Spectroscopic Properties as a Function of Fluorine Content in Eu^{3+}:PMMA

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ABSTRACT: In this work europium was used as a spectroscopic probe of the local environment about a lanthanide dopant in a fluorinated copolymer of poly(methyl methacrylate) (PMMA). Fluorination of PMMA was achieved through copolymerization with heptafluorobutyl methacrylate (HFBMA). Samples were characterized for their refractive index, glass transition temperature (T_g), and optical emissions via prism coupling, differential scanning calorimetry, and fluorescence spectroscopy respectively. The refractive index and T_gs were found to decrease linearly with fluorine content. The hypersensitivity ratio, which is defined as the ratio of integrated emission intensity between the $^5D_0 \rightarrow {}^7F_2$ hypersensitive transition and $^5D_0 \rightarrow {}^7F_1$ magnetic dipole transition in Eu^{3+}, was found to decrease by $\sim$60% when the HFBMA copolymer content exceeded about 75% by weight. This implies a change in the local environment about the rare earth dopant that is dependent on the copolymer concentration and is likely due to changes in solubility between the ligand and host environment. The results show that fluorination of PMMA can be useful to tailor refractive index, glass transition, and the spectroscopic properties of active dopants. ©2006 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 44: 1592–1596, 2006
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INTRODUCTION

The development of silica-based optical fiber in the 1970s brought about a revolution in telecommunications, providing bandwidth that could never have been accomplished through electrical transmission means. Progress since the early days of fiber technology has brought the attenuation of silica fibers down to near-theoretical values at 1550 nm, the standard wavelength of operation for telecommunication systems.[1] However, as effective a material as silica is for long-haul applications, it possesses certain disadvantages for short-haul applications. The fiber is too brittle at the larger diameters (*e.g.* $\sim$1 mm) needed for large volume premise installation and is costly and difficult to splice together at small core diameters. Here, polymers display several advantages over silica, as they provide potential solutions to all of these issues. Polymers may offer an answer to the question of how to replace the "last mile" of copper wire still used in many telecommunication applications today.[1–7] The successful commercialization

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of such networks requires the development of active polymer optical materials for use in devices such as fiber amplifiers. Researchers have sought to accomplish this through the use of rare earth doped polymers, much like in silica fibers.[1,3,5,8–19]

One issue that arises in the making of such amplifiers is the local symmetry around the rare earth. The rare earth may be located in a symmetric or asymmetric site, and there can be practical reasons for desiring one or the other. For example, the commercially useful emission from erbium in the telecommunications window of 1550 nm is considered to be optimized by a symmetric site. This improves the stability of the signal, important for wavelength division multiplexing applications.[20] An asymmetric site would be desirable in making a europium doped fiber amplifier for use at 614 nm, where the intensity of this peak improves with the asymmetry of the site.[21,22] The symmetry of the site is dependent on the interaction between the host, rare earth, and, when used, the ligand.

Thus, selection of the host is an important consideration. In making both passive and active fibers, optical absorption also plays a vital role in the selection of a host polymer. Most polymers consist of large numbers of C—H bonds, which give an absorption (C—H stretching overtones) in the region of the 1550 nm telecommunications window. It is well known that substitution of the hydrogen with heavier elements will decrease the energy of these vibrations, thus reducing the attenuation at 1550 nm. As a result, much of the recent research into polymer optical fibers has focused on replacing hydrogen with deuterium, fluorine, or chlorine.[5] Thus the current interest in chlorinated, fluorinated, and deuterated polymers stems from the need for low absorptions in the 1550 nm telecommunications window.

In this work, a study was undertaken using poly(methyl methacrylate) (PMMA) and a fluorinated acrylate, 1H,1H-heptafluorobutyl methacrylate (HFBMA) to investigate the changes in site symmetry brought about by the replacement of C—H bonds with C—F bonds (see Fig. 1). This effect is observed using trivalent europium doped samples of these polymers. Doping is accomplished through the use of a fluorinated organic complex (see Fig. 1c). The europium ion is frequently used to study the local environment of rare earths in a variety of materials.[21–27] Europium provides strong, easily measured emission peaks in the visible range. The transitions in this range are not easily quenched, making them useful in higher phonon energy materials such as polymers. In addition, europium emission peaks can provide information regarding the ion's site symmetry.[21,22,24,26,27] Europium doping may be used to perform phonon sideband analysis, which gives information on the rare earth's local phononic environment.

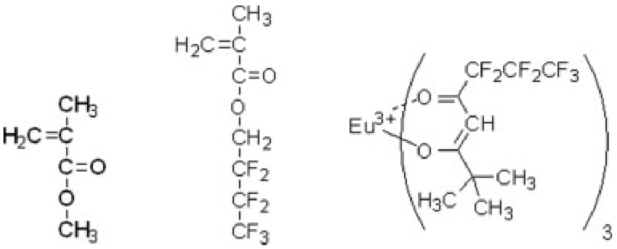

Figure 1. (left) methyl methacrylate, (middle) 1H,1H-heptafluorobutyl methacrylate, and (right) the europium complex used for doping the PMMA copolymers.

EXPERIMENTAL

Sample Preparation

Methyl methacrylate (99% purity) and benzoyl peroxide (97% purity, radical initiator) were purchased from Aldrich (Aldrich, Milwaukee, WI). 1H,1H-heptafluorobutyl methacrylate (HFBMA, >98% purity) was purchased from SynQuest Labs (Alachua, FL). The desired ratio of MMA and HFBMA (2 g total), along with 0.5 wt % europium and 0.7 wt % benzoyl peroxide, were combined and sonicated until all of the benzoyl peroxide and rare earth complex had dissolved. This solution was then placed into a glass tube of 0.75 cm diameter and ~20 cm height. A positive nitrogen pressure was supplied through the open end of the tube. These samples were heated in an oil bath at 60 °C for 48 h, the tubes unsealed, and followed by a post cure in a vacuum oven at 120 °C and about 500 Torr for 3 days. The polymer rod could then be removed from the glass tube. Samples were prepared at twenty weight percent increments of MMA monomer. The dopant used in this work was europium tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionate), purchased from Aldrich in powder form with a purity of >99% (Resolve-Al EuFOD, Aldrich, St. Louis, MO). All samples were doped at 0.5 wt % concentrations and synthesized following the procedures given elsewhere.[8]

Spectroscopic Characterization

All emission data were obtained using a PerkinElmer LS 50B luminescence spectrometer (PerkinElmer, Wellesley, MA). Scan rates were 50 nm/min with a 5 nm slit size from 575 to 635 nm with a 310 nm pump. Spectra were normalized to the magnetic dipole emission occurring at 590 nm. All measurements were taken at room temperature.

Refractive Index Measurements

Polymer films were prepared by dip coating the polymer solutions in toluene onto a silicon wafer. Silicon wafers were obtained from Wafer World (West Palm Beach, FL). Refractive index measurements at a wavelength of 632.8 nm were obtained using a Metricon Model 2010 prism coupler system (Metricon, Pennington, NJ). The instrument measures an area of ~1 mm/run. A prism (no. 200 P-1), optimized for measuring refractive indices between 1 and 1.80, was used to make the measurements. Measurements were taken at room temperature and averaged over five spots on each film.

Differential Scanning Calorimetry

All differential scanning calorimetry (DSC) data were obtained using a TA Instrument DSC Q1000 (TA Instruments, Newcastle, DE). Samples for determining glass transition temperature (T_g) were run through three heating cycles at 10 °C/min using a liquid nitrogen cooling system and determination of T_g was made from the third run. Sample sizes were between 5 and 10 mg each.

RESULTS AND DISCUSSION

Copolymer samples were characterized in terms of T_g by DSC and refractive index using the Metricon Model 2010. These results are shown in Figure 2. The T_g for the homopolymerized HFBMA (PHFBMA) was found to be 60 °C, which is not high enough to make this the homopolymer of direct interest for most optical applications. Copolymerization with MMA increases the T_g and refractive index as expected because of the decrease in volume fraction of plasticizing and nonpolar fluorocarbon side chains respectively. It should be noted, though not shown, that the width of the glass transition feature in the DSC scans was constant, to within the experimental error, as a function of HFBMA content. This, coupled with the observed linearity in refractive index and T_g with HFBMA content, suggests that the samples were copolymers and that no microphase separation occurred. Further, at dopant concentrations above 1 wt % the samples did become opaque, which may suggest microphase separation. At levels below ~0.75 wt % the samples are all clear. For this reason, in this study the dopant levels were fixed below this limit (0.5 wt %). Here, however, the interest is directed toward studying the effects of changing copolymer composition on the rare earth ion site symmetry.

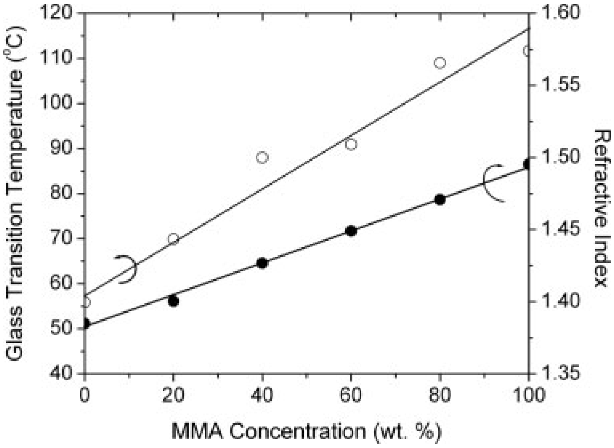

Figure 2. Glass transition temperature and refractive index at 632.8 nm of poly(MMA-*co*-HFBMA) by weight percent MMA. Trend line added as a guide to the eye.

Emission spectra for the Eu^{3+} doped copolymers from 575 to 635 nm, excited at 310 nm, are shown in Figure 3. For viewing clarity, only four of the six spectra obtained are shown. Major 4f transitions from Eu^{3+} have been labeled. The spectra were normalized to the $^5D_0$ to $^7F_1$ transition intensity at 590 nm. The $^5D_0$ to $^7F_1$ transition is a magnetic dipole transition and thus its intensity is independent of environment and can be used as a reference.[21]

Information on the site symmetry of the rare earth can be gained from Figure 3. Site symmetry, in instances such as this relating to the spectroscopic properties of lanthanide dopants, is defined as the crystal field that directly influences the optical transitions of the dopant. This includes the effects of the host on dopant (ground and excited state) absorption and emission linewidths and line-strengths as well as on the energy level dynamics such as radiative emission lifetimes and multiphonon relaxation rates of the dopant. In general, transitions between 4f energy levels in rare earths are not affected by their environment owing to the shielding provided by the outerlying 5s and 5p electrons. However, transitions

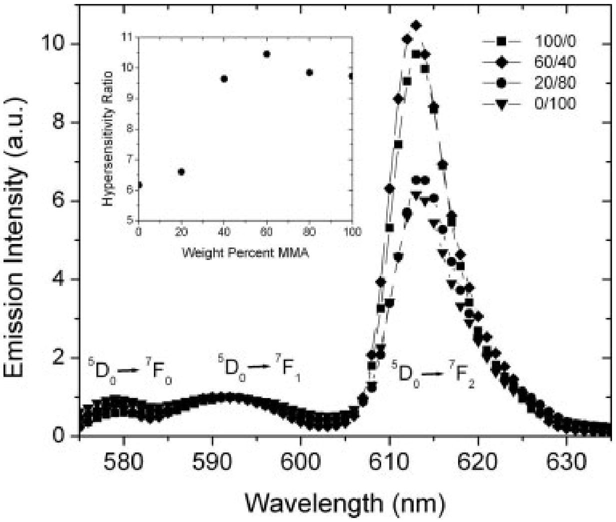

Figure 3. Emission spectra from 0.5 wt % europium doped poly(MMA-*co*-HFBMA), 310 nm pump, normalized to the 590-nm peak. Inset: Hypersensitivity ratio as a function of weight percent.

with total angular momentum quantum number difference $\Delta J = 2$ are known to be more sensitive to their local environment, and thus they are termed hypersensitive. The $^5D_0$ to $^7F_2$ emission ($\Delta J = 2$) in europium is an example of such a transition.[21] If the rare earth resides in a center of symmetry, the intensity of these hypersensitive transitions is small, but the intensity increases as the site becomes more asymmetric. More specifically, in a more symmetric site, the intensity of the $^5D_0$ to $^7F_2$ emission is nearly 0, with some small intensity resulting from the very weak vibronic-allowed transition, and the intensity increases as the site becomes more asymmetric.[21] Here the $^5D_0$ to $^7F_1$ magnetic dipole transition can be used as a reference point. The ($^5D_0 - {}^7F_2$)/($^5D_0 - {}^7F_1$) fluorescence intensity ratio is commonly referred to as the hypersensitivity ratio and is used as a measure of rare earth site symmetry.[21] Clearly, from Figure 3 the intensity of the hypersensitive transition relative to the intensity of the $^5D_0$ to $^7F_1$ is significantly large, especially for the samples with high PMMA content. Thus, the relative strength of this hypersensitive transition in the fluorescence spectra indicates that the rare earth is located in an asymmetrical environment.

The change in the hypersensitivity ratio with changing copolymer composition is plotted in the inset of Figure 3. The data indicate that the hypersensitivity ratio remains essentially unchanged until PHFBMA becomes the significantly dominant component, indicating some type of local symmetry structural change. At that point, the site symmetry begins to increase, as reflected in the decrease in the hypersensitivity ratio with increasing PHFBMA content (decreasing PMMA content).

The observation of an effect on site symmetry should not be surprising. The ligand being used in the Eu^{3+} complex contains fluorine, as does HFBMA, while MMA does not. Therefore, it seems reasonable to expect that the solubility of the ligand in each of these polymers would be different, despite both being acrylates. The change in the symmetry of the rare earth ion site can therefore likely be explained as resulting from the solubility of the ligand in the two polymers. Of the three pertinent interactions—HFBMA–ligand, MMA–ligand, and ligand–ligand, we can assume that the fluorocarbon–fluorocarbon interactions are more favored than the others; therefore, HFBMA-ligand interactions compete with ligand–ligand interactions both thermodynamically and kinetically, based on the molar excess of HFBMA in the copolymers studied. This competition results in less aggregation and reduced quenching tendency from nearby metal centers in addition to providing a more flexible ligand field environment from the solvating fluorocarbon side chains in HFBMA.

However, it should also be noted that at a wavelength of 310 nm, it is reasonable to assume that the host polymer is what is actually being excited, followed by an energy transfer process to the europium ion. Therefore, the emission intensities may also be influenced by the efficiency of this energy transfer, which may be dependent on the copolymer concentration. The significance of this effect is not fully understood now.

These results provide additional insight into the local environment about the rare earth. One may have expected that the large size of the ligand would yield little symmetry influence from the host polymer itself. If this were the case, then the selection of ligand would have been far more important than the choice of host polymer in the symmetry of the site. However, these results show that the symmetry is influenced by the polymer even for relatively large rare earth complexes. Thus, it can be concluded that, in this case, the local environment experienced by the rare earth extends beyond the ligand and into the host polymer.

These findings may represent a way of tuning the output of a device fabricated from these materials. The strength of the 614 nm emission relative to the 590 nm emission can be adjusted by simple choice of comonomer composition.

CONCLUSIONS

Copolymers have been made from methyl methacrylate and HFBMA in 20 wt % increments. These have been doped with 0.5 wt % europium using the ligand shown in Figure 1c. This study investigated the changes in site symmetry induced by using a fluorinated acrylate as compared with PMMA. Asymmetric or symmetric rare earth ion sites may be desirable depending on the application. It was noted that the asymmetry of the rare earth ion site decreased significantly with increasing PHFBMA content in the host. It is suggested that this results from the different solubilities of the ligand in the two polymers.

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