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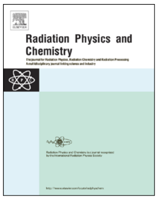

Radiation Physics and Chemistry

Functionalization of polymer surfaces by radiation-induced grafting for separation of heavy metal ions

E.M. Kornacka*, G. Przybytniak, L. Fuks, M. Walo, K. Łyczko

Institute of Nuclear Chemistry and Technology, Dorodna 16, 03-195 Warsaw, Poland

HIGHLIGHTS

- Two monomers were copolymerized on polypropylene filter by radiation grafting.
- Grafting has changed thermal characteristic of polypropylene matrix.
- Contribution of monomers in the grafted layer was determined by IR spectroscopy.

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ABSTRACT

The reported investigations were focused on the elucidation of the most important factors influencing radiation-induced grafting, particularly on studying the relationship between layer structure formed via copolymerization and content of monomers in the initial solution. Sorption capacity of the prepared by radiation grafting adsorber was evaluated by gamma radiometer using $^{152}Eu^{3+}$ as a marker monitoring depletion of the radioisotope from the feed solution.

When two monomers, AAc and AAm, contributed in the formation of grafted layer, their input into copolymerization was not proportional to their concentrations in the feed solution. It was confirmed that grafting of the monomers shows synergetic effect as the yield of copolymerization exceeds degree of grafting achieved for the individual components.

1. Introduction

Radiation induced grafting offers many advantages that might be commercialized: simplicity in controlling parameters of processing, uniform grafting of monomers or other low molecular weight moieties at ambient temperature, flexibility and good reproducibility of treatment. The adsorbent fabricated in this way can be applied to concentrate radioactive isotopes which reveal chemical affinity to the ligands present in the grafted layers (e.g. Hegazy et al., 1999, 2001). Therefore, selection of suitable radiation grafted groups complexing chosen metal ions seems to be promising way for the development of novel separation technique. The method might be applied for the production of trivalent ion adsorbents.

The aim of this research was to elucidate the contribution of two selected monomers in the construction of grafted layer and to assess their role in adsorption of europium cation. Graft copolymerization of two monomers, AAc and AAm, was conducted via simultaneous grafting. The introduction of carboxyl groups increases hydrophilic properties of the polymeric matrix (polypropylene) enhancing its affinity toward cation attraction, and subsequently production of complex/chelate compounds.

Characterization of the sorbents was performed using the gravimetric method, thermal measurements, EPR and ATR-FTIR spectroscopes. Sorption properties of the prepared materials were determined using LG-1 gamma radiometer constructed at the Institute of Nuclear Chemistry and Technology. This equipment was applied for the measurements of solutions radioactivity before and after sorption. The sorption capacity indirectly reveals construction of the grafted layers as well as their usefulness for the coordination of selected metal ions. It is known that the coordination chemistry of trivalent lanthanides does not differ neither along the series nor from the actinide series (Sharma and Tomar, 2008) thus obtained data can be extrapolated for both groups of elements.

2. Materials and methods

2.1. Materials and their irradiation

Following materials were used in this work: polypropylene (PP) filter of microporous structure (20 μm), acrylic acid (AAc) and

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* Corresponding author. Tel.: +48 22 504 1321; fax: +48 22 504 1313.
E-mail addresses: e.kornacka@ichtj.waw.pl, e.m.kornacka@gmail.com (E.M. Kornacka).

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acrylamide (AAm) purchased from Aldrich Chemical Company Inc. Copper chloride delivered by Aldrich Chemical Company Inc. was used without any purification. Methanol was purchased from Chempur Co.

PP filter was washed with double distilled water in an ultrasonic bath and dried at 60 °C under vacuum. Then the samples were immersed in the solution containing 0.7 parts by volume of methanol and 0.3 parts by volume of aqueous solutions of monomers in a ratio AAc:AAm=0:100; 20:80; 40:60; 60:40; 80:20 and 100:0.

2.2. Radiation-induced grafting

Before irradiation the PP filters were kept for 24 h in the water/methanol solutions of monomers. Simultaneous grafting was performed by exposure of the samples to gamma-rays in a Issledovatiel ^{60}Co-chamber (dose rate 0.97 kGy/h) to a dose of 10 kGy. $CuCl_2$ was used as an inhibitor of homopolymerization at a concentration of 5×10^{-4} M.

Upon grafting, the PP filters covered with layers of polymerized AAc and/or AAm were kept at 50 °C for 0.5 h to continue chain growth, then washed for 0.5 h in an ultrasonic water bath and dried under vacuum at 80 °C until a constant weight. The degree of grafting was determined gravimetrically and expressed as follows:

Degree of grafting (%)=$[(w_g - w_o)/W_o] \times 100\%$where w_g and w_o represent the weights of grafted and initial samples, respectively.

2.3. Thermal analysis

Phase transitions were determined using a TA Instruments DSC apparatus with nitrogen flow and heating rate of 10 °C/min. The melting and crystallization behavior of the samples was studied during the first heating/cooling cycle. The measurements were performed in the temperature range from 25 to 200 °C. About 5 mg of the sample inserted in the pan was heated, then kept for 5 min at 200 °C and gradually cooled.

Thermal decomposition of the polymers was performed on a TA Instruments TGA Q500 apparatus. Analyses were conducted over the temperature range from 30 °C to 600 °C with a programmed temperature increment of 10 °C/min under nitrogen atmosphere.

2.4. EPR spectroscopy

Radicals produced in the studied systems were monitored and identified by Electron Paramagnetic Resonance (EPR) spectroscopy using an X-band ESP 300 Bruker spectrometer equipped with the WinEPR software.

2.5. ATR-FTIR spectroscopy

ATR-FTIR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer. The spectra were collected in the range of 4000–650 cm^{-1} at a resolution of 4 cm^{-1} by means of an accessory designed for the single reflection ATR technique equipped with ZnSe crystal.

2.6. Sorption

The grafted polymeric sample before using as a sorbent was activated by 0.5 h consecutive treatment with 1.0 M HCl, 1.0 M NaCl and water. Europium radioisotope $^{152}Eu^{3+}$ (10^{-7} M in 1 M NaCl solution) was used as a marker monitoring sorption capacity. pH values of the initial solutions (pH=4.95) was adjusted by adding 0.05 M NaOH or HCl and was controlled using a combined glass electrode connected to a pH meter (of the HI-221 type, Hanna Instruments Co.). It was found that batch sorption equilibrium was reached after 2 h shaking using programmable roto-shaker MultiBio RS-24 (Biosan, Latvia). Home-made gamma radiometer LG-1 was used to determine the initial and equilibrium radioactivity of the solutions.

3. Results and discussion

The PP filter of the developed boundary surface facilitating penetration of the low molecular weight species was applied as a matrix, whereas acrylamide with growing content of acrylic acid enhancing hydrophilic features of the grafted layers, were used as grafted monomers.

Grafting yield measurements: The PP-g-AAc–AAm sorbent was prepared via simultaneous method of grafting applying the methanol/water solutions of monomers at various concentrations. The results shown in Fig.1 (diagram A) indicated that grafting of acrylamide is more efficient than acrylic acid, and the highest yield was achieved when the contribution of the components was in a proportion of AAc/AAm=40:60. Course of the graph unambiguously reveals that the radiation induced processes in the system comprising two monomers, namely AAc and AAm, demonstrate a synergetic effect as under such conditions the efficiency of grafting prevails over the additive effect arising from the weight contribution of the monomers.

Thermogravimetric analysis in ambient gas (nitrogen): Thermal characteristic of grafted PP depends on the nature of mers. The initial weight loss below 100 °C was due to the presence of small amount of structural water in the samples, Fig. 2. The thermograms of PP-g-AAc and PP-g–AAm show distinct zone of thermal degradation of maximal rate at about 460 °C (T_{m3}). For PP-g-AAc the small peak below 400 °C is due to decarboxylation combined with the emission of carbon dioxide.

Contrary to this findings, the PP-g-AAc–AAm system is more thermally sensitive as the first step of decay starting at low temperatures achieves maximal mass loss rate just at $T_{m1}=217$ °C, and second one at $T_{m2}=390$ °C. In both stages the thermal decomposition deepens with increasing concentration of AAm and reaches maximum for AAc:AAm=20:80. The signal position is in correlation with T_{m3} which increases insignificantly when thermal decay at T_{m1} and T_{m2} becomes more intensive. The first stage decomposition at around T_{m1} was due to dehydration as well as loss of ammonia by P(AAc–AAm) copolymer followed by the formation of imide group via cyclisation (Thakur et al., 2011). The second stage at T_{m2} might correspond to decrosslinking of the

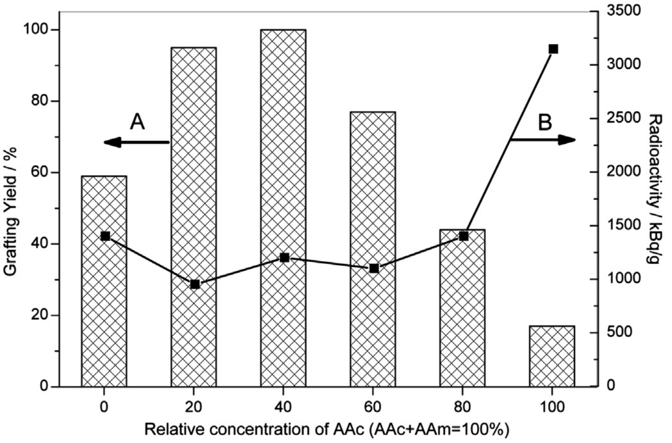

Fig. 1. Effect of monomer concentrations on the grafting yield for the system PP-g-AAc—AAm (diagram A). Radioactivity per gram of grafted layers resulting from sorption of europium radioisotope $^{152}Eu^{3+}$ (graph B).