

# $\gamma$ -Radiation-Induced Graft Copolymerization of Acrylic Acid onto Poly(ethylene terephthalate) Films: A Study by Thermal Analysis

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**ABSTRACT:** The grafting of acrylic acid onto poly(ethylene terephthalate) films with  $\gamma$  radiation was carried out. The effects of different parameters, such as the monomer concentration, inhibitor concentration, and irradiation dose, on the grafting yield were investigated. The grafting yield depended on these parameters, and its maximum value was obtained at a 1.5% inhibitor concentration and a 40% monomer concentration. The obtained grafting films were characterized with water swelling measurements, differential scanning calorimetry, and thermogravimetric analysis. The results of differential scanning calorimetry showed decreases in the heat capacity step and the glass-transition tempera-

ture with increasing grafting yield. The ability of poly(ethylene terephthalate) to crystallize and the size of the crystalline domains were affected by the grafting. The grafted poly(ethylene terephthalate) that was obtained was tested as an ion exchanger for copper, nickel, cobalt, and lead. The capacity of the grafted films for ion recovery was dependent on the grafting yield. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 198–203, 2006

**Key words:** crystallization; glass transition; ion exchangers; radiation

## INTRODUCTION

The graft copolymerization of functional monomers is an effective method for the modification of the chemical and physical properties of polymer surfaces. Several methods have been proposed for initiating graft copolymerization, including ionizing radiation, ultraviolet light, plasma treatment, decomposition of chemical initiators, and oxidation of polymers. The radiation-induced grafting technique is an important method because of its extensive penetration of the polymer matrix and its rapid and uniform formation of radicals for initiating grafting in many kinds of polymers.<sup>1–5</sup> A wide range of applications of radiation-grafted materials have been discovered over the years. Grafting processes have been developed particularly for wool, cotton, and synthetic materials to improve flame retardation, permanent press, dyeing soil release, antistatic properties, and other properties.

The  $\gamma$ -radiation-induced graft copolymerization of acrylic acid (AAc) onto different substrates, such as polypropylene,<sup>6</sup> cellulose triacetate,<sup>7</sup> polycarbonate,<sup>8</sup> poly(vinyl alcohol),<sup>9</sup> waste rubber,<sup>10</sup> and silicon rubber,<sup>11</sup> has attracted the attention of many investiga-

tors. According to Morlay et al.,<sup>12</sup> poly(acrylic acid) and its copolymers are useful for separating the metal ions of  $\text{Cu}^{2+}$  in solutions.

Poly(ethylene terephthalate) (PET) is one of the most studied polymers because of its important commercial significance and the very wide possibilities of the physical state (wholly amorphous, thermally or strain-induced semicrystalline states).<sup>13–15</sup> The radiation-induced graft copolymerization of various monomers onto PET has been investigated earlier on many occasions.<sup>16–18</sup> The aims of this work were to prepare modified PET through the grafting of AAc monomers (PET-g-AAc) with a simultaneous  $\gamma$ -irradiation grafting method, to study the effects of different parameter such as the monomer concentration, inhibitor concentration, and irradiation dose on the grafting yield, and to investigate the characterization of the grafted films by means of differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

## EXPERIMENTAL

### Materials

The PET film (0.5 mm) had a number-average molecular weight of 31,000 g/mol (supplied by the Carolex Society, France). Experimental measurements were performed on isotropic, amorphous PET films on the basis of birefringence and density measurements. AAc

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(99% purity; Fluka, Switzerland) was used as received. The other chemicals were reagent-grade and were used as supplied.

## Techniques

### $\gamma$ -Radiation source

The irradiation of samples was carried out with a  $^{60}\text{Co}$   $\gamma$  cell of the Russian dissolved type at room temperature at a dose rate of 2.15 kGy/h.

### Graft copolymerization

Strips of PET were washed with acetone, dried at 50°C in a vacuum oven, weighed, and then immersed in a monomer solution. Ferric chloride ( $\text{FeCl}_3$ ) was introduced into the reaction mixture to avoid the formation of homopolymers by direct irradiation grafting. The reaction mixture was deaerated with bubbling nitrogen gas for 7 min, sealed, and then exposed to the  $^{60}\text{Co}$   $\gamma$  source at different doses. The obtained grafted films were removed and washed thoroughly with hot distilled water for 10–15 min and were soaked overnight in water at room temperature to ensure the extraction of residual monomers and homopolymers from the films. The obtained films were then dried in a vacuum oven at 50–60°C for 24 h and weighed. The degree of grafting was determined by the percentage increase in the weight as follows:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where  $W_0$  and  $W_g$  represent the initial and final weights of the films, respectively.

### Swelling measurements

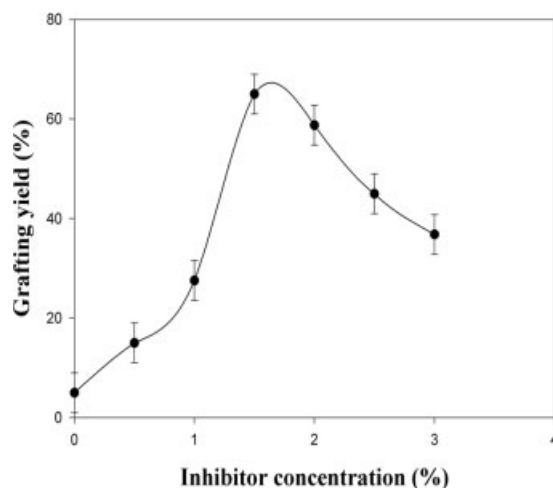
Clean and dried grafted PET films of known weights were immersed in distilled water for 24 h at 20°C. The films were removed, blotted with absorbent paper, and immediately weighed. The percentage of swelling in water was calculated as follows:

$$\text{Swelling (\%)} = \frac{W_s - W_0}{W_0} \times 100 \quad (2)$$

where  $W_0$  and  $W_s$  represent the weights of the initial and swollen films, respectively.

### Thermal analysis

The thermal analysis of the grafted films was performed with the help of a Setaram DSC131 apparatus (France). Calibration was achieved by the determination of the temperature and the enthalpy of fusion of



**Figure 1** Effect of the inhibitor ( $\text{FeCl}_3$ ) concentration on the grafting yield of AAc onto PET (radiation dose = 100 kGy; monomer concentration = 50 wt %).

indium and zinc. Calorimetric measurements were made under a nitrogen atmosphere at a heating rate of 10°C/min. TGA was carried out with a Mettler TGA50 apparatus (Switzerland) at a heating rate of 10°C/min under a nitrogen atmosphere.

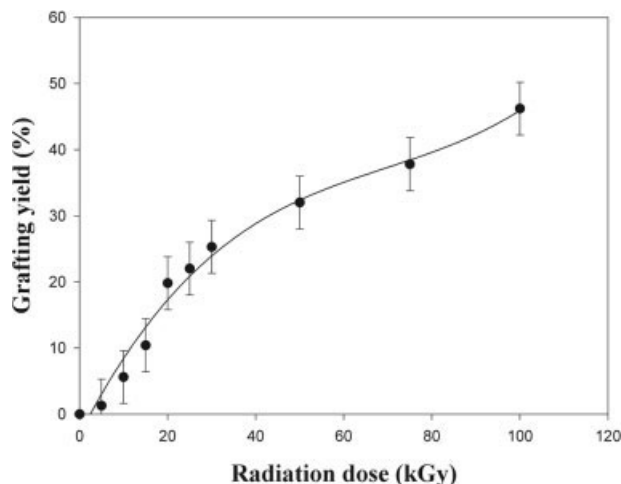
## RESULTS AND DISCUSSION

### Effect of the inhibitor concentration

AAc is known as a water-soluble monomer. Therefore, the entire grafting reaction was carried out in an aqueous medium. However, the irradiation of AAc in water results in homopolymer formation. Additives are used in a wide range of radiation polymerization processes to accelerate the rate of reaction and reduce homopolymerization.<sup>19,20</sup> The effect of the  $\text{FeCl}_3$  concentration, as an inhibitor, on the grafting yield of AAc onto PET is shown in Figure 1. The grafting yield of AAc increases with increasing inhibitor concentration up to 1.5 wt %, after which it starts to decrease. Such behavior is explained in the literature and has been attributed to the formation of complexes between AAc and iron ions.<sup>10,21</sup> Increasing the concentration of the inhibitor above the stoichiometric value allows the excess iron ions to move toward the surface of PET films, leading to an inhibition of the grafting process.

### Effect of the radiation dose

The effect of the irradiation dose on the grafting yield of AAc onto PET was studied. The results are shown in Figure 2, which illustrates the grafting yield increases with an increasing radiation dose in a nonlinear form. Increasing the radiation dose above 100 kGy results in increasing formation of the homopolymer.



**Figure 2** Effect of the irradiation dose on the grafting yield of AAc onto PET (AAc concentration = 50 wt %;  $\text{FeCl}_3$  concentration = 1.5 wt %).

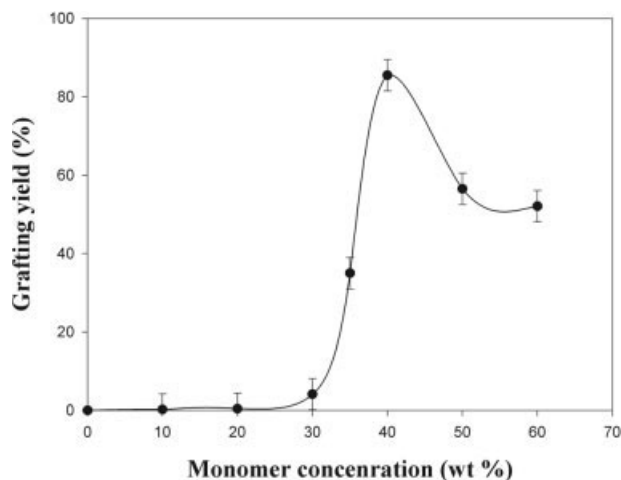
### Effect of the monomer concentration

The effect of the monomer concentration on the grafting yield of AAc on PET has been investigated, and the results are given in Figure 3. The grafting yield increases with increasing monomer concentration up to 40%. Furthermore, an increase in the monomer above these values reduces the grafting yield. This can be attributed to the increase in the viscosity of the medium due to the increase in the monomer concentration. This increase in the viscosity hinders the movement of the monomers toward the substrates and consequently reduces the grafting yield.

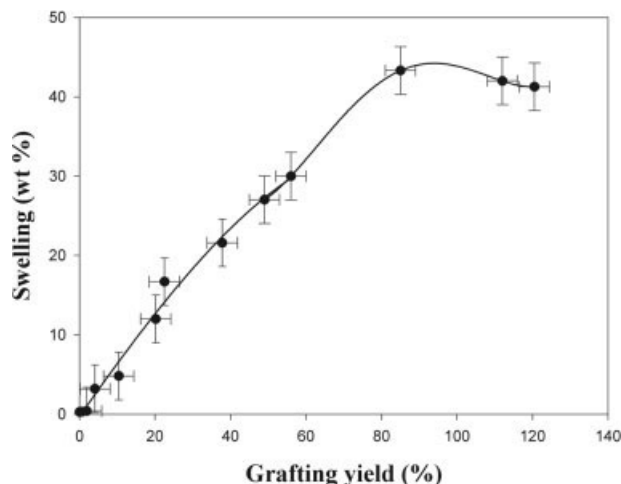
### Characteristics of grafted PET

#### Swelling measurements

The swelling of the samples in distilled water was carried out, and the results are shown in Figure 4. As



**Figure 3** Effect of the monomer concentration on the grafting yield of AAc onto PET (radiation dose = 100 kGy;  $\text{FeCl}_3$  concentration = 1.5 wt %).

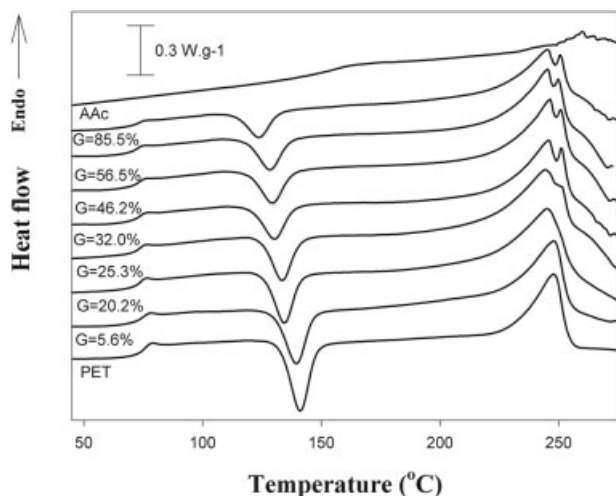


**Figure 4** Effect of the grafting yield on the equilibrium swelling of PET-g-AAc.

expected, the grafting of hydrophilic monomers such as AAc onto PET should improve the hydrophilic properties of the polymer substrate. Consequently, the swelling increases with the degree of grafting up to 80%, and a further increase in the grafting yield leads to a leveling off of the swelling. This behavior has been observed for the grafting of AAc onto low-density polyethylene and polypropylene films and can be attributed to the increase in the crosslinking content at high degrees of grafting and the association of carboxylic acid groups, which result in the hindering of the diffusion and mobility of water molecules into the bulk of the grafted copolymer.<sup>22</sup>

#### Thermal analysis

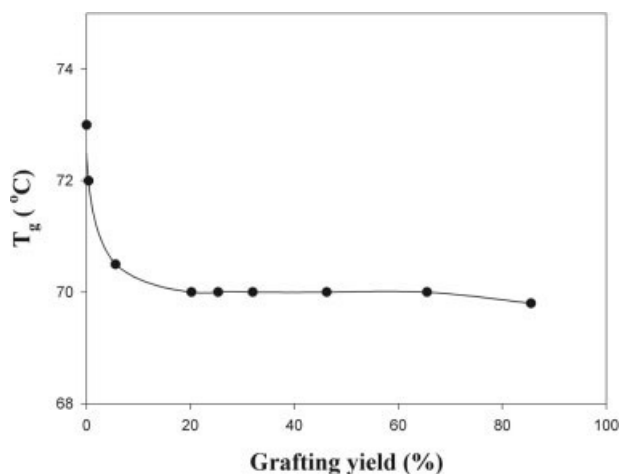
**DSC investigations.** DSC is a very useful technique for evaluating the glass-transition temperature ( $T_g$ ) of the amorphous phase in the polymer before and after grafting. To compare DSC data, all samples (grafted, ungrafted, and AAc) were subjected to the same thermal cycles and radiation dose (100 kGy). The DSC results for all the samples are displayed in Figure 5. For visibility, the different curves have been shifted along the heat flow axis. The DSC curve of the ungrafted PET film exhibits, at a high temperature, an endothermic peak due to the melting of the crystalline phase during the DSC scan. Between the  $T_g$  and melting temperature ( $T_m$ ) range, we can observe an exothermic peak for this sample,<sup>23</sup> which is due to the cold crystallization of a part of the amorphous phase during heating. The DSC curve of the AAc sample irradiated at 100 kGy shows a glass transition at  $150^\circ\text{C} < T_g < 170^\circ\text{C}$  and an endothermic peak at about  $260^\circ\text{C}$ , which could be due to the degradation confirmed by TGA (shown later in Fig. 10). The DSC curves of the grafted films are quasisimilar to the



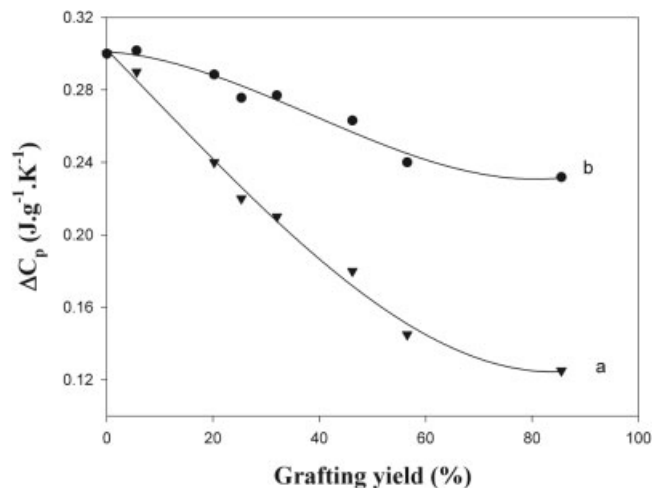
**Figure 5** Normalized DSC curves for ungrafted and grafted PET. The curves have been shifted for visibility.

ungrafted PET curve, with a supplementary peak appearing in the melting peak. This supplementary peak appears in the same temperature range as the degradation of AAc, and this is probably due to the degradation of AAc. Increasing the degree of grafting shifts the cold-crystallization temperature toward the glass transition, with a concomitant reduction of the crystallization enthalpy ( $\Delta H_c$ ).

In the temperature range of the glass transition (Fig. 5), the change in the heat capacity ( $\Delta C_p$ ) indicates the glass transition. The values of  $\Delta C_p$  ( $\text{J g}^{-1} \text{K}^{-1}$ ) are calculated from the difference in the thermal heat capacities between the liquid and glassy states at the  $T_g$  midpoint, and the masses used for calculation are the whole masses of the samples. Figure 6 reports the variation of  $T_g$  versus the degree of grafting.  $T_g$  decreases with an increasing degree of grafting up to 10%. Above these value,  $T_g$  is quasi-independent of



**Figure 6** Variations of  $T_g$  versus the grafting yield for ungrafted and grafted PET.

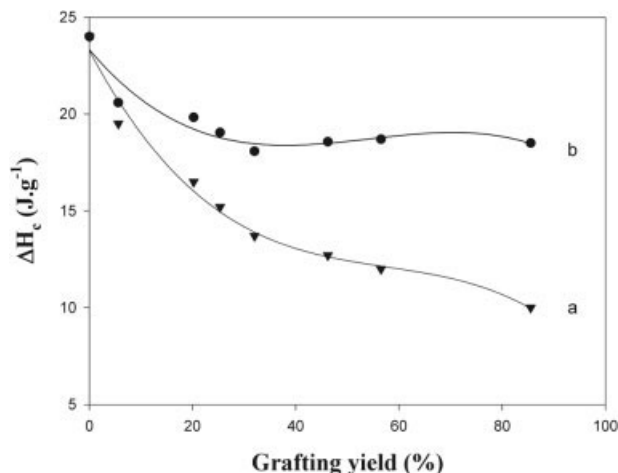


**Figure 7** Variations of  $\Delta C_p$  (difference of the thermal heat capacities between the liquid and glassy states at the  $T_g$  midpoint) versus the grafting yield for ungrafted and grafted PET: (▼) normalized for the whole mass of the sample and (●) normalized for a fraction mass of PET.

the degree of grafting and is close to  $70^\circ\text{C}$ . The graft copolymerization proceeds on the surface of the films by the formation of branched-chain structures. Such a branched chain structure plays a diluting role and could be responsible for the observed drop in  $T_g$ .<sup>24</sup> Therefore, the decrease in  $T_g$  is perhaps a result of the increase in the space available for molecular motion and the decrease in the cohesive energy density with the introduction of AAc.

The variations of the heat capacity step ( $\Delta C_p$ ) at the glass transition shows an important decrease with an increasing degree of grafting [Fig. 7(a)]. The decrease in  $\Delta C_p$  in Figure 7(a) could be due to the decreases of the fraction mass of PET in the grafted samples [Fig. 7(b)]. The  $\Delta C_p$  values normalized for a fraction mass of PET still show a decrease with increasing grafting yield, but this decrease can be attributed to the appearance of a rigid, amorphous part of PET that does not participate in glass transition. This rigid part is probably the part linked to the AAC monomers and modified by the grafting. Such behavior cannot be explained in terms of the susceptibility of PET toward the effect of  $\gamma$  radiation because all the grafted and ungrafted samples were subjected to the same radiation dose (100 kGy).

The effect of the grafting on the crystallinity has been investigated by many authors.<sup>25</sup> Some authors have stated that a slight decrease in the crystallinity occurs, and this has been taken as an indication that the graft copolymerization proceeds not only on the surface of the films but also in the amorphous part. DSC has also been used to explore the change in the ability to crystallize of PET before and after grafting. The results are shown in Figure 8(a).  $\Delta H_c$  decreases with an increasing degree of grafting. This decrease in

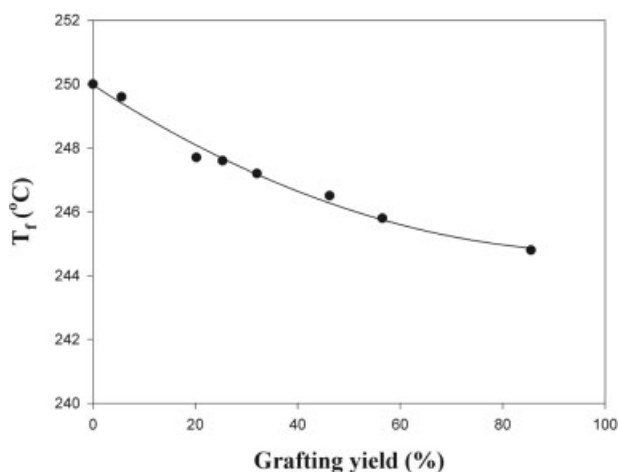


**Figure 8** Variations of  $\Delta H_c$  versus the grafting yield for ungrafted and grafted PET: (▼) normalized for the whole mass of the sample and (●) normalized for a fraction mass of PET.

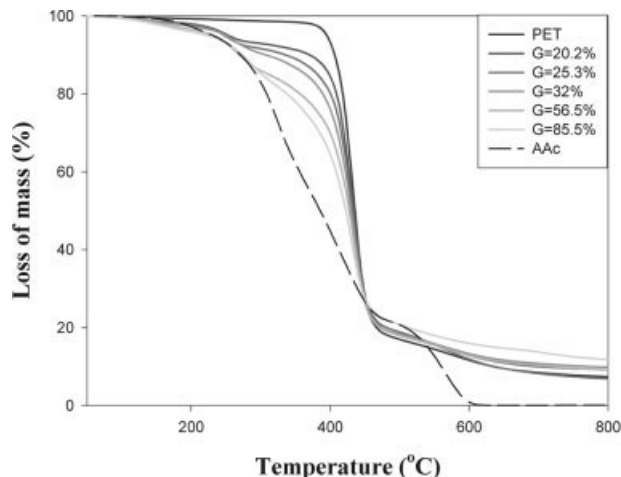
$\Delta H_c$  can be explained not only by the reduced weight fraction of the PET part in the grafted samples [Fig. 8(b)] but also to the reduction of the ability to crystallize the PET amorphous phase because the grafting process forms irregular structures opposing the crystallization.

Like the glass transition, the melting depends on the presence of diluents and the structure of the chains. For various reasons, in general  $T_m$  varies in the same direction as  $T_g$ .<sup>24</sup> The variations of the crystalline  $T_m$  of grafted PET versus the degree of grafting are plotted in Figure 9.  $T_m$  slightly changes with a changing degree of grafting. Such a decrease can be explained by the change in the size of the crystalline domains that appear during the DSC scan.<sup>26</sup>

**TGA investigation.** TGA was carried out at heating rate of 10°C/min under a nitrogen atmosphere, and the



**Figure 9** Variations of the melting temperature ( $T_m$ ) versus the grafting yield for ungrafted and grafted PET.

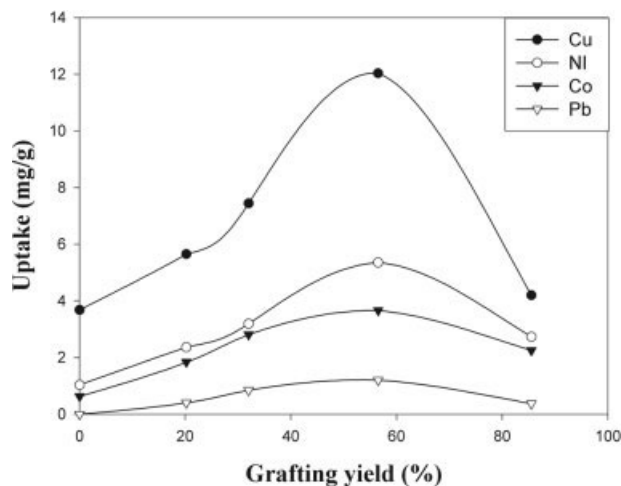


**Figure 10** Variations of the loss of mass (%) versus the temperature for ungrafted and grafted PET.

results are given in Figure 10, indicating that the PET thermal decomposition takes place in two stages. The PET film degrades at about 435°C, whereas its graft copolymers show supplementary stage decomposition at low temperatures. This supplementary stage decomposition starts from 250°C for the samples with a low degree of grafting and reaches 285°C for the high degree of grafting. Also, the extent and rate of weight loss for this stage increase with an increasing grafting yield. With respect to the thermal decomposition of AAc irradiated to 100 kGy, we can observe that such decomposition starts at about 260°C. Therefore, it is evident that this supplementary stage decomposition can be attributed to the decomposition of AAc grafted onto the PET films. For the initial decomposition positions of the grafted samples, there are no significant changes with respect to the temperature. From these data, it can be concluded that graft copolymerization proceeds only on the surface of the samples grafted.

#### Ion-exchange capacity

Poly(acrylic acid) is known as a water-soluble polymer and can be used for heavy-metal recovery either in their soluble state or as crosslinked hydrogels. Also, grafted polymers containing this monomer were investigated as ion exchangers. The recovery of copper, cobalt, nickel, and lead from their salt solutions with an initial concentration of 100 ppm was carried out. The clean and dried grafted PET films were immersed in metal ion solutions for 24 h to attain the maximum ion uptake. The results are presented in Figure 11, which illustrates the variation of the ion uptake versus the degree of grafting. The ion uptake increases with the grafting yield up to its maximum at about 60%. A decline in the metal uptake at a higher grafting yield is due to a highly crosslinked network structure formed



**Figure 11** Effect of the grafting yield on the ion uptake of PET-g-AAc.

via hydrogen bonding. Such crosslinking density restricts more diffusion of the metal solution, causing a decrease in its uptake. The efficiency of grafted PET toward ion recovery can be arranged in the following order: copper > nickel > cobalt > lead. Such a sequence indicates that the grafting film is highly selective for  $\text{Cu}_2^+$  in comparison with the other metal ions investigated. Also, it seems that the stability of the Cu-metal/polymer complex is higher than those obtained for others. The ionic radii and complexation stability play important roles in the selectivity of grafted polymers and their affinity toward different metal ions. From these results, it can be assumed that the  $\text{Cu}_2^+$ -metal/polymer complex is more stable than the other metal/polymer complexes formed. As a result, copper is more selective than the other metals investigated here.

### CONCLUSIONS

On the basis of these results, it can be concluded that PET is susceptible to radiation-induced graft copolymerization of AAc. Modified PET (PET-g-AAc) can be used for heavy-metal recovery from solutions. Thermal analysis with DSC has shown that the grafting of AAc onto PET affects the mobility of the chain of PET and consequently its  $T_g$  and  $\Delta C_p$  values. Moreover, the

grafting forms structural irregularities that inhibit the crystallization and change the size of crystalline domains that appear during the DSC scan.

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