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Synthesis, Characterization, and Fluorescence Properties of Aniline-g-Poly(styrene-co-maleic anhydride) and Its Lanthanide Complexes

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ABSTRACT: Copolymers of aniline-*g*-poly(styrene-*co*-maleic anhydride) (AP/SMA) and its lanthanide(III) (Ln) ion complexes [Ln–AP/SMA (where Ln = La, Eu, Tb, or Yb)] were synthesized and characterized by elemental analysis, Fourier transform infrared spectroscopy, ^{1}H-NMR analysis, thermogravimetry–differential thermal analysis, and differential scanning calorimetry. At room temperature, the fluorescence spectra showed that the AP/SMA polymer had a strong, broad emission band at 300–550 nm (maximum wavelength = 381 nm) under excitation at 293 nm. Moreover, the respective characteristic emissions of Eu(III) and Tb(III) ions were observed in their Ln(III) complexes. Both the Eu(III) complexes and Tb(III) complexes showed excellent solvent resistance, good thermal stability, high quantum yield, and a long fluorescent lifetime. Therefore, the AP/SMA polymer and the fluorescent Ln–AP/SMA complexes have a promising future in applications of fluorescence materials. In addition, the reaction spontaneously reached equilibrium only after 5 min in the water phase; this showed that AP/SMA has good application prospects in the adsorption of Ln ions. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 3432–3439, 2013

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INTRODUCTION

Because 4f electrons are shielded by filled 5s and 5p electrons, and the spectra exhibit characteristic emissions arising from f–f transitions; with the negligible influences of the environment, lanthanide (Ln) elements have an advantage over other metals in the development of fluorescent materials.[1] Europium and terbium ions are of special interest because of their particularly suitable spectroscopic properties, but their absorption bands are weak and narrow. To enhance absorption, Ln ions are usually chelated with certain ligands, which possess both the functional properties of polymeric matrices and the emission properties of Ln coordination compounds. Macromolecular lanthanide complexes (MLnCs) are of great interest because of their unique physicochemical properties and various applications as functional materials.[2,3] In particular, the magnetic and luminescent properties of MLnCs have aroused much attention for decades.[4,5] Until now, because of their characteristic emissions, such as red emissions for Eu(III) and green emissions for Tb(III), which are suitable for photosynthesis, MLnCs have been an increasingly attractive subject area for researchers of light-conveying agricultural films.[6] Because of the potential applications of these solid materials as light-conveying agricultural films, study of the solid state is extremely important and requires more fundamental research.

Our group is committed to macromolecular Ln coordination compounds, including carboxylic acid and amide groups that have strong coordination capabilities and excellent thermal stability.[3,7] In our studies, poly(styrene-*co*-maleic anhydride) (SMA) has been chosen as an intermediate, mainly because of its low production costs and ease of preparation and modification.[8–10] The copolymer of aniline-*g*-poly(styrene-*co*-maleic anhydride) (AP/SMA) was prepared by the reaction of an aniline with a ringlike anhydride group via a simple and effective approach. Then, the Ln–AP/SMA complexes were synthesized in an aqueous solution by an easy path. The reaction approached chemical equilibrium in only 5 min. All of the previous phenomenon inspire us to enrich and separate Ln ions from the low-concentration solution used this macromolecular polymer. The preliminary results indicate that the coordination capability increases with increasing pH value, and the carboxylic groups, as bidentate ligands, participate in the coordination with Ln(III) ions, including two coordinated water molecules in the structural unit of the Ln–AP/SMA complexes. The Eu–AP/SMA and Tb–AP/SMA complexes exhibit respective characteristic

Table I. GPC Analysis of AP/SMA Polymer

	GPC molecular weight							
Polymer	M_n (Da)	M_w (Da)	MP	M_z (Da)	$M_z + 1$ (Da)	M_w/M_n	M_z/M_w	$M_z + 1/M_w$
AP/SMA	14818	23545	28757	34877	47695	1.59	1.48	2.03

M_n, number-average molecular weight; M_w, weight-average molecular weight; MP, the peak position molecular weight; M_z, z-average molecular weight.

emissions of Eu(III) and Tb(III) ions with narrow and strong emission lines. This demonstrates that the AP/SMA polymer in the extraframework channels succeed in sensitizing Eu(III) and Tb(III) ion emission. In addition, Eu(III) complexes and Tb(III) complexes reveal a high quantum efficiency (Φ) and long lifetime (τ), and no fluorescence quenching behavior is observed with increasing Ln(III) ion content.

EXPERIMENTAL

Materials

Maleic anhydride and aniline were provided by Alfa Aesar (Beijing, China). Maleic anhydride, dissolved in chloroform and filtered, was recrystallized to eliminate maleic acid. Styrene was supplied by Sigma-Aldrich (Shanghai, China) and was washed with 10% aqueous sodium hydroxide to remove the inhibitor, and then, it was washed with water until it was neutral and then dried with anhydrous magnesium sulfate. Hydrated Ln nitrates, $Eu(NO_3)_3{\cdot}6H_2O$ and $Tb(NO_3)_3{\cdot}6H_2O$ were prepared by the dissolution of 2–3 g of the corresponding oxides (Alfa Co.) in concentrated nitrate acid (a few drops of hydrogen peroxide was needed in the case of Tb_4O_7); then, the solution was heated to evaporate the excess acid. Other analytical-reagent-grade chemicals were supplied by Alfa Aesar and were used without further purification.

Measurements

The average molecular weight of AP/SMA was estimated by an SN-01A gel permeation chromatograph with tetrahydrofuran as a carrier (Table I). The contents of C, H, and N in the ligands and complexes were determined on an Elemental Vario-EL instrument (Table II). The Ln(III) ion contents were determined by ethylene diamine tetraacetic acid titration with xylenol orange as an indicator. The vibration spectra from 4000 to 400 cm^{-1} were recorded on a Nicolet 170 XET IR spectrometer (with KBr discs). ^1H-NMR spectra were measured on a Varian Mercury-300 MB NMR spectrometer. Fluorescence spectra, luminescence τ values, and quantum yields for the Ln(III) complexes were recorded on a single-photon counting spectrometer (Edinburgh FLS 920 fluorescence spectrophotometer) with a microsecond pulse lamp as the excitation. Thermogravimetry (TG)–differential thermal analysis (DTA) was carried out on a WCT-2C thermal balance, and differential scanning calorimetry (DSC) was accomplished by an STA PT1600 instrument.

Synthesis of the AP/SMA Polymer

SMA was prepared according to literature methods.[11] A mixture of styrene (30 g, 288 mmol) and maleic anhydride (27 g, 277 mmol) was added to toluene (500 mL) at 85 ± 1°C under stirring for 6 h with benzoyl peroxide (1% of monomer) as initiator. The generated precipitate was washed repeatedly with toluene to remove the unreacted monomers and initiator and then dried in a vacuum oven for 48 h at 40°C to a constant weight (yield = 83.61%). An ethyl acetate (100 mL) solution of SMA (10.0 g, maleic anhydride content = 98.5 mmol) was added to a three-necked flask equipped with a condenser. Then, aniline (16.5 mL, 181.25 mmol) dissolved in the ethyl acetate (100 mL) was added dropwise to the mixture under stirring at 45°C. A yellow precipitate appeared after a period (ca. 1 h after the addition of aniline). The reaction mixture was stirred for 24 h. A light yellow aminolysis product appeared; it was filtered and washed several times with toluene and ethyl acetate and then dried *in vacuo* for 24 h at 40°C to a constant weight (71.33%). The weight-average molecular weight (M_w) of AP/SMA obtained from gel permeation chromatography (GPC) was 23545 g/mol, as summarized in Table I.

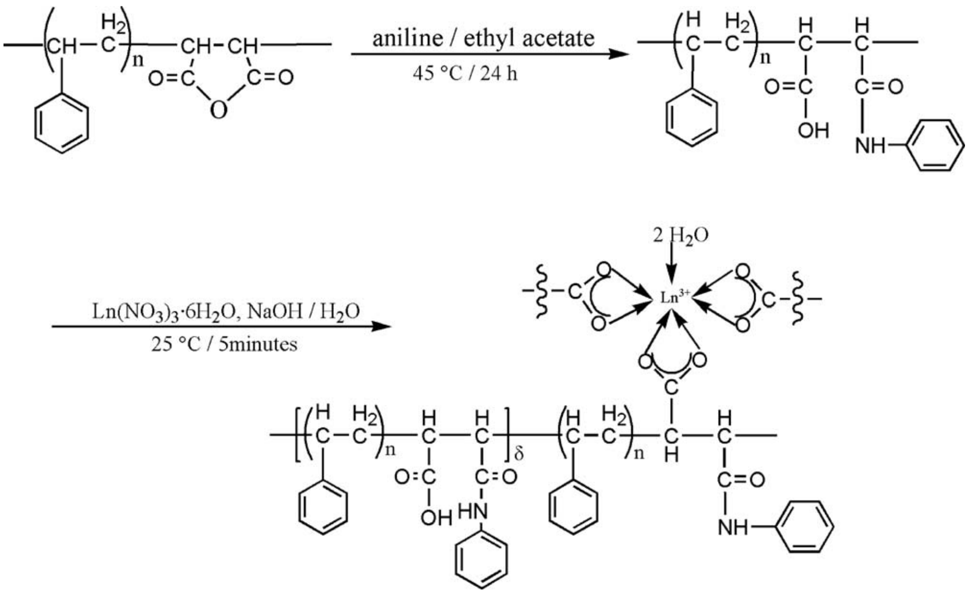
Synthesis of the Ln–AP/SMA Complexes

The AP/SMA [0.5 g, content of carboxylic groups (COOH) = 0.423 mmol] was dissolved with a dilute NaOH solution (31.5 mL, 0.01*M*) to transform part of the carboxylic groups (90%) to carboxylates. Afterward, the aqueous solution

Table II. Elemental Analysis of the Polymer and Its Complexes

Compound	C (%)	H (%)	N (%)	Ln (%)	$(n)^a$	$(\delta)^b$
SMA	69.52 (69.54)	5.959 (6.116)			0.969	
AP/SMA	62.65 (63.01)	5.904 (5.741)	4.598 (4.798)	0	0.969	
La–AP/SMA	60.87 (60.90)	5.497 (5.478)	2.998 (3.087)	8.69 (8.70)	0.969	0.521
Eu–AP/SMA	58.54 (59.20)	5.455 (5.344)	3.489 (3.509)	10.93 (11.05)	0.969	0.280
Tb–AP/SMA	57.64 (58.24)	5. 276 (5.431)	3.368 (3.419)	11.92 (12.04)	0.969	0.202
Yb–AP/SMA	56.01 (56.08)	5.267 (5.233)	3.254 (3.309)	12.57 (12.58)	0.969	0.206

[a] The molar ratio of styrene to maleic anhydride.
[b] δ in the Ln–AP/SMA complexes.



Scheme 1. Reaction process of the Ln–AP/SMA complexes.

of $Ln(NO_3)_3{\cdot}6H_2O$ was added dropwise to the solution and stirred for 5 min at room temperature, and a white precipitate formed. The Ln–AP/SMA complexes were separated from the solution by centrifugation, washed with water and acetone three times, and then dried *in vacuo* for 24 h at 40°C. The synthesis routes for the ligand and complexes are shown in Scheme 1.

RESULTS AND DISCUSSION

Compositional Analyses of the Polymer and Complexes

The molar ratio of carboxyl groups, which was equal to the anilino groups in the copolymer, was determined by neutralization titration and elemental analysis. The data (Table II) indicate that each Ln(III) ion was bonded to three carboxylic groups in the chain of the copolymer (not necessarily in only one chain) to form stable and repeatable units (Scheme 1). Here, *n* is the molar ratio of styrene to maleic anhydride in the polymeric ligands, and δ is the number of uncoordinated carboxylic groups (COOH) in the Ln(III) complexes. The values of *n* and δ were calculated from eqs. (1) and (2):

$$n=\frac{\frac{W_{C'}}{12.01}-2CV}{4CV} \tag{1}$$

$$\delta=\frac{W_{C''}\times M_{Ln}}{12.01\times W_{Ln}\times(10+8n)\times 3}-1 \tag{2}$$

where $W_{C'}$ is the mass percentage of carbon atoms in the SMA ligand, C is the concentration of KOH (0.1 M), V is the volume (L) of the solution of KOH (0.1*M*) consumed by per gram of SMA ligand, $W_{C''}$ is the mass percentage of carbon atoms, M_{Ln} is the molecular weight of Ln(III) ions, and W_{Ln} is the determined content of Ln(III) ions in the Ln(III) complexes. The experimental results show that *n* was 0.969. The content of maleic anhydride in the SMA ligand was about 9.85 mmol/g; this was determined by acid–base titration with phenolphthalein as an indicator.

X-Ray Diffraction (XRD)

XRD analysis revealed that the AP/SMA polymer had similar diffraction patterns to the Ln(III) complexes (Figure 1). The peak at a 2θ of nearly 20° indicated a random structure in these solid compounds. Both the AP/SMA polymer and the Ln(III) complexes were amorphous because of the presence of packing disruptive groups and subsistence as a side chain. However, the patterns of the former were considerably stronger in intensity; this suggested that the Ln(III) complexes had a relatively lower degree of crystallization.[12] This means that the Ln(III) complexes possessed good plasticity; this is expected to give them potential application value in light-conversion film materials.

IR Analysis

The IR spectrum of the AP/SMA polymer was quite different from those of the Ln(III) complexes, whereas the spectra of all

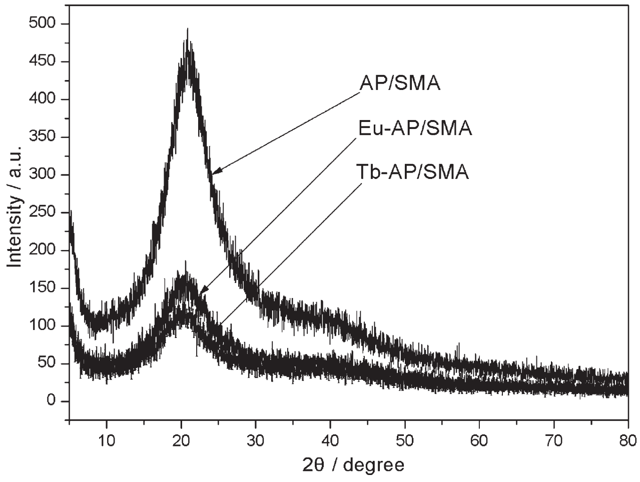


Figure 1. XRD curves (5–80°) of the AP/SMA polymer and Ln–AP/SMA complexes.

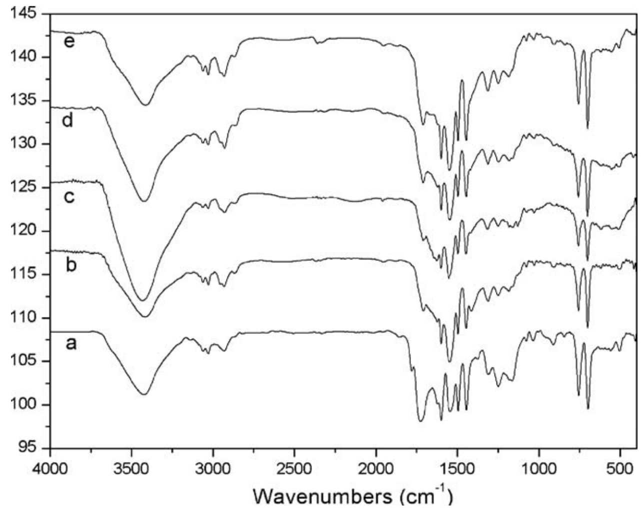


Figure 2. Fourier transform infrared spectra of compounds (a) AP/SMA, (b) La–AP/SMA, (c) Eu–AP/SMA, (d) Tb–AP/SMA, and (e) Yb–AP/SMA.

of the Ln(III) complexes were similar to each other (Figure 2). Characteristic IR bands were assigned and are summarized in Table III.

The IR spectra show that the AP/SMA polymer and the Ln–AP/SMA complexes had absorption bands at 1704–1710 and 3414–3434 cm^{-1} assigned to $\nu_{(C=O)}$ and $\nu_{(O-H)}$, respectively, of carboxylic groups. For the Ln(III) complexes, the featured absorption bands of $\nu_{(C=O)}$ at 1710 cm^{-1} were still observed; this was attributed to the fact that the carboxylic groups were not entirely coordinated in the copolymer chains. The results were consistent with the composition determination about the δ value. Two strong absorption bands at 1412–1414 and 1597–1598 cm^{-1}, assigned to the symmetric vibration absorption [$\nu_{s(COO-)}$] and asymmetric vibration absorption [$\nu_{as(COO-)}$] of the carboxylic groups,[13] were present for the Ln(III) complexes. In addition, the difference of symmetric vibration absorption and asymmetric vibration absorption $\Delta\nu$ ($\Delta\nu = \nu_{as(COO-)} - \nu_{s(COO-)}$) of the Ln–AP/SMA complexes (Table III) ranged from 183–186 cm^{-1}; this was smaller than that of Na–AP/SMA (196 cm^{-1}). This indicated that the symmetry of the carboxylic group was C_{2v} (the same as that of the free ion) in the Ln(III) complexes, and the carboxylic group was a bidentate chelate coordinated with Ln(III) ions.[14,15] The absorption peaks at about 1310 and 1444 cm^{-1} were attributed to ν_{C-N} of Ar—N and O═C—N,[16] which existed in the AP/SMA polymer and Ln(III) complexes, respectively. This confirmed that the ringlike anhydride group in SMA was opened by aniline. In addition, the peaks of $\nu_{C=O}$ and δ_{N-H} in both the AP/SMA polymer and Ln(III) complexes showed no significant differences in position and intensity; this proved that the carbonyl oxygen and amide nitrogen did not participate in coordination.

^{1}H-NMR Analysis

The SMA and AP/SMA polymer were characterized by ^{1}H-NMR spectroscopy (Figure 3). The SMA and AP/SMA polymer had similar structural units, and the hydrogens in each structural unit had close relaxation times. Therefore, a broadening of the characteristic peak shape and peak widths occurred. As depicted in Figure 3(a), a pack of peaks was discovered at 6.8–8 ppm and corresponded to the chemical shift of the aromatic hydrogen in the styrene.[17] The peaks of the package of methylene and methine appeared in the high-frequency zone.[18] There were characteristic peaks of the carboxyl groups (12–13 ppm), as shown in Figure 3(a), which indicated that part of hydrolysis occurred in the process of the copolymerization of styrene and maleic anhydride. Thus, this reaction should be operated under anhydrous conditions. According to Figure 3(b), there was a set of doublets, triplets, and multiplets in the range 6.5–7.1 ppm; these were attributed to the aromatic hydrogen of aniline.[17] The N—H proton (8.10 ppm) appeared in the spectra of the AP/SMA polymer; this was further evidence that the ringlike anhydride group in SMA was opened by aniline.

Fluorescent Properties

The excitation and emission spectra of the AP/SMA polymer and Ln–AP/SMA complexes (Ln = Eu or Tb) were measured in the solid state with excitation and emission slit widths of 5.0 nm (Table IV and Figure 4) at room temperature. When excited at 293 nm, the AP/SMA polymer exhibited a broad emission band at 300–550 nm (maximum wavelength = 381 nm). As shown in Figure 4(b), several sharp lines in the range 300–500 nm were ascribed to the intraconfigurational 4f–4f transitions of the Eu(III) ions: $^7F_0 \rightarrow {}^5F_4$ (303 nm), $^5H_6$ (318 nm), $^5D_4$ (362 nm), ^5G_J (376 nm), $^5L_7$ (383 nm), $^5L_6$ (395 nm), and $^5D_3$ (417 nm), respectively.[19,20] We found that the excitation intensity at 395 nm was the highest in the excitation spectrum; this is very attractive for applications such as the red component of tricolor luminescence materials.[19,21] Under excitation at 395 nm, the emission bands were assigned to $^5D_0 \rightarrow {}^7F_0$ (579 nm), $^5D_0 \rightarrow {}^7F_1$ (592 nm), $^5D_0 \rightarrow {}^7F_2$ (615 nm), $^5D_0 \rightarrow {}^7F_3$ (651 nm), and $^5D_0 \rightarrow {}^7F_4$ (699 nm), respectively.[22] The $^5D_0 \rightarrow {}^7F_0$ was a strongly forbidden transition, which was indicative of a distinct Eu(III) ions emitter center in the Eu–AP/SMA complexes.[23] The

Table III. Characteristic IR Bands (cm^{-1}) of the Polymer and Its Complexes

Compound	ν_{OH}	ν_{C-N}	ν_{COO-}	ν_{N-H}	$\nu_{as\text{-}COO-}$	$\nu_{s\text{-}COO-}$	$\Delta\nu_{as\text{-}s}$
AP/SMA	3424	1309/1443	1710/1620	1545			
Na-AP/SMA	3426	1314/1443	1704/1625	1544	1596	1400	196
La-AP/SMA	3414	1310/1444	1707/1622	1546	1597	1414	183
Eu-AP/SMA	3434	1313/1446	1710/1627	1551	1598	1412	186
Tb-AP/SMA	3421	1310/1444	1710/1620	1544	1598	1414	184
Yb-AP/SMA	3414	1311/1444	1709/1620	1546	1598	1412	186

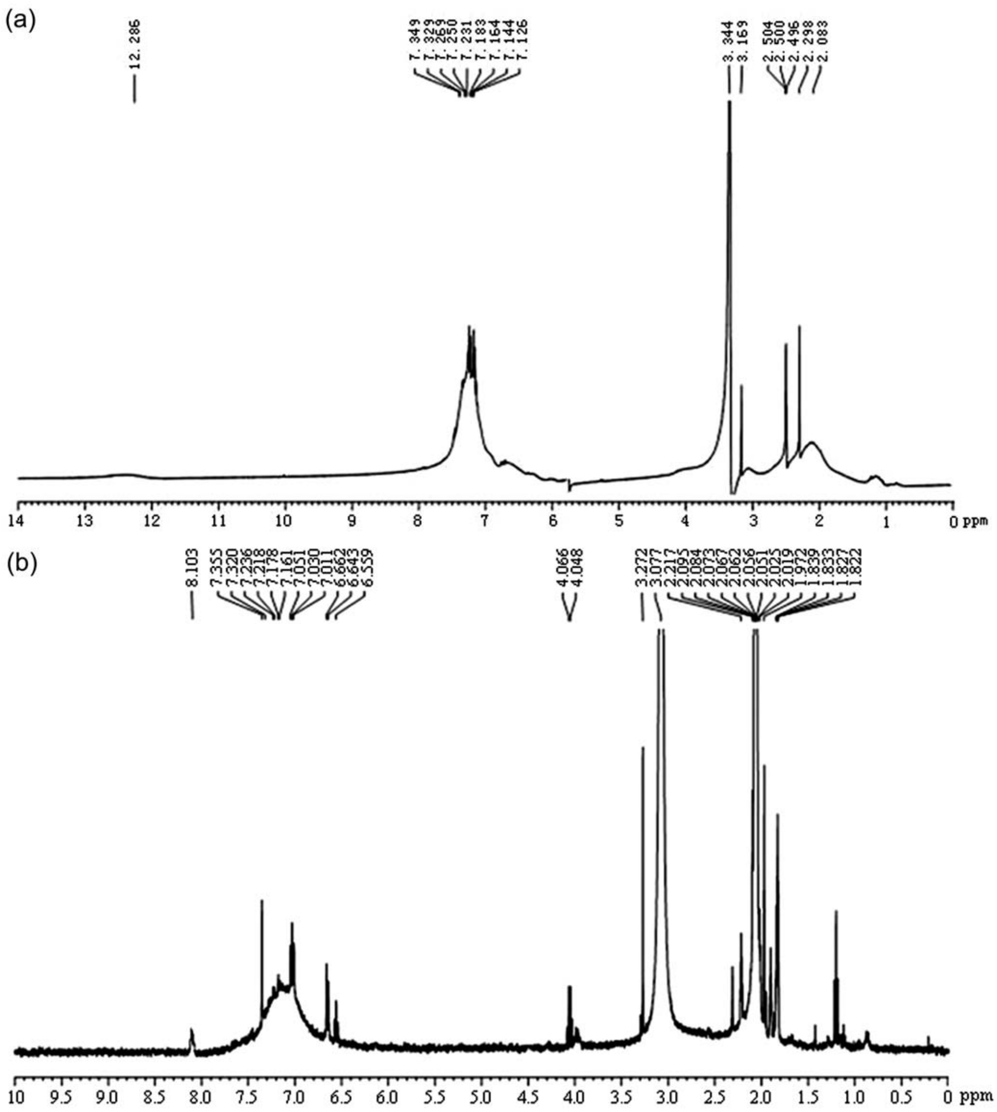


Figure 3. ^{1}H-NMR spectra of the SMA and AP/SMA polymer.

Table IV. Fluorescence Spectral Data of the Polymer and Its Complexes

Compound	λ_{ex} (nm)	λ_{em} (nm)	(RFI)[a]	Transition
AP/SMA	293	381	3968	
Eu-AP/SMA	395	579	182	$^5D_0 \rightarrow {}^7F_0$
		592	410	$^5D_0 \rightarrow {}^7F_1$
		615	2130	$^5D_0 \rightarrow {}^7F_2$
		651	40	$^5D_0 \rightarrow {}^7F_3$
		699	153	$^5D_0 \rightarrow {}^7F_4$
Tb-AP/SMA	353	490	1613	$^5D_4 \rightarrow {}^7F_6$
		545	4928	$^5D_4 \rightarrow {}^7F_5$
		584	572	$^5D_4 \rightarrow {}^7F_4$
		620	410	$^5D_4 \rightarrow {}^7F_3$

[a] The relative fluorescence intensity.

λ_{em}: the maximum emission wavelength; λ_{ex}: the maximum excitation wavelength.

$^5D_0 \rightarrow {}^7F_1$ was a magnetic dipole transition and was insensitive to the crystalline field.[24] The asymmetric ratio ($^5D_0 \rightarrow {}^7F_2/{}^5D_0 \rightarrow {}^7F_1$) was about 6.27; this suggested that the Eu(III) ion was at the center of an asymmetric coordination field.[25,26] The $^5D_0 \rightarrow {}^7F_2$ transition was the most intensive; this indicated a highly polarizable chemical environment around the europium site.[27] As shown in Figure 4(c), the spin-forbidden transition $^7F_6 \rightarrow {}^9D_J$ (ca. 285 nm) was attributed to the $4f^8$–$5d^1$ transition of the Tb(III) ions.[28] Other excitation bands represented the 4f–4f transitions of the Tb(III) ions: $^7F_6 \rightarrow {}^5H_6$ (305 nm), $^5H_7$ and $^5D_{0,1}$ (319 nm), $^5G_2$ and $^5L_6$ (341 nm), $^5L_9$ and $^5G_4$ (353 nm), $^5L_{10}$ (369 nm), and $^5D_3$ and $^5G_6$ (378 nm).[28,29] Under excitation at 353 nm, four emission bands were assigned to $^5D_4 \rightarrow {}^7F_6$ (490 nm), $^5D_4 \rightarrow {}^7F_5$ (545 nm), $^5D_4 \rightarrow {}^7F_4$ (584 nm), and $^5D_4 \rightarrow {}^7F_3$ (620 nm) transitions. The $^5D_4 \rightarrow {}^7F_5$ emission band was obviously stronger than the other emission bands. In addition, the asymmetric ratio ($^5D_4 \rightarrow {}^7F_5/{}^5D_4 \rightarrow {}^7F_6$) was about 2.88; this indicated that the Tb(III)

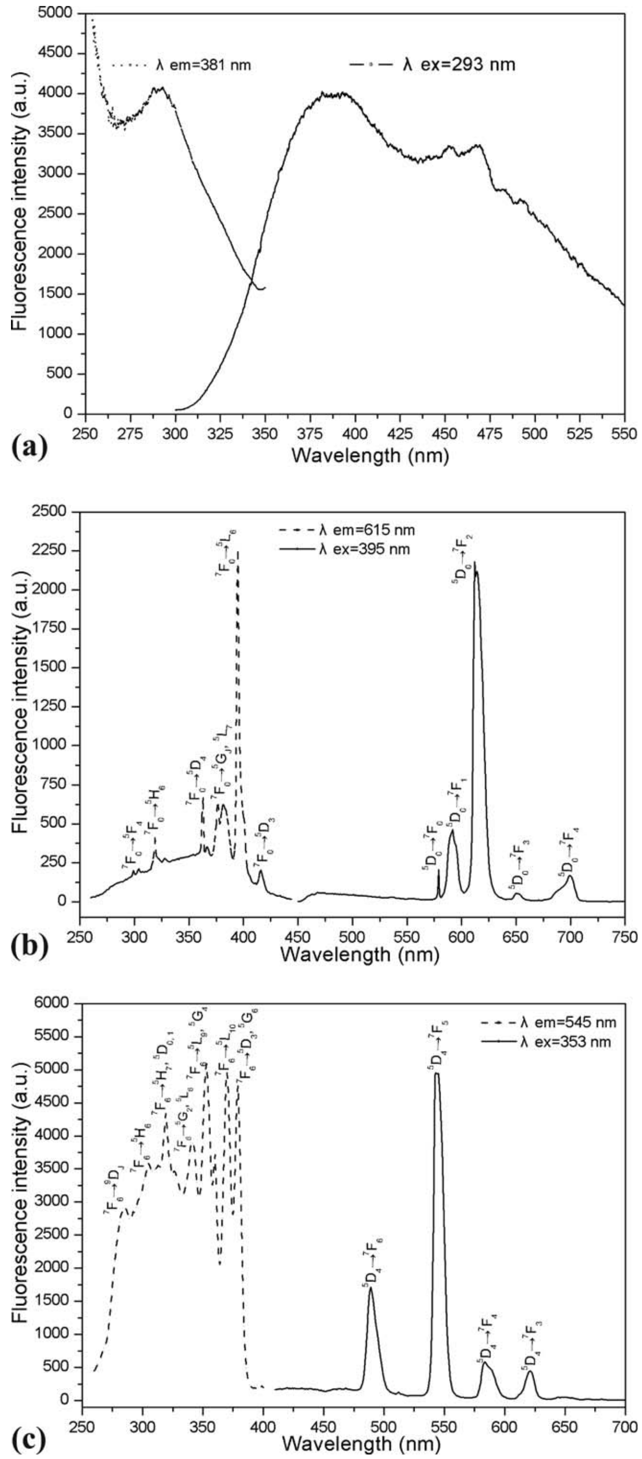


Figure 4. Excitation and emission spectra in solid powder: (a) AP/SMA polymer, (b) Eu–AP/SMA complex, and (c) Tb–AP/SMA complex.

ion was at the center of an asymmetric coordination field.[30] Each emission band was very narrow; this demonstrated that the Tb(III) complexes had a high color purity.[31]

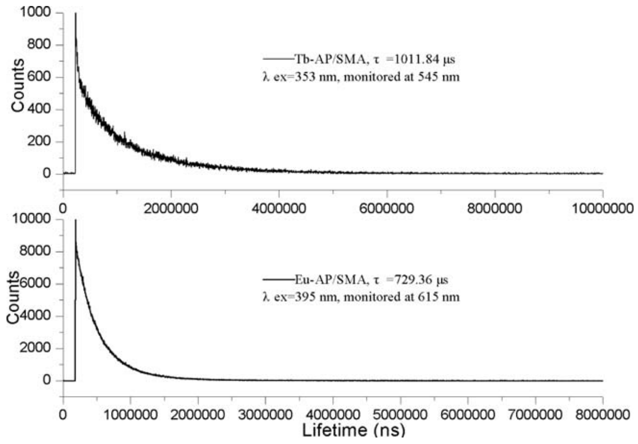


Figure 5. Luminescent decay curves of the Ln–AP/SMA complexes (Ln = Eu and Tb) in solid powder.

The decay curves for the Eu(III) and Tb(III) complexes were fit with a single exponential model (Figure 5). The absolute Φ and τ were 53.6% and 729.36 *μ*s, respectively, for the Eu(III) complex and 20.3% and 1011.84 *μ*s, respectively, for the Tb(III) complex. The relatively higher Φ (53.6%) suggested the direct excitation of Eu(III) ions, and the AP/SMA polymer had little influence on the luminescence of the Eu(III) complex.[32] However, the relatively lower Φ (20.3%) was due to the back-transfer process occurring in the Tb(III) complex.[33] The value of τ corresponded to the presence of O—H oscillators in the Ln–AP/SMA complexes.[32] In addition, the effect of the Ln(III) ion content on the characteristic emission intensity was studied with excitation and emission slit widths of 5.0 nm. As shown in Figure 6, the emission intensity increased with increasing Ln(III) ion content, without typical fluorescence concentration quenching behavior. The results were attributed to the presence of a large steric hindrance in the Ln(III) complexes.[34,35]

Effect of the pH Value on the Number of Free Carboxyls

As shown in Figure 7, *δ* in the structural units of Ln(III) complexes was closely dependent on the pH value. At low pH values, large numbers of uncoordinated carboxylic groups appeared in the structural units. The results were attributed to the fact that the polymeric AP/SMA was a weak organic acid, so

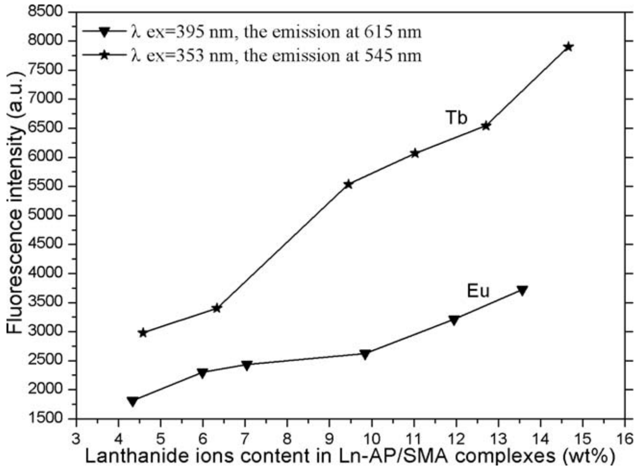


Figure 6. Fluorescence intensity of the Ln–AP/SMA complexes versus different Ln(III) ion contents.

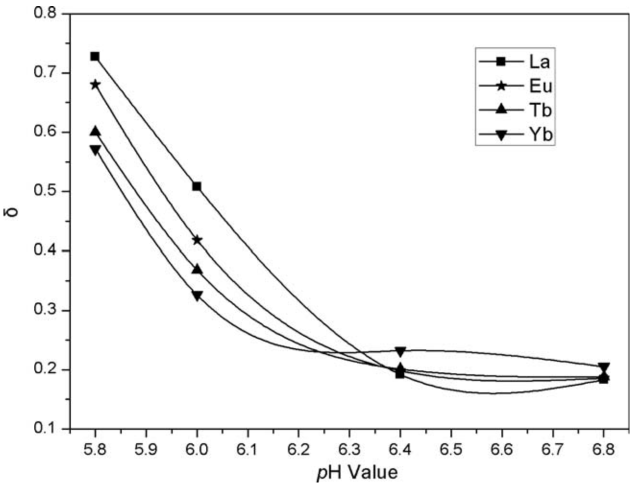


Figure 7. Relationship between the pH and δ value of the Ln–AP/SMA complexes (Ln = Eu and Tb).

the Ln(III) ions could not replace the protons in the carboxylic groups at higher acidity. At the same pH values for these different Ln(III) complexes, the number of uncoordinated structural units decreased with increasing Ln(III) ion atomic number. These results suggest that the smaller radius of the Ln(III) ion resulted in a higher coordination ability.[36] In addition, δ in the Yb–AP/SMA complexes increased with pH values greater than 6.4; this was explained by the presence of hydrolysis reactions above this pH in the Yb(III) ion aqueous solution.[37]

Thermal Properties

The thermal behavior of the Ln–AP/SMA complexes was studied. Samples (10 mg) were placed in a crucible and heated up to 800°C at a rate of 10°C/min in inert nitrogen with Al_2O_3 as a reference material. The TG–DTA and DSC curves of the Ln(III) complexes (Ln = La, Eu, Tb, or Yb) were all studied; herein, we only show the curves of the Eu(III) complex to illustrate the decomposition process (in Figure 8).

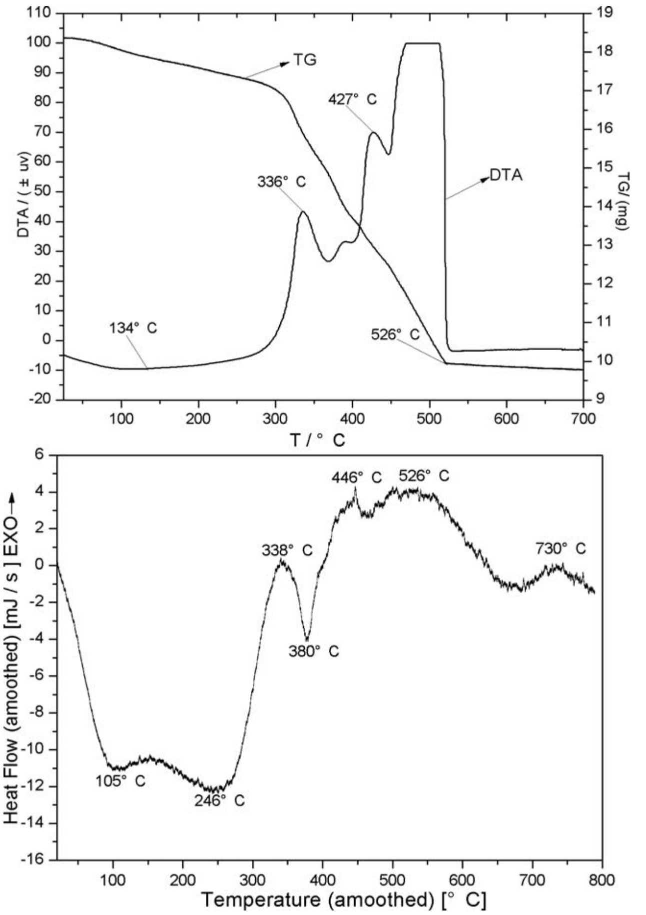


Figure 8. TG–DTA and DSC curves of the Eu–AP/SMA complex (T = temperature).

The first mass loss of about 4.10% was absorbed water in the sample; this corresponded to the endothermic peak on the DSC curve around 105°C. The second mass loss of about 3.03% was in the temperature range 120–195°C and corresponded to the endothermic peak on the DTA curve around 134°C. However, the relatively higher temperature for water loss confirmed that the water was coordinated with the Eu(III) ions in the inner sphere. Accordingly, the number of coordinated water molecules in the structural unit of the Eu–AP/SMA complex was calculated to be 2; this was consistent with the element analysis.[12] Subsequently, the third thermal decomposition process in the temperature range 200–315°C with a weight loss of 8.64% was attributed to loss of water in the formation of acid anhydride from the carboxyl groups.[38,39] As shown, a corresponding endothermic peak around 248°C on the DSC curve occurred. The final decomposition stage for the Eu–AP/SMA complex was a continuous oxidation decomposition process, which was demonstrated by the continuous exothermic peak on the DTA curve up to 427°C. Such a high decomposition temperature suggested that the Eu–AP/SMA complex had a high thermal stability. The remaining residue, about 15.67%, corresponded to the theoretical product (14.88%), and this coincided with the general formula of the oxides (Eu_2O_3). The thermal behaviors of all of the Ln–AP/SMA complexes were very similar. It was clear that their decompositions occurred in the same way.

CONCLUSIONS

According to the previous discussion, it was obvious that the AP/SMA polymer could form stable complexes with Ln(III) ions. The experimental results show that the number of coordinated water molecules in the structural units of the Ln–AP/SMA complexes was 2 and the complexes had three-dimensional crosslinked structures. The carboxylic groups partially coordinated with Ln(III) ions and acted as bidentate ligands in the Ln–AP/SMA complexes. Two kinds of Ln–AP/SMA complexes (Ln = Eu and Tb) exhibited the respective characteristic emissions of Eu(III) and Tb(III) ions, respectively, with narrow and strong emission lines, and no fluorescence quenching behavior was observed with increasing Ln(III) ion content. Thus, these fluorescence Ln(III) complexes have potential application in fluorescence materials. In addition, because the reaction is carried out in the water phase and because equilibrium can be reached easily within 5 min, the AP/SMA polymer possesses good application prospects and theoretical significance in the adsorption of Ln ions.

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