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Radiation grafting of pH-sensitive acrylic acid and 4-vinyl pyridine onto nylon-6 using one- and two-step methods

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HIGHLIGHTS

- A new binary graft of 4VP and AAc onto Ny_6 films was synthesized by γ-radiation.
- The binary grafted material has potential application for heavy ion retention.
- The two-step method shows better conditions in swelling and reversibility properties.
- Surface distribution of monomers was evaluate by XPS characterization.

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ABSTRACT

Acrylic acid (AAc) and 4-vinyl pyridine (4VP) were γ-ray grafted onto nylon-6 (Ny_6) films via pre-irradiation oxidative method. These monomers were grafted using a one-step method to render Ny_6-g-(AAc/4VP). A two-step or sequential method was used to render (Ny_6-g-AAc)-g-4VP. Random copolymer branches were obtained when the grafting was carried out via one-step method using the two monomers together. The two-step method was applied to graft chains of 4VP on both Ny_6 substrate and previously grafted AAc chains (Ny_6-g-AAc). The two types of binary copolymers synthesized were characterized to determine the amount of grafted polymers, the thermal behavior (DSC and TGA), the surface composition (XPS), and the pH responsiveness. In the two-step process, it is possible to achieve a higher graft yield, better control of the amount of each monomer, good reversibility in the swelling/deswelling process and shorter time to achieve equilibrium swelling.

1. Introduction

Nylon-6 (Ny_6) has attracted considerable interest due to its physicochemical and mechanical properties, especially its heat resistance. In addition, Ny_6 is a material with moderate water uptake capacity (9.5 wt%), which limits its application in the environmental decontamination and biomedical fields. Therefore, grafting reactions of Ny_6 with hydrophilic monomers have been reported to improve its water absorption and retention (Nayak, 1979; Takigami et al., 1984). Other reports have described grafting of polymer materials with stimulus-responsive monomers/polymers that exhibit relatively abrupt and large physical or chemical changes in response to low-intensity stimuli, such as temperature, pH, and ionic strength (Byung et al., 2003; Bucio et al., 2005; Liu and Urban, 2010). These species possess certain functional groups, such as amides, amines, carboxylic acids or epoxy groups, that can be grafted on the surface or in the bulk matrix by applying different chemical methods (Siow et al., 2006; Wang et al., 2006; Schmidt and Schmidt-Naake, 2007; Truica-Marasescu et al., 2007). Among the suitable techniques, ionizing radiation, ultraviolet light, plasma and chemical initiators are useful approaches for grafting polymers (Bucio and Burillo, 1996; Bucio et al., 2001; Burillo et al., 2006; Chen et al., 2007). Gamma radiation (γ) grafting is an attractive method for obtaining a modified material without chemical initiators or other additives that is applicable to nearly all polymer–monomer combinations (Clough, 2001). Taher et al. (2000) studied γ-radiation grafting of AAc and acrylamide (AAm) onto Ny_6 for separation of radioactive europium in wastewater. Other authors have grafted a combination of these monomers onto Ny_6 for use as cation-exchange membranes in different practical

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applications, especially for the separation of heavy metals in water. However, anionic/cationic membranes obtained by radiation grafting onto low-density polyethylene (LDPE) are more effective for the retention of heavy ions than the cationic ones (El-Sayed et al., 1997, 2000). According to previous reports, binary grafting of AAc and 4-vinyl pyridine (4VP) onto Ny_6 is an alternative that is effective for heavy ion uptake.

The aim of this study was to synthesize pH-sensitive binary grafting copolymers containing AAc/4VP grafted onto Ny_6 with gamma radiation using two different pre-irradiation oxidative methods (i.e., one- and two-step methods). The one-step method is one of the more practical approaches for producing random copolymers. However, block copolymers are often prepared following a sequential method, such as the two-step approach. The effect of the swelling capacity, pH sensitivity and reversibility on the swelling/deswelling behavior was evaluated for all of the synthesized materials. The Ny_6 films modified with AAc/4VP have the potential for application as cation-exchange membranes for the separation of selected heavy metals in wastewater.

2. Experimental

AAc and 4VP, which were supplied by Aldrich Co (USA), were vacuum distilled for purification. Methanol and dimethylformamide (DMF), which was obtained from JT Baker (México), were used as received. The Ny_6 films that were 75 mm thick with a molecular weight of 32700 g mol^{-1} were provided by the Good Fellow Co, USA. The Ny_6 films were cut into 1.2 cm × 4.0 cm pieces, washed with methanol for 24 h and vacuum dried.

2.1. Binary grafting via one-step method [Ny_6-g-(AAc/4VP)]

The Ny_6 films were irradiated in air at room temperature with a ^{60}Co γ source (Gammabeam 651 PT; Nordion Co., Canada) at a dose rate of 5.8 kGy h^{-1} with absorbed doses ranging from 10 to 40 kGy. The pre-irradiated samples (previously weighed) were placed in glass ampoules containing a solution mixture containing a monomers/solvent ratio of 60/40 or 80/20 (v/v). The monomer solution was prepared with an AAc/4VP ratio of 40/60 or 80/20 (v/v), and the solvent was prepared with a methanol/water ratio of 20/80 or 60/40 (v/v). To avoid an exothermic reaction between AAc and 4VP, the addition of the components in the mixtures was as follows: methanol, AAc and finally 4VP. The ampoules were saturated with argon for 20 min, sealed and heated at different temperatures. The grafted films were extracted by stirring in hot water and then in methanol for 24 h. The grafted films were dried under vacuum. The weight percentage of the grafted material was calculated as:

$$g\ (\%) = [(W_f - W_i)/W_i]100 \quad (1)$$

where W_f and W_i are the masses of the Ny_6 films after and before grafting, respectively. The composition of the chains grafted onto Ny_6 was measured by elemental analysis (Columbia analytics, USA) Scheme 1.

2.2. Binary grafting via two-step method [(Ny_6-g-AAc)-g-4VP]

2.2.1. Grafting of AAc onto nylon

To obtain Ny_6-g-AAc, AAc was grafted onto Ny_6 using the pre-irradiation oxidative method at a dose rate of 5.8 kGy h^{-1} with doses of 10 or 20 kGy. The pre-irradiated films were placed in glass ampoules containing a solution of 20% (v/v) AAc in methanol/water (70/30 v/v). The ampoules were saturated with argon for 20 min, sealed and heated to 50 °C for 45 min to achieve the desired grafting percentages (30–110%). The grafted films were washed with hot water for 24 h and methanol for 12 h to extract the residual monomer and homopolymer (PAAc). The grafting percentage was estimated using Eq. (1).

2.2.2. Grafting of 4VP onto Ny_6-g-AAc

4VP was grafted onto Ny_6-g-AAc using the pre-irradiation oxidative method at a dose rate of 5.8 kGy h^{-1} with 20 kGy dose. The pre-irradiated Ny_6-g-AAc films were placed in glass ampoules containing a solution of 4VP (40% v/v) in DMF/water (30/70 v/v). The ampoules were saturated with argon for 20 min, sealed and heated at different temperatures (from 40 to 80 °C) for different time periods. The grafted polymers were repeatedly washed with a solution of acetic acid in water (5% v/v), DMF and then methanol to extract both the residual 4VP monomer and homopolymer (P4VP). The grafting percentage was estimated using Eq. (1).

2.3. Swelling behavior

The grafted copolymers were immersed in distilled water and weighed at different times. The swelling percentage was determined using Eq. (2):

$$S_w(\%) = 100[(W_t - W_d)/W_d] \quad (2)$$

where W_t and W_d are the masses of the swollen polymer at time t and the dry polymer, respectively.

The sensitivity to pH was evaluated at room temperature by immersion in phosphate buffer solutions with a pH range of 2.0–9.0 for 30 min (the equilibrium swelling time). The pH values were determined using a HI 4212 potentiometer (Hanna Instruments, CA). The critical pH was identified as the inflection point of the S_w (%) in the equilibrium swelling time as a function of pH plot. The effect of the reversibility on the swelling/deswelling behavior was evaluated by comparing the largest and smallest swelling in a pH range of 2.2–7.0 and a temperature range of 20–25 °C at the equilibrium swelling time.

2.4. Characterization of the grafted polymers by infrared analysis

Fourier-transform infrared-attenuated total reflection (FTIR-ATR) spectra were recorded from 650 to 4000 cm^{-1} using a Perking Elmer Spectrum 100 (Perkin Elmer Cetus Instruments, Norwalk, CT) equipped with a Universal ATR sampling accessory and a diamond tip.

2.5. Thermogravimetric analysis (TGA)

A TGA instrument (SDT Q600) was employed to determine the thermal decomposition of the grafted copolymer. TGA analysis was performed in a nitrogen atmosphere as the temperature increased from room temperature to 700 °C with a heating rate of 10 °C min^{-1}.

2.6. Surface analysis

X-ray photoelectron spectroscopy (XPS) analyses were performed on both the pristine Ny_6 sample and Ny_6 grafted with AAc/4VP using an AES-XPS PHI-548 spectrometer after exciting the samples with an un-monochromatized Al Kα line at 1486.6 eV. The instrument base pressure was 2×10^{-8} Pa. The energy scale was calibrated using thick films of copper with a line at 932.67 eV for Cu $2p_{3/2}$. The survey scans were obtained in the 1200-(−20) eV energy interval at 1.0 eV per step and pass energy of 200 eV. The high-resolution XPS scans were measured with a step size of 0.2 eV and pass energy of 50 eV (constant pass energy mode).