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Lanthanide coordination polymer/PMMA hybrid polymeric films: in-situ composition and photoluminescent properties

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In this paper, formation of binary and ternary lanthanide coordination polymers of 2-hydroxynicotinic acid and 1,10-phenanthroline was achieved through the polymerization process of MMA monomer. Then the transparent hybrid thick films were in-situ composed with lanthanide (Ln = Dy, Tb, Eu) coordination polymers ($[Ln(HnicO)_3]_n$, $[Ln(HnicO)_3 \cdot phen]_n$) and polymethyl methacrylate (PMMA). The luminescence properties and energy transfer for these polymeric composite films were studied with absorption spectra, IR spectra, fluorescent emission spectra in detail. All the hybrid thick films composed with dysprosium, terbium and europium coordination polymers show respective characteristic emission of the lanthanide ions. Besides, terbium and the europium complex co-doped thick films also have been achieved. In the terbium and the europium complex co-doped thick films, luminescent intensity of Eu^{3+} have been improved with the adding of the terbium complex.

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1. Introduction

Luminescent rare earth organic complexes are of both fundamental and technical interest due to their characteristic luminescence properties, such as extremely sharp emission bands, long lifetime, and potential high internal quantum efficiency**,** which make them suitable candidates for applications as light emitting diode (LED), laser materials, optical signal amplification, and fluoroimmunoassay [1-6]. The luminescence of rare earth ions stems from the intra- 4f transitions, which in principle are forbidden transitions, resulting in relatively low emission efficiency. An effective approach to increase the luminescent efficiency is to modify these complexes with different kinds of ligands possessing broad and intense absorption bands, which make the absorbed photon energy to transfer to the higher energy levels of rare earth ions [7-9]. Some papers were reported on the luminescence behavior of Eu^{3+} and Tb^{3+} complexes with β-diketone [10, 11] and aromatic carboxylic acid [12, 13] in sol–gel derived host materials. Unfortunately, it is not easy to obtain transparent and uniform material and the inorganic matrix has some disadvantage such as poor mechanistic properties that restrict its practical application.

The growing importance of polymer films in integrated optic technology makes it interesting to study the incorporation of rare-earth complexes in a polymer. Rare-earth complexes doped polymers are important because they possess the properties of the complexes while they can be processed from solution and are mechanically flexible. However, in recent years, rare earth ions-containing polymers have attracted much attention for their potential applications in the fields of fluorescence and laser systems, optical communication devices, polymer optical fiber amplifier and integrated waveguide, etc [14, 15]. The main reason is that polymer-based rare earth luminescent materials can be processed easily, which is an advantage in the fabrication of optical components. In addition to that, encapsulating rare earth ions with organic ligands makes it possible to incorporate them into polymers hosts up to higher concentrations and concentration quenching sets in at higher concentrations [16].

As early as in 1963, Wolff and Pressley [17] studied the lasing and luminescent properties of mixed systems of $[Eu(TTA)_3(H_2O)_2]$/ PMMA. More and more europium complex/polymer mixed systems have been studied recently [18,19].The property of a rare-earth ion transition that is most influence by the surrounding environment is the observed metastable-state lifetime, which should be maximized for efficient laser property [20]. As an optical polymer material, particular interest in PMMA arises from its low cost, simple synthesis, refractive index tailor ability with molecular weight, best optical transparency and resistance to laser damage [8]. These characteristics make it suitable as a host material for rare earth ions and organic dye doping.

In this paper, the hybrid thick films were composed that by choosing the two kinds of rare earth complexes ─$[Ln(HnicO)_3]_n$, $[Ln(HnicO)_3 \cdot phen]_n$ (Ln = Eu, Tb, Dy) which have chain-like structure and the MMA were in situ polymerization method by the initiator action of ABIN.

We also tried the co-doped method to study the properties of europium and terbium complexes in the hybrid thick films. The luminescence properties of these hybrid polymeric thick films were studied in detail. SEM microscope indicates that the luminescent hybrid thick films show very homogenous and uniform structure.

2. Experimental

Methyl methacrylate (MMA) was previously treated using dilute sodium hydroxide solution in order to get rid of impurity which hinders the polymerization of monomers. The $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = Dy), the 2-hydroxynicotinic acid (the molar ratio 3:1) or $Ln(NO_3)_3{\cdot}6H_2O$ (Ln = Eu, Tb, Dy), the 2-hydroxynicotinic acid and the 1,10-phenanthroline (the molar ratio 1:3:1) were dissolved into ethanol solvent, then the pH value of the result solutions were adjusted to about 7, respectively. After stirred several minutes, 7.5 ml methyl methacrylate was added to mixtures. Then the Azo bis iso butyronitrile (ABIN) (about 0.005 g) used as the initiator and catalyst for polymerization was added into the mixed solution. After heated several minutes, the mixture solution became viscous and then put along the microscopic glass slides. The thick films were achieved after drying in the 60 °C oven.

Ultraviolet absorption spectra were measured with Agilent 8453 spectrophotometer. The luminescence (excitation and emission) spectra were determined with Perkin – Elmer LS-55 spectrophotometer with excitation slit width = 10 nm, emission slit width = 5 nm, respectively. The micrograph was measured with scanning electronic microscope (SEM, Philps XL-30).

3. Results and discussion

These hybrid thick films were synthesized by the same method and the properties were studied in detail. Fig. 1 shows the ultraviolet absorption spectra of the hybrid thick film composed with the four lanthanide ions coordination polymers. The absorption specta of $Ln(HnicO)_3]_n$, (Ln = Eu, Tb, Dy) has two peaks which is at 223 and 344 nm that corresponds to the characteristic absorption of pyridine cycle's (2-hydroxynicotinic acid) π → π* and n → π* transition. When using water as solvent, the two absorption peaks of 1, 10-phenanthroline lies at 228 nm and 265 nm respectively. But in the absorption spectrum of $[Ln(HnicO)_3{\cdot}phen]_n$ (Ln = Eu, Tb, Dy) we can find three peaks which is at 226, 264, 309 nm. Different from the absorption spectra of the second ligand 1, 10-phenanthroline, a broad peak appears around 309 nm and the peak around 264 nm is lower than that of the second ligand. So we deduced that there are chemical bond between the rare earth ion and the two ligands. This indicates that the nicotinic acid derivative and the 1, 10-phenanthroline are the energy absorption donor for the luminescence of rare earth ion in the hybrid thick films.

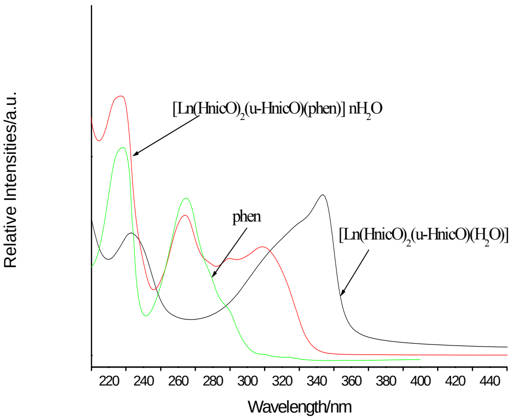


Fig. 1. Ultraviolet absorption spectra of hybrid $[Dy(HnicO)_3]n$, $[Dy(HnicO)_3{\cdot}phen]n$ and 1,10-phenanthroline.

In the IR spectra of the complexes $[Ln(HnicO)_3]_n$ (Ln = Eu, Tb, Dy) the pyridine V(c-c) and V(c-N) stretches of the pyridinic ring show no shifts ,so we concludes that the coordination to the Ln^{3+} does not involve the nitrogen atom. The band assigned to the ketone V(c=O)stretch in the ligand (1741 cm^{-1}) is not seen in the spectra of the lanthanide complexes, in agreement with the coordination of the respective oxygen atom to the lanthanide(III) ions. And The asymmetric mode Vas (CO_2) of the carboxylate group shows 10 cm^{-1} shifts to higher wavenumber on coordination when compared to the free ligand (at 1629 cm^{-1}), showing that the carboxylate oxygen is also bound to the lanthanide. In the infrared and Raman spectra, the symmetric mode Vs (CO_2) shows higher shifts (around 30 cm^{-1}) to lower wavenumber on coordination. The 2-hydroxynicotinate ion coordinates through O,O-chelation to lanthanides as registered for the complexes $[Ln(HnicO_3]_n$ [21,22] From these analyses and the previous investigation we can deduce the coordination fashion of the complexes $[Ln(HnicO)_3]_n$ which shows in Fig. 2(a). And from the coordination fashion we can conclude that lanthanide complexes with pyridinecarboxylic acids usually form polymeric chain structures, with the carboxylate groups as a bridge between lanthanide ions [Fig. 2 (b)]. The IR spectra of the complexes $[Ln(HnicO)_3]_n$ have some similar characteristics to that of $[Ln(HnicO)_3]_n$ complex except that we can find the V(C-N) vibration of 1, 10-phenanthroline shows about 10 cm^{-1} shifts (from 1558 to 1520 cm^{-1}). So in the complexes $[Ln(HnicO)_3{\cdot}phen]_n$ the coordination to Lanthanide (III) ions involves the nitrogen atom of 1, 10-phenanthroline. The coordination fashion of this kind of complex is shown in Fig. 2 (c). The IR spectra of PMMA-lanthanide system is only the simple mixture of two component respective spectra.

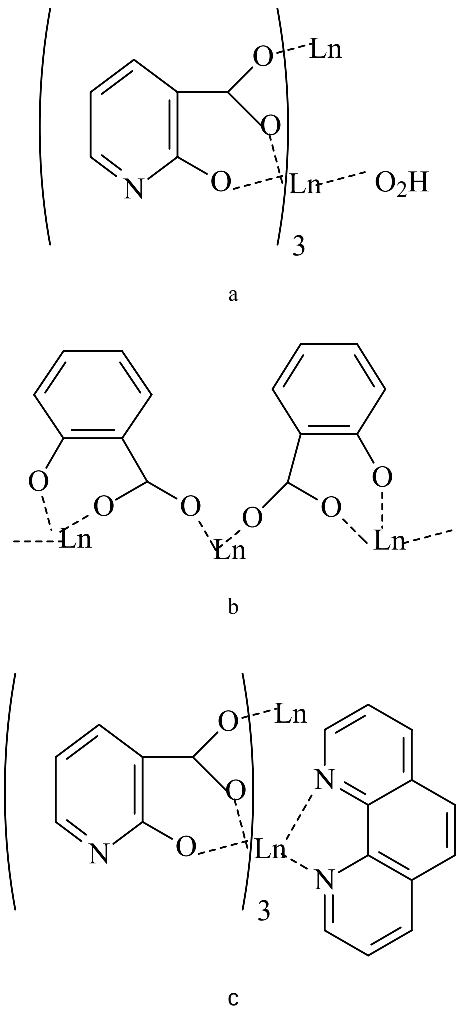


Fig. 2. Molecular fragment mode scheme of binray complex and ternary coordination polymers [Ln(HnicO)$_3$]n and [Ln(HnicO)$_3$·phen]n.

Fig. 3 shows different doping concentration emission spectra of hybrid polymeric thick films composed by [Dy(HnicO)$_3$]n (A) and [Dy(HnicO)$_3$·phen]n (B) and MMA respectively. It can be seen clearly that the characteristic blue line at about 483 nm and the yellow line at 574 nm of Dy^{3+} ions both appear under about 340 nm in the spectra, which correspond to the dysprosium characteristic emission from the $^4F_{9/2}$ excited state to $^6H_{15/2}$ and to the $^6H_{13/2}$ state, respectively. Moreover, we can also find that the luminescent properties strongly depend on the doping concentration in the polymer. When the concentration of Dy^{3+} complex increases up to 0.025 mmol/7.5 ml, the intensity shows the strongest and decreases at higher dysprosium complex concentrations. This is a typical property named concentration quenching of lanthanide doped system due to mutual Dy^{3+} – Dy^{3+} interactions. We can find the emission intensity of PMMA- [Dy(HnicO)$_3$·phen]n system does not improve obviously comparing to that of PMMA-[Dy(HnicO)$_3$]n system [Fig. 3 (C)]. So we deduce that in the two kinds of dysprosium complex, 2-hydroxynicotinic acid ligand is the primary energy absorption donor for the luminescence of the dysprosium ions.

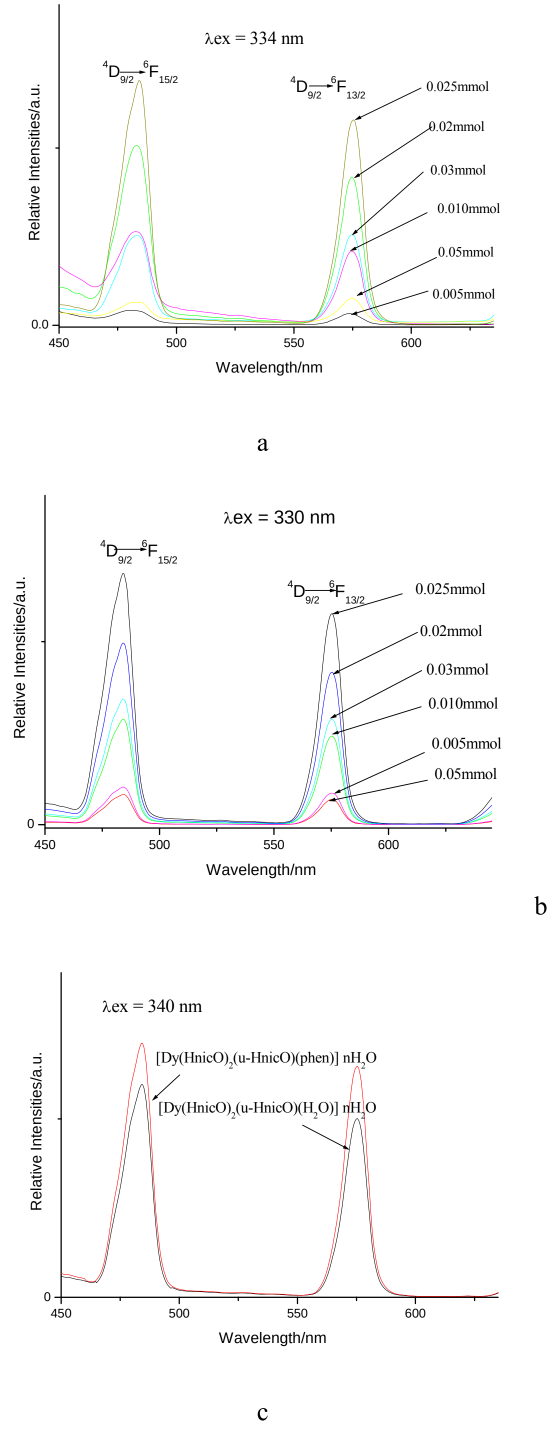
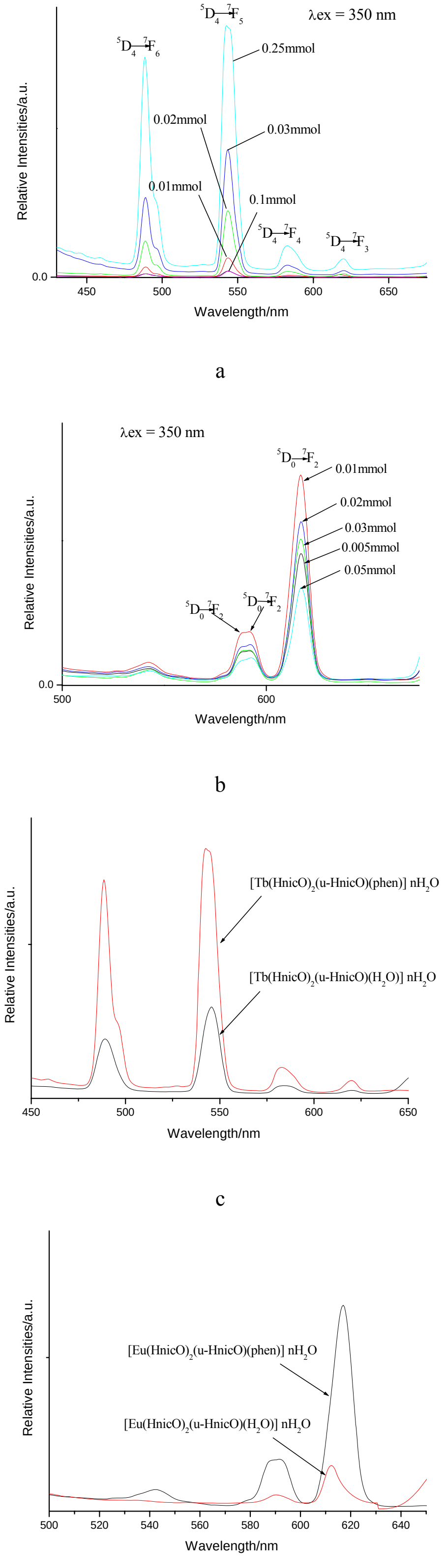


Fig. 3. Emission spectra of [Dy(HnicO)$_3$]n/PMMA and [Dy(HnicO)$_3$·(phen)]n/PMMA hybrid films.

The terbium and europium coordination polymer also have been achieve. Fig. 4 (A) exhibits clearly that concentration quenching effect for [Tb(HnicO)$_3$·phen]n excited under the excitation wavelength of 340 nm. The intensity shows a maximum value at a doping concentration of 0.025 mmol/7.5 ml and then decreases at higher terbium concentrations by metal ions aggregation. The characteristic emission can be seen obviously at 489 nm and 546 nm ($^5D_4 \rightarrow {}^7F_J$, J = 6, 5) originating from low energy transfer of Tb^{3+}. Besides, we can also observe the weak emission (586, 620 nm) corresponded to the $^5D_4 \rightarrow {}^7F_J$ (J = 4, 3) transition of Tb^{3+} from its high excite state of $^5D_4$ level [18]. Upon UV excitation, we also obtain the emission spectra of [Eu(HnicO)$_3$·phen]n/PMMA. From the spectra B, we also see the concentration quenching when the doping quantum is up to 0.01 mmol/7.5 ml due to the mutual Eu^{3+}-Eu^{3+} interaction. As for the Eu^{3+}, the characteristic emission can be seen obviously ($^5D_0 \rightarrow {}^7F_J$) (J = 1, 2) originating from low energy transfer of Eu^{3+}. The dominated red peak located at about 613 nm, which comes from the hypersensitive transition $^5D_0 \rightarrow {}^7F_2$ with $J = 2$. As we known, in the bulk material the emission of the Eu^{3+} concludes the weak emission (536.5, 556.5 nm) corresponded to the $^5D_1 \rightarrow {}^7F_J$ ($J = 1, 2$) transition of Eu^{3+} from its high excited state of $^5D_1$ level except characteristic emission ($^5D_0 \rightarrow {}^7F_J$) (J = 1, 2). However, It is difficult to exhibit these emissions for europium complex. We can see clearly that the emission intensity of PMMA- [Ln(HnicO)$_3$·phen]n (Ln = Tb, Eu) system has been improved obviously comparing to that of PMMA-[Ln(HnicO)$_3$]n (Ln = Tb, Eu) system when chooses the same doped concentration from the spectra C and D, especially for the europium complex.(Fig. 4 D) So we conclude that the 1,10-phenanthroline is excellent ligand for the Tb^{3+} and Eu^{3+} ions that is the primary energy absorption donor for the luminescence of the these two rare earth ions in the complex.

Fig. 5 shows the emission spectra of two complex [Tb(HnicO)$_3$·phen]n and [Eu(HnicO)$_3$·phen]n co-doped with MMA. We can see clearly the characteristic emission of the Tb^{3+}(488, 543 nm)and Eu^{3+} ions (617 nm) in the Fig. 4 (A). A broad peak appears at about 590 nm and the peak of the Tb^{3+} at 582 and 620 nm can't be found .The intensity of the Eu^{3+} ion characteristic peak at 617 nm have been improved follow the adding content of the terbium complex. The dependence of luminescent intensity of Eu^{3+} on the content of terbium complex is relevant to a triplet–triplet intermolecular energy transfer from ligand in [Tb(HnicO)$_3$·phen]n to that in [Eu(HnicO)$_3$·phen]n in PMMA.[23] Besides, an important factor that accounts for the fluorescence enhancing of europium ion luminescence is the energy transfer between Eu^{3+} and Tb^{3+} ion. The resonance energy level of Eu^{3+} ($^5D_0$) is lower than that of Tb^{3+} ($^5D_4$). It is possible that the Eu^{3+} in the mixed complex diverts a large portion of the energy from the $^5D_4$ level of the Tb^{3+}, thus promoting the luminescence enhancing of the Eu^{3+} [24].



a

b

c

d

Fig. 4. Emission spectra of [Ln(HnicO)$_3$]n/PMMA and [Ln(HnicO)$_3$·(phen)]n/PMMA hybrid films (Ln = Tb, Eu).

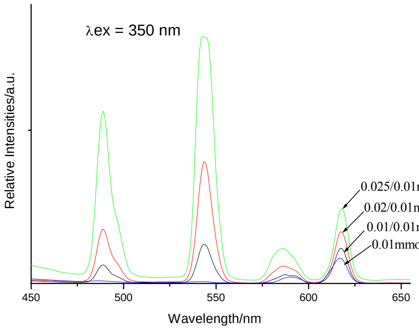
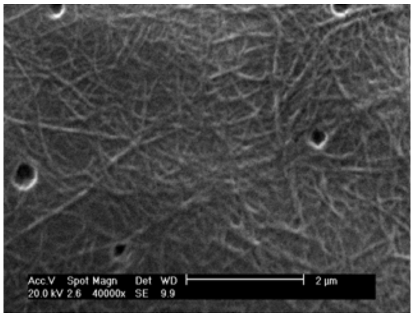
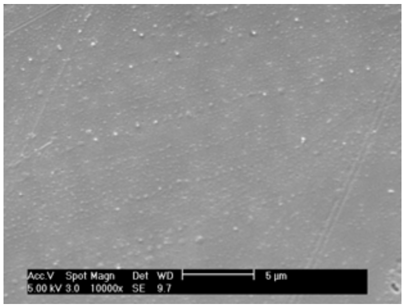


Fig. 5. Emission spectra of Tb(HnicO)$_3$·(phen)]n/Eu(HnicO)$_3$·(phen)]n/PMMA hybrid films.

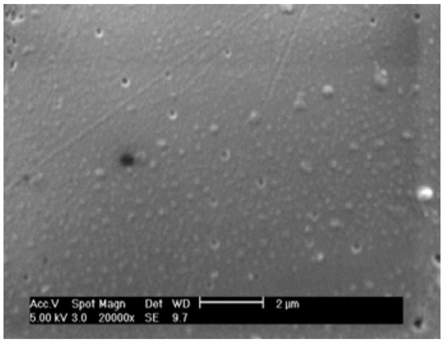
Finally we detected the SEM microscopes of part hybrid polymeric thick films (shown in Fig. 6). It can be found that these coordination polymers can be dispersed in the PMMA homogeneously and they compose very uniformly to interpenetrate together. Beside that we find all of them have the similar chain polymeric structures in the SEM spectra. As shown in Fig. 2, the structure of this kind of Lanthanide complexes is inclined to chain-like. This polymeric chain structure plays important part in avoiding lanthanide ions concentration quenching in the polymer environment which is advantage for the luminescence of polymeric films. Due to the interaction between complex and the PMMA does not belong to chemical action so that we can find the phase separation phenomena in this kind of thick films.



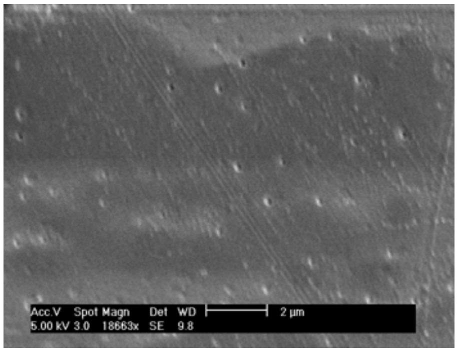
A [Dy(HnicO)$_3$]n / PMMA



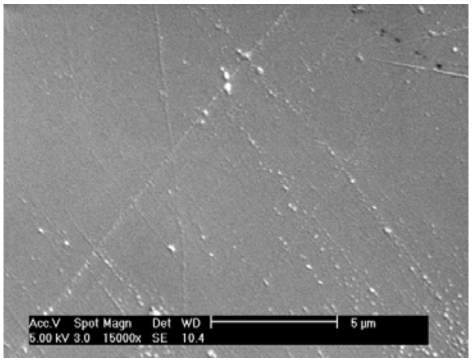
B [Dy(HnicO)$_3$·phen]n / PMMA



C ([Tb(HnicO)$_3$·phen]n / PMMA



D ([Eu(HnicO)$_3$·phen]n / PMMA



E [Tb(HnicO)$_3$·phen]n / [Eu(HnicO)$_3$·phen]n / PMMA

Fig. 6. SEM of [Ln(HnicO)$_3$]n / PMMA and [Ln(HnicO)$_3$·phen]n / PMMA hybrid films.

4. Conclusion

In summary, controlling the formation of dysprosium, terbium and europium coordination polymers accompanied by the polymerization of methyl methacrylate, the coordination polymers of [Ln(HnicO)$_3$]n and [Ln(HnicO)$_3$·phen]n (Ln = Dy, Eu, Tb) with infinite chain polymeric structures were in situ composed with methyl methacrylate (MMA) and the transparent hybrid polymeric thick films were achieved. The emission spectra indicate that all the hybrid thick films composed with the three kinds of rare earth coordination polymers show the corresponding characteristic emission of lanthanide ions. The second ligand 1, 10-phenanthroline is more benefit for the luminescence of the terbium and europium coordination polymers than in dysprosium coordination polymers. And for the Eu^{3+} and Tb^{3+} complexes co-doped thick films, we deduce that the reason of the fluorescence enhancing of Eu^{3+} luminescence is the energy transfer between Eu^{3+} ions and Tb^{3+} ions. By the emission spectra of these polymer films, we find that the hybrid composite polymeric film is a suitable substrate for the luminescence of these lanthanide ions complexes.

Acknowledgements

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