Eu$^{3+}$ ions in the modified matrix polyethylene/poly(acrylic acid)

Fluorescence studies

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Summary

Ion exchange between H$^+$ and Eu$^{3+}$ 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 Eu$^{3+}$-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
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=0.918 g/cm³, MI=1.15 g/10 min) 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 containig 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 0.5 g of Eu₂O₃. The concetrated 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 xylene 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 394 nm and the fluorescence spectra were obtained in the region of 570-640 nm. The fluorescence intensity of the Eu³⁺ ions in the solution