

Characterization of thermo and pH sensitivity of binary graft copolymers onto polytetrafluoroethylene

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Abstract. The temperature sensitivity (low critical solution temperature LCST), and pH sensitivity of binary grafting of two monomers *N*-isopropylacrylamide NIPAAm (temperature responsive) and acrylic acid AAc (pH responsive) onto poly(tetrafluoroethylene) PTFE, was studied for the graft copolymers with different grafting percentages, the reversibility of the phase transition from hydrophilic to hydrophobic behavior with change in temperature and pH were also studied. Poly(NIPAAm) has a low critical solution temperature of about 33 °C, but in case of the binary grafting the LCST shift to the lower temperature; probably due to the formation of hydrogen bonds between dimethylamino and acrylic acid groups.

Key words: LCST, binary grafting, intelligent polymers, PTFE

Resumen. En este trabajo se estudió la sensibilidad a la temperatura (LCST) y sensibilidad al pH del injerto binario de 2 monómeros, la *N*-isopropilacrilamida NIPAAm (con respuesta a la temperatura) y el ácido acrílico AAc (con respuesta al pH) en politetrafluoroetileno PTFE a diferentes porcentajes de injerto. Se estudió la reversibilidad en la transición de comportamiento hidrofílico a hidrofóbico con el cambio en temperatura y pH. La P(NIPAAm) tiene una temperatura de solución crítica (LCST) de aproximadamente 33 °C, pero en el caso del injerto binario estudiado la LCST se desplaza a temperaturas mas bajas, debido probablemente a la formación de puentes de hidrógeno entre los grupos amino de la NIPAAm y los grupos ácidos del ácido acrílico.

Palabras clave: LCST, injerto binario, polímeros inteligentes, PTFE.

Introduction

The unique property of intelligent polymeric materials, which exhibit significant changes in properties to response to small changes in external stimuli, such as temperature [1], and pH [2], offers potential applications relevant to industry [3, 4, 5], to the environment and to biomedical field [6-8]. These applications include drug delivery systems, temperature sensitive coatings, flocculating agents, smart catalysis and others.

Poly(*N*-isopropylacrylamide) PNIPAAm is a temperature sensitive polymer that has been widely investigated as a result of the reversible macromolecular phase transition from hydrophilic to a hydrophobic behavior at about 32 °C, which is known as its lower critical solution temperature (LCST), and actually there is interest in the use of materials that respond to two stimuli, with emphasis on pH/temperature sensitivity [2, 9-12], mainly about PNIPAAm/PAAc (Poly(acrylic acid)). With respect to grafted systems, Wen [13] studied the temperature-responsive character of acrylic acid (AAc) and NIPAAm binary photografting onto celluloses.

This paper focuses on the thermal and pH properties of a binary graft copolymer onto poly(tetrafluoroethylene) (PTFE-g-(NIPAAm/AAc)), over a wide range of pH and temperature values, and about they reversibility behavior; PTFE films was chosen because of its excellent mechanical, physicochemical and chemical properties. AAc was selected as co-monomer because the AAc grafted chains acted as reaction sites to introduce various functions through the carboxyl groups. Radiation grafting was chosen as one of the easy methods well studied by others to graft NIPAAm or AAc to several polymeric films; binary grafting onto PTFE was studied by our group [2]. In that paper, monomers reactivity ratios of AAc (r_1) and

NIPAAm (r_2) were determined; they were 0.35 and 0.01 respectively, this values indicate that co-monomers sequence in the grafted copolymer was highly alternating, with some random placement. Dependence of grafted copolymers composition on the monomers feed was also studied, and for one initial composition from 0.2 to 0.8 mol fraction of AAc, a constant composition of about 0.75 mole fraction of AAc was obtained in the formed copolymer.

Experimental

NIPAAm supplied by Aldrich, was recrystallized from *n*-hexane/toluene (1/1 in volume ratio) and AAc (Materiales Plásticos SA de CV México) was distilled under a reduced pressure before use. PTFE films (donated by Laboratoire de chimie Macromoléculaire sous Rayonnement CNRS France) of 85 mm thick and size of 1.5 × 2 cm were washed in methanol for 24 h, and then dried under reduced pressure to a constant weight. All the solvents were analytical grade, from Aldrich.

PTFE samples were irradiated in air at a dose rate of 5.7 kGy/h and radiation doses from 5 to 30 kGy, with a ⁶⁰Co γ source (Gammabeam 651 PT, Nordion International Inc.), with an activity of about 25,000 curies (Ci). The irradiated films were placed in ampoules which contained aqueous solutions of AAc and NIPAAm mixtures with different molar ratio, and constant total monomers concentration of 6 M, as it was published by Palacios [2]. The ampoules were deaerated by bubbling argon during 20 min and sealed. Then, they were heated at temperature of 50 °C for 15 h. After heating, the samples were washed with water and methanol for 24 h to extract un-reacted monomers as well as homopolymer formed

during the grafting reaction. The grafted samples were dried under vacuum to a constant weight. The grafting yield was determined by the equation: Grafting (%) = $[(W_1 - W_0)/W_0] \cdot 100$ where W_1 and W_0 are weights of the grafted and initial films respectively.

For a measured of limited swelling %, the grafted samples were immersed into phosphate buffer solution at pH 7 at different period of time in a thermostatic water bath at 22 °C, until the equilibrium swelling of the samples was reached; before weight the swelled samples at each period of time, excess of solution on the films surface was wiped by filter paper. The swelling % of samples was calculated as follows: Swelling (%) = $[W_2 - W_1]/W_1 \cdot 100$, where W_2 and W_1 are weights of the swelled and dry films respectively.

Samples were swelled at different temperatures and constant pH, to determine the LCST of the samples, and swelled at different pH from 2.2 to 8 and constant temperatures, to found the critical pH point of the grafted samples.

Thermo-reversibility of the grafted films was determined by swelling and deswelling kinetics, at 20 °C until a limit swelling of 3 h, and then at 40 °C, this procedure was carried out several times; at pH 2.2 and 7; the pH reversibility was determined by swelling and deswelling at pH 2.2 during 2 h, and then to pH 8 during the same time; this procedure was also carried out several times in both cases at room temperature of 20 °C.

Thermo sensitivity was defined as the ratio of the grafted samples swelling at 20 and 45 °C, and pH sensitivity as the ratio of the swelled grafted samples at pH 8 and 2.2.

Buffer solutions were prepared with different concentrations ratios of Na_2HPO_4 0.2 M. and citric acid 0.1 M.

Results and discussion

Relationships between the equilibrium swelling of the films at different pH of the buffer solutions at 22 °C are shown in Fig. 1, the equilibrium swelling was found at about 2 h for both pH determined. The swelling percentage increased with pH of the solution. At pH 2.6, the films are less hydrophilic and present hydrogen bonding between the carboxylic moieties and between the two macromolecular species NIPAAm and AAc as can be seen in Fig. 2. At pH 8 there was no interaction between them. Fig. 3 shows the swelling percentages as a function of pH. The swelling percentage increased with grafting, but the pH critical point, found on the inflection point of the plot, was more or less constant, which is about 4.8, lower than the critical pH point of the acrylic acid of about 5.5; this point is not well defined in films with grafting of 17.5 %. Before this pH critical point, the film showed hydrophobic behavior. The pH sensitivity of films increased with grafting amount; pH sensitivity of films with 17.5, 48.6, and 83.5 % grafting were 1.8, 3.4, and 6 respectively. Fig. 4 shows the swelling percentage of the films with different ratio of AAc/NIPAAm and different grafting percentages as a function of pH. The same critical pH point of about 4.8; was

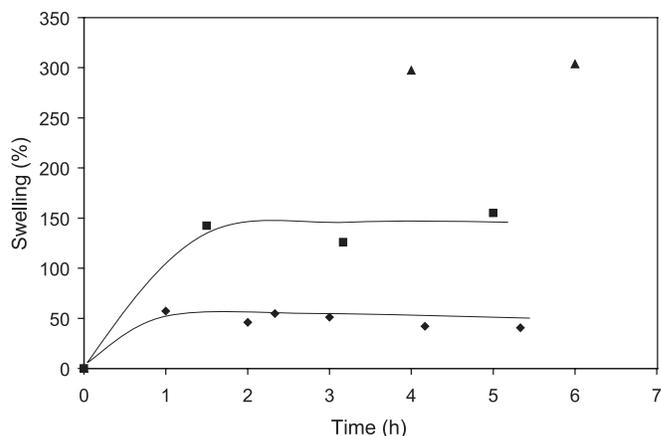


Fig. 1. Swelling % of films with 83.5 % grafting as a function of time, at different pH, constant temperature of 22 °C, and monomer concentration 50/50: ◆◆ 2.6; ■■ 5; ▲ 8.

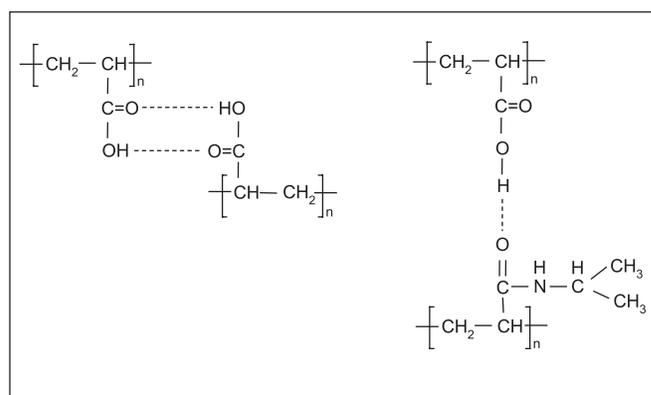


Fig. 2. Hydrogen bonding between two units of acrylic acid, and between acrylic acid and *N*-isopropylacrylamide.

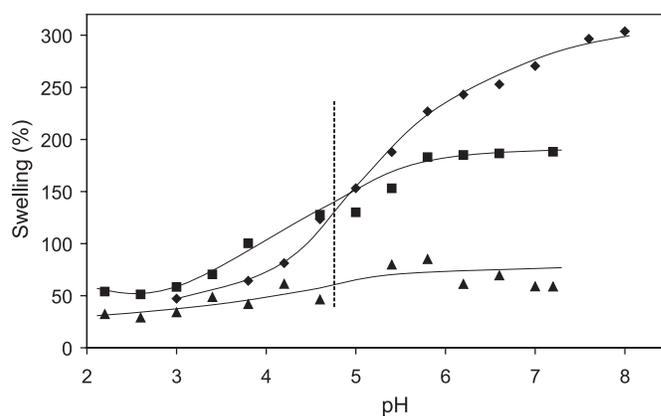


Fig. 3. Swelling % of films as a function of pH, at different grafting %, and constant temperature of 20 °C and monomer concentration of 50/50; ▲▲ 17.5 %; ■■ 48.6 %; ◆◆ 83.5 %.

observed but with a higher inflexion point in the sample with less amount of AAc (35%). Bian [14] has also observed this behavior in the studies of complexation between poly(diethylacrylamide) PDEA and poly(acrylic acid) PAAC. At low PAAc concentrations, there is no interaction between the two polymers, and therefore, a high hydrophilic behavior was observed, but in the films with 35 % of AAc, this behavior is also due to higher grafting percentage. The critical pH point was constant at any grafting % and monomers concentration relation, in the binary grafting system onto PTFE there was only change in the pH sensitivity with increase in grafting percentage.

The low critical solution temperature (LCST) of poly (NIPAAm) was found at 32 °C; and in the binary grafting onto PTFE, it shifted to lower temperatures. Fig. 5 shows the LCST of a film with 83.5 % grafting at two different pH, the LCST of binary grafting film shifted to 25 °C when the pH of solution was 3 (before the critical point of 4.8) and to 22 °C when the pH was 8., (after the pH critical point) where the hydrogen bond of the monomer was destroyed. The LCST is significantly affected by the variation in pH, as the hydrophilic content of the copolymer changes and this effect was also observed by Jones [12] in copolymers of both monomers. The shift to lower temperatures of the LCST was probably due to the formation of hydrogen bonds between AAc and -C=O groups of NIPAAm, and -OH groups of AAc which protect the system from exposure to water, and result in a hydrophobic contribution to LCST. The thermal sensitivity (relation between swelling % at 20 °C and 40 °C) in 50/50 AAc/NIPAAm film with 83.5 % grafting, was 3.8 at pH of 3 and 1.4 at pH of 8, and this indicates almost three times more water absorption in the hydrophilic behavior than in the hydrophobic one. Fig. 6 shows the reversibility on the effect of swelling and deswelling at pH 2.2 and 8, in the binary films with 43 and 83 % graft and at a constant temperature of 10 °C. A good reversibility on the effect of swelling and deswelling at 20 and 40 °C was found only after two or three cycles of the process. Fig. 7 shows the variation on contact angle as a function of

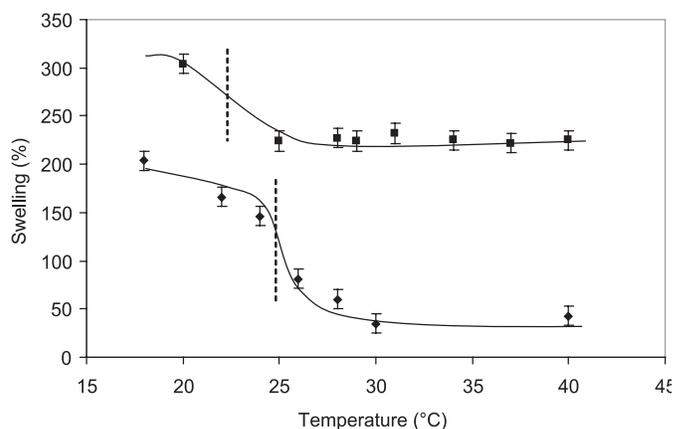


Fig. 5. Swelling % as a function of temperature, at different pH and 83.5 % grafting; ◆◆ pH 3; ■■ pH 8, (monomer concentration 50/50).

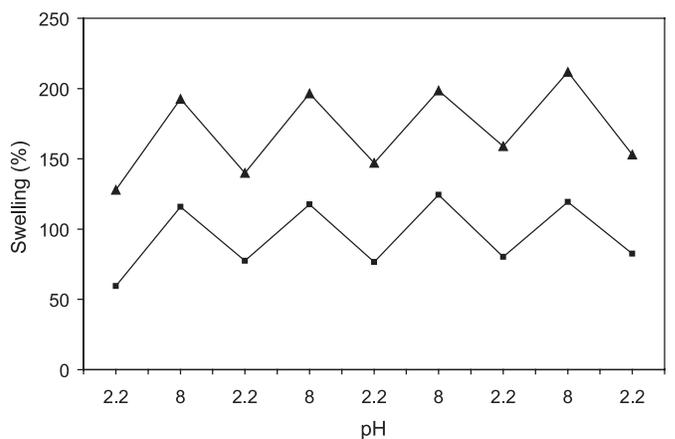


Fig. 6. Reversibility on the swelling-deswelling-reswelling cycle as a function of pH; ■■ 43 % grafting; ◆◆ 83 % grafting.

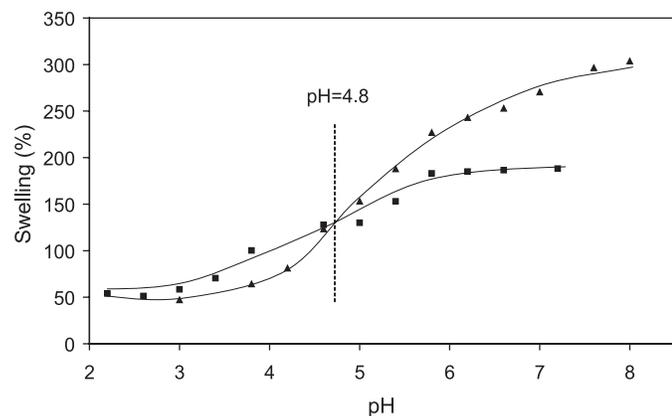


Fig. 4. Swelling % as a function of pH, at room temperature and different grafting % and relation of AAc/NIPAAm; ■■ 50/50 monomer concentration and 49 % grafting; ▲▲ 35/65 monomer concentration and 80 % grafting.

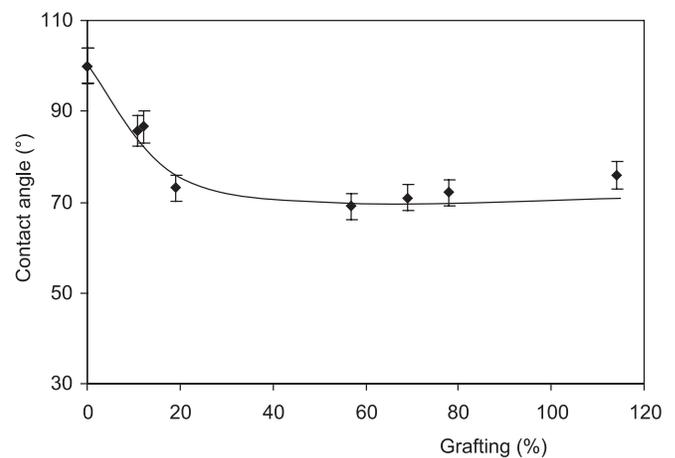


Fig. 7. Variation in contact angle of water with films as a function of grafting % onto PTFE of binary AAc/NIPAAm grafted film, at 20 °C, and pH 7.

grafting percentage of samples, hydrophilicity (decrease of contact angle) increases with grafting, up to about 30 % grafting when all PTFE surface was covered with the graft copolymer of AAc/NIPAAm. This was observed by Adem [15], in the surface characterization of this binary grafting onto PTFE by X-ray photoelectron spectroscopy (XPS).

Conclusions

Binary graft copolymerization with the temperature responsive monomer NIPAAm and the pH responsive AAc onto PTFE, resulted in a dual sensitive polymer material to both temperature and pH. They exhibit phase transitions in water absorption resulting from both polymer-water and polymer-polymer interactions. There is hydrophobic contribution to the LCST because of intermolecular interactions via hydrogen bonds. Films of PTFE with binary grafting present a good reversibility on swelling-deswelling process in water. The grafted film showed a limited swelling change in about 2 hours. Faster response may be achieved for the interpenetrate networks of both monomers, which is being carried out at present.

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