Eu³⁺/Block copolymer nanostructured hybrid materials

K D Gatsouli, S Pispas and E I Kamitsos

Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vass. Constantinou Ave., 11635 Athens, Greece

Email: pispas@eie.gr

Abstract. The synthesis and spectroscopic characterization of a series of nanostructured organic-inorganic hybrid materials based on functional diblock copolymers and Eu³⁺ salts is reported. The organic block copolymers were prepared by anionic polymerization and contain a block carrying functional groups, able to complex with Eu³⁺ cations (i.e. ethylene oxide, 2-vinylpyridine, sulfonate or methacrylic acid units) and a “neutral” non-interacting hydrocarbon block as a structure participating component (i.e. polystyrene or poly(tert butylstyrene)). In these materials the diblock is acting as the nanostructured matrix (having lamellar, cylindrical or spherical morphologies) as well as the inorganic cation fixation agent, whereas the Eu³⁺ component provides the optical response to the hybrids. The novel materials were characterized using infrared and fluorescence spectroscopy.

1. Introduction
Lanthanide complexes exhibit very efficient light emission intensity under ultraviolet excitation. However, despite their interesting optical properties they have so far been excluded from practical use as tunable solid-state lasers or photoluminescence and electroluminescence devices, essentially due to their poor thermal stability and mechanical properties. One of the strategies adopted in recent years, to improve the thermal stability, the mechanical and light emission properties of lanthanide ions, is their incorporation into polymeric matrices and sol-gel derived organic-inorganic nanostructured hybrids. The major interest in this approach is the possibility of preparing multifunctional nanoscale organic-inorganic frameworks with tunable designs and suitable features. Here we report on the synthesis and spectroscopic characterization of a series of nanostructured organic-inorganic hybrid materials based on functional diblock copolymers and Eu³⁺ salts.

2. Experimental Part

2.1. Synthesis of Block Copolymers
The synthesis of the block copolymers has been achieved by anionic polymerization high vacuum techniques involving extensive purification of reagents, sequential monomer addition and selective post-polymerization chemical transformation reactions. In this way poly(styrene-b-methacrylic acid) (SMA), poly(styrene-b-ethylene oxide) (SEO), poly(sulfonated styrene-b-tert butyl styrene) (suStBS) and poly(styrene-b-2-vinylpyridine) (S2VP) copolymers were synthesized. The polymers were characterized by size exclusion chromatography, ¹H-NMR and attenuated total reflectance FTIR (ATR-FTIR) in order to obtain the exact molecular characteristics and to confirm the uniformity of the samples. The overall molecular weight, polydispersity, the composition and the morphology of the
block copolymers used are shown in table 1. The morphology of each block copolymer depends on the volume fraction of each block2.

2.2. Sample Preparation
At first 5w/v% solutions of each polymer in dimethylformamide (DMF) were prepared. A weighed amount of europium nitrate, Eu(NO3)3, was added in each solution in the desirable functional group:Eu ratio. Two samples of each polymer were prepared with ratios 2:1 and 4:1, apart from the poly(sulfonated styrene)-b-tert butyl styrene) case where 1:1, 2:1 and 4:1 ratios were prepared. The solutions were stable after the addition of Eu(NO3)3 for several weeks.

Table 1: Molecular characteristics of the employed block copolymers

| Block Copolymer | Molecular Structure | Volume Fraction | Mw | I | Percentage |
|-----------------|--------------------|-----------------|----|---|------------|
| Poly(styrene-b-ethylene oxide) (SEO) | ![Molecular Structure](image1) | Cylinders of PEO | 70,900 | 1.01 | 75% wt PS |
| Poly(sulfonated styrene-b-tert butyl styrene) (suStBS) | ![Molecular Structure](image2) | Lamellae | 147,000 | 1.03 | 52% wt suPS |
| Poly(styrene-b-2-vinylpyridine) (S2VP) | ![Molecular Structure](image3) | Lamellae | 70,400 | 1.01 | 44% wt PS |
| Poly(styrene-b-methacrylic acid) (SMA) | ![Molecular Structure](image4) | Spheres of PMA | 44,900 | 1.06 | 16% wt PMA |

2.3. Measurements
Solid films were formed by casting the prepared solutions, onto glass plates or silicon wafers, in order to be investigated by fluorescence or infrared spectroscopy, respectively. The photoluminescence spectra were measured on a double-grating excitation and a single-grating emission spectrofluorometer (Fluorolog-3, model FL3-21, Jobin Yvon-Spex). Infrared spectra were measured in transmission on a Fourier transform instrument (Bruker Optics, Equinox 55) by averaging 100 scans at 8 cm⁻¹ resolution. All measurements were performed at room temperature.

3. Results and Discussion
Well-defined narrowly distributed block copolymers were prepared by anionic polymerization. The block copolymers have a microphase separated morphology depending on their composition (table 1). Europium nitrate was dispersed completely in the solution of the polymers resulting in homogenous solutions. The quality of the films derived from these solutions onto glass or silicon was very good on either substrate, as the surface was smooth and no island formation was observed.

Representative IR spectra of poly (styrene-b-methacrylic acid) (SMA) and poly(styrene-b-ethylene oxide) (SEO) based composites are shown in figures 1 and 2, respectively. In the case of SMA the frequencies of the C-O stretching modes at 1269 cm⁻¹ and of the C=O at 1708 cm⁻¹ in pure block copolymer (figure 1), shift drastically with COOH: Eu ratio indicating the incorporation of europium into the poly(methacrylic acid) phase. The vibration modes of C-O-C stretching at 1065 cm⁻¹, 1113 cm⁻¹ and 1145 cm⁻¹ of poly(styrene-b-ethylene oxide) (SEO) (figure 2) also shift indicating the complexation of europium ions with the ether oxygens of the poly(ethylene oxide) block. A small shift in the -SO3 stretching vibrations, at 1033 cm⁻¹ and 1175 cm⁻¹ of the pure poly(sulfonated styrene-b-tert butyl styrene) copolymer, is observed leading to the conclusion that europium ions were
complexed with the functional group of the copolymer (spectra not shown). A similar situation takes
place in the poly(styrene-b-2-vinylpyridine) case where pyridine ring stretching modes at
1431 cm\(^{-1}\), 1471 cm\(^{-1}\), 1567 cm\(^{-1}\) and 1593 cm\(^{-1}\) shift due to europium interaction with the pyridine
units\(^3\). In all samples the shifts increase with the concentration of the europium ions. Therefore, the
complexation of europium ions with the functional groups drives the incorporation of europium ions
into the functional block phase in each copolymer.

Figure 1. IR transmittance (left) and fluorescence (right) spectra of the pure SMA (solid line), SMA +
Eu(NO\(_3\))\(_3\) with different COOH:Eu ratios (COOH:Eu=4:1, dashed line, and COOH:Eu=2:1, dotted
line) and Eu(NO\(_3\))\(_3\) (dash-dot line).

Figure 2. IR transmittance (left) and fluorescence (right) spectra of the pure SEO (solid line), SEO +
Eu(NO\(_3\))\(_3\) with different EO:Eu ratios (EO:Eu=4:1, dash line, and EO:Eu=2:1, dot line) and Eu(NO\(_3\))\(_3\)
dash-dot line).

Figures 1 and 2 also depict the fluorescence spectra of the pure and the hybrid composites based on
(poly(styrene-b-methacrylic acid) and poly(styrene-b-ethylene oxide)) as well as pure europium nitrate
under excitation at 394 nm. Five europium emission peaks were observed at 578 nm \(\left(\frac{5}{2}D_0-\frac{7}{2}F_1\right)\),
591 nm \(\left(\frac{5}{2}D_0-\frac{7}{2}F_2\right)\), 615 nm \(\left(\frac{5}{2}D_0-\frac{7}{2}F_3\right)\), 649 nm \(\left(\frac{5}{2}D_0-\frac{7}{2}F_4\right)\) and 694 nm \(\left(\frac{5}{2}D_0-\frac{7}{2}F_4\right)\) and they are
characteristic of the f-f transition of Eu\(^{3+}\) ions\(^4,5\). These bands are not observed in the pure block
copolymers. It is noted that no shift of the Eu\(^{3+}\) bands could be observed in any of the hybrids studied.
The observed f-f transitions are direct evidence of incorporation of Eu\(^{3+}\) into the diblock copolymers. The hybrids show strong fluorescence, suggesting that the copolymers used are suitable matrices for achieving the desired optical performance in the final materials, under conditions of good mechanical stability accompanied by ease and flexibility in terms of process ability. The absence of frequency shifts in the fluorescence spectra is in line with the fact that the coordination sphere of Eu\(^{3+}\) in the composites is dominated, at least partially, by oxygen ligands.

4. Conclusions
Nanostructured hybrid materials based on functional block copolymers and Eu\(^{3+}\) ions were prepared and studied in film form. FT-IR characterization of the copolymers / Eu\(^{3+}\) hybrids showed the complexation of the cation within the functional block of each copolymer. The final materials preserve the optical properties of the lanthanide ion, as evidenced by fluorescence spectroscopy, and exhibit good mechanical stability and ease of process ability, stemming from the polymeric nature of the block copolymer matrices.

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6. References
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