

# Grafting of Polypropylene and Its Potential Use as Metal Ion Adsorption Resin

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Received 19 December 2007; accepted 31 August 2008

DOI 10.1002/app.29306

Published online 19 March 2009 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Polypropylene (PP) was modified by radical grafting of acrylic acid (AA) in the melt by using dicumyl peroxide (DCP) as initiator. To reach a high grafting degree (GD) without substantially modifying PP-chain structure, a few runs were carried out by employing butyl 3-(2-furanyl)propenoate (BFA), which is a coagent able to preserve the molecular weight (MW) of PP macromolecules in the presence of radical grafting reagents. All the samples were extracted with selective solvents to remove unreacted chemicals and free poly(acrylic acid) (PAA), and the GD was accurately determined by using the FTIR methodology. The GD ranged from 1.51 to 4.67 mol %. High-temperature size permeation chromatography analysis was used to evaluate

MW behavior, confirming the control exerted by the presence of BFA on the degradation reactions. DSC, TGA, and SEM analyses were performed to analyze the chemical modification effects on the polymer products' thermal and morphological properties. Finally, selected samples, with a particle size distribution in the range 100–850  $\mu\text{m}$ , were tested as metal ion adsorption resins. Al(III), Cr(III), Zn(II), Cd(II), Pb(II), and Hg(II) were studied, and the highest adsorption efficiency values (in percentage) were obtained for Al(III) (15–20%) and Hg(II) (25–30%). © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 290–298, 2009

**Key words:** adsorption; metal-polymer complexes; resins

## INTRODUCTION

The use of isotactic polypropylene (PP) in some technological fields is restricted principally because of the lack of functionalities. The most interesting applications of PP are related to biomedical, fibers, membranes, metal-polymer bonding, composites, blending, and paint adhesion fields, which generally request the presence of polar groups on the surface or inside the polymer bulk.

Reactive extrusion is the most widespread method to introduce functionalities into polyolefin substrates, in particular the free radical-induced grafting process.<sup>1</sup> This process involves a free radical initiator (most commonly a peroxide), monomer or macromonomer, and polyolefin as well as coagents when required. The success of a grafting experiment is usually measured in terms of the grafting degree (GD; the fraction of the monomer that is grafted onto the polymer backbone). To maximize the GD,

to minimize side reactions (for example, the functionalizing monomer homopolymerization) and to control the structure of the grafted product, it is important to control the temperature, residence time, polyolefin, initiators, monomers, and coagents' nature and amounts.<sup>1</sup> For example, during the melt-radical functionalization of PP using maleic anhydride (MAH) and its derivatives<sup>2–8</sup> as grafting species, the formed macroradicals undergo beta-scission reaction, an undesirable reaction responsible for chain breaking, which dramatically reduces the macromolecules length, thus changing the structure of the pristine polymer and consequently its final mechanical properties.

Recently, the polymer structure and GD can be controlled using furan derivatives (as coagents), which are able to control and limit the PP degradation during the melt-radical reaction with MAH.<sup>9–11</sup>

This article proposes the use of a PP-like supported polymer that is able to interact with metal ions from an aqueous solution because of its suitable characteristics such as high ratio stiffness/impact, good solvent resistance (insoluble in water), good thermal stability, convenience particle characteristics, and low production costs. For the proposed

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Contract grant sponsors: CIPA, PETROQUIM SA, CONICYT.

TABLE I  
Grafting Reaction Conditions: Experimental Procedure, Feed Amounts, and End Torque Values<sup>a</sup>

Abbreviation	DCP (mol %)	AA (mol %)	BFA (mol %)	Remarks	End torque (N m)
PH0130	–	–	–	–	0.90
F1PPAA1	0.1	2.9	–	Reaction mode: Method 1	0.45
F1PPAA2	0.1	5.8	–	Reaction mode: Method 1	0.55
F2PPAA1	0.1	2.9	0.2	Stoichiometric ratio: BFA/primary radicals	1.73
F2PPAA2	0.1	5.8	0.2	Stoichiometric ratio: BFA/primary radicals	2.61
F3PPAA2	0.1	5.8	–	Reaction mode: Method 2	0.40

<sup>a</sup> All the runs were carried out at 180°C, 50 rpm, 10 min.

application, the melt radical modification of a PP powder by grafting onto the macromolecular backbone of acrylic acid (AA) was performed.

The chemical modification of PP using AA has been approached in the literature with different methodologies as follows: ultraviolet irradiation in the presence of benzophenone,<sup>12</sup> etching oxidation,<sup>13</sup> emulsion,<sup>14</sup> suspension process,<sup>15</sup> plasma functionalization,<sup>16</sup> and melt-radical grafting reaction.<sup>17,18</sup> In particular, Flores-Gallardo et al.<sup>17</sup> obtained a GD in the range 0.6–3.0 (mol %) depending on the feed ratio initiator/monomer in the presence of styrene, which was used as coagent. Rao et al.<sup>18</sup> reported a GD value of 3.90 (wt %) using benzoyl peroxide (BPO) and 5.60 (wt %) using dicumyl peroxide (DCP) as initiators.

By focusing the attention on surface-grafting methodologies and by taking into account the application of our interest, some related literature has been found: electron beam irradiation (EBI), plasma, gamma rays, and photoinduced grafting were applied directly onto different PP-based materials such as nonwoven fabric, membranes, and fibers. The products were used to react with different ionic species: Cu(II), rare earth ions, nitrogen, and phosphorus compounds.<sup>19–27</sup> In particular, Lin and Hsieh<sup>20</sup> found retention values around 50% for Cu(II) with low concentrations of metal ion (95 ppm) and a moderate temperature (40°C) by using fibrous morphology with high GD (120 wt %).

The modification of PP with AA and the adsorption properties of the chemically modified PP toward different metal ions in aqueous solutions are reported here. The traditional and current industrial modification technique of melt-radical grafting reaction was used (reactive extrusion).

The evaluation of chemically modified PP-like metal ion adsorption resin, by taking into account the intrinsic and extrinsic variables that influence the adsorption process, requires a very high GD (related with the ion exchange sites)<sup>28</sup> to achieve useful retention properties. However, reaching a high GD by using melt-radical grafting approach is not easy because the mechanism involves adverse reactions

that affect the final mechanical properties of the modified PP.<sup>1–4</sup> Thus, for our purposes, the mechanical stability of the resins used depends on ion adsorption. Generally, by increasing the amount of peroxide and/or monomer, higher GDs are achieved; however, in an extreme situation (for example, using a large amount of initiator, more than 1 wt %<sup>9,10,29</sup>), a viscous liquid PP is obtained because of the degradation process.

Therefore, to control both grafting level and molecular weight evolution during the radical grafting in the melt, we designed one set of reactions of PP with AA (see Table I) using butyl 3-(2-furanyl)propenoate (BFA) as coagent, which was patented by the University of Pisa and kindly supplied for this research.<sup>9–11</sup>

All the samples obtained in the presence or absence of BFA were comparatively characterized in terms of GD, MW, thermal, and morphological properties, and finally they were tested as metal ion adsorption resin.

## EXPERIMENTAL SECTION

### Materials

Isotactic polypropylene homopolymer (PP) powder PH0130, supplied by PETROQUIM S.A. (Chile), with a melt-flow rate (MFR) of 0.1 g/10 min (2.16 kg/230°C) was used. Ethylene-acrylic acid copolymer (EAA) containing 20 wt % of AA with a melting point of 99–101°C and density of 0.96 g cm<sup>-3</sup> was purchased from Aldrich. DCP was used without further purification. AA was purified by distillation under reduced pressure. Butyl 3-(2-furanyl)propenoate (BFA) was prepared as reported in the literature.<sup>9,27,30</sup> The ion exchange resin Amberlite IRP-64 100–400 wet mesh with an ion exchange capacity of 10 mequiv g<sup>-1</sup> (dry) was purchased from Aldrich.

For metal ions aqueous solutions, salts of Zn(NO<sub>3</sub>)<sub>2</sub> × 6H<sub>2</sub>O, Al(NO<sub>3</sub>)<sub>3</sub> × 9H<sub>2</sub>O, Cr(NO<sub>3</sub>)<sub>3</sub> × 9H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Cd(NO<sub>3</sub>)<sub>2</sub> × 4H<sub>2</sub>O, and Hg(NO<sub>3</sub>)<sub>2</sub> × H<sub>2</sub>O (p.a. grade, Merck) were used as received. The solutions were prepared with double-distilled

water whose conductivity was lower than  $1 \mu\text{S cm}^{-1}$ .

### Melt-radical grafting procedures

PH0130 grafting reactions were performed in a Brabender Plastograph Mixer (mixer chamber  $20 \text{ cm}^3$ ) preheated at  $180^\circ\text{C}$  and rotor speed of 50 rpm. Different reagents addition methodologies were used generating three series of samples:

Method 1: The PP powder was filled into the chamber under nitrogen atmosphere. When the polymer was completely molten, after 4 min, a mixture between AA and DCP was added dropwise using a syringe. This method generates the F1PPAA series.

Method 2: The PP was preimpregnated with a mixture of AA and DCP under nitrogen atmosphere during 30 min. Then the so-treated PP powder was filled into the chamber under nitrogen atmosphere. This method yields F3PPAA.

During all the runs (time was 10 min), torque and temperature evolution were measured by Brabender Mixing software WinMix. The recovered polymer was melt-pressed into films (1.3–1.5 mm thickness) and then cut. The small pieces of the grafted PP were grinded under liquid nitrogen to obtain particles with sizes in the range 850–100  $\mu\text{m}$ . Finally, the modified PP particles were extracted with boiling water for 16 h and methanol for 8 h for samples prepared without using BFA; while the modified PP particles were extracted with boiling water for 16 h and acetone for 8 h in the case of samples prepared by using BFA with the aim to remove free AA homopolymer and unreacted chemicals, respectively. In both cases, the residue was dried under vacuum at  $80^\circ\text{C}$  for 6 h.

### Characterization

#### FTIR analysis

The grafted PP (FPPAA series) was characterized by Fourier transform infrared spectrometer (FTIR; before and after extractions) with a Perkin-Elmer 1760-X FTIR spectrometer onto films obtained by casting from xylene solutions on KBr windows.

To determine the GD, a calibration curve was done using compatible blends of PP and polar copolymer (EAA) containing AA units (20 wt %).<sup>31</sup> The relative absorbance obtained from IR analysis was plotted against the ratio of PP/AA in the blends. The blends were prepared by solution blending (xylene) and carefully characterized by FTIR. The GD was reported as a function of the ratio between the area of the characteristic peak: the signal at  $1710 \text{ cm}^{-1}$  corresponding to the stretching of the carbonyl

group ( $\text{C}=\text{O}$ ) coming from AA and the signal at  $1167 \text{ cm}^{-1}$  corresponding to the stretching of methyl group ( $\text{C}-\text{CH}_3$ ) coming from PP.

In the case of the samples modified in the presence of BFA (F2PPAA series), a deconvolution procedure was applied<sup>9,29,32</sup> by taking into account the presence on the carbonyl region of  $\text{C}=\text{O}$  stretching due to the ester derivative (the BFA). Two Lorentzian-shaped bands were considered in the range between 1750 and  $1650 \text{ cm}^{-1}$  (1)  $\nu_{\text{C}=\text{O}}$  of the carboxylic acid ( $1710 \text{ cm}^{-1}$ ) and (2)  $\nu_{\text{C}=\text{O}}$  of the ester (BFA) ( $1737 \text{ cm}^{-1}$ ), whose absorbance changed by varying the functionalization degree. The deconvolution was performed by using a nonlinear least-squares method of fitting (NLSF; Origin 6.0 software) by optimizing the value area for each peak, the half width of the band and the peak's maximum by starting with determined values and varying them within a predetermined range.

#### SEC analysis

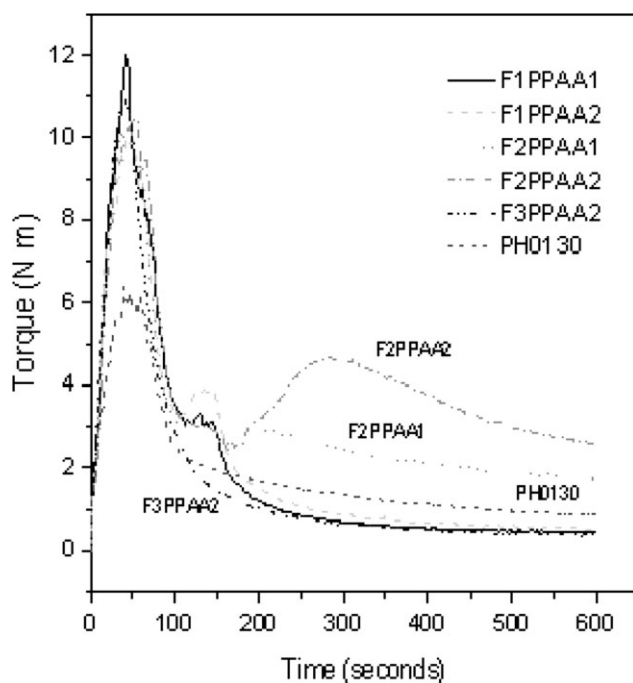
Molecular weights of the FPPAA sample series were determined by size exclusion chromatography (SEC) using a Waters Alliance GPCV 2000 series System apparatus equipped with three Waters Styragel HT 6E columns (MW 5000–10,000,000) and one Waters Styragel HT 3 column (MW 500–30,000) with an average particle size of 10  $\mu\text{m}$ ; a differential refractive index (DRI) and a differential viscometer as detectors. Polymer solutions were prepared with amounts of 2.5–3.0 mg of polymer in 4 mL of 1,2,4-trichlorobenzene (TCB) containing a small amount of antioxidant (BHT) to prevent any degradation and eluted at  $145^\circ\text{C}$ ,  $1 \text{ mL min}^{-1}$  flow rate. The calibration was made with narrow polystyrene standards, and the calculations were performed using Millennium software.

#### Porosity measurements

Porosity measurements for intrusion mercury were performed in Micromeritics AutoPore IV-9510 with penetrometer of 15 bulb and stem volume 1.8360 mL for PH0130 original powder and grafted. The sample was previously dried under vacuum at  $80^\circ\text{C}$  for 8 h.

#### DSC and TGA analysis

Thermal analysis was carried out using a Mettler-Toledo DSC 821 differential scanning calorimeter (DSC) in the temperature range  $20$ – $190^\circ\text{C}$  at a heating rate  $20^\circ\text{C min}^{-1}$ . The residues of all solvent extractions of the grafted PP samples were analyzed. The instrument was previously calibrated by using In as standard reference. Thermogravimetric analyses (TGA) were performed in Mettler-Toledo TGA/



**Figure 1** Behavior of the mixing torque for the samples modified with AA (all) and with BFA (F2PPAA 1-2).

SDTA 821 at the temperature range 40–600°C and heating rate 10°C min<sup>-1</sup>.

#### SEM analysis

Scanning electron microscopy (SEM) was performed by JEOL-JSM 6000380 LV on particle surface for the grafted PP after sputtering with gold.

#### Solid-phase extraction experiments

The FPPAA series and commercial resin were evaluated by batch method. The batch method was performed using a 7.5-mL culture tube previously cleaned with ethanol solutions. Then, 0.05 g of polymer were put in contact with 5 mL of a metal ion solution using the culture tube. The metal ion stock solutions were prepared taking into account the molecular weight of the monomeric unit of the functional polymers, and the corresponding amount of metal ion was calculated using a mol ratio of functional group and metal ion of 20 : 1. The system was introduced in a bath and kept at room temperature (20°C) at 140 rpm for 1 h. Then, the samples were filtered using a water-saturated filter paper, Whatman No. 1, and then the filtrate was collected in a 50-mL flask. The metal ion concentration was determined by atomic absorption spectrometry (AAS) through a spectrometer UNICAM Solaar 5M Series. The contact experiments in the batch method were done in triplicate to get an appropriate reproducibility of the metal ion retention property.

The adsorption of the metal ions from aqueous solution was expressed in adsorption efficiency (%) and calculated by the following equation:

$$\text{Adsorption efficiency (\%)} = \frac{C_{SS} - FD \times C_{NA}}{C_{SS}} \times 100$$

where the  $C_{SS}$  is the concentration of the stock solution,  $FD$  is a dilution factor equal to ten (10) and  $C_{NA}$  is the concentration of the non-adsorbed metal ion in the filtrate.

## RESULTS AND DISCUSSION

### Grafting experiments

The free radical grafting of AA onto PP (see Table I) was carried out in a Brabender internal mixer, and the torque/time curve was collected for each sample (see Fig. 1). F2PPAA1 and F2PPAA2 samples were prepared by adding BFA in a stoichiometric ratio with respect to the amount of primary radicals (theoretically calculated by considering the production of two primary radicals per mole of DCP, Table I). For these samples, an increment of the torque was observed as soon as the reagents' feeding was finished and the value remained over the other samples (including the virgin PP) until the end of run (for all reaction time).

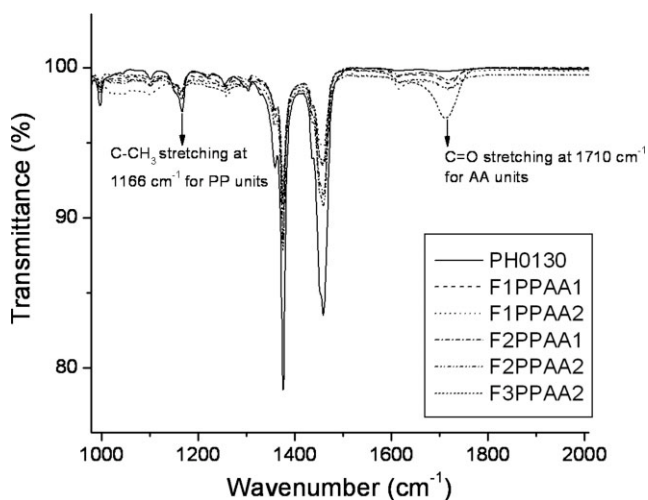
The end torque values (see Table I) are significantly higher (2.9 times for F2PPAA2 and 1.9 times for F2PPAA1) with respect to pure PP, and the effect is even more dramatic with respect to the samples prepared by using AA and peroxide alone: 3.8 times for F2PPAA1 with respect to F1PPAA1 and 4.8 times for F2PPAA2 with respect to F1PPAA2. This behavior indicates that the presence of BFA is able to maintain the viscosity of modified PP, suggesting a certain control of the PP degradation reaction I; in contrast, this clearly occurred when BFA was not used (i.e., run F1PPAA series).

To determine the quantitative effect of BFA on the molecular weight of grafted PP, the SEC analysis of all the samples was performed (see Table II). For all the samples, decreases of molecular weight,

**TABLE II**  
**SEC Data of Grafted PP**

Sample	$M_n \times 10^{-3}$ (Da)	$M_w \times 10^{-3}$ (Da)	$M_n/M_w$	$[\eta]$ (dL g <sup>-1</sup> )
PH0130 <sup>a</sup>	93	347	3.7	1.34
F1PPAA1	56	123	2.2	0.57
F1PPAA2	47	118	2.5	0.54
F2PPAA1	67	194	2.9	0.66
F2PPAA2	72	248	3.5	0.79
F3PPAA2	46	118	2.6	0.48

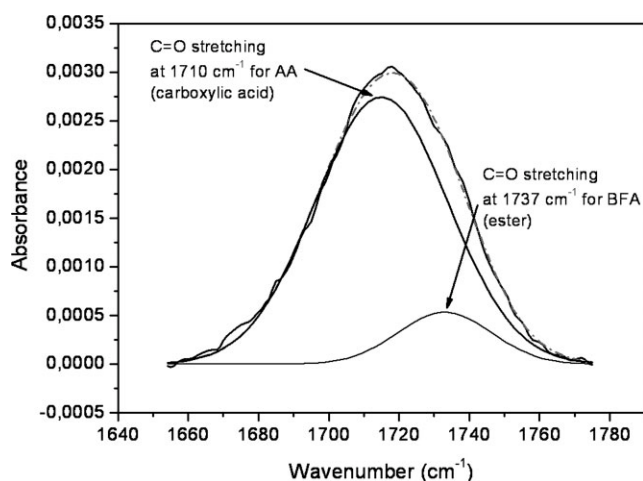
<sup>a</sup> PP processed in Brabender at working conditions.



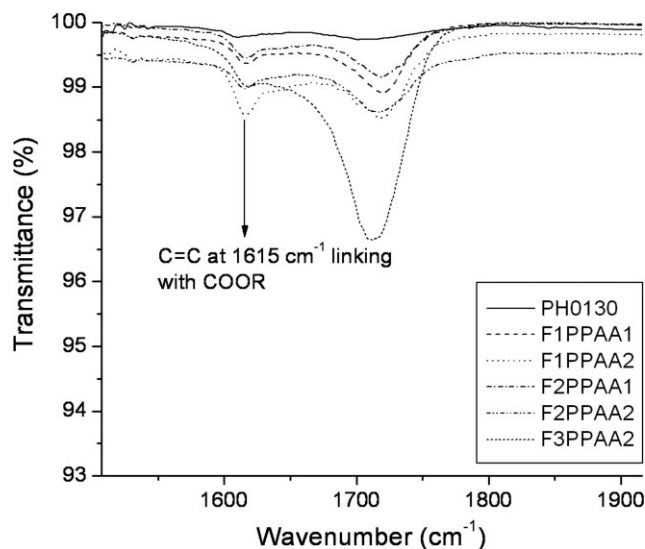
**Figure 2** FTIR spectra in the range 950–2000  $\text{cm}^{-1}$  of grafted PP samples with variable amounts of AA and BFA.

polydispersity, and intrinsic viscosity were observed, indicating that a certain extent of degradation reaction took place in the molten phase. This extent was less severe for samples assisted with the coagent, indicating BFA's effective influence on degradation control as demonstrated by Coiai et al.<sup>9</sup> In particular, the polydispersity of the sample F2PPAA2 is close to pure PP (even if a decreasing of  $M_n$  and  $M_w$  was observed), suggesting the occurrence of both breaking and coupling macroradicals reactions.<sup>10,30</sup>

The FTIR spectra of the grafted PP samples after removing the free homopolymer by solvent extraction are shown in Figure 2. They confirm AA grafting as follows: the C=O stretching at  $1710\text{ cm}^{-1}$  is clearly evident and its intensity depends on the grafted amount. After the deconvolution procedure, because of the contemporary grafting of different carboxyl species,<sup>29,32</sup> the presence of the ester C=O



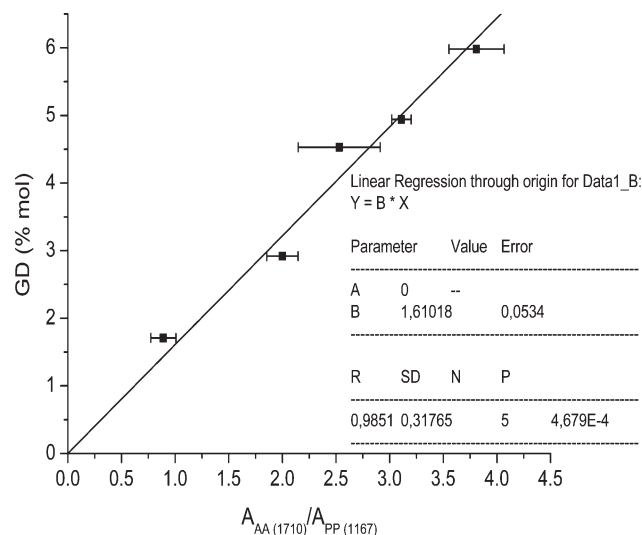
**Figure 3** Deconvolution of the C=O peak signal for PP-grafted samples with BFA and AA.



**Figure 4** FTIR spectra for the range 1500–1950  $\text{cm}^{-1}$  of the grafted PP samples.

stretching was highlighted for the samples F2PPAA1 and F2PPAA2 confirming the grafting occurrence of BFA<sup>9,10</sup> (see Fig. 3). By observing an enlargement of IR spectra in the region between 1400 and  $1900\text{ cm}^{-1}$  (see Fig. 4), the presence of an unsaturation was highlighted, suggesting the possible occurrence of termination reactions by radical disproportionation as already reported.<sup>9,10</sup> The PP treated in the melt under the same condition (PH0130) showed carbonyl absorptions that are completely negligible with respect to grafted samples, suggesting that the possible thermoxidation process induced by temperature does not occur in these conditions.

To quantitatively assess the GD values of grafted PP samples, a calibration curve was arranged as described in the "Experimental Section." Figure 5



**Figure 5** Calibration curve obtained by blending PP with EAA.

TABLE III  
Grafting Degree Values, Conversion, and Efficiency Data for Grafted Samples

Sample	GD <sub>AA</sub> (mol %)	AA conv. <sup>a</sup> (%)	AA Eff. <sup>b</sup>	GD <sub>BFA</sub> <sup>c</sup> (mol %)	BFA conv. <sup>a</sup> (%)	BFA Eff. <sup>b</sup>	Functionality × macromolecules <sup>d</sup>
F1PPAA1	2.86	94.1	14.3	–	–	–	38
F1PPAA2	4.67	78.5	23.3	–	–	–	52
F2PPAA1 <sup>c</sup>	1.51	49.7	7.5	0.11	55.0	0.5	24
F2PPAA2 <sup>c</sup>	1.85	30.8	9.2	0.14	70.0	0.7	32
F3PPAA2	2.90	49.9	14.5	–	–	–	32

<sup>a</sup> Percentage of grafted AA and BFA units with respect to the AA and BFA concentration in the feed.

<sup>b</sup> Efficiency = mol ratio between the FD and the amount of primary radicals (Eff = FD/2[ROOR]).

<sup>c</sup> The FD<sub>BFA</sub> values were calculated by considering the  $\epsilon_{\text{BFA}}$  ( $1.10 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-2}$ ) and the  $\epsilon_{\text{PP}}$  ( $1.22 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-2}$ ) calculated for the Atofina hopolymer<sup>10</sup> and using the deconvolution procedure explained in the Experimental Section.

<sup>d</sup> Calculated as  $M_n/\text{monomeric unit weight} \times \text{GD}/100$ .

shows linear variation of GD (mol %) versus the integral absorbance ratio of AA (deriving from EAA copolymer) and PP units at least up to 5 mol % of AA units corresponding to a blend ratio PP/EAA = 73.7/26.3 wt %. The best-fit equation of the simulation procedure was employed for each modified PP, and the corresponding GDs were calculated, as shown in Table III. The FTIR spectra were obtained and the absorbance signals were analyzed using samples that were accurately washed with water, methanol, and acetone to remove unreacted peroxide, monomer, coagent, and any possible poly (acrylic acid) (PAA) homopolymer chains and BFA oligomers.<sup>10</sup>

A good grafting level in all the runs was generally reached; conversion of the monomer ranged from 31 to 94% depending on the monomer/peroxide ratio, the presence of BFA, and the applied methodology. The efficiency values suggested the insertion of at least 10–24 monomer units per primary radicals: when considering AA's homopolymerization capability under the adopted condition, segments with more than 10 AA monomer units were successfully grafted. An increase of the GD is expected when the monomer is increased (at certain level) by maintaining the initiator amount constant, as observed for the samples F1PPAA1 and F1PPAA2 (see Table III). However, when the BFA coagent is added, only a slight increment of the GD is obtained by increasing the AA amount (samples F2PPAA1 and F2PPAA2), and the GD is generally reduced by the presence of BFA as observed by comparing run F2PPAA2 (1.85 mol %) with the run F1PPAA2 (4.67 mol %), which was performed using same amounts of AA and DCP. This result was recently evidenced in the BFA-assisted radical functionalization of PP with MAH and was justified by considering the specific reactivity of the radicals formed by BFA addition.<sup>10</sup> The lack of transfer reactions of macroradicals bearing BFA and their tendency to terminate by coupling or disproportionation<sup>10</sup> probably affect the length of AA-grafted chains

(that decreased); in spite of this evidence, the functionality distribution per chain (see Table III) was almost unchanged for all the samples (except F1PPAA2), suggesting a more homogeneous distribution of AA along the backbone for the samples obtained with BFA showing a good control of MW. Thus, even if GD decreased, because of the molecular weight control, a high amount of functionalities per chain can be reached by maintaining the structure and thus the mechanical stability of PP unchanged.

After solvent extractions, a mass balance analysis was performed for all the samples (see Table IV). A larger amount of extractable fractions, mainly containing oligomers and/or homopolymerization products of AA (see Fig. 6), were obtained, as expected, for samples characterized by a lower grafting level (F2PPAA1, F2PPAA2, F3PPAA1).

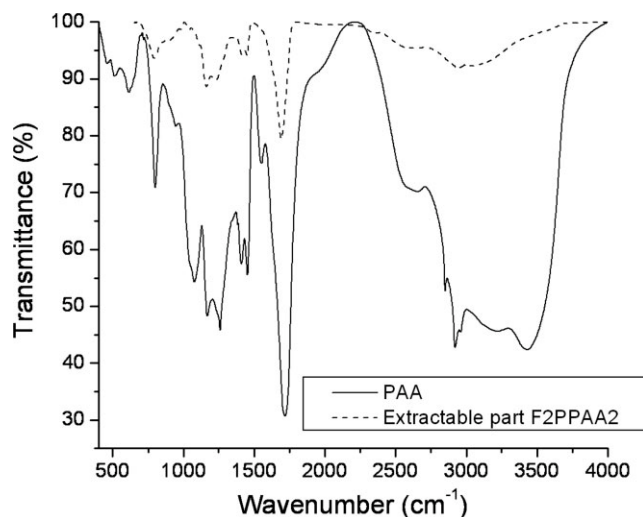
By comparing the samples F1PPAA2 and F3PPAA2 (see Table III), a significant reduction of the GD was observed when changing the methodology but maintaining the reagents' amounts. Flores-Gallardo et al.<sup>17</sup> suggested that a higher GD is reached when PP particles are preimpregnated; however, this does not seem to be the case here and a reduction of GD was observed when applying the second method. This result can be explained by the PP particles' morphology, which shows a porosity

TABLE IV  
Solvent Extraction Results for Grafted Samples

Sample	Solvent soluble fraction (wt %)	Residue (wt %)
F1PPAA1 <sup>a</sup>	0.5	99.5
F1PPAA2 <sup>a</sup>	0.8	99.2
F2PPAA1 <sup>b</sup>	1.2	98.8
F2PPAA2 <sup>b</sup>	1.5	98.5
F3PPAA2 <sup>a</sup>	1.2	98.8

<sup>a</sup> Extraction with hot water for 16 h and hot methanol for 8 h in continuous way.

<sup>b</sup> Extraction with hot water for 16 h and hot acetone for 8 h in continuous way.

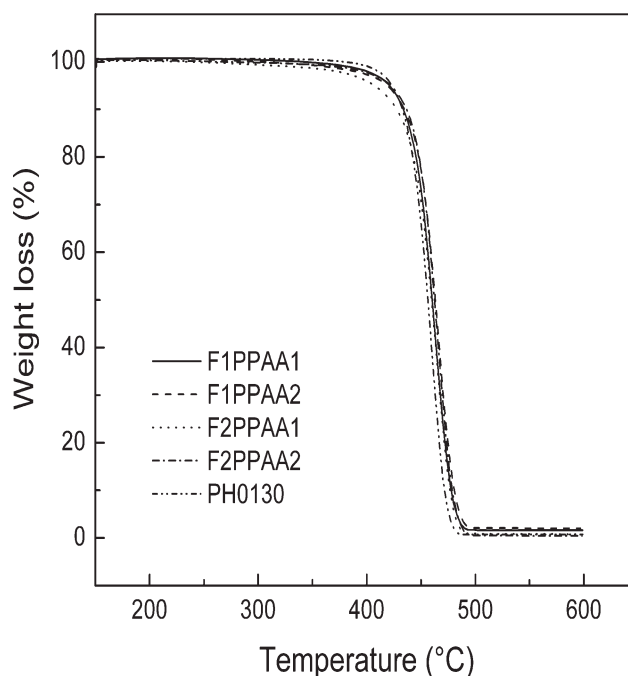


**Figure 6** FTIR spectra for the extractable part of the sample F2PPAA2 compared with pure poly(acrylic acid) (PAA).

value of 6.1%. After impregnating solution AA plus DCP, micelles<sup>33</sup> containing both the reagents are trapped in particle voids. In these conditions, the initiator was located in the liquid monomer, and thus it is more able to start the homopolymerization reaction rather than forming macroradicals into polymer chains, and therefore decreasing the GD.

Thermal stability of grafted samples was tested by TGA analysis (see Fig. 7): no significant variation of the onset temperature was observed when comparing the mass loss curves of different grafted PPs, where the degradation path was completely comparable with the pristine polymer one.

The crystallization temperature (determined by DSC measurements) for all the samples showed an increment with respect to pure PP (Table V), indicating the nucleation effect of the grafted AA chains during the crystallization of PP chains. A small increment of the crystallinity ( $\chi$ ) for the samples F2PPAA1 and F2PPAA2 (both with BFA) with respect to pure PP was observed. This result can be related to the possible formation of more branched structure



**Figure 7** Thermogravimetric analyses of the grafted PP samples.

because of some coupling reactions, characteristic of the presence of BFA in the radical process.<sup>10</sup>

#### Solid-phase extraction technique experiments: Batch method

On the basis of the previous results summarized in Tables II and III, we selected the grafted PP samples with the highest GD and molecular weight (related with the best mechanical strength) to carry out the solid-phase extraction (SPE) experiments (F1PPAA1, F1PPAA2, and F2PPAA2). In this type of experiments, unwashed samples were used because the possible free PAA present in the samples might act as extra coupling agent during the interaction with metals ions in aqueous solutions.

**TABLE V**  
Thermal Properties of PP-Grafted Samples

Sample	$\chi^a$ (%)	Crystallization		Melting	
		$T_{c,peak}$ (°C)	$\Delta H_c$ (J g <sup>-1</sup> )	$T_{m,peak}$ (°C)	$\Delta H_f$ (J g <sup>-1</sup> )
PH0130	45	106.5	95.7	152.9	95.2
F1PPAA1	43	113.3	91.1	155.6	90.1
F1PPAA2	44	114.5	99.3	155.7	92.9
F2PPAA1	48	111.6	96.0	157.0	100.8
F2PPAA2	47	114.0	95.9	158.1	98.2
F3PPAA2	45	114.6	96.3	155.7	94.4

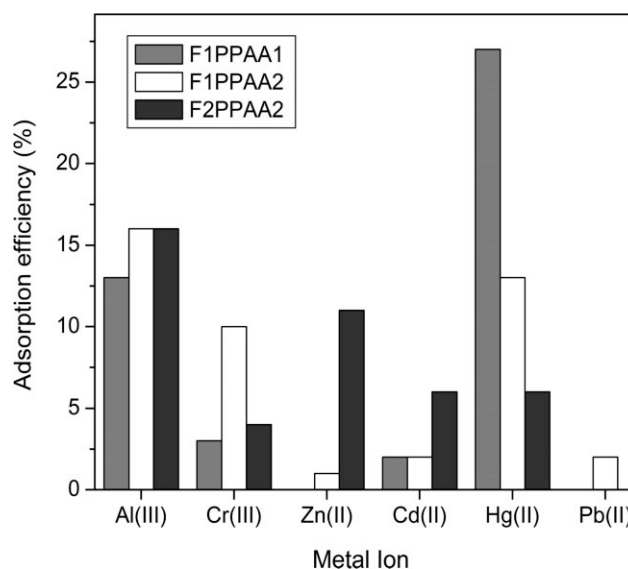
<sup>a</sup> The relative crystallinity ( $\chi$ ) of the samples was calculated with the expression:  $\chi = \frac{\Delta H_f}{\Delta H_f^0} \times 100\%$ . Where  $\Delta H_f^0$  is the heat of fusion of the 100% crystalline polymer, for PP was taken 209.0 J g<sup>-1</sup>.<sup>35</sup>

Thermal stability characterization and adsorption efficiency (expressed by %) are necessary to compare grafted PPs with the conventional and current ion exchange resins. In the case of thermal stability, the literature indicates that the recommended working temperature for an ion exchange resin bearing the same functional groups ( $\text{COO}^-$ ), such as copolymer of AA and divinylbenzene, is around  $120^\circ\text{C}$ .<sup>34</sup> In our case, for all grafted PPs, the loss of physical stability is around  $140^\circ\text{C}$  when the PP crystals begin to melt (see Table V) and degradation starts at around  $450^\circ\text{C}$  (see Fig. 7), indicating a comparable thermal stability of the grafted PPs samples with the commercial ion exchange resin. However, the SPE experiments were carried out at  $20^\circ\text{C}$  because this temperature should be more adequate for a possible industrial application.

Comparing the metal ion adsorption efficiency (%) of the chemically modified PP (sample F2PPAA2) for  $\text{Al}^{3+}$  in comparison with the commercial resin (AMBERLITE IRP-64), values around 81% were found for the commercial resin in contrast with 17% for the sample F2PPAA2. Even when the difference seems to be very high, it is important to highlight that the proposed grafted PP has low GD (1.85 mol %) and a broad particle size distribution (100–850  $\mu\text{m}$ ). As a result, the system is more heterogeneous, and the density of the chemically modified PP is lower than  $1\text{ g cm}^{-3}$ , making the contact experiment less efficient (the PP particles float in the aqueous medium). The only characteristic that these functional polymers have in common is the presence of the same functional group (carboxylic acid), although it is well known that different ion exchangers bearing the same groups can exhibit significant different properties because a group's strength depends on the nature of the supporting hydrocarbon structure.<sup>34</sup>

Figure 8 shows the adsorption efficiency (%) of metals ions of the grafted PPs: the highest adsorption is observed for Al(III) and Hg(II) for all the systems evaluated here. In particular, the F2PPAA2 sample is the only one showing a significant interaction with Zn(II), thus indicating that the electron withdrawing group substituent and the heteroaromatic ring of the BFA grafted molecule can influence the metal ion stabilization.

Comparing the adsorption efficiency of the samples F1PPAA2 and F2PPAA2 for the metal ion Al(III) (see Fig. 8), it can be observed that both show similar retention values (16%); however, these samples have different GD (4.67 and 1.85 mol %, respectively). This result can be explained by considering that the presence of the BFA induces a positive effect on the homogeneity of the F2PPAA2 sample (see Table III) because of the molecular weight control exerted by the presence of the coagent, and this effect can improve the adsorption in spite of the low GD



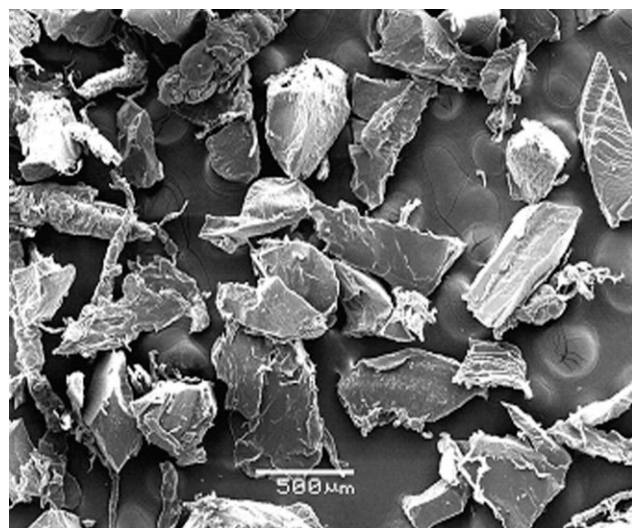
**Figure 8** Metal ion retention of grafted PP at pH 5 (> pKa of the acrylic acid 4.5) and at pH 2 for the Hg(II).

reached for the sample F2PPAA2. Moreover, this behavior only occurs for the trivalent ion, Al(III) suggesting that Al(III) is more sensitive to sample homogeneity rather than the amount of the functional group available on the polymer surface. Also in this case, as in the case of Zn(II), the chemical nature of the BFA grafted onto the PP backbone may positively influence the adsorption efficiency for Al(III).

In the case of Hg(II), a high level of adsorption (25–30%) was found for the sample F1PPAA1 at pH 2 in comparison with the sample F1PPAA2. As we mentioned in a previous paragraph that this experiment was performed considering the unwashed grafted PPs samples, and thus higher adsorption is expected for the F1PPAA1 sample since these samples have the higher conversion of AA (94.1%) in comparison with F1PPAA2 (78.5%), indicating that the F1PPAA1 could have more functionalities on the surface coming from the grafting reaction and the AA homopolymerization. The adsorption efficiency behavior of the divalent metal ion Hg(II) suggests that it is more sensitive to the amount of the functional group available on the polymer surface than to sample homogeneity.

At pH 2, the formation of a linear adduct between the weak acid Hg(II) and the partially deprotonated carboxylate ligand ( $\text{COO}^-$ ) is possible. The retention behavior of Al(III) at pH 5 is expected for the resins because of the hard acid nature of the trivalent ion and the hard base nature of the carboxylate ligand ( $\text{COO}^-$ ) when the experimental conditions are above the pKa of the AA (3.5–8)<sup>34</sup>. For the other metal ions, the carboxylic acid group acts as a weak acid ion exchanger because of their lower metal ion adsorption.





**Figure 9** SEM micrograph of F2PPAA2 particles.

The counter ions present in the aqueous solutions ( $H^+$ ,  $OH^-$ , and  $NO_3^-$ ) are the same for all the evaluated systems, possessing the same hard base nature as the carboxylate ligand. Therefore, we can assume that the influence in the stabilization of the metal-polymer adduct will be similar for all of metal ions.

The morphological characteristic of the grafted PP particles was evaluated, finding a particle size distribution in the range 100–850  $\mu m$  with an irregular laminate shape (see Fig. 9) and not porous. It was found to be mechanically stable at room temperature during the experiment.

### CONCLUSIONS

PP modified with AA in the presence of radical initiator and BFA coagent has been prepared with high conversion of monomers and has been used as a polymer-supported reactive reagent to remove metal ions. The coagent was able to react in the molten phase producing grafting together with a significant reduction of the PP backbone degradation by maintaining almost the same functionality amount per chain obtained for samples produced without BFA.

All the grafted PP samples showed interesting metal ion adsorption properties considering the low content of the functional carboxylic/carboxylate groups. In particular, the presence of the BFA-grafted species together with short AA chains affected the ion adsorption in SPE experiments, suggesting a synergic effect of different parameters as follows: GD, functionalities distribution, molecular weight. In fact, even the AA-grafted samples, characterized by a lower GD value, showed a positive stabilizing effect toward Al(III) and Zn(II). The highest adsorption efficiency (in percentage) values were obtained for Al(III) 15–20% and Hg(II) 25–30%.

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