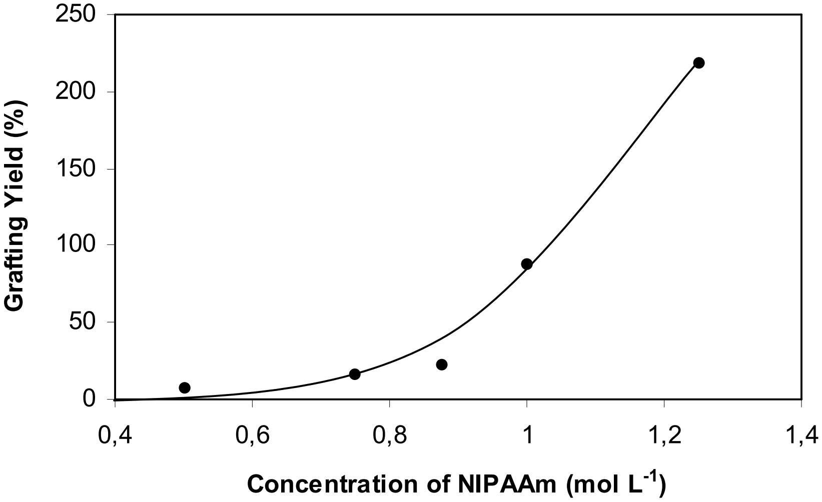

Figure 3. Dependence of the grafting yield of P(NIPAAm) onto pre-irradiated PP-g-DMAEMA 100% graft for increasing concentration of monomer. Pre-irradiation dose 100 kGy, graft temperature 60°C, and reaction time 5h.

Characterization

The grafting of DMAEMA and NIPAAm onto PP films was confirmed by FTIR-ATR. Figure 4 shows the spectra of PP film which exhibited signals at 1373 and 1450 cm^{-1} due to symmetrical and asymmetrical bending vibrations of CH_3 groups respectively. Also it showed stretching vibrations at 2914 and 2837 cm^{-1} for CH_2 groups; DMAEMA with a band at 1715 cm^{-1} due to the C=O group and a signal at

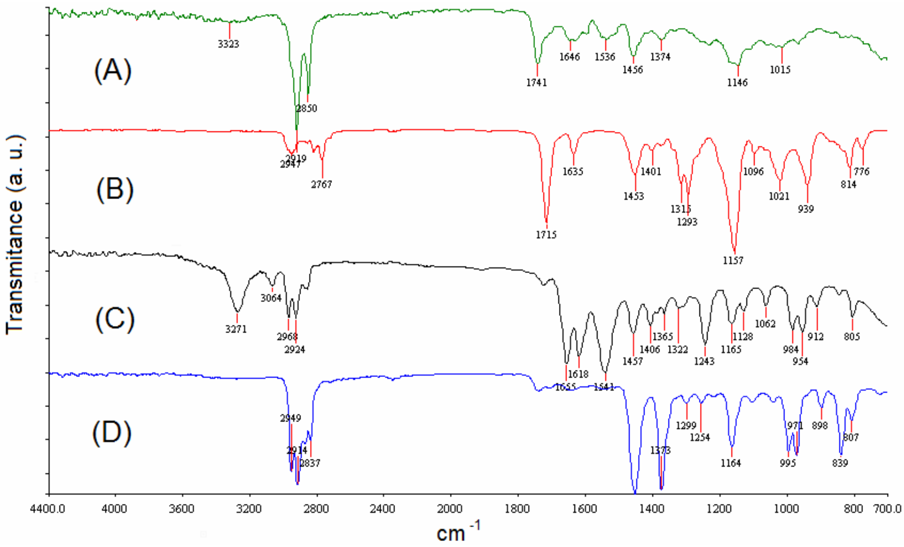

Figure 4. FTIR-ATR spectra of (PP-g-DMAEMA 215 %)-g-NIPAAm 16 % (A), DMAEMA (B), NIPAAm (C), and PP film (D).

1157 cm^{-1} attributed to the stretching vibration of C-C(=O)-O; NIPAAm showed a signal due to the C=O group at 1655 cm^{-1}, a band at 3271 cm^{-1} for the stretching vibration of the N-H group and a strong signal at 1541 cm^{-1} for the bending vibration N-H. Finally, PP-g-DMAEMA-g-NIPAAm film exhibited peaks around 1741 cm^{-1} (C=O from DMAEMA), 1646 cm^{-1} (C=O from NIPAAm), stretching vibrations due to N-H at 3323 cm^{-1} and a characteristic absorption for secondary amides at 1536 cm^{-1} corresponding to bending vibrations of N-H groups. These bands confirmed the binary graft copolymerization [43-45].

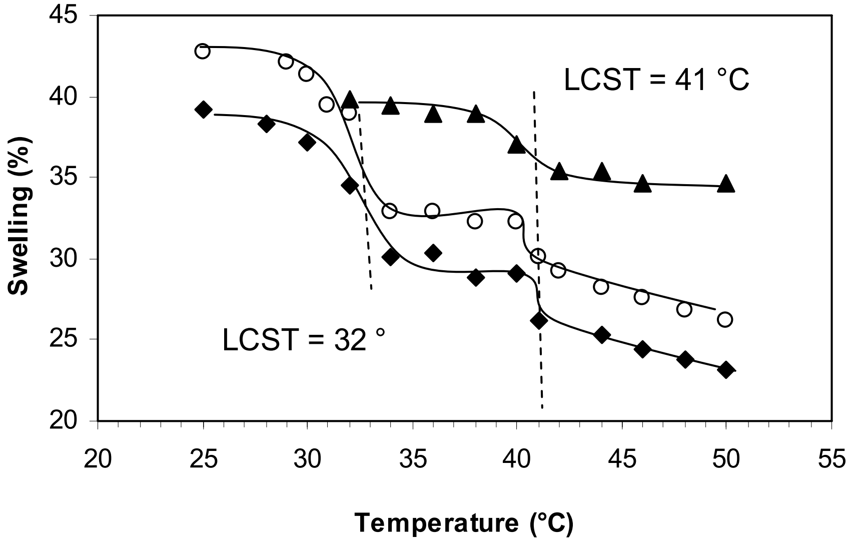

Figure 5. Swelling percent as a function of temperature of PP-g-DMAEMA 133% (▲), PP-g-DMAEMA)-g-NIPAAm 238 % (○), and (PP-g-DMAEMA)-g-NIPAAm 370 % (♦).

Figure 5 shows the temperature-dependent swelling percent of PP-g-DMAEMA and (PP-g-DMAEMA)-g-NIPAAm with a graft percentage of DMAEMA of about 100 percent, and two different graft percentages of NIPAAm in a temperature range of 20–50 ºC in distilled water at neutral pH. The graph indicates that as the temperature is increased, the percent swelling decreased. For (PP-g-DMAEMA)-g-NIPAAm, a drastic decrease at 32 ºC is observed as the LCST of P(NIPAAm) is reached; however, a second smaller change also occurs at 41 ºC, and it is attributed to the LCST of P(DMAEMA). Usually, the main reason for this behavior can be attributed to structural changes in the copolymer. At temperatures below the LCST chains have a coil structure, and the hydrophilic groups of the copolymer form hydrogen bonds with water molecules. When the temperature is raised above the LCST, chains have a globular structure and hydrogen bonds are formed between hydrophilic groups, which cause a release of water molecules and a decrease in the percent swelling.

Figure 6 shows the contact angle of water as a function of temperature at pH 7. The two LCST values determined for the binary graft copolymer surface, by the variations of the contact angle formed by a water drop at temperatures ranging from 27 to 52°C, were found to be 30°C for P(NIPAAm) and 40 ºC due to P(DMAEMA). When the temperature is raised above each of the LCST values, the binary graft copolymer surface becomes more hydrophobic and an increase of the contact angle is observed. These LCST values are similar to those determined from swelling measurements. The LCST was examined by DSC. Figure 7 shows the DSC thermogram for (PP-g-DMAEMA)-g-NIPAAm. It exhibited an endothermic peak at 31 ºC which corresponds to LCST of P(NIPAAm).This value is in accord with those obtained by swelling and water contact angle measurements. The DSC thermogram did not show an expected endothermic peak around 40°C due to LCST of P(DMAEMA) even though this behavior was observed by measurements of swelling and water contact angle.

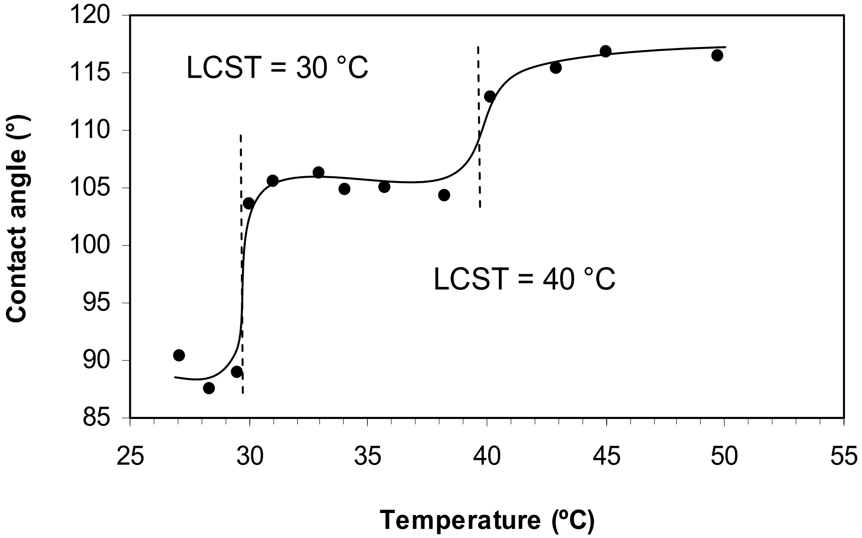

Figure 6. Influence of temperature on contact angle of water for (PP-g-DMAEMA, 66%)-g-NIPAAm 73% at pH 7.

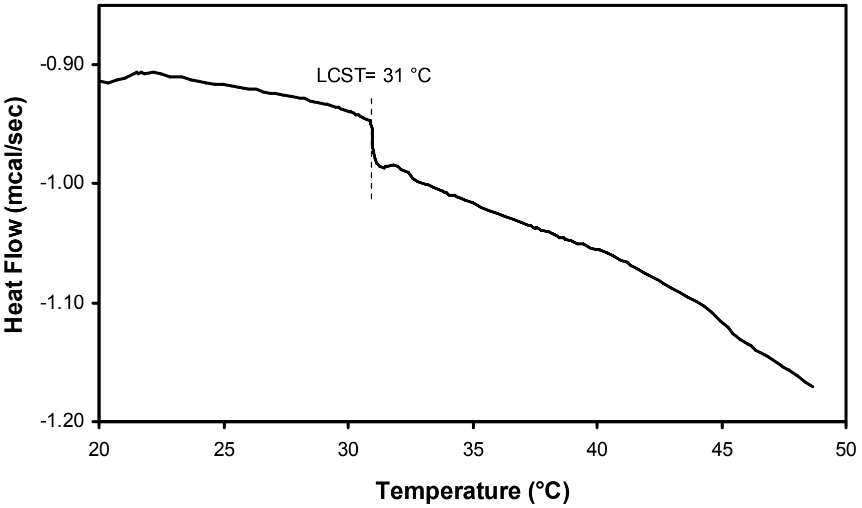

Figure 7. DSC thermogram of (PP-g-DMAEMA 87 %)-g-NIPAAm 28 %, with water at a heating rate of 1°Cmin^{-1} from -10 to 50°C.

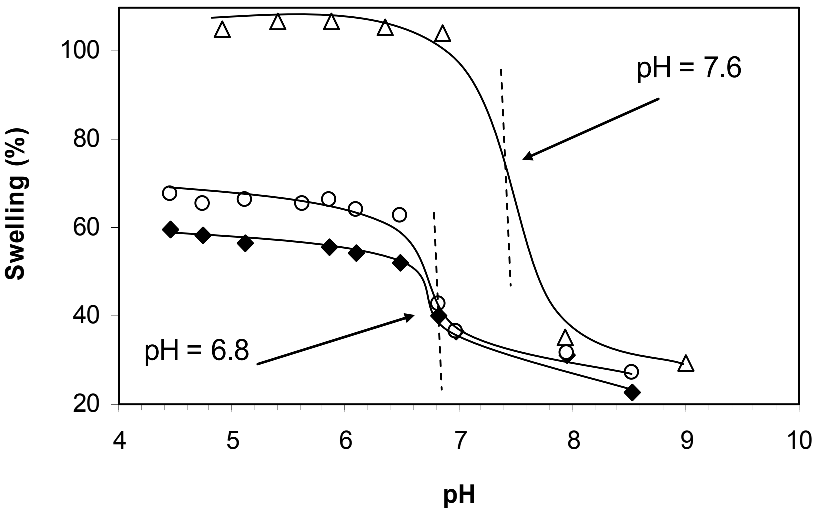

Figure 8. Swelling % as a function of pH of PP-g-DMAEMA 140 % (Δ), (PP-g-DMAEMA)-g-NIPAAm 240 % (♦), and PP-g-DMAEMA)-g-NIPAAm 81 % (○) at room temperature.

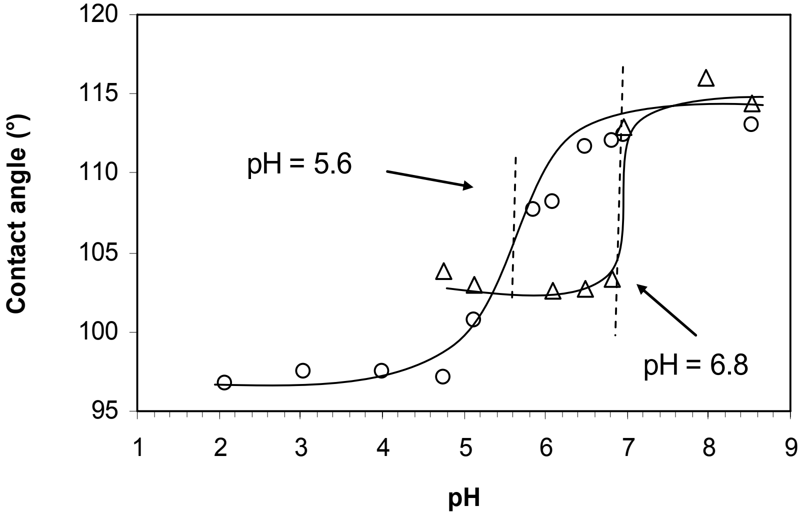

Figure 9. Effect of solution pH on contact angle of water for PP-g-DMAEMA 69 % (Δ), and (PP-g-DMAEMA, 61%)-g-NIPAAm 30% (○) at room temperature.

Figure 8 shows the swelling behavior for PP-g-DMAEMA, and (PP-g-DMAEMA)-g-NIPAAm films containing various graft percentages of NIPAAm plotted as a function of pH. The swelling percent for PP-g-DMAEMA changes dramatically at pH 7.6. This value is in accord with those reported in the literature [46-47]. When pH value is lower than 7.6, the tertiary amine moieties of the P(DMAEMA) are protonated and

solvated by water molecules. On the other hand, when pH is increased further than 7.6 amine moieties are deprotoned which permit the formation of hydrogen bond between them that cause a less exposition to water molecules decreasing the swelling %. (PP-g-DMAEMA)-g-NIPAAm exhibited a critical pH at 6.8. A percent swelling decrease is observed by comparing with PP-g-DMAEMA. This is because there are hydrogen bond interactions through amine groups of P(DMAEMA) chains and amide moieties of PNIPAAm chains which causes a less exposition to water molecules. Also, as can be seen in the Fig. 7, binary graft copolymer showed a lower critical pH point than PP-g-DMAEMA. This shift could be explained due a hydrophobic contribution of NIPAAm [48]. For a polybase, as hydrophobicity increases, a minor degree of ionization is required to enable the transition; therefore, the transition pH will be lowered. These results were confirmed by measuring water contact angle (Fig. 9).
The thermal properties of these polymers are summarized in Table 1. Glass transition temperatures (T_g) were easily determined by DSC. The thermal stability data (10% wt loss) for the modified PP are as expected: ungrafted PP was 428°C, PP-g-DMAEMA was 321°C and (PP-g-DMAEMA)-g-NIPAAm was 319°C which indicates that the good stability of PP films is conserved. A melting point, T_m, due to PP was observed for both PP-g-DMAEMA and (PP-g-DMAEMA)-g-NIPAAm. This could indicate that the graft process occurs mainly on an amorphous region of PP.

Table 1. Thermal Properties of Polypropylene and modified Polypropilenes

Sample	TGA (°C) (10%wt loss)*	% Char Yield (600°C)*	T_g (°C) (1st heating)*	T_m (°C) (1st heating)*
PP film	428	1.26		170.4
PDMAEMA	318	6.88		
PNIPAAm	367	1.58	86.8	
PP-g-DMAEMA	321	3.49	128.5	170.9
(PP-g-DMAEMA)-g-NIPAAm	319	2.70	131.9	168.2

* measured at 10°Cmin^{-1} under nitrogen

Conclusions

(PP-g-DMAEMA)-g-NIPAAm films were prepared by a two step method by using a mutual irradiation technique to graft DMAEMA onto PP films and a pre-irradiation method to graft NIPAAm onto PP-g-DMAEMA. FTIR-ATR confirmed the graft of DMAEMA and NIPAAm. It was observed that the grafting efficiency of NIPAAm onto PP-g-DMAEMA increased with the pre-irradiation dose, reaction time, and monomer concentration whereas the grafting yield decreased when the temperature was increased. The binary graft copolymer films exhibited good mechanical properties. The LCST and pH critical point were conserved on PP-g-DMAEMA and (PP-g-DMAEMA)-g-NIPAAm films. This last one showed two LCST's due to P(NIPAAm) and P(DMAEMA) at 32 and 40 ºC respectively.

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