Synthesis and Near Infrared Properties of Rare Earth Ionomers

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SYNOPSIS

Fully exchanged, anhydrous ionomers of ethylene-*co*-acrylic acid (EAA) copolymers and ethylene-*co*-methacrylic acid (EMAA) copolymers containing Dy^{+3}, Er^{+3}, Sm^{+3}, Tb^{+3}, Tm^{+3}, and Yb^{+3}, and mixtures of them, were synthesized and studied in the near infrared region by reflection and Fourier Transform Laser Raman spectroscopies. The EAA copolymers ranged from 1.4 to 8.7 mol % acid and the EMAA copolymers were 7.3 and 16.2 mol % acid. The ionomers were shown to be essentially free of carboxylic acid groups, water, or other forms containing O — H groups and were characterized by infrared and other methods. They are light and heat stable, and become thermoplastic and moldable at ca. 220°C under pressure. When excited at 1.064 μ with a Nd : YAG laser, these ionomers exhibit novel, lanthanide-dependent near infrared luminescence and strong Raman scattering in the near infrared region. The strongest luminescence is observed with Sm^{+3} ionomers. The Dy^{+3} ionomer Raman-shifts this source to emit light most strongly in the 1.53–1.55 μ range where the ionomer also transmits light well. © 1996 John Wiley & Sons, Inc.

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INTRODUCTION

The incorporation of rare earth, or lanthanide, ions in suitable host materials has generated great interest in the past few years, because they can impart to these materials some valuable optical properties. In fact, materials with rare earth ions incorporated in them have been used successfully as optical waveguides, fiber amplifiers, and narrow band lasers.[1–8] In addition, these materials also can exhibit luminescence,[9,10] frequency upconversion,[11–17] and other energy transfer processes[18] whose occurrence is related to ion–ion interactions between neighboring lanthanide ions. Until now, most materials of this type have comprised rare earth ions in metal fluoride or silica glass hosts. For example, erbium-doped silica is being used as the core material in optical fibers,[3,4] Nd-doped glasses are being used as lasers,[7,8] and other rare earth ion-doped glasses, such as thulium, holmium, and ytterbium combined with erbium in silica or metal fluoride glass hosts are used as frequency upconverters from the infrared to the visible range.[11–17]

The host material has an impact on the solubility of the rare earth ion and the kinds of structures these ions adopt. The ionic structures, especially the aggregation of lanthanide ions, is a key to some of the energy transfer processes. Overall, the host material can strongly influence the absorption, emission, and fluorescence behavior of the materials.[19] The preparation of glasses with rare earth ions often is limited by the high-temperature phase relationships between the glass-forming components. It is of interest to find new materials that can incorporate lanthanide ions of all types over a broad concentration range in a system that promotes the ion aggregation, which is responsible for some of the important energy transfer processes. Naturally, the near infrared absorbance must be low in the regions where O — H vibrational overtones contribute, so such materials must be free of water, carboxylic acid groups, and other sources of O — H.

Studies have been performed[20–23] on polymeric materials formed by reacting the salts of trivalent

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lanthanide ions (written Ln^{3+}) with polymers to complex them with various functional groups. In the field of ionomers, particularly, Okamato and coworkers[21-23] have synthesized and studied the properties of rare earth ions complexed to COO— functional groups attached to a polymeric backbone. For example, they reacted lanthanide acetates with various polymers including polyacrylic acid, polymethacrylic acid, styrene-acrylic acid copolymer, and polymethylmethacrylate-methacrylic acid in solution and studied the fluorescence properties of the resultant materials. Okamoto and coworkers also synthesized a number of carboxy-benzoyl- and carboxy-naphthoyl-substituted polystyrene ionomers and exchanged them partially with Eu^{3+} ions.[22,23] In one case, Eu^{3+} ions neutralized by two carboxylates from 2-benzoyl benzoic acid was also neutralized by a third carboxylate of a 4-vinylbenzoate-2/-benzoic acid and this compound was copolymerized with styrene to form a CH_2Cl_2 soluble compound. Their studies, which addressed questions of ion clustering in ionomers, showed that the fluorescence intensity increased and then decreased with increasing Ln^{+3} concentration in the materials. This fluorescence quenching can occur if there is energy transfer occurring between rare earth ions which are within 1 nm of each other, so its occurrence was interpreted as evidence for cluster formations in these matrices. These ionomer matrices, however, typically were not fully exchanged or dry, so they would not satisfy the near infrared requirements for optical materials.

Ionomers based on ethylene and either ethylene-*co*-acrylic or ethylene-*co*-methacrylic acid copolymers also could form ion clusters and, if fully exchanged with lanthanide ion and dried, be free of groups containing the O—H moiety. Thus, they could exhibit the optical and magneto-optic properties of interest. Moreover, acid copolymers in the near zero to about 40 wt % acid range should be able to incorporate any or all of the lanthanides and to do so over a composition range from near zero to about 5.4 mol % lanthanide ions (1.4–16.2 mol % acid). This would provide a new class of optically interesting materials with compositional flexibility.

In this article we report the synthesis of rare earth ionomers in which the complete neutralization of the carboxylate groups is achieved. The near infrared properties also are reported. The base polymers included in this study were a series of five ethylene-*co*-acrylic acid copolymers with increasing acrylic acid content and two ethylene-*co*-methacrylic acid copolymers with different methacrylic acid contents. One key to the synthetic approach is to react the acid copolymers with the acetylacetonate complexes of the rare earth ions in a very dilute solution under refluxing conditions to maximize the amount of ion exchange. About 85% of the acid groups can be neutralized in this way, but to achieve complete neutralization of the carboxylate groups additional steps must be taken. We report this preparation and the characterization of the new ionomers containing Dy^{+3}, Er^{+3}, Sm^{+3}, Tb^{+3}, Tm^{+3}, and Yb^{+3}. Of particular importance is the phenomena they exhibit in the near infrared region, where most optical communication occurs. The reflectance spectra and the Fourier Transform Raman Spectra in this near infrared region are reported.

EXPERIMENTAL

The new lanthanide ionomers were prepared by incorporating the trivalent lanthanide metal ions into ethylene-*co*-acrylic acid (EAA) and ethylene-*co*-methacrylic acid (EMAA) copolymers. The synthesis of the materials was accomplished by a three-step process: first, the reaction of the copolymers with the acetylacetonate salts of the trivalent lanthanide metal, $Ln(acac)_3$, in a very dilute solution; second, heating under refluxing conditions and filtration; and finally, a heat treatment in vacuum. The ethylene-*co*-acrylic acid copolymers were produced by the Dow Chemical Co. as Primacor and the ethylene-*co*-methacrylic acid copolymers used in this synthesis were experimental samples kindly provided by Dr. Robert Statz of the DuPont Co. Five different Primacor ethylene-*co*-acrylic acid copolymers, Primacor 3150 ($M_w = 9.88 \times 10^4$, $M_n = 1.67 \times 10^4$), 3340 ($M_w = 8.19 \times 10^4$, $M_n = 1.64 \times 10^4$), 3440 ($M_w = 8.0 \times 10^4$, $M_n = 1.71 \times 10^4$), 60758.03 ($M_w \sim 1 \times 10^5$, $M_n \sim 2 \times 10^4$), and 5990 ($M_w = 1.71 \times 10^4$, $M_n = 8.4 \times 10^3$), which have acrylic acid contents of 1.38, 2.3, 3.6, 5.0, and 8.7 mol %, were used. Two copolymers of ethylene-*co*-methacrylic acid have methacrylic acid content of 7.3 and 16.2 mol % ($M_w \sim 1.9 \times 10^5$, M_n 4.5×10^4) and are identified as EMAA (7.3 mol %) and EMAA (16.2 mol %). The lanthanide ionomers have mole percents of Ln^{+3} of one-third these values. The $Ln(acac)_3$ hydrated complexes were obtained from Johnson-Matthey Chemical Co.

In a typical preparation, stoichiometric amounts of the polymer and the $Ln(acac)_3$ salt, corresponding to a 3 : 1 mole ratio of acid groups in the copolymer to Ln^{+3} in the $Ln(acac)_3$, were calculated and a 75% excess of the lanthanide complex was taken (to drive the exchange process); the acid copolymer was dissolved in tetrahydrofuran (THF) under refluxing conditions to form a very dilute solution (e.g., 0.50 g of 16.2 mol % EMAA in 1.00 L of THF). The

$Ln(acac)_3$ salt was dissolved in methanol to form a dilute solution [e.g., 0.50 g $Ln(acac)_3$ dissolved in 0.030 L of methanol]. The methanolic solution containing the dissolved lanthanide salt (or salts) was added dropwise to the polymer/THF solution over a 2–3-h period with constant stirring. The resultant solution was refluxed for ca. 48 h and then the product was precipitated in an excess of cold methanol. The resultant, finely powdered precipitate was filtered and air dried overnight. The infrared spectra of the powders showed only very weak bands for the acetylacetonate vibrations, confirming that most of the excess $Ln(acac)_3$ (which had been taken to drive the process) remained in the methanol. It also showed that 85–90% of the acid groups had been neutralized. The powder then was heated at ca. 250°C for 48 h at a pressure of ca. 30 mm Hg. For spectroscopic measurements a few milligrams of the material were taken and molded into thin films at ca. 220°C for 20 min at a pressure of 1.4–3 kpsi. Elemental analyses of the representative samples of the ionomers with each copolymer were performed by Galbraith Laboratories (Knoxville, TN). A typical analysis is that of the Sm-EAA (8.7 mol % acid) ionomer, which gave Sm 12.12% (calc.), 12.93% found. C 68.85% (calc.), 66.87% found; H 11.05% (calc.), 10.68% found. The calculated values are for a complete replacement of H^+ in the original acid copolymers and do not consider decarbonylation.

Infrared spectra of the ionomers were measured using a Perkin Elmer 1600 FTIR Spectrometer in the 400–4000 cm^{-1} range. The far infrared spectra of the films were measured in the 200–650 cm^{-1} range using an IBM 98 (Bruker IFS 113V) FTIR Spectrometer with a resolution of 2 cm^{-1}. Raman spectra of the ionomers were measured using a Bruker RFS 100 FT-Raman Spectrometer in the 70–3500 cm^{-1} range (Stokes side) using a cw, monomode, Nd : YAG laser operating at a frequency of 9396.7 cm^{-1} as the excitation source. The source was defocused to avoid heating and was incident at ca. 1.4×10^4 W/m^2. Fluorescence spectra were measured using a Spex DM1B Raman Spectrometer with 488 nm as the excitation source frequency. Near infrared spectra were measured on a Nicolet 740 FTIR Spectrometer with a resolution of 4 cm^{-1}.

RESULTS

Synthesis and Characterization

The infrared spectra of the powders produced by the reactions carried out in solution under these extremely dilute conditions showed that 85–90% of the carboxylate groups had been neutralized with Ln^{+3}. This is shown in Figure 1b, by comparison to the acid in spectrum 1a. Most of the excess lanthanide complex remained in the methanol solution, although small amounts of partially reacted lanthanide complex remained. By contrast, reactions performed using more concentrated solutions and with faster addition of the $Ln(acac)_3$ solution to the polymer/THF solution gave materials that precipitated quickly and had much lower degrees of neutralization.

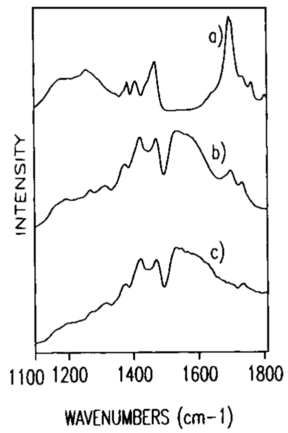

Figure 1. Infrared spectra (1100–1850 cm^{-1}) EMAA (16.2 mol % MAA) series: (a) EMAA (16.2 mol % MAA), (b) EMAA (16.2 mol % MAA) refluxed with $Yb(acac)_3$ for ca. 48 h, (c) after heat treatment, 250°C for 48 h. The absorbance scale and the display offset are arbitrary.

The powder precipitates that were obtained by the current method, as described in the Experimental section, were heated to allow atomic rearrangements and to achieve further neutralization. This was done in vacuum to prevent oxidation. The heating was done at increasing temperature until it was found that heating at ca. 250°C in vacuum caused the disappearance of the carboxylic acid features in the infrared spectra, as well as the full development of Ln^{3+} (COO—) complexation. This is most apparent from the decrease of the intensity of the infrared band at 1700 cm^{-1} for the 16.2 mol % EMAA, acid copolymer (Fig. 1a), to that of the precipitate after reaction in solution, with $Yb(acac)_3$ (Fig. 1b), to its absence (Fig. 1c) after the heat treatment. Simultaneously, the broad, strong features in the 1500–1650 cm^{-1} region, due to the lanthanide carboxylate complexation, grow to become stronger than the 1465 cm^{-1} mode for the amorphous ethylenic backbone. The spectra of these ionomers change throughout the far and mid infrared to reflect the development of these structures.

The far infrared spectra in the 300–600 cm^{-1} region are shown in Figure 2 for the case of the erbium ionomers formed from EAA, ranging from 3.6 mol

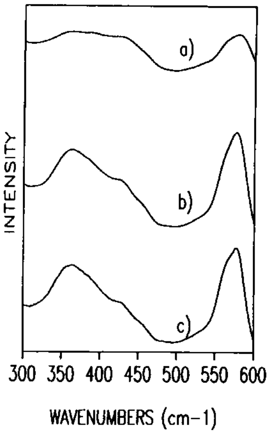

Figure 2. Far infrared spectra (300-600 cm^{-1}) of EAA series. (a) Yb + ER-EAA (2.9 mol % Ln^{+3}), (b) Er-EAA (1.7 mol % Er^{+3}), (c) Er-EAA (1.2 mol % Er^{+3}). The absorbance scale and display offset are arbitrary.

% acid to 8.7 mol % acrylic acid. A band that is centered at ca. 430 cm^{-1} for the Er-EAA (0.45 mol % Er^{+3}) becomes more intense for the materials that have higher Ln^{+3} content. This band may be assigned to a vibration of the Ln^{+3}-carboxylate complex which is approximately the Ln — O stretching frequency. This band becomes more intense when the amount of Ln^{+3} in the material is increased. Spectrum 2a shows the ionomer with ca. 2.9 mol % Ln^{+3} (Yb^{3+} + Er^{3+} in a 50 : 50 mass ratio) in which this band has become very strong and shifted slightly to ca. 420 cm^{-1}.

The spectra of the EMAA copolymer at 16.2 mol % acid and its reaction products are shown in the mid infrared regions of 500–1100 cm^{-1} in Figure 3 and 1100–1800 cm^{-1} in Figure 1. In the mid infrared region (500–1100 cm^{-1}), a band that appears at ca. 560 cm^{-1} in the acid form spectrum (Fig. 3a) shifts to a higher frequency (ca. 578 cm^{-1}) when reacted with $Yb(acac)_3$. This band is assigned to C — O — R linkage[24] but a vibration consisting of C — C — C wagging motions also can contribute in this region.[25] A band at ca. 782 cm^{-1} in the acid form shifts to ca. 792 cm^{-1} when it is neutralized. It is assigned to the O — C — O bending motion.[24] The band at ca. 643 cm^{-1}, which is assigned to the COO^- wagging motion in the acid form,[24] shifts to ca. 655 cm^{-1} when neutralized. A band at ca. 945 cm^{-1} in the spectrum of the acid form, which is assigned to the deformation of the hydrogen bonded O — H bond of the unionized carboxyl,[26] is reduced in intensity when the acid form is reacted with $Yb(acac)_3$. It practically disappears after the heat treatment of the powder. This band has been shown to be temperature dependent and has been observed to disappear when ethylene-*co*-acrylic acid and ethylene-*co*-methacrylic acid ionomers are heated.[27]

The two components of the vibrations at ca. 1260 and 1170 cm^{-1} in the acid form (Fig. 1a) weaken in intensity when the ionomer is reacted with $Yb(acac)_3$ (Fig. 1b) and practically disappear after the heat treatment at 250°C (Fig. 1c). As noted above, the band at ca. 1700 cm^{-1} in the acid form assigned to the asymmetric stretching vibration of the carboxylic acid moiety becomes far less intense after the ionomer is refluxed with $Yb(acac)_3$ (Fig. 1b). It disappears when the material is heated at 250°C (Fig. 1c). A new broad band from ca. 1500 to 1665 cm^{-1} appears in the neutralized forms and is assigned to the asymmetric vibration of the lanthanide-coordinated carboxylate ion. Okamoto[21,22] also observed the appearance of broad bands in the 1500–1700 cm^{-1} region in some lanthanide carboxylate complexes. It is interesting to note that spectra of the Yb^{3+}/Er^{3+} mixed rare earth ionomer system (Fig. 4) show that they are quite similar to those with only one type of ion.

Near Infrared Spectra

The near infrared region diffuse reflectance spectra of the thermally treated powdered materials containing Er^{+3}, Sm^{+3}, and Dy^{+3} in the 900–2000 nm range are shown in Figures 5–7. The bands in the near infrared spectra are broad with full widths at half height (FWHH) of several hundred wavenumbers due to the disordered nature of the polymer and in particular the environments of the lanthanide ions. This leads to different ions in an ionomer hav-

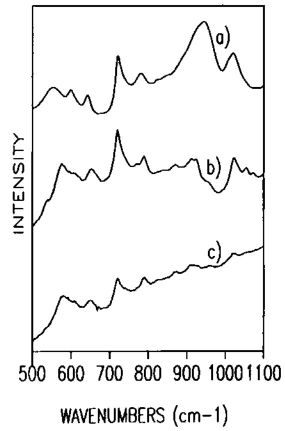

Figure 3. Infrared spectra of (500-1100 cm^{-1}) EMAA (16.2 mol % MAA) series. (a) EMAA (16.2 mol % MAA), (b) EMAA (16.2 mol % MAA) refluxed with $Yb(acac)_3$ for ca. 48 h, (c) after heat treatment, 250°C for ca. 48 h. The absorbance scale and the display offset are arbitrary.

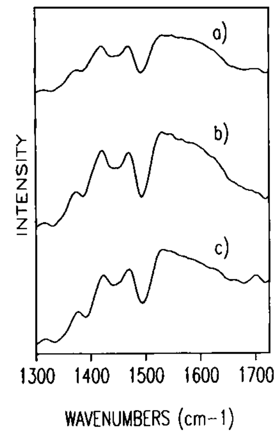

Figure 4. Infrared spectra (1300–1750 cm^{-1}) EMAA (16.2 mol % MAA) series. (a) Er-EMAA (5.4 mol % Er^{3+}), (b) Yb-EMAA (5.4 mol % Yb^{3+}), (c) Yb + Er EMAA (5.4 mol % Ln^{3+}). The absorbance scale and display offset are arbitrary.

ing somewhat different energy levels. This distribution of environments is reflected in their absorption, emission, and excited-state decay behavior. In glasses the broadening of spectral lines due to the inhomogeneity of the matrix has been known to range from ca. 300 to 500 cm^{-1}.[28,29] The spectra for both for EAA and EMAA ionomers containing Er^{+3} are shown in Figure 5. Spectrum 5a is that of the material containing ca. 2.9 mol % Er^{+3}, because the base polymer ethylene-*co*-acrylic acid copolymer contained 8.7 mol % acrylic acid. Spectrum 5b is that of the material containing ca. 5.4 mol % Er^{+3}, because the base polymer ethylene-*co*-methacrylic acid copolymer contained 16.2 mol % methacrylic acid.

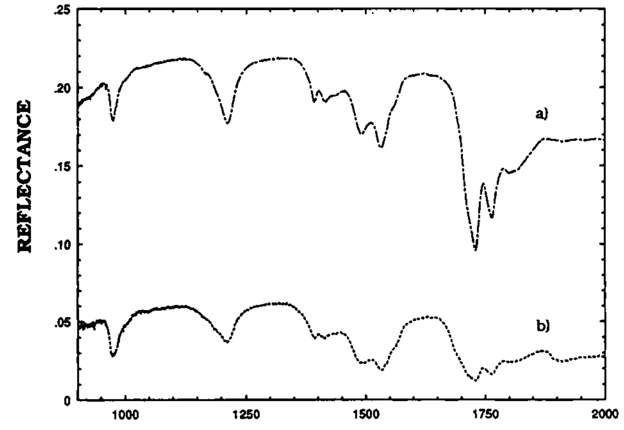

Figure 5. Near infrared reflectance spectra (900–2000 nm). (a) Er-EAA (2.9 mol % Er^{+3}), (b) Er-EMAA (5.4 mol % Er^{+3}).

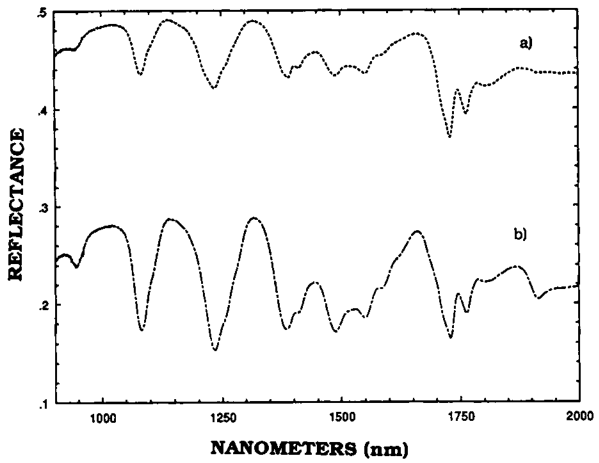

Figure 6. Near infrared reflectance spectra (900–2000 nm). (a) Sm-EAA (2.9 mol % Sm^{+3}), (b) Sm-EMAA (5.4 mol % Sm^{+3}).

The ground state for Er^{+3} is $^4I_{15/2}$.[30] The transitions assigned to this ion, given in Table I, are those of the broad bands observed at ca. 1529 and 975 nm. The $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition occurs at 1529 nm, which is consistent with the frequency at which this transition was observed in heavy metal fluoride (HMF) glasses.[30] The transition from the $^4I_{15/2}$ level to the $^4I_{11/2}$ level occurs at 975 nm in these ionomers and at 972 nm for HMF glasses.[30]

The near infrared transitions for the ionomers containing Sm^{+3} are shown in Figure 6. Spectrum 6a shows the material that contains ca. 2.9 mol % Sm^{+3}, complexed to ethylene-*co*-acrylic acid copolymer, Sm-EAA (8.7 mol % AA). This is called Sm-EAA (2.9 mol % Sm^{3+}). Spectrum 6b is that of the

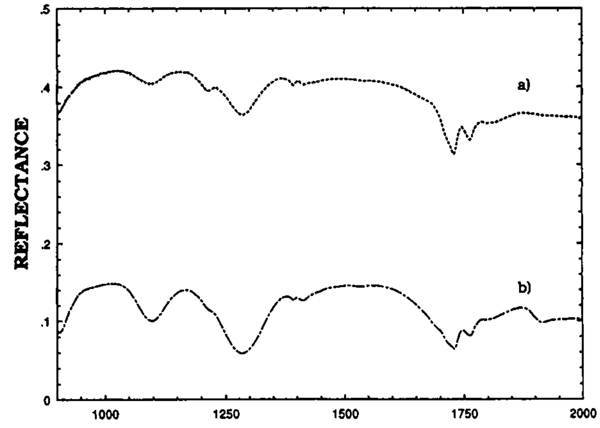

Figure 7. Near infrared reflectance spectra (900–2000 nm). (a) Dy-EAA (2.9 mol % Dy^{+3}), (b) Dy-EMAA (5.4 mol % Dy^{+3}).

Table I. Er^{+3}

Analogous Transition in Er^{3+}-Free Ion	Band Observed in Ionomers (nm)	Band Observed in HMF Glasses (nm)
$^4I_{15/2} \rightarrow {}^4I_{13/2}$	1529	1529
$\rightarrow {}^4I_{11/2}$	975	972

Table III. Dy^{+3}

Analogous Transition in Dy^{3+}-Free Ion	Band Observed in Ionomers (nm)	Band Observed in HMF Glasses (nm)
$^6H_{15/2} \rightarrow {}^6F_{11/2}$	1286	1280
$\rightarrow {}^6F_{9/2}$	1090	1100

Sm-EMAA (5.4 mol % Sm^{+3}) ionomer. The ground state for Sm^{+3} is $^6H_{5/2}$ and the various transitions are shown in Table II. Two intense bands occur at ca. 1079 and 1235.7 nm, for both the materials, which correspond to the $^6H_{5/2} \rightarrow {}^6F_{9/2}$ and $^6H_{5/2} \rightarrow {}^6F_{7/2}$ transitions, respectively. The other bands for Sm^{+3} occur at ca. 942, 1385, 1485, 1550, and 1585 nm and are assigned as indicated in Table II.

The near infrared reflectance spectra for the materials containing Dy^{+3} are shown in Figure 7. Spectrum 7a is that of the Dy-EAA (2.9 mol % Dy^{+3}), and spectrum 7b is that of the Dy-EMAA (5.4 mol % Dy^{+3}) ionomer. The transitions are shown and assigned in Table III based on the $^6H_{15/2}$ ground state for Dy^{+3}. The two major bands occur at ca. 1093 and 1286 nm for both the materials, and correspond to the $^6H_{15/2} \rightarrow {}^6F_{9/2}$ and $^6H_{15/2} \rightarrow {}^6F_{11/2}$ transitions. These frequencies are in agreement to the absorption frequencies observed for Dy^{+3} in HMF glasses[30] and are shown in Table III.

The other bands observed in these near infrared spectra can be assigned to overtones of vibrational bands of the polymers themselves. For example, the two bands at ca. 1728 and 1761 nm are the overtones of the C — H stretching vibrations, whose fundamentals occur at ca. 3508 (2850 cm^{-1}) and 3424 (2920 cm^{-1}) nm, respectively. The overtones for the CH_2 vibrations of the polymer occur at ca. 1380 and 1414 nm, and the fundamental vibrations occur at ca. 6830 nm (1460 cm^{-1}) and 7040 nm (1420 cm^{-1}), respectively. The O — H overtone that would occur at ca. 1470 nm (6802 cm^{-1}) is absent in the materials containing Dy^{+3} and Sm^{+3}, which have undergone the heat treatment and are virtually O — H free. For the Er^{+3}-containing materials (which also have undergone the heat treatment), a band at ca. 1485 nm is observed that could be due in part to O — H overtones, although the fundamental region (ca. 3400 cm^{-1}) does not show significant absorption.

Table II. Sm^{+3}

Analogous Transition in Sm^{3+}-Free Ion	Band Observed in Ionomers (nm)	Band Observed in HMF Glasses (nm)
$^6H_{5/2} \rightarrow {}^6F_{1/2}$	1586	1580
$\rightarrow {}^6F_{3/2}$	1550	1545
$\rightarrow {}^6H_{15/2}$	1485	1460
$\rightarrow {}^6F_{5/2}$	1385	1383
$\rightarrow {}^6F_{7/2}$	1235	1234
$\rightarrow {}^6F_{9/2}$	1078	1083
$\rightarrow {}^6F_{11/2}$	942	947

Raman Spectra

The Raman spectra (Stokes side) of the ionomers were measured using a Nd : YAG laser as the excitation source operating in the near infrared region at 9396.7 cm^{-1}. The spectra of the ionomers were measured with the source laser beam defocused to minimize heating of the ionomers. If sample heating contributed to the near infrared emission, it would be evident at least in the highest Raman frequency region. However, the spectra have only vibrational Raman bands in the 2800–3200 cm^{-1} region. The spectra of the EMAA ionomers complexed with Sm^{+3} are shown in the 200–3200 cm^{-1} range in Figure 8. In addition to the narrow vibrational Raman bands expected for such a compound, new broad bands appear in the ca. 200–1100 cm^{-1} range, and 1700–2200 cm^{-1} ranges appear in the spectrum of the Sm-EMAA (5.4 mol % Sm^{+3}) ionomer, as shown in spectrum 8a. Spectrum 8b shows the Raman scattering in the same range for the lower concentration ionomer Sm-EMAA (2.4 mol % Sm^{+3}). The new bands from ca. 200 to 1100 cm^{-1} and from ca. 1700 to 2200 cm^{-1} are lower in relative intensity for the ionomer with lower Sm^{+3} concentration. Therefore, the main new features, for the Sm^{3+}-containing ionomers, are the growth of the broad features in the 200–1100 and 1700–2200 cm^{-1} regions and a band centered at ca. 2600 cm^{-1}, in addition to the vibrational Raman spectrum of the polymers.

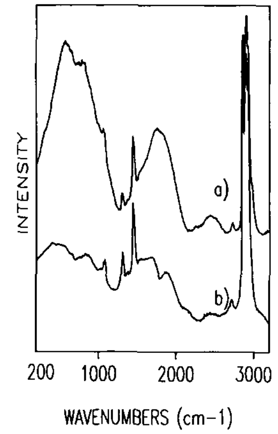

Figure 8. FT-Raman spectra in the 200–3200 cm^{-1} region (1.064 μ source). (a) Sm-EMAA (5.4 mol % Sm^{+3}), (b) Sm-EMAA (2.4 mol % Sm^{+3}). The absorbance scale and the display offset are arbitrary.

Figure 9 shows the Raman scattering in the 200–3200 cm^{-1} range for the series of EAA ionomers complexed with increasing concentrations of Sm^{+3}. The spectrum of the Sm-EAA (0.45 mol % Sm^{+3}) ionomer is shown in spectrum 9c. There are two vibrational bands at ca. 1060 and 1125 cm^{-1} that change in shape as the concentration of Sm^{+3} in the ionomers increases. The band at 1060 cm^{-1} is assigned to the skeletal C — C stretching vibration for amorphous polyethylene and the band at 1127 cm^{-1} is assigned to an internal mode of polyethylene.[31] The band at ca. 1060 cm^{-1} broadens in Figure 9b and 9c and the band at 1127 cm^{-1} almost disappears when the Sm^{+3} concentration is higher. In Figure 9b a new, broad band appears from ca. 300 to 800 cm^{-1}; in Figure 9c the same band band appears in the same region from ca. 160 to 900 cm^{-1}. In addition, the band at ca. 1295 cm^{-1} in Figure 9c becomes relatively less intense with respect to the band at ca. 1440 cm^{-1} when the Sm^{+3} concentration increases. The bands at ca. 1295 and 1440 cm^{-1} can both be assigned to the stretching, vibrational modes of amorphous polyethylene.[31]

The Raman scattering spectra for the EMAA ionomers with three different rare earth ions incorporated in the ionomer are shown in Figure 10. Spectrum 10a shows the ionomer that contains Sm^{+3}, spectrum 10b shows the ionomer that has Dy^{+3}, and spectrum 10c is that of the Er^{+3}-containing ionomer. The broad, intense bands that appear in the ionomer complexed with Sm^{+3} are less intense and broad when the rare earth ion in the ionomer is Dy^{+3}, and these bands are virtually absent when the rare earth ion is Er^{+3}.

The new broad features seen in the FT-Raman spectra of the Sm^{3+} and Dy^{3+} ionomers do not appear in the spectrum of the analogous Er^{3+} ionomers. These three series were studied together because their electronic transitions have different relationships to the frequency of the FT-Raman laser source. One transition for Sm^{3+} systems is quite close to the Nd : YAG laser line at 9396.7 cm^{-1}. A transition for the Dy^{3+} systems is close enough to the 9396.7 cm^{-1} laser line that when the band for this transition is broadened, there is enough overlap with the source to cause excitation. There are no Er^{3+} transitions near the exciting line.

Although the FT-Raman bands do not appear to be resonantly enhanced in any of these systems, at

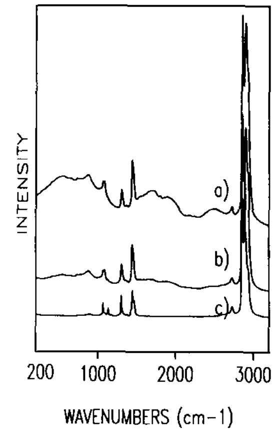

Figure 9. FT-Raman spectra in the 200–3200 cm^{-1} region (1.064 μ source). (a) Sm-EAA (2.9 mol % Sm^{+3}), (b) Sm-EAA (1.7 mol % Sm^{+3}), (c) Sm-EAA (0.45 mol % Sm^{+3}). The absorbance scale and the display offset are arbitrary.

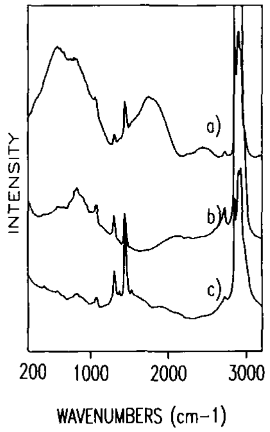

Figure 10. FT-Raman spectra in the 200–3200 cm^{-1} region (1.064 μ source). (a) Sm-EMAA (5.4 mol % Sm^{+3}), (b) Dy-EMAA (5.4 mol % Dy^{+3}), (c) Er-EMAA (5.4 mol % Er^{+3}). The absorbance scale and the display offset are arbitrary.

least in the commonly understood usage of the term resonance Raman, the new, broad features clearly are associated with the presence of the rare earth ions and their overlap with the exciting line. They increase in intensity when the metal ion concentration increases, and their relative intensity is such that it is strongest for Sm^{3+}, weaker for Dy^{3+}, and absent for Er^{3+}. They can be understood as follows.

As noted above, in the case of the Sm^{3+} ionomers the new, broad bands are in the ca. 200–1100, 1700–2200, and ca. 2500 cm^{-1} regions, with maxima at about 540, 1700, 1900, and 2300 cm^{-1}. The Sm^{3+} ions in the ionomers give rise to regions in the electronic density of states peaked near the excited states of the free Sm^{3+} ions. The new, broad infrared bands are listed in Table II, where they are compared with the band positions for Sm^{3+} in HMF glasses and labeled with the transitions of Sm^{3+}-free ion states.

The proximity of the Sm^{3+} ions in the ionomers containing higher concentration of rare earth ions can introduce or enhance energy transfer mechanisms that are unimportant when the ions are well separated. When the Sm^{3+} ions are excited by the laser source at 9396.7 cm^{-1}, the ions in the manifold of $^6F_{9/2}$ states with energy matching that of the source get excited. Those Sm^{3+} ions that are in excited states can transfer their energy to neighboring Sm^{3+} ions. The energy transfer can either occur within the same manifold of states or to a manifold that is lower in energy. For the manifold comprising the $^6F_{9/2}$ excited levels, the peak is at 9276 cm^{-1} as seen from the near infrared spectra. A state at ca. 9276 cm^{-1} can relax to the ground electronic state, which has the $\mu(M-O)$ vibration in the n = 1 state at ca. 420 cm^{-1}. Thus, this transition emits a photon at ca. 8850 cm^{-1} and this appears in the FT-Raman spectrum at ca. 550 cm^{-1}.

Energy transfer from the $^6F_{9/2}$ manifold populates the $^6F_{7/2}$ manifold, whose peak lies at 8097 cm^{-1} above the ground electronic state. It can relax to the same ground state mentioned above [i.e., the ground state with n = 1 for the $\mu(M-O)$ vibration at ca. 420 cm^{-1}], resulting in the FT-Raman band at ca. 1720 cm^{-1}. A schematic diagram of these processes is shown in Figure 11a.

The remaining FT-Raman transitions can be accounted for by relaxation from the $^6F_{5/2}$ manifold. The transitions can occur from both the maximum and minimum energies associated with this manifold. The maximum is at ca. 7500 cm^{-1} and the minimum is at ca. 7200 cm^{-1}. Relaxation from the state at ca. 7500 cm^{-1} to the ground electronic state, which has the vibrational level in the n = 1 state, will appear in the FT-Raman spectra at ca. 2300 cm^{-1}, whereas relaxation from the state at ca. 7200 cm^{-1} to the ground state itself will show up at ca. 2200 cm^{-1} in the spectrum.

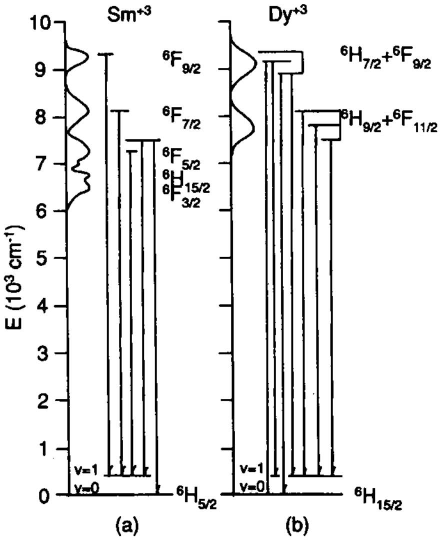

Figure 11. Schematic diagram for the energy transfer and relaxation processes that occur in Sm^{+3} and Dy^{3+} ionomers. (a) Energy transfer processes in Sm^{3+} ionomers, (b) energy transfer processes in Dy^{3+} ionomers.

The energy transfer processes thus populate the $^6F_{9/2}$, $^6F_{7/2}$, and $^6F_{5/2}$ manifold and the subsequent relaxation of their states to the ground state with $n = 0$ or 1 [for the $\mu(M-O)$ vibration] leads to the broad bands observed in the FT-Raman spectra.

For the Dy^{3+}-containing ionomers, there exists a manifold of states whose energy is fairly close to that of the laser source. The appearance of the broad bands in the 300–1100 and 1700–2200 cm^{-1} ranges can be explained by energy transfer between closely spaced Dy^{3+} ions and their subsequent relaxation to the ground state. The $^6F_{9/2}$ manifold centered at ca. 9175 cm^{-1} can become populated when the ionomer is irradiated by the laser source. A transition from the maximum (which is at ca. 9390 cm^{-1} for this manifold) to the ground state with the $\mu(M-O)$ vibration in the n = 1 state will show up at ca. 420 cm^{-1}, whereas relaxation from the minimum of this manifold (at ca. 8850 cm^{-1}) to either the ground state with $n = 0$ or 1 will show up as bands in the FT-Raman spectra at ca. 550 or 1000 cm^{-1}, respectively. Similarly transitions from the $^6F_{11/2}$ manifold (peaked at ca. 7775 cm^{-1}) to the ground state with $n = 0$ or 1 will show in the 1700–2000 cm^{-1} range in the FT-Raman spectra. A schematic diagram of the energy transfer processes in Dy^{3+} ionomers is shown in Figure 11b.

Er^{+3} does not have an electronic transition that is close in energy to that of the pump energy and therefore we do not see the energy migration processes that we see in the other two ionomer series.

Fluorescence Spectra

The fluorescence spectra of two Tb^{3+}-containing EAA ionomers are shown in Figure 12. The ionomers were excited using an argon ion laser operating at 20492 cm^{-1}. The spectrum in Figure 12a is that of the EAA ionomer containing ca. 1.7 mol % Tb^{3+} and spectrum 12b is that of the EAA ionomer containing ca. 0.45 mol % Tb^{3+}. The peak at ca. 18440 cm^{-1} is assigned to the $^5D_4 \rightarrow {}^7F_5$ transition, which occurs for HMF glasses at 0.543 μ (18416 cm^{-1}).[30] The bands at ca. 17160 and 16980 cm^{-1} can be assigned to the crystal field split $^5D_4 \rightarrow {}^7F_4$ transition, which occurs at 0.583 μ (17152 cm^{-1}) for HMF glasses,[30] and the peak at ca. 16092 cm^{-1} is assigned to the $^5D_4 \rightarrow {}^7F_3$ transition, which occurs at 0.62 μ (16103 cm^{-1}) for HMF glasses.[30] The fluorescence bands are broad and extend over a few hundred wavenumbers for each transition.

DISCUSSION

The synthetic method used for the ionomers has achieved complete neutralization of the carboxylate groups by the trivalent rare earth ions. As mentioned above, the synthesis involved the reaction of the polymer and the rare earth ion acetylacetonate salt in a very dilute solution and refluxing for ca. 48 h under this condition. The product of this reaction (obtained after precipitation in excess cold methanol, filtration, and air drying) showed that ca. 85% of the acid groups had been complexed when characterized by infrared methods. The infrared spectra also showed very weak features characteristic of the acetylacetonate salt in the 700–750 cm^{-1} region. The next step involved heating the finely powdered product in vacuum at 250°C for ca. 48 h. When the infrared spectra of these materials were taken, there was virtually no evidence of unreacted carboxylate functionalities. The heat treatment to complete the neutralization process probably involves at least two paths. The first path involves the further reaction of unreacted carboxylate groups with some of the excess acetylacetonate ligands in the ionomer, either on partially substituted Ln^{+3} or on $Ln(acac)_3$, which adheres to the ionomer. Due to the heat treatment, mobility increases, and those rare earth ions that had less than the three carboxyl groups required for balancing the +3 charge could rearrange to satisfy this requirement and release acetylacetonate. The second path is the decomposition of any small amount of the acid form carboxylate groups remaining through a decarbonylation process. The amount of acid form groups removed through the second step presumably is quite small because no clear evidence for formation of anhydrides at this stage is seen in the infrared spectra.

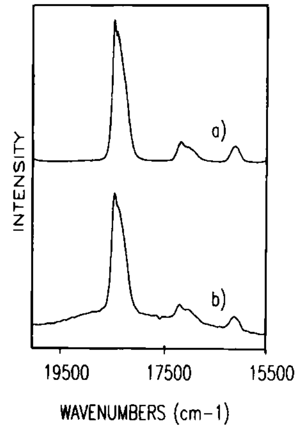

Figure 12. Fluorescence spectra in the 500–5000 cm^{-1} region. (a) Tb-EAA (1.7 mol % Tb^{+3}), (b) Tb-EAA (0.45 mol % Tb^{+3}). The intensity scale and the display offset are arbitrary.

Ionomers whose rare earth ions comprise a 50 : 50 by wt. mixture of Yb^{3+} and Er^{3+} also were synthesized. Materials containing both Yb^{+3} and Er^{+3} have exhibited interesting optical properties.[14] They enable frequency upconversion (from the infrared to the visible), because Yb^{3+}, which has an electronic transition ($^2F_{5/2} \rightarrow {}^2F_{7/2}$) at 1.0 μ in HMF glasses, absorbs light at ca. 1.0 μ and then transfers energy to a nearby Er^{+3} ion. The excited Er^{+3} state emits light in the visible when it relaxes to the ground state. The mid infrared spectrum of an Er^{3+}/Yb^{3+} EMAA ionomer (Fig. 4) showed that the carboxylate-Yb^{+3}/Er^{+3} complexes formed are quite similar to the individual rare earth ion complexes. This illustrates the wide synthetic utility of this ionomer approach, in particular, the incorporation of a range of lanthanides and mixtures of lanthanides.

The near infrared and FT-Raman characterization of the ionomers resulted in the observation of particularly interesting phenomena. The near infrared spectra show the virtual absence of O—H-containing groups in the Dy^{+3}- and Sm^{+3}-containing ionomers. For the Er^{+3}-containing ionomers the band ca. 1.48 μ might be due in part to the presence of a small amount of O—H-containing groups that could be removed by further heat treatment. In addition, the spectra in the near infrared region show that most of the electronic transitions are broadened by several hundred wavenumbers. The broadening of the spectral line indicates that the rare earth ions find themselves in different environments and thus vibrate within a frequency range.

The FT-Raman spectra provide some information about the energy transfer processes that occur in these ionomeric materials. For the Sm^{+3}-containing ionomers, the pump laser frequency is very close to the $^6H_{15/2} \rightarrow {}^6F_{9/2}$ electronic transition, and this energy is absorbed by those Sm^{+3} ions whose optical transition energy nearly matches this frequency. This energy then is transferred to neighboring, closely spaced, Sm^{+3} ions whose electronic states are at energies other than that of the excitation. Some of the Sm^{+3} ions can relax to a lower vibrational level and then emit photons that account for the broad bands in the 100–500 cm^{-1} region of the Raman scattered spectra, whereas other Sm^{+3} ions can relax to lower electronic levels such as $^6F_{7/2}$ and $^6F_{5/2}$. The photons emitted when the ions relax from these electronic levels to the ground electronic vibrational state can account for the bands observed in the 1500 to 2200 cm^{-1} region in the Raman spectra.

In another study[32] we observed that these luminescence bands do not occur in the FT-Raman spectra of ionomers containing similar concentrations of Sm^{+3} ions incorporated in a polysiloxane (PSI) ionomer matrix. The backbone of the PSI ionomer is quite flexible and the extent of aggregation presumably is low. In the ionomers reported in this article, we believe that the host material (ethylene-*co*-acrylic acid, ethylene-*co*-methacrylic acid) is responsible for rare earth ion aggregation, which leads to the novel aggregate-related luminescence.

A similar explanation can be given for the bands seen in the Dy^{+3}-containing ionomers, whose electronic transition $^6H_{15/2} \rightarrow {}^6F_{9/2}$ lies at ca. 9150 cm^{-1}. This leads to the absorption of the exciting line because a small fraction of the Dy^{+3} ions absorb at a frequency very close to the exciting frequency (as observed from the near infrared spectra). Subsequent relaxation to either lower electronic levels, such as the $^6F_{11/2}$ (at ca. 7775 cm^{-1}) or to other low-lying vibrational levels account for the broad bands that appear from ca. 300 to 900 cm^{-1} and from ca. 1700 to 2200 cm^{-1}. The Dy^{+3}-containing ionomers Raman shift the source from 1.064 to 1.53 μ and they also transmit in the 1.53–1.55 μ range.

Er^{+3} does not have an electronic transition that is close to the pump laser frequency, so we do not observe the energy transfer processes that were observed in the ionomers mentioned above.

Earlier studies[19] have shown that rare earth ion aggregation, in glasses especially, often leads to phenomena such as cooperative frequency upconversion (from the infrared to the visible range) or luminescence. The energy transfer observed here as a result of rare earth ion aggregation could result in cooperative upconversion or luminescence and is under investigation.

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