Macromol. Symp. ***186*****,** *51–56 (2002)*

Optical Absorption Spectra from Rare-Earth Ions in Polymers: The Effect of the Polymer Host

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Summary: A Molecular Dynamics (MD) based modified Judd/Ofelt approach has been used to simulate UV-VIS absorption spectra for different concentrations of $Er(CF_3SO_3)_3$ (erbium triflate) in the amorphous polymer host poly(ethylene oxide), PEO. The simulations have been performed for systems containing both single-chain PEO and PEO with an attached side-chain. Effects on the optical properties of the introduction of side-chains are demonstrated. Qualitative inspection of the calculated spectra would suggest that similarities in the crystal field experienced by individual Er ions in qualitatively different local environments will make structural information difficult to access from this procedure.

Introduction

A wide range of crystalline and inorganic glassy rare earth (RE) ion hosts now exist for optical applications of different kinds and in different optical regions [1-2]. It is generally believed that RE ions in polymer hosts will also find many interesting and innovative applications in the coming years. In principle, any material with negligible absorption in a given optical region can be considered as a potential host material for RE ions in optical devices. Polymers have the main advantage of being considerably cheap and easier to process. However, it is only recently that we have seen this increased interest in the use of polymers as RE ion hosts. The apparent lack of earlier interest would seem to stem from problems associated with the high-frequency O-H and C-H bond vibrations in polymers, which increase non-radiative energy transfer, shorten excited-state lifetimes, and thereby quench optical transitions. These difficulties can be overcome in several ways [3]. The lifetimes of the RE excited states must remain long, implying that this non-radiative energy transfer must be minimised. This can be achieved by trapping the RE ions in chelate-type or colloidal

CCC 1022-1360/00/$ 17.50+.50/0

hosts, and ensuring that the high-frequency vibrations avoid the inner-sphere energy transfer region. RE-containing polymers developed for use in optical telecommunication applications include acrylates, polyimides, and olefins. The RE ion most commonly used in is Er^{3+} - the ion on which we focus here.

The overriding goal of this work is to endeavour to forge a link between optical properties and the local structure of the Er^{3+} ions in the polymer host poly(ethylene oxide) (PEO) . It has long been known that these are intimately related in crystalline materials, *i.e.*, the optical properties are determined by the crystal field experienced by the lanthanide ion [4-5]. In amorphous polymer hosts, the local structures experienced by the RE ion itself are provided by the anions and the polymer-host atoms. Intuitively, different local structures around the RE ions will result in different optical properties. This relationship has been probed in calculations for the Cl^- anion [6], although such monoatomic anion systems are difficult to synthesise because of the low solubility of $ErCl_3$ in PEO. In this work, we have therefore chosen the bulkier triflate ion ($CF_3SO_3^-$) as counter-ion to Er^{3+}, and have attempted to further encourage amorphicity in the host by adding a PEO-type side-chain to the polymer backbone.

Method

The approach used here combines experimental absorption spectroscopy and computational techniques, although the main focus has been in the theoretical area. A strategy has been evolved for deriving the local structure of RE ions in a crystalline host, and for establishing how this structure relates to the optical properties of the material, *e.g.* [7]. Here we extend the method to the treatment of polymer hosts.

Molecular Dynamics (MD) simulation first provides a sequence of representative local environments for the RE ions, and thereby a dynamical picture of their local environments. This is needed to derive their optical properties. The contributions to the absorption spectra from the RE ions in their different local environments are then calculated and accumulated in a histogram to give the total theoretical spectrum. The total spectrum and the individual contributions are then used to establish the RE ion environments present in the material, and how these influence the resulting spectra.

In the MD simulations, the intramolecular potentials used have been described by three- or four-body interactions, while the intermolecular potentials have been described by two-body interactions of the Born-Mayer-Huggins form. These potentials are derived from quantum-chemical calculations or taken from libraries of reliable potentials; their sources are listed in Table 1. The MD simulations are performed with a NpT barostat); a time-step of 0.5 fs is used for a total of 1 ns, *i.e.,* 2×10^6 time-steps.

Table 1. Sources of the potentials used in the simulations.

Potential	Source
Intramolecular potentials: PEO	[8]
Intramolecular potentials: triflate ion	[9]
Intramolecular potentials: sidechain	[10]
Intermolecular potentials: PEO – triflate ion	[11]
Intermolecular potentials: Er^{3+} - PEO	[6]
Intermolecular potentials: Er^{3+} - triflate ion	[12]

MD simulations thus provide a dynamical picture of the RE ion in different local environments. The spectral contribution to the total absorption spectra from each ion in each of these environments in the simulation box is calculated from 300 snapshots taken at 1000-step intervals in the MD simulation, after the system has reached equilibrium.

For each RE ion and snapshot, the different eigenstates of the $4f$ electrons involved in the optical transitions are generated by several perturbation terms in the Hamiltonian: coulomb interaction, spin-orbit interaction, "crystal-field" interaction depending on the environment surrounding the Er^{3+} ion and linear and non-linear configuration interactions. The energies and eigenvectors needed for the construction of the spectrum are then obtained by diagonalizing a 364×364 energy matrix.

The matrix elements are described in the *SLJM* representation and the different states are assigned according to Racah algebra [13]. Judd-Ofelt theory [4-5] describes the electric-dipole transitions between J manifolds in the $4f$ shell of the RE ions. In this work, the theory is extended by considering transitions between JM_j levels. The crystal-field parameters generated for each MD snapshot are calculated from a monopole contribution, thus making the crystal-field description somewhat primitive by neglecting the covalency in the system.

Results and discussion

Different concentrations of $Er(CF_3SO_3)_3$ have been studied in the $Er(CF_3SO_3)_3(PEO)_n$ system for n = 100, 50, 28.6 and 25, and for polymers with and without a side-chain.

The MD simulations suggest that $Er(CF_3SO_3)_3$ dissolved in PEO (with and without side-chain) results in a number of qualitatively different coordination environments for the Er^{3+} ion. The Er^{3+} ions are generally found to have coordination numbers ranging from 7 to 10, with an average value of 9; this is in good agreement with experiment, and suggests that our MD potentials are reasonably appropriate. The Er^{3+} ion shows a striking tendency to coordinate to polymer or triflate oxygens; only a few Er ions were found to coordinate in any other way (*e.g.,* to a triflate fluorine). A rich variation in the coordination-types of the different Er^{3+} ions in the simulation; the coordination number to triflate oxygens range from 1 to 6. All triflate ions coordinate to Er^{3+} ions along only one of their three S-O bonds. These variations in coordination might well suggest that the crystal-field parameters should be significantly different for different Er^{3+} ion environments, and thus contribute differently to the spectrum.

It was found, however, that the differences between calculated shapes and positions of the peaks do not reflect the qualitatively different coordination types, as was the case for $ErCl_3$ in PEO [6] (Figure 1). This must be a result of the more similar crystal field experienced by the RE ions in their apparently different local environments. This is, in turn, a consequence of the similar partial charge on the ether and triflate oxygens. Such small differences between environments can be perhaps better detected by an improved description of the crystal field, which takes more explicit account of covalency.

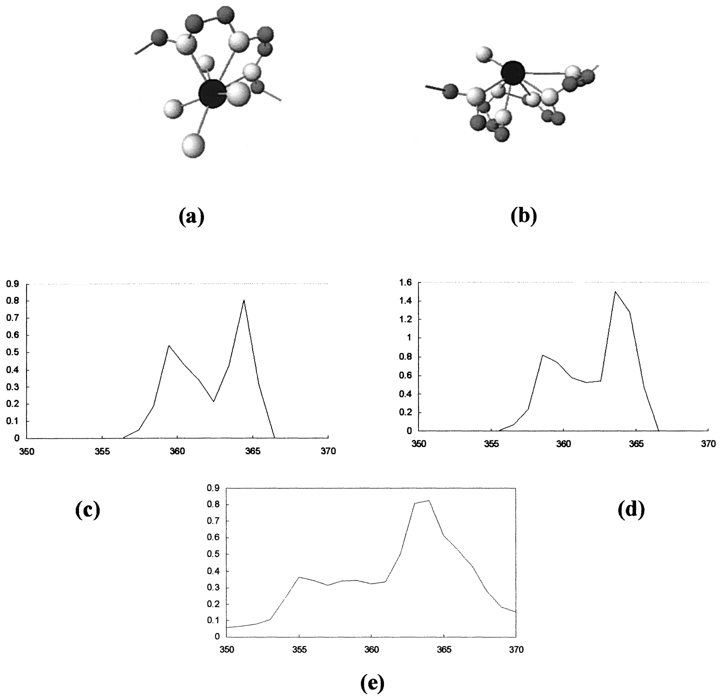

Figure 1. Two different local Er^{3+} environments in $Er(CF_3SO_3)_3(PEO)_{25}$ (a and b), their calculated spectral contributions (c and d), and the corresponding experimental peak (e).

The calculated absorption spectrum obtained agrees quite well with the experimental spectra for $Er(CF_3SO_3)_3$ in PEG400, which is a short-chain PEO providing the same local geometries around Er^{3+} (Figure 2). The differences that arise derive from the free-ion parameters used in the perturbation Hamiltonian, and from experimental line-broadening effects.

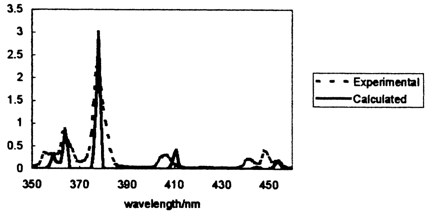

Figure 2. Comparison between a part of the experimental and calculated spectrum for $Er(CF_3SO_3)_3(PEO)_{25}$.

Further, the MD simulations indicate very similar local coordination types around Er^{3+} for the two polymer-host types. This is because the ions tend to avoid the side-chain attachment region and the end-groups during the simulations. The calculated spectra thus become very similar (Figure 3), indicating that amorphicity could be improved by adding side-chains to the polymer hosts.

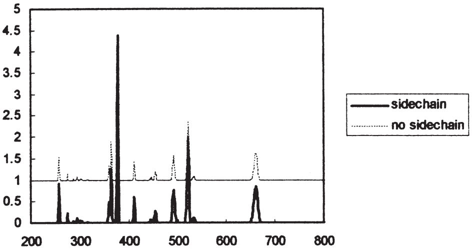

Figure 3. Comparison between calculated spectra for the $Er(CF_3SO_3)_3(PEO)_{25}$ systems with and without a side-chain.

Conclusions

A variety of different Er coordination types appear in the simulations; these might well have been expected to contribute differently to the spectrum. However, this is not apparent from the spectral calculations, suggesting a high degree of covalency in the system. The agreement between calculated and experimental absorption spectra is relatively good (the differences originate chiefly in differences in the free-ion parameters and in the crystal-field model used in the calculations) and the amorphicity of the polymer host can be increased by adding side-chains to the polymer backbone without changing the optical properties significantly.

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