RARE EARTH METAL CONTAINING POLYMERs: ENERGY
TRANSFER FROM URANYL TO EUROPIUM IONS IN IONOMERS

Y. Okamoto, Y. Ueba, I. Nagata, E. Banks,
B.A. Garetz and J.M. Khosrofian

Department of Chemistry and Polymer
Research Institute, Polytechnic Institute
of New York, Brooklyn, N.Y. 11201

Abstract

Various ratios of Eu and UO2 acetates were
prepared by dissolving Eu and UO2 acetates in
acetic acid and removing acetic acid in vacuum.
The fluorescence intensities at 616 nm of these
mixed acetates were measured under excitation at a
wavelength of 429 nm. Strong energy transfer from
UO2+ to Eu3+ was observed. This result indicated
that these ions were in very close contact in this
system. Various concentrations of Eu3+ and UO2+
salts of polymers containing carboxyl ligands were
prepared and fluorescence properties of these
polymers were investigated. The polymers investi­
gated were poly(methacrylic acid)(PMA), and co­
polymers of styrene-acrylic acid (PSAA) and methyl
methacrylate-methacrylic acid (PMM/MA). When
Eu3+ and UO2+ were introduced to the polymers of
PSAA and PMM/MA, very effective energy transfer
from UO2+ to Eu3+ was observed because of the
proximity of these metal ions in ionic aggregates
of these ionomers. However, the PMA-UO2 and Eu
salts did not show energy transfer even when a
large excess of UO2+ was added to the polymer. The
PMA salts are reported to have no ion aggregate
structure; it is concluded that Eu3+ and UO2+
ions were uniformly dispersed throughout the poly­
mer system so that the distances between these ions
were far beyond the energy transfer range.
The fluorescence lifetimes of the PHM/MA-UO$_2^{2+}$ and Eu$^{3+}$ salts investigated were found to be comparable to glass studies on similar systems. Samples displayed lifetimes of 330±20 μs at 25°C.

Introduction

The structures of synthetic polymers containing metal ions have been extensively investigated in recent years(1,2). A host of techniques, including small angle X-ray scattering, electron microscopy and Raman spectroscopy has been used to elucidate the structures of ion-containing polymers. It has been suggested that certain polymers contain submicroscopic aggregations of ionic groups(2,3). Various structures of the ionic aggregates have been proposed and these depend on the composition of polymers, nature and concentration of metal ions, and temperature.

In the arsenal of spectroscopic techniques, fluorescence measurements offer particular advantages, since they are sensitive and can be employed at relatively low concentrations of the luminescent species(4). Thus, we have initiated a study of the structures of ion-containing polymers using trivalent lanthanide ions as fluorescent probes.

The fluorescence intensity of samples containing uniformly dispersed Eu$^{3+}$ acetate in polystyrene or poly(methyl methacrylate) was found to increase linearly with Eu content. However, the Eu$^{3+}$ salts of copolymers of methacrylate-methacrylic acid (PHM/MA) and styrene-acrylic acid (PSAA) displayed typical concentration quenching behavior, reaching a maximum at 3-5 weight % Eu and decreasing with further increases in Eu content(5). This result shows that the ion-containing polymers contain ionic aggregates, in agreement with a recently proposed model. Such aggregates would create locally high Eu ion concentrations, whose interactions lead to concentrations quenching at low overall Eu concentrations.

Considerable effort has been devoted to the