

Eu³⁺ ions in the modified matrix polyethylene/poly(acrylic acid)

Fluorescence studies

Maria Irismar N. Ximenes¹, Osvaldo A. Serra², and Glaucione G. de Barros³

¹Departamento de Quimica, Universidade de Brasilia, Brasilia, Brasil

²Departamento de Quimica, Universidade de Sao Paulo, Ribeirao Preto, Brasil

³Departamento de Quimica, CP 152 928, Universidade de Brasilia, 70919 Brasilia, Brasil

Summary

Ion exchange between H⁺ and Eu³⁺ ions was studied in the material modified by *in situ* sorption and thermal polymerization of acrylic acid in low density polyethylene films (LDPE-PAA). The effects of the temperature and film thickness on the ion exchange were observed using fluorescence spectroscopy. The ion exchange was investigated at 60, 70 and 80°C and was most efficient at 80°C. At this temperature 42% of the ion exchange at the saturation time was observed in the matrix (200 μm thick). The percent of ion exchange at saturation increases with the matrix film thickness reaching 72% of Eu³⁺ ions in LDPE-PAA. Ion exchange occurs mainly in the film surface or in the neighbouring layers.

Introduction

Low density polyethylene can be modified by acrylic acid sorption and *in situ* thermal polymerization and grafting at 60-90°C (1). Using this method materials such as low density polyethylene/poly(4 vinyl pyridine), low density polyethylene/poly(methyl methacrylate), and low density polyethylene/poly(acrylic acid), have been prepared in our laboratory (2,3). The latter material containing carboxylic groups is of interest for studies of rare earth complexes yielding an organic polymer matrix with fluorescent functions. The fluorescence of the rare earths makes them suitable as a probe for fluorescence investigations of ionic aggregates in polymeric materials (4,5). In this way, rare earth ion complexes of ionomers have been studied at low concentration due to the high sensibility of this technique (6). The fluorescence technique can also be used to elucidate ion aggregation in various ion-containing polymers (6,7). For example, studies of energy transfer from uranyl to europium ions in ionomers showed evidence of dispersed submicroscopic regions of ionic aggregates (7).

In this paper, the distribution of carboxylate groups of poly(acrylic acid) in LDPE matrix were studied using the europium ion probe. The fluorescence properties of the

composite matrix LDPE/PAA/Eu³⁺ were also investigated.

Experimental

Materials

Acrylic acid (AA) was supplied by Aldrich Chem. Co. and Cia Quimica Rhodia Brasileira. It was distilled prior to use under vacuum and stored at 18°C. Hydroquinone monomethyl ether (HMME) was supplied by Cia Quimica Rhodia Brasileira. It was purified by successive crystallization in acetone.

Europium (III) oxide, Eu₂O₃ 99,99% was supplied by Alfa Inorganics Ventron Co.. The other reagents were of analytical grade and they were used without any further purification.

Low density polyethylene (LDPE) sheets (d=0,918g/cm³, MI=1.15g/10min) were supplied by Poliolefinas (Sao Paulo). The films (3x4 cm) were immersed in toluene for 24 hr and dried before use. The characteristics of the polymer were checked by IR spectroscopy and X-ray diffraction (8). The degree of crystallinity of LDPE was 50% as measured by X-ray diffraction.

Methods

a) Sorption and thermal polymerization of AA in LDPE.

The sorption and *in situ* thermal polymerization of AA (80% by unit volume of aqueous solution containing 350 or 500 ppm of HMME) in LDPE films followed the method described in our previous work(1,3). The thicknesses of the films used were 90, 200, 250, 270 and 310 μm. The mass increase of LDPE films was obtained by gravimetry as described in the literature(9).

b) Synthesis of EuCl₃.6H₂O from Eu₂O₃.

Europium (III) oxide was dried at 100°C for 2h. A stoichiometric amount of HCl was added to 0.5g of Eu₂O₃. The concentrated solution was diluted with water, filtered and kept over a water bath for evaporation. The addition of successive amounts of water during the evaporation process was necessary to eliminate the excess HCl and to reach a pH= 4-5 in the solution. The salt was recrystallized, filtered, dried under vacuum at room temperature and heated for 30 min. at 100°C. A 10 mM aqueous solution of EuCl₃.6H₂O was prepared. It was titrated with EDTA using xylenol orange as indicator (10).

c) Ion exchange H⁺ ↔ Eu³⁺ in LDPE-PAA matrix.

A film of LDPE-PAA was carefully folded in several layers and immersed in 3.6 ml of a 10 mM EuCl₃.6H₂O aqueous solution into a quartz cell. The cell was tightly sealed and heated at a specific temperature (60, 70 and 80 °C). The fluorescence spectra were taken periodically from the homogenized cell solution at room temperature. The film in the cell was kept out from the optical pathway. The Eu³⁺ ions were excited at 394nm and the fluorescence spectra were obtained in the region of 570-640 nm. The fluorescence intensity of the Eu³⁺ ions in the solution

showed a linear behavior so that, the fluorescence intensity of the peak at 591nm was used as the basis to calculate the percent ion exchange $H^+ \leftrightarrow Eu^{3+}$. The fluorescence intensity of the peak at 591 nm of a 10mM $EuCl_3 \cdot 6H_2O$ solution was assumed to be 100%. The percent of ions in the solution after each thermal treatment was calculated as follows:

$$\% \text{ of } Eu^{3+} \text{ ions} = \frac{I_f}{I_1} \cdot 10^2$$

and, in the matrix

$$\% \text{ of } Eu^{3+} \text{ ions} = 100 - \frac{I_f}{I_1} \cdot 10^2$$

where,

I_f = fluorescence intensity at 591nm of the $EuCl_3 \cdot 6H_2O$ solution after thermal treatment;

I_1 = fluorescence intensity at 591nm of the 10mM $EuCl_3 \cdot 6H_2O$ solution.

The fluorescence spectrum of the dehydrated LDPE-PAA matrix after ion exchange was obtained under the same conditions as that used for the solution. The matrix was placed in a sample holder such as to get the maximum fluorescence intensity in the region of 570-670nm.

Physical Measurements

FTIR spectra were taken using a Nicolet Model 5ZDX Spectrophotometer.

Fluorescence spectra were obtained by use of a Perkin Elmer Model MPF 44B and a Spex Fluolog-2 attached to a Datamate and Multiprocessor.

Results

a) Ion exchange $H^+ \leftrightarrow Eu^{3+}$ in the matrix LDPE-PAA.

The characteristics of thermally modified matrices, LDPE-PAA, used for ion exchange $H^+ \leftrightarrow Eu^{3+}$ (including the data after the ion exchange) are given in Table 1.

Fig. 1 shows FTIR spectra of LDPE-PAA modified matrix (Fig. 1a) and LDPE-PAA after its immersion in 10mM $EuCl_3 \cdot 6H_2O$ aqueous solution at 60°C (Fig. 1b). The presence of a peak at 1770 cm^{-1} characteristic of carbonyl group and the absence of insaturation confirm the presence of PAA in LDPE matrix (Fig. 1a). A peak at 1550 cm^{-1} is characteristic of stretching vibration mode of carboxylate groups (Fig. 1b). This is an evidence of the ion exchange $H^+ \leftrightarrow Eu^{3+}$ in the modified matrix LDPE-PAA after the thermal treatment. Consequently, coordination between the polymeric matrix and the rare earth metal complex has formed.

The fluorescence spectrum of 10 mM $EuCl_3 \cdot 6H_2O$ solution is shown in Fig. 2a. The emission spectrum (excitation at 394 nm) showed three fluorescence intensity peaks characteristic of Eu^{3+} ions. The more intense lines are due to the transition ${}^5D_0 \rightarrow {}^7F_1$ (at 591 nm) and transition ${}^5D_0 \rightarrow {}^7F_2$ (at 618nm). The ratio between the fluorescence intensity peaks at 591nm and 618nm was 3:1. A typical

emission spectrum of the dehydrated LDPE-PAA-Eu³⁺ complex is shown in Fig.2b. The spectrum was similar to that of the solution (Fig. 2a). However, the ratio between the fluorescence intensity peaks was 1:4. This is evidence for interaction between the Eu³⁺ ions and the carboxylate groups in the matrix. From the literature it is known that the relative position of fluorescence lines varies only slightly with changes of the environment but their intensities are very sensitive to the changes of environment (11).

Table 1. Ion exchange H⁺ ↔ Eu³⁺ in films of LDPE-PAA

Sample	Saturation Time (h)	*% PAA in LDPE-PAA Matrix	*% Eu ³⁺ in LDPE-PAA Matrix	Film Thickness (μm)	Heating Temp. (°C)
A ₁	6	4.1	29	200	60
A ₂	22	4.5	42	200	80
B ₁	7	3.0	7	90	60
B ₂	23	3.1	14	250	60
B ₃	6	3.3	16	310	60
C ₁	4	2.6	5	90	60
C ₂	22	2.5	27	90	70
C ₃	18	2.7	29	90	80
C ₄	22	3.5	21	200	70
C ₅	18	3.5	28	200	80
C ₆	18	12.9	28	200	80

* see Experimental

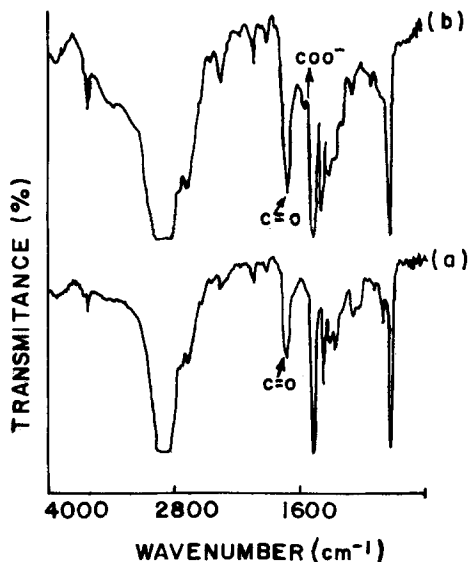


Fig. 1 FTIR Spectra
LDPE-PAA film (a); LDPE-PAA after ion exchange in a EuCl₃.6H₂O solution (b). Film thickness, 200 μm; PAA, 4.5 %; Eu³⁺, 45 %.

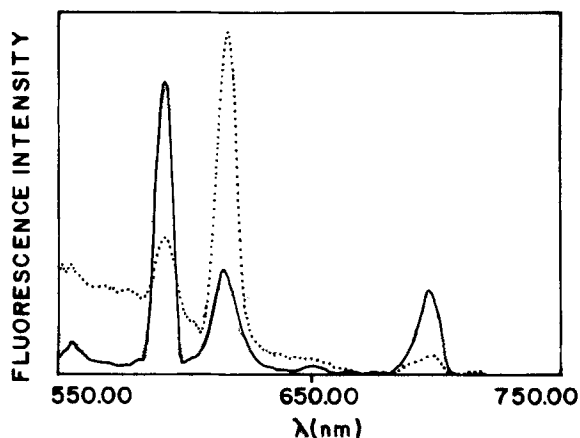


Fig.2 Fluorescence Spectra
 10 mM $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ solution (-); LDPE-PAA matrix after
 ion exchange $\text{H}^+ \leftrightarrow \text{Eu}^{3+}$ (.....); Excitation: 393 nm;
 60°C; PAA, 3.5 %, Eu^{3+} , 7%.

b) Temperature effect of the ion exchange $\text{H}^+ \leftrightarrow \text{Eu}^{3+}$ in
 LDPE-PAA matrix.

The fluorescence spectra of the $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ solution containing sample A₁ (Table 1) after heating 0, 2, 6 and 22 hours at 60°C is shown in Fig. 3. The apparent saturation of the matrix by Eu^{3+} ions was observed after heating the sample for 6 hours. The swelling of the matrix immersed in the $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution did not effect the measurements more than 5% as confirmed by calculations using previous data (3).

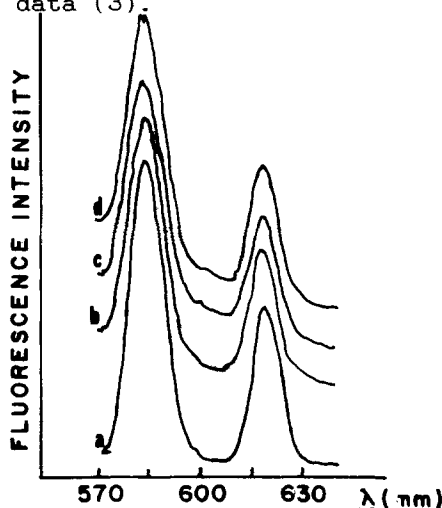


Fig. 3 Fluorescence Spectra of the $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ solution
 during thermal treatment of sample A₁ at 60°C.
 Heating time: 0 h (a); 2 h (b); 6 h (c); 22 h (d).

Fig. 4 shows the percent ion exchange of Eu^{3+} ions in LDPE-PAA versus time, at 90 μm film thickness at several temperatures (60, 70 and 80°C).

A saturation time of 4h was observed for the sample treated at 60°C (C_1 , Table 1) and of 18-22 h for the samples treated at 70 and 80°C (C_2 and C_3 , Table 1). Identical saturation times (18-22h) were found for samples C_4 and C_5 (film 200 μm thick) heated at 70°C and 80°C (Fig. 5). The ion exchange in the matrix at saturation time (4h) was 5% in sample C_1 (90 μm thick), and 27-29% in samples C_2 and C_3 at the saturation time of 18-22h (Fig.4). The longer saturation time observed at temperatures higher than 60°C might be due to the formation of LDPE-PAA- Eu^{3+} complexes at the matrix surface, limiting the diffusion of hydrated Eu^{3+} ions to the inner layers of the film.

The percent of ion exchange at saturation was directly dependent of the temperature (Fig. 6).

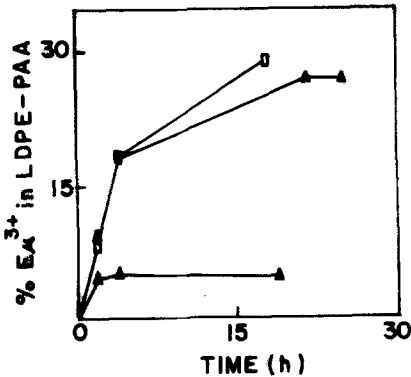


Fig.4 Ion exchange $\text{H}^+ \leftrightarrow \text{Eu}^{3+}$ vs time in LDPE-PAA. 60°C(▲-▲); 70°C(▲-▲); 80°C(□-□); PAA, 2.6 %; film thick., 90 μm .

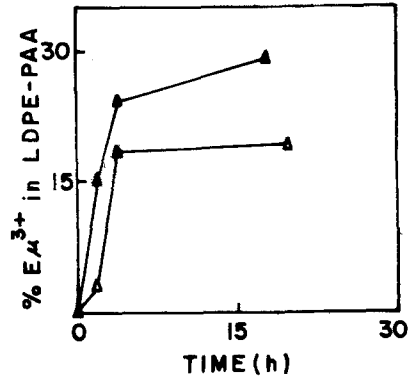


Fig.5 Ion Exchange $\text{H}^+ \leftrightarrow \text{Eu}^{3+}$ vs time in LDPE-PAA. 70°C(▲-▲); 80°C(▲-▲); PAA, 3.5 %; film thick., 200 μm

c) Effect of film thickness on ion exchange $\text{H}^+ \leftrightarrow \text{Eu}^{3+}$ in LDPE-PAA matrix.

The percent of ion exchange of Eu^{3+} in LDPE-PAA versus time using films thicknesses of 90, 250 and 310 μm is shown in Fig.7. The ion exchange was observed at 60°C to prevent effects due to surface ion exchange. A increase of the percent of ion exchange with time was observed. Fig.8 shows the percent of ion exchange at the saturation time versus the film thickness. The percent of Eu^{3+} ions in the matrix was directly dependent on the film thickness (90 to 310 μm). This suggests that ion exchange of the hydrated Eu^{3+} ions into the matrix is not diffusion controlled. It is known from previous work (3) that the PAA chains in the modified matrix LDPE-PAA are localized mainly at or next to the surface using films 90-210 μm thick. The exchange observed might be preferentially occur at the surface. This means that the Eu^{3+} ions exchanged at the surface block the diffusion of hydrated ions toward the inner layers of the film.

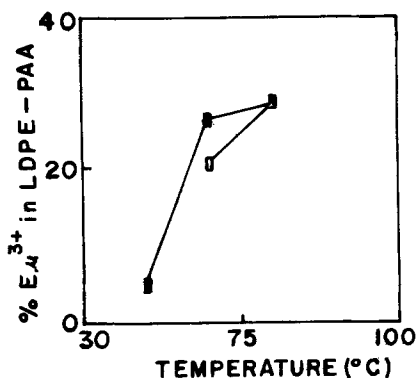


Fig. 6 Temperature effect on the ion exchange $H^+ \leftrightarrow Eu^{3+}$ in LDPE-PAA. Film 200 μm thick, 3.5% PAA (□-□); film 90 μm thick, 2.6% PAA (■-■).

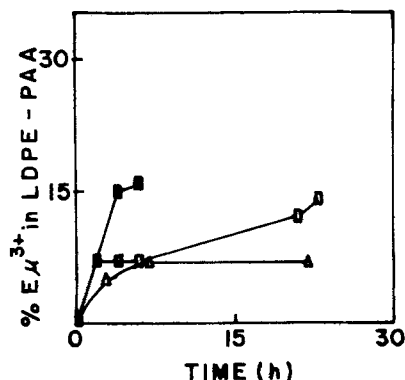


Fig. 7. Ion exchange $H^+ \leftrightarrow Eu^{3+}$ vs time in LDPE-PAA. Film thick.: 90 μm (▲-▲); 250 μm (□-□); 310 μm (■-■); 60°C, PAA, 3.1%.

d) Effect of the amount of PAA in LDPE on ion exchange $H^+ \leftrightarrow Eu^{3+}$.

Fig. 9 shows the percent of Eu^{3+} at the saturation time versus percent of PAA in the matrix, using film thicknesses of 90 and 200 μm and heating them to 60°C and 80°C. The Eu^{3+} ion exchange increases with the amount of PAA in the matrix. An ion exchange of 28% was observed using a 200 μm thick film containing 3.5% of PAA and 42% of ion exchange in the matrix at the same thickness but containing 4.5% of PAA.

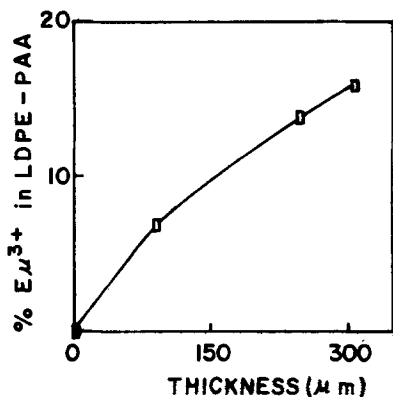


Fig. 8 Effect of the film thickness in the $H^+ \leftrightarrow Eu^{3+}$ exchange in LDPE-PAA; 60°C.

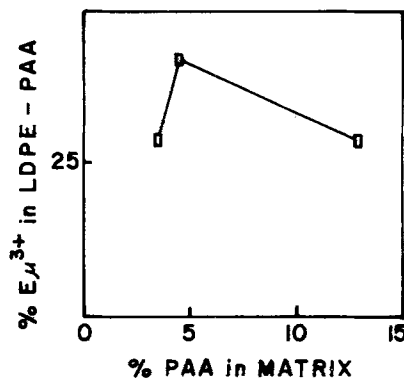


Fig. 9 Ion exchange $H^+ \leftrightarrow Eu$ vs % PAA in LDPE-PAA. Film 200 μm thick; 80°C.

However, at higher PAA matrix concentration the Eu^{3+} exchange in the matrix decreased. This confirms the suggestion that the ion exchange producing a polymer- Eu^{3+} complex occurs preferentially at the surface of the matrix. The formation of the polymer-complex at the film surface limits the diffusion of the hydrated ions to deeper layers in the matrix.

Further investigations, particularly of the uranyl ions exchange in LDPE-PAA matrix and simultaneous exchange Eu^{3+} and UO_2^{2+} ions in the matrix, are under way. The evidence of energy transfer from UO_2^{2+} to Eu^{3+} ions in the matrix are being also investigated.

Acknowledgement

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