Polymer Bulletin 60, 79–87 (2008)
DOI 10.1007/s00289-007-0827-0

Polymer Bulletin

Thermo and pH Sensitive Copolymer Based on Acrylic Acid and N-Isopropylacrylamide Grafted onto Polypropylene

Yessica S. Ramírez-Fuentes, Emilio Bucio (✉), and Guillermina Burillo

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

Received: 9 April 2007 / Revised version: 26 June 2007 / Accepted: 17 August 2007

Summary

Binary graft copolymerization of pH sensitive of acrylic acid (AAc) and thermosensitive N-isopropylacrylamide (NIPAAm) monomers onto polypropylene films (PP), was carried out by two step method, and their pH and thermal sensitivity were studied. Graft polymerization of AAc onto PP was carried out by a pre-irradiation oxidative method using a ^{60}Co gamma radiation source (Gammabeam 651-PT, Nordion International Inc.) NIPAAm was grafted onto PP-g-AAc a second step. The influence of synthesis conditions, such as pre-irradiation dose, reaction time, monomer concentration, and reaction temperature was studied. The PP samples grafted with the binary monomers were characterized with thermogravimetric analysis and differential scanning calorimetry. The lower critical solution temperature (LCST) and pH critical were obtained by swelling and water contact angle determinaions.

Introduction

Stimuli-responsive polymers are defined as polymers that undergo relatively large and abrupt physical or chemical changes in response to small external changes in the environmental conditions. Names coined for stimuli-responsive polymers include stimuli-sensitive, intelligent, smart, or environmentally sensitive polymers [1-6]. Poly(N-isopropylacrylamide) (PNIPAAm) is the most popular polymer among the temperature sensitive polymers since it exhibits a sharp phase transition close to 32°C [7]. The important and useful feature of the PNIPAAm/water system resides in the ability to tailor its lower critical solution temperature (LCST) by incorporating comonomers with hydrophilic or hydrophobic groups in the polymer or by adding solvents, simple salts or surfactants to the polymer/water solution [8, 9]. Preparation and characterization of temperature sensitive PNIPAAm hydrogels have been emphasized in recent years, due to their versatile applications in biomedicine, biotechnology, and drug delivery systems [10]. PNIPAAm hydrogels are well known for their discontinuous phase separation near their phase transition temperature or LCST and exhibit a sudden shrinking in volume at a temperature right above LCST [11]. In order to obtain a hydrogel that dramatically changes its swelling degree in water, the gel constituents must be insoluble above or below a certain temperature, called the lower or upper critical solution temperature (LCST or UCST, respectively) [12]. These transitions are mainly controlled by the rapid alteration in hydrophilicity and hydrophobicity among the hydrogel sub-groups, and this structural collapse takes place upon heating [13]. The hydrogels that exhibit pH and electro-sensitivity are comprised of polyelectrolytes and polyampholytes, while the thermoresponsive hydrogels have special chemical structures of hydrophilic–hydrophobic balance and exhibit LCST. Polymeric hydrogels which are pH sensitive such as poly(acrylic acid) (PAAc) the promoted the drug release in acidic medium and retarded the release in alkaline medium [14]. Many structural factors (charge, concentration and pKa of the ionizable group, degree of ionization, crosslink density and hydrophilicity) influence the degree of swelling of ionic polymers. In addition, a property of the swelling medium (pH, ionic strength and the counter ion and its valency) affects the swelling characteristics [15]. Copolymers of PNIPAAm with several comonomers including acrylic acid (AAc), 4-pentenoic acid, N-acryloxysuccinimide, allylamine, 2-(dimethylamino)ethylmethacrylate, 2-(dimethylamino)propylmethacrylamide, 2-(dimethyl)acrylamide, 3-acrylamidophenylboronic acid, maleic acid, citraconic anhydride, itaconic acids, etc.; which exhibi both temperature and pH sensitivities have been used in diverse application [16]. The complexes are formed at low pH and that the molecular weight of PAAc and solution properties such as pH and ionic strength influence the stability and structure of inter polymer complexes [17]. Radiation processing has many advantages over other conventional methods, radiation processes differs from chemical initiation, because no catalyst or additives are needed to initiate the reaction [18-20].

Experimental

Grafting

N-isopropylacrylamide (NIPAAm, 97%) and Acrylic acid (AAc) were supplied from Aldrich Chemical Co. NIPAAm was recrystallized from hexane/toluene (1/1, v/v) solution before use and AAc was distilled in vacuum before use. Polypropylene films (PP) from PEMEX, thickness of 60 μm and 1x5 cm in size were washed in methanol before use. Hexane and toluene from Baker were used as received.

PP films were irradiated in air at a dose rate of 2.4 kGy/h and several different total pre-irradiation doses with a Co-60 source with an activity of 22,000 Curies. The irradiated films and 5.8 molL^{-1} of AAc aqueous solution were charged in glass ampoules, the system was deaerated by bubbling with argon gas for 20 min and then sealed and placed in a water bath at 50°C, for various periods of time. The grafted films PP-g-AAc were then washed with water for 24 to 72 h to extract the residual poly(acrylic acid) that had formed. Grafting of NIPAAm onto PP-g-AAc was carried out using the same procedure at a dose rate of 2.4 kGy/h at a different total radiation dose, a monomer concentration of 1molL^{-1} in water, and a reaction temperature of 50°C. Grafted copolymer films were extracted in water for 24 h in order to remove remaining monomers and homopolymer.

Characterization

Decomposition temperatures were determined in nitrogen atmosphere by Thermogravimetric Analysis, using a TGA Q50 (TA Instruments, New Castle, DE). Differential Scanning Calorimetry was performed using a DSC 2010 calorimeter (TA Instruments, USA). FTIR-ATR (attenuated total reflection) spectra were taken using a Perkin-Elmer Paragon 500 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT). The measurements of the contact angle for various samples were carried out at room temperature, 1 minute after water drops were deposited onto the graft PP surface. In order to examine temperature-sensitive behaviors of PP-g-AAc and (PP-g-AAc)-g-NIPAAm copolymers, swelling ratios at different temperatures and pH were measured. For determination of equilibrium water absorbency, the samples were immersed into distilled water for different periods of time. The excess of solution on the copolymer films was removed with filter paper, and the swollen samples were weighed. The vials with copolymer films were placed in a temperature controlled bath at room temperature in phosphate buffer solutions of pH values from 2 to 8, during 3 h to obtain the pH critical point. The swelling % was determined by the equation:

$$\text{Swelling (\%)} = [(Ws - Wd) / Wd] \text{ X } 100 \qquad (1)$$

Where Ws and Wd are weights of the swollen and initial films respectively.

Results and Discussions

Figure 1 shows the spectra of (a) PP films with absorption bands characteristic of CH_2 (2913 and 1453 cm^{-1}), and CH_3 (1373 cm^{-1}); (b) PAAc with bands around 1694 cm^{-1} corresponding to C=O and 2920 CH_2; (c) PNIPAAm with characteristic C=O (1629 cm^{-1}), N-H (3283 and 1535 cm^{-1}) and CH_3 (2968 cm^{-1}) bands; (d) (PP-g-AAc)-g-NIPAAm film, presented peaks around 1702 cm^{-1} (C=O from AAc), 1643 cm^{-1} (C=O from NIPAAm); characteristic absorption of the (N-H)group 1540 cm^{-1}. These spectra confirmed binary graft copolymerization.

Figure 2 shows the water uptake of (PP-g-AAc)-g-NIPAAm as a function of time. The swelling of selected samples at different absorbing time in distilled water was measured. The swelling rate indicates that the initial swelling process is due primarily to the water penetrating into the copolymer film through capillary and diffusion. Then the penetrated water is absorbed by hydrophilic groups and amide groups through formation of hydrogen bonds. The swelling is fast during the first 20 min and gradually slows down until the equilibrium swelling is reached. The swelling rate and equilibrium swelling time was at 60 minutes.

Figures 3a shows the typical swelling behavior of four PP-g-AAc films containing various graft percentages of AAc plotted as a function of pH. Figure 3b shows similar results for (PP-g-AAc)-g-NIPAAm. Swelling for both polymer systems is significant at a pH above 8 (the pH critical point ranges from 6.6 to 7.0), where the hydrogen bond interaction between AAc units (Figure 3a) and between AAc and NIPAAm units (Figure 3b) is destroyed at this higher pH value, allowing the system to exhibit hydrophilic behavior. This contrasts to the hydrophobic behavior observed at lower pH values (before the pH critical point) attributed to hydrogen bond interaction between acrylic acid through carboxylic moieties and between AAc and NIPAAm, through carboxylic acids and amide groups. A higher grafted AAc content results in a higher content of the ionized carboxylate groups and greater hydrophilicity at higher pH values which causes a higher swelling ratio. The swelling ratio increases dramatically with increasing pH after the critical pH point is exceeded.

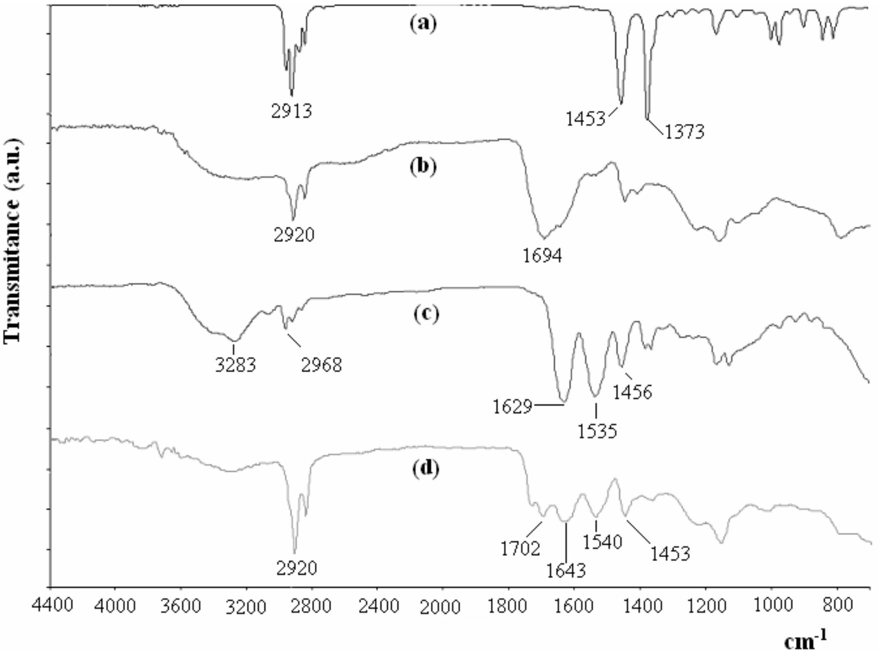

Figure 1. FTIR-ATR spectra of (a) PP film; (b) PAAc; (c) PNIPAAm; and (d) (PP-g-AAc 1219% graft)-g-NIPAAm 46% graft.

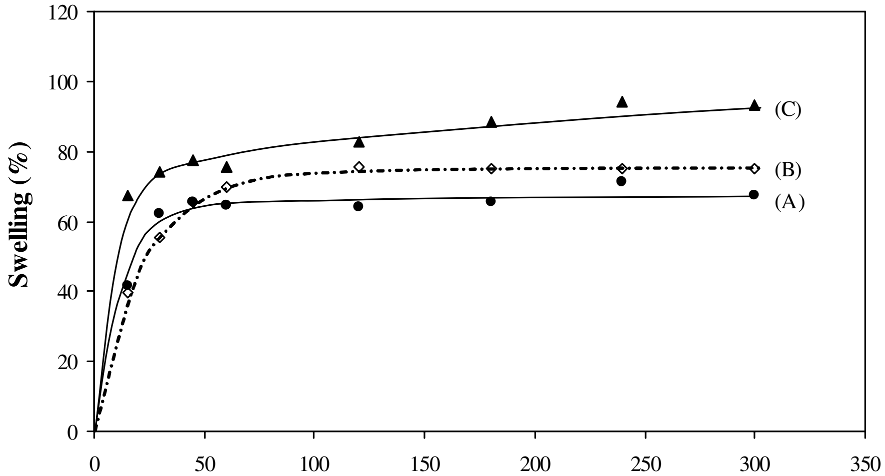

Figure 2. Swelling percent of (A) (PP-g-AAc 250%)-g-NIPAAm 70%; (B) (PP-g-AAc 1220%)-g-NIPAAm 47%; and (C) (PP-g-AAc 277%)-g-NIPAAm 358% , as a function of swelling time.

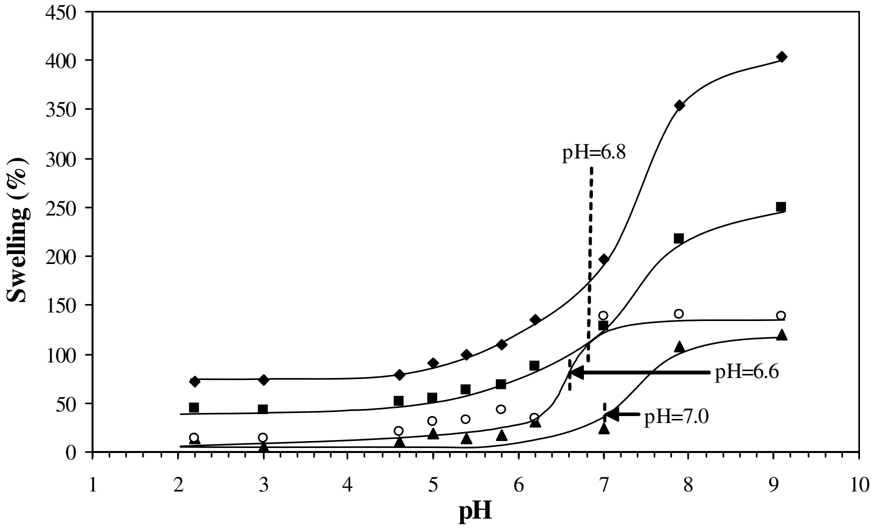

Figure 3a. Swelling % as a function of pH of PP-g-AAc 915% (♦); 570% (■); 92% (▲); and 45% (○).

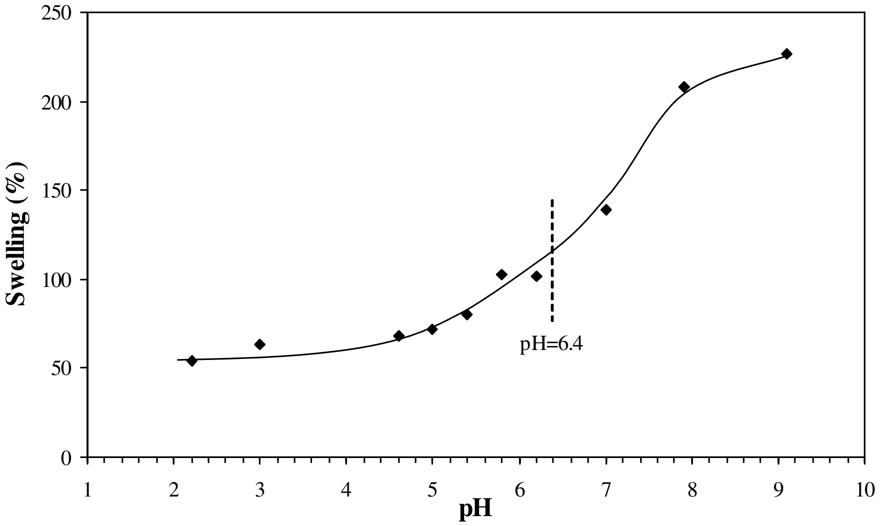

Figure 3b. Swelling % as a function of pH of (PP-g-AAc 1220% graft)-g-NIPAAm 47% graft.

Figure 4 shows the typical temperature-dependent swelling ratio of four thermo sensitive copolymer films with different graft percentages, over the temperature range of 20–40°C in distilled water (pH 7.0). The equilibrium swelling ratios for all of the films exhibit similar temperature dependence. As the temperature was increased, the swelling ratio decreased, with the most drastic decrease being observed at around the LCST (about 31–31.5°C) of PNIPAAm. Generally, the main reason for this distinctive characteristic of the thermo responsive films can be attributed to the unique and rapid alternation of the hydrophilic and hydrophobic states. At temperatures below the LCST, the hydrophilic groups of the copolymer films form hydrogen bonds with water molecules. These bonds act cooperatively to form a stable shell of hydration around the hydrophobic groups, resulting in greater water uptake and producing a larger swelling ratio. When the temperature exceeds the LCST, the hydration shell of PNIPAAm collapses abruptly. These results indicate that the thermo-sensitive properties of the hydrogels rise mainly from PNIPAAm and the graft copolymer composition can be used to control the swelling ratio.

Figure 5 shows the contact angle of water as a function of pH (at ambient temperature) for the polymers. PP-g-AAc 45% graft and (PP-g-AAc 41%)-g-NIPAAm 180%. The pH critical point, defined here as the mid point in the sigmoid dependence was in both cases determined to be at approximately pH 5 for both samples grafted. These critical pH points were lower than those measured for similar samples by swelling measurements.

The LCST value determined from surface properties, by the variations of the contact angle formed by a water droplet at temperatures ranging from 22 to 55°C, was found to be 32°C (Figure 6) even for sample with AAc (73% graft) and NIPAAm (228% graft) by prepared by the two step method. This value is according with the LCST determined from swelling measurements (between 31and 31.5°C) [20].

Figure 7 illustrate the reversibility of the swelling and deswelling kinetics of the copolymers films with different graft percentage as the pH is alternated between 2.2 and 8 in water.

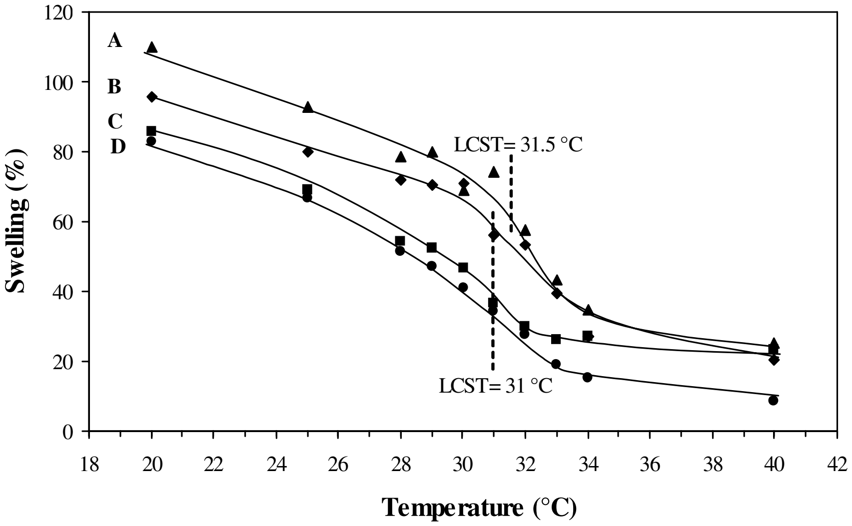

Figure 4. Swelling % as a function of temperature; lower critical solution temperature (LCST) of (PP-g-AAc)-g-NIPAAm: AAc 266%, NIPAAm 111%(▲); AAc 41%, NIPAAm 18%(♦); AAc 73%, NIPAAm 1050%(■); AAc 72%, NIPAAm 840%(●).

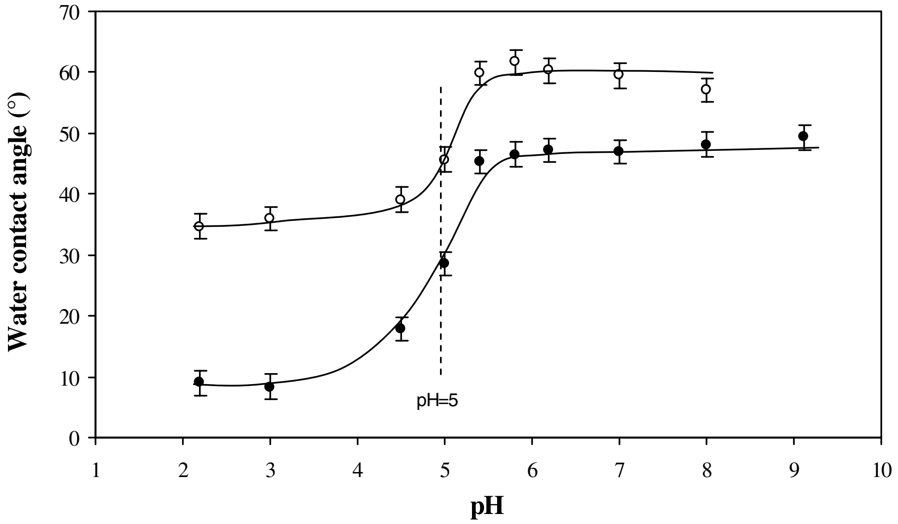

Figure 5. Variation of water contact angle with pH for samples of PP-g-AAc 45% graft (●) and (PP-g-AAc 41%)-g-NIPAAm 180% graft (○).

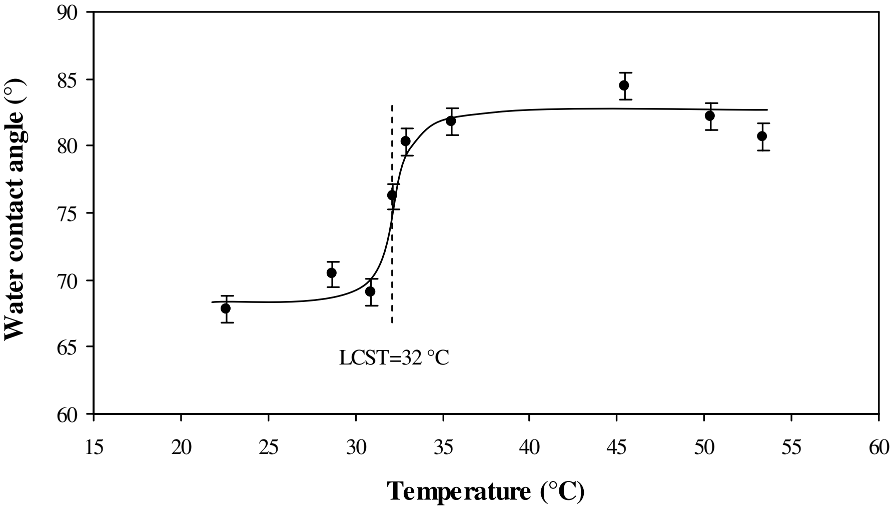

Figure 6. Temperature dependence of the water contact angle of (PP-g-AAc, 73%)-g-NIPAAm 228% graft at pH 7.

The thermal properties of the polymers are summarized in Table 1. Glass transition temperature (Tg) could be easily determined by DSC. The values ranged between 112.5 and 158°C. Tm values for PP alone and modified with PAAc and PNIPAAm were between 169.8 and 170.4. The thermal stability data (10% wt loss) for the modified PP were as expected: PP alone was 420°C, PP-g-AAc was 360°C and (PP-g-AAc)-g-NIPAAm was 208°C, indicating good stability (see Table 1).

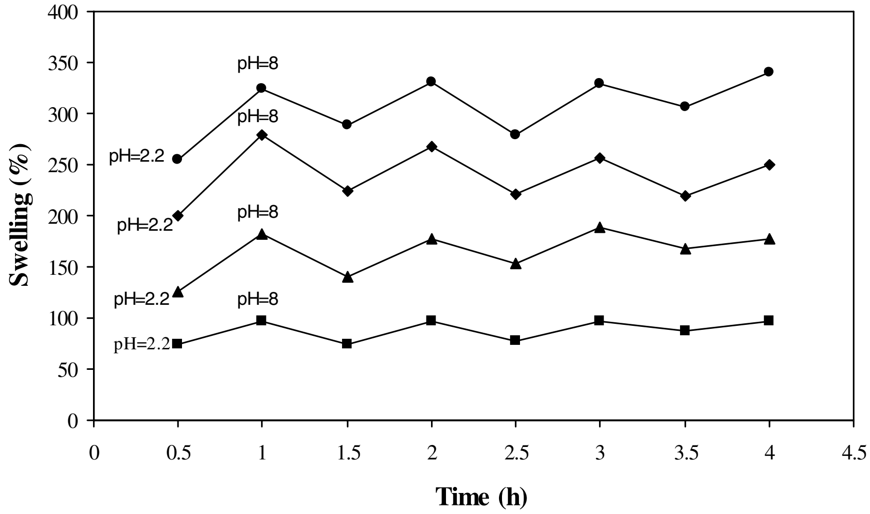

Figure 7. Reversibility of swelling-deswelling effect as a function of time by varying the pH from 2.2 to 8, PP-g-AAc 45% graft (■); PP-g-AAc 92% graft (▲); PP-g-AAc 570% graft (♦); and (PP-g-AAc 1220%)-g-NIPAAm 47% graft (●).

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	1.54		170.4
PAAc	215	17.45	142.8	213.1
PNIPAAm	159	2.70	158.0	
PP-g-AAc	360	8.79	112.5	171.6
(PP-g-AAc)-g-NIPAAm	208	12.71	129.8	169.8

* measured at 10°C/min in nitrogen

Conclusions

NIPAAm onto PP-g-AA films were prepared in two steps, using a pre-irradiation method. The FTIR-ATR was used to confirm that PP had been grafted to form the binary system. The grafting efficiency increased with the time and with pre-irradiation dose; the grafting yield which results was between 33 and 1500% for AAc onto PP, and the graft copolymer of NIPAAm onto PP-g-AAc was between 45 and 530%. The swelling ratio depended on the de graft contents. All films presented good mechanical properties. The LCST and pH critical point were conserved on the binary grafted films.

Acknowledgements. The authors are grateful to M. Cruz and M. L. Escamilla from ICN-UNAM, for technical assistance. This work was financially support by DGAPA-UNAM (Grant No. IN200306)

References

1. Jeong B., Gutowska A. (2002) Trends Biotechnol 20: 305.
2. Kikuchi A., Okano T. (2002) Prog Polym Sci. 27: 1165.
3. Hoffman A. S., et al. (2000) J Biomed Mater Res 52: 577.
4. Galaev L. Y., Mattiasson B. (2000) Trends Biotechnol 17: 335.
5. Qiu Y., Park K. (2001) Adv Drug Deliv Rev 53: 321.
6. Seok-Gil E., Hudson S. M. (2004) Prog. Polym. Sci. 29: 1173.
7. Yoo M. K., Sung Y. K., Cho C. S., Lee Y. M. (1997) Polymer 38: 2759.
8. Winnik F. M., Ottaviani M. T., Turro N. J. (1991) Macromolecules 25: 6007.
9. Schild H. G., Muthukumai M., Tirrell D. A. (1991) Macromolecules 24: 948.
10. Maolin Z., Min Y., Jian S., Jinshan W., Hongfei H. (1998) Radiat. Phys. Chem. 52: 313.
11. Hirokawa Y., Tanaka T. (1984) J Chem Phys 81: 6379.
12. Bromberg1 L. E., Ron E. S. (1998) Advanced Drug Delivery Reviews 31: 197.
13. Xian-Zheng Z., Da-Qing W., Chih-Chang C. (2004) Biomaterials 25: 3793.
14. Loo-Teck N., Hiroshi N., Isao K., Kumao U. (2005) Radiat. Phys. and Chem. 73: 117.
15. Mahdavinia G. R., Pourjavadi A., Hosseinzadeh H., Zohuriaan M. J. (2004) Eur. Polym. J. 40: 1399.
16. Pişkin E. (2004) International Journal of Pharmaceutics 277: 105.
17. Mun G. A., Nurkeeva Z. S., Khutoryanskiy V. V., Sarybayeva G. S., Dubolazov A. V. (2003) Eur. Polym. J. 39: 1687.
18. Huiliang W., Wenxiu C. (2006) Radiat. Phys. and Chem. 75: 138.
19. Palacios O., Roustam A., Burillo G. (2003) Polymer Bull. 51: 191.
20. Bucio E., Burillo G., Adem E., Coqueret X. (2005) Macromol. Mater. Eng. 290: 745.