



Synthesis and fluorescent properties of europium–polymer complexes containing naphthoate ligand

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Abstract

Eu–polymer complexes containing naphthoate (Nap) ligand were synthesized through copolymerization of Eu(Nap)₂AA with methyl methacrylate or styrene. Their luminescent properties were investigated. The Eu–polymer phosphors exhibited an intense red emission under UV excitation, the emission intensities were much stronger than that of Eu(Nap)₂AA complex and that of Eu(Nap)₂AA-doped polymers of the same Eu content. Energy transfer processes and environmental effects were found to make contributions to the luminescence enhancement. Typical relationships between emission intensity and Eu content exhibited some extent of concentration quenching in our studies. However, ⁵D₀ lifetime results suggested that the quenching phenomena can not be accounted for by deactivation of ⁵D₀ state through exchange or multipolar interactions. Ligand energy migration along or cross many chains can interpret the emission concentration quenching phenomena reasonably. © 1998 Elsevier Science S.A.

Keywords: Rare earth; Fluorescence; Polymer complex; Exciton migration

1. Introduction

In recent years, interest in rare earth ions-containing polymers has been greatly stimulated by their potential use in fluorescence and laser systems [1,2]. Okamoto and other researchers have synthesized polymers containing coordination groups and studied the fluorescent properties of the complexes [3–5]. However the synthesis of functional polymers with good energy donor capability was found to be very complicated [6,7], and as a result made the use of polymer phosphors uneconomical. Furthermore, the direct reaction of the polymer ligands with RE ions usually form low coordination number complexes and ion aggregates [8,9], resulting in weak emission of the polymer phosphors. Considering the synergetic effects of RE ions coordinating with polymers and low molecular weight ligands, it is promising to synthesis RE-containing polymer complexes with specific luminescent properties by combining the functional polymers with low molecular organic ligands, because many low molecular ligands are at hand, and mild reaction conditions are easy to adjust. To date,

limited attention has been paid to the synthesis and characterization of the RE–polymer–organic ligand ternary complex, and the energy transfer process has hardly been considered. In this paper, we have synthesized Eu–polymer complexes through copolymerization of Eu–acrylate–di(naphthoate) salt with methyl methacrylate or styrene. The polymer complexes prepared by this novel method exhibited more intense Eu³⁺ typical fluorescence than Eu(Nap)₂AA-doped polymers and Eu(Nap)₂AA monomer. All these Eu–polymer complexes can be cast into clear thin films with good thermal and moisture stable properties.

2. Experimental

2.1. Materials

Eu₂O₃ (99.99 wt.%) was purchased from Shanghai Yao Long Non-Ferrous Metals Limited and used without further purification. Styrene, acrylic acid and methyl methacrylate were purified before use. 2,2-Azoisobutyronitrile (AIBN) was recrystallized twice from methanol (m.p. = 103 °C). Other chemicals were analytical grade.

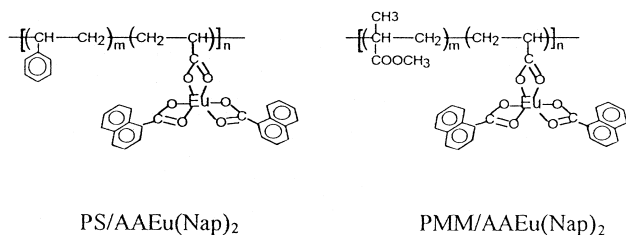
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2.2. Eu–acrylate–di(naphthoate) salt ($\text{Eu}(\text{Nap})_2\text{AA}$)

$\text{Eu}(\text{Nap})_2\text{AA}$ was prepared by neutralization of a mixture of acrylic acid and naphthoic acid in a 1.2:2 mole ratio with freshly prepared $\text{Eu}(\text{OH})_3$ in 50% ethanol aqueous solution. The salt obtained was washed with a small portion of ethanol, and dried under vacuum at room temperature for 24 h. The IR spectrum of the salt showed the antisymmetric and symmetric COO^- stretching vibrations at 1538 and 1406 cm^{-1} and vinyl moiety absorption at 990, 910 cm^{-1} . Eu content determined by ICP was 25.2% (calculated 26.9%).

2.3. Copolymers of $\text{Eu}(\text{Nap})_2\text{AA}$ with styrene (PS/AAEu(Nap)₂) and methyl methacrylate (PMM/AAEu(Nap)₂)

The $\text{Eu}(\text{Nap})_2\text{AA}$ –styrene copolymers with different Eu content were synthesized as follows: For example, 0.2 g $\text{Eu}(\text{Nap})_2\text{AA}$ was dissolved in 2 ml methanol and mixed with 4 g styrene, the homogeneous solution was placed in a tube and 0.02 g AIBN was added. The solution was degassed by three freeze–thaw cycles under vacuum, then sealed and heated in an oil bath at 60 °C for 4 h. The viscous homogenous solution was then dissolved in THF and purified by reprecipitating with methanol, and dried under vacuum at 60 °C for 24 h. 1.1 g (27% yield) white powdery copolymer was obtained, the Eu content was 1.06 wt.%. The copolymer of $\text{Eu}(\text{Nap})_2\text{AA}$ with methyl methacrylate (MMA) was obtained by the procedure described above. The Eu content in both copolymer systems is in the range of 0.1–2.8 wt.%. The copolymers are shown schematically as:



2.4. Instruments

Absorption spectra were recorded on a UV-240 spectrophotometer. TG measurements were carried out using a DU Pont 1090 thermal analyzer. FTIR spectra were recorded on a Nicolet Magna 550 FTIR spectrometer. Excitation and emission spectra were measured on a Hitachi MPF-4 spectrophotometer equipped with an automatic compensation and procalibration system. The powder samples were used for this purpose. A fluorescence lifetime measurement was carried out with a Nd:YAG pumped tunable dye laser ($\lambda_{\text{ex}} = 348$ nm, pulse duration is 7 ns).

3. Results and discussion

Eu –polymer complexes are highly soluble in CHCl_3 , THF, etc., and can be easily cast into transparent thin films. Both the UV extinction value of naphthoate ligand and Eu content in each polymer complex sample interpreted the mole ratio of $\text{Eu}:\text{Nap}$ to be 1:1.98 and 1:1.93 for PMM/AAEu(Nap)₂ and PS/AAEu(Nap)₂ systems respectively. The infrared spectrum of PS/AAEu(Nap)₂ (Eu content, 2.2 wt.%) has no absorption bands in the region of 1720–1670 cm^{-1} which corresponding to the $\text{C}=\text{O}$ stretching vibrations of the naphthoic acid and acrylic acid. The above results illustrated that the $\text{Eu}(\text{Nap})_2\text{AA}$ moiety attaches to the polymer backbones as a whole and the dissociation of AA and Nap groups is negligible during the copolymerization and the following purification processes. In considering the good solubility of $\text{Eu}(\text{Nap})_2\text{AA}$ in methanol, few free $\text{Eu}(\text{Nap})_2\text{AA}$ monomers can still stay in the copolymers through precipitating from THF into methanol. The above result suggested that with one of the coordinate ligands linked to the polymer chains directly, the $\text{Eu}(\text{Nap})_2\text{AA}$ moiety is much more uniformly dispersed in polymer matrices, which is important in optical applications. Meanwhile such structure character gives the polymer complexes a much more stable luminescent property to chemical treatment than $\text{Eu}(\text{Nap})_2\text{AA}$ -doped polymers. TGA analysis showed that the polymer complexes have a good thermal stability; there are no apparent weight loss and decrease of emission intensity up to 320 °C.

Fig. 1 shows the UV absorption spectra of Eu –polymer complexes in THF solution. The absorption spectra of different Eu –polymer complexes are very similar, and exhibit a superposition of absorption bands characteristic of $\text{Eu}(\text{Nap})_2\text{AA}$ complex and pure PS or PMMA. The absorption due to naphthoate ligand at 240 nm is buried

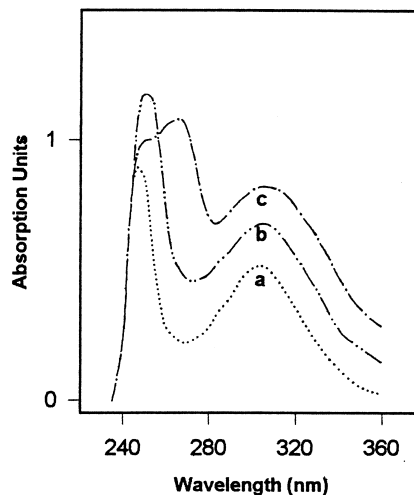


Fig. 1. Absorption spectra of (a) $\text{Eu}(\text{Nap})_2\text{AA}$; (b) PMM/AAEu(Nap)₂; (c) PS/AAEu(Nap)₂ in THF solvent.

under the carboxyl $\pi-\pi^*$ absorption of PMMA at 240 nm and phenyl $\pi-\pi^*$ absorption of PS at 260 nm. The broad band at 298 nm can be assigned to naphthoate $\pi-\pi^*$ transition, its absorption intensity consistent with the $\text{Eu}(\text{Nap})_2\text{AA}$ moiety content in polymer complexes.

Fig. 2 shows the excitation and emission spectra of $\text{Eu}(\text{Nap})_2\text{AA}$ monomer and PS/AAEu(Nap)₂, PMM/AAEu(Nap)₂ polymer complexes. The excitation spectra of different Eu-polymer complexes, obtained by monitoring the emission intensity of the Eu^{3+} band at 615 nm, are quite similar. However, they show striking differences from that of the $\text{Eu}(\text{Nap})_2\text{AA}$ monomer. The excitation spectra of polymer complexes are dominated by strong broad absorption at 300 nm, with intensity dropping slowly in the region of 250–330 nm. The $\text{Eu}(\text{Nap})_2\text{AA}$ complex features a excitation band at 300 nm with a long shoulder toward lower wavelengths, furthermore the normal f-f absorption of Eu^{3+} in the region of 350–400 nm is also prominent. A comparison of the absorption spectra (Fig. 1) with the excitation spectra shows reasonable overlap between the naphthoate absorption in the UV region with the strong absorption in the excitation spectra. The excitation bands corresponding to absorption of PMMA and PS for polymer complexes are also prominent. From the above results, we can conclude that the emission in $\text{Eu}(\text{Nap})_2\text{AA}$ is mainly sensitized by the naphthoate $\pi-\pi^*$ transition whereas that of Eu-polymer complexes are sensitized not only by ligand absorption at 298 nm but by the polymer matrices absorption at about 240–250 nm. The emission spectra of Eu-polymer complexes, excited at 300 nm, do not show significant differences and all exhibit ligand-sensitized emission typical of Eu^{3+} ions. The assignment of observed bands to appropriate f-f transitions is straightforward. Five luminescence lines centered at 580, 592, 614, 650, 690 nm may be attributed to the $^5\text{D}_0-^7\text{F}_0$, $^5\text{D}_0-^7\text{F}_1$, $^5\text{D}_0-^7\text{F}_2$, $^5\text{D}_0-^7\text{F}_3$, $^5\text{D}_0-^7\text{F}_4$ transitions respectively. Such a spectrum character suggests a low symmetric binding site around Eu^{3+} . As depicted in Fig. 2, the

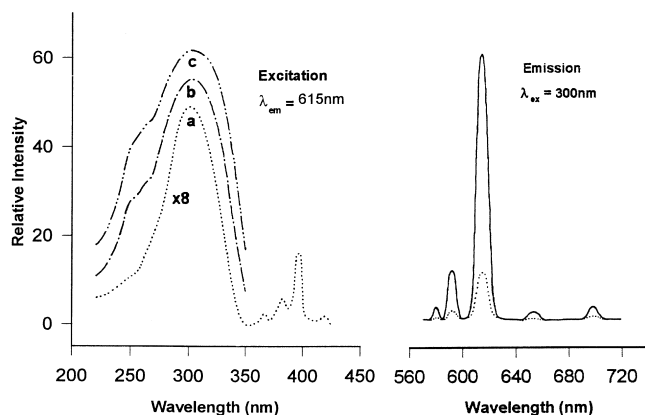


Fig. 2. Excitation spectra of (a) $\text{Eu}(\text{Nap})_2\text{AA}$; (b) PMM/AAEu(Nap)₂; (c) PS/AAEu(Nap)₂. Emission spectra of $\text{Eu}(\text{Nap})_2\text{AA}$ (...) and copolymers at Eu^{3+} content 2 wt.% (—).

relative positions of Eu^{3+} emissions in both the Eu-polymer complex and the $\text{Eu}(\text{Nap})_2\text{AA}$ complex do not show noticeable changes, but the emission intensities change greatly even with the minor changes of environment. The emission intensity of PMM/AAEu(Nap)₂ at Eu content 2 wt.% is comparable with that of $\text{Eu}(\text{TTA})_3$ and is about eight times that of $\text{Eu}(\text{Nap})_2\text{AA}$ complex under 300 nm excitation. Then what is the main effect accounting for the enhancement of Eu^{3+} emission in polymer complex? The inner coordination sphere of Eu^{3+} in both Eu-polymer complexes and $\text{Eu}(\text{Nap})_2\text{AA}$ complex is quite similar. The only difference lies in that: in polymer complexes the mean distance between two $\text{Eu}(\text{Nap})_2\text{AA}$ moieties is longer than in the complex. The above result suggested that $\text{Eu}(\text{Nap})_2\text{AA}$ moiety content plays a dominant role in determining the emission intensity of Eu^{3+} . This phenomenon will be further discussed.

Typical relationships between fluorescence intensity and Eu content in polymer complexes of PS/AAEu(Nap)₂ and PMM/AAEu(Nap)₂ and $\text{Eu}(\text{Nap})_2\text{AA}$ -doped polymers are shown in Fig. 3. In the PMM/AAEu(Nap)₂ system, the emission intensity increases with the increase of Eu content and reaches a maximum at 2.2 wt.%. The PS/AAEu(Nap)₂ system has a maximal emission intensity at 1.5 wt.%. $\text{Eu}(\text{Nap})_2\text{AA}$ -doped polymers exhibit typical emission concentration quenching as described in the literature [8]. The optimum Eu contents in both PMMA and PS systems are 1.8 wt.% and 1.1 wt.% respectively. It is surprising to compare the above results with that reported in the literature [3]. The linear relationship between fluorescence intensity and RE content in $\text{RE}(\text{AcO})_3$ -doped PMMA system was observed within 1.2 wt.%. In RE-containing polymers, emission concentration quenching always interprets formation of ion aggregates in which RE ions lie in close proximity to one another [9], and the exchange mechanism is predominately responsible for the emission quenching under this condition. However, ion aggregates can not be easily formed when the RE ions

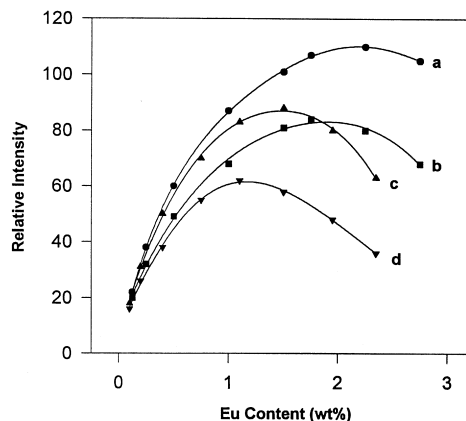


Fig. 3. Relationship between fluorescence intensity and Eu^{3+} content in (a) PMM/AAEu(Nap)₂; (b) $\text{Eu}(\text{Nap})_2\text{AA}$ -doped-PMMA; (c) PS/AAEu(Nap)₂; (d) $\text{Eu}(\text{Nap})_2\text{AA}$ -doped-PS ($\lambda_{\text{ex}} = 300$ nm).

are dispersed in PS or PMMA matrices in the form of organic complexes, as in the case of RE(AcO)₃-doped polymer, in which the ions are wrapped around by organic ligands and have little chance to form ion aggregates. On the other hand, another mechanism corresponding to electrostatic multipolar interaction between RE ions has been used to explain the concentration quenching phenomena in rare earth- β -diketone chelates doped PMMA matrix [10]. The optimum Eu content turned out to be 1.2 wt.% for Eu(DBM)₃ doped PMMA film. Then what are the dominant effects contributing to the emission concentration quenching in our experiment? Concerning the above results and discussions, we are inclined to say that electrostatic multipolar interaction may be an important effect accounting for emission concentration quenching in polymer complexes. In an effort to achieve further confirmation: we have measured the luminescence lifetimes of Eu(Nap)₂AA and polymer complexes with different Eu content. The lifetimes of ⁵D₀ level are shown in (Table 1).

No significant changes of lifetime were observed for various Eu-polymer complexes, in agreement with the presence of metal sites with very similar chemical environments [11,12]. Furthermore, τ values recorded at 77 K are almost identical with those at room temperature, implying feeble thermal deactive process. It is known that concentration quenching through exchange or multipolar interactions will cause a decrease of the ⁵D₀ lifetime. However, the lifetimes of the Eu(Nap)₂AA complex and copolymers of different Eu contents, as shown in Table 1, are almost identical. This result suggested that concentration quenching can not be accounted for by deactivation of the ⁵D₀ state through exchange or multipolar interactions. Van Uitert et al. have demonstrated that Eu³⁺ self-quenching by multipolar interaction is much more efficient for the ⁵D₁ state than for the ⁵D₀ state [13]. Upon excitation at 300 nm, the direct resonant transfer from the ligand T₁ level (21316 cm⁻¹ for Naphthoate) [14] to the ⁵D₁ level (19300 cm⁻¹) of Eu³⁺ is possible. But quenching through the ⁵D₁ state should have a low efficiency in the Eu-polymer complexes owing to the relatively longer distance between Eu³⁺ ions and the short lifetime nature of the ⁵D₁ state. One can infer from the above results that besides electrostatic multipolar interaction there may exist another dominate mechanism accounting for the emission concentration quenching in Eu-polymer complexes.

Exciton migration had been used to interpret rare earth emission quenching in solid complexes [11,12]. This process is favoured when ligands coupling caused by a

series of Coulomb interactions is strong [15]. In Eu(Nap)₂AA complex ligand excitation energy migration is evident from monitoring the naphthoate emissions. When Gd(Nap)₂AA was excited at 300 nm, the strong broad band ligand emissions at 438 and 538 nm were observed. However, when the (Eu_{0.01}Gd_{0.99})(Nap)₂AA complex was excited at 300 nm, no significant emissions from the naphthoate ligand were observed while sharp Eu³⁺ emission is dominant, only small amounts of Eu³⁺ traps were needed to quench the ligand fluorescence. Under this condition, the rate of energy migration through the complex until a killer site is reached is larger than the rate of the intramolecular energy transfer, and as a result only weak emission of Eu³⁺ in solid Eu(Nap)₂AA complex was observed while in solution it is highly fluorescent. Exciton migration in polymers containing chromophores was first confirmed by Cozzens and Fox [16]. In the exciton migration process, the T₁ state can be easily quenched by paramagnetic species (e.g. O₂) or by intrinsic traps of the polymer; the polymer matrix itself participated both as an acceptor of energy from excitons and as a medium for the triplet energy migration [17]. It has been reported that in styrene-vinylnaphthlene copolymer, exciton migration was efficient even with naphthlene moiety content as low as 10⁻³ mole fraction [18]. In PS/AEu(Nap)₂ of 2.0 wt.%, the total mole fraction of naphthoate ligand is about 0.02. It seems likely that such a ligand content is high enough for ligand exciton to migrate through the polymer matrices, causing apparent concentration quenching. As shown in Fig. 3, both PMM/AEu(Nap)₂ and PS/AEu(Nap)₂ show emission concentration quenching, with the latter being more efficient. This phenomenon suggested that this kind of ligand exciton migration is favoured among similar molecules but it can also occur between dissimilar molecules if the excited states involved are close in energy. In PS the π -stacking interaction between aromatic rings makes the exciton migration process more efficient than in PMMA. The exciton migration process which competes with the ligand to metal transfer process is negligible in low Eu content polymer complexes and becomes more apparent with the increase of Eu content. It is argued that it is the very energy migration process, along or across polymer chains, that enhances the probability that the exciton will encounter a quencher and consequently causes Eu³⁺ emission concentration quenching.

A careful examination of Fig. 3 found that the emission intensity is in the order of PMM/AEu(Nap)₂ >

Table 1
⁵D₀ lifetimes (τ) of Eu(Nap)₂AA and polymer complexes of different Eu content (μ s)

Eu content wt. %	Eu(Nap) ₂ AA	PMM/AEu(Nap) ₂					PS/AEu(Nap) ₂				
		0.11	0.52	1.06	1.90	2.80	0.10	0.41	1.21	1.75	2.28
τ 300 K	1.28	1.23	1.25	1.22	1.25	1.26	1.20	1.20	1.21	1.18	1.25
τ 77 K	1.30		1.25			1.27		1.21			1.26

PS/AAEu(Nap)₂ ≥ Eu(Nap)₂AA-doped PMMA > Eu(Nap)₂AA-doped PS, in agreement with the sequence of concentration quenching efficiency. Upon copolymerization, Eu³⁺ emission intensity is apparently enhanced. Fluorescence intensity of PMM/AAEu(Nap)₂ at 2 wt.% is about 1.8 times that of Eu(Nap)₂AA-doped PMMA of the same Eu content, and PS/AAEu(Nap)₂ is about twice that of Eu(Nap)₂AA-doped PS at an Eu content of 1.5 wt.%. Fig. 4 shows the X-ray diffraction patterns of different Eu-containing polymers, using PMMA, PS and Eu(Nap)₂AA as contrasts. In the atactic PMMA, two broad diffraction peaks centered at 2θ = 12° (8.615 Å) and 17.9° (4.539 Å) were observed. In the PMM/AAEu(Nap)₂ system, the diffraction intensity of the two main non-crystalline peaks centered at 12° and 17.9° 2θ decreases apparently with the increase of Eu content. However, in Eu(Nap)₂AA-doped PMMA (Eu content 2.8 wt.%) the peak at 12° 2θ almost disappears while the peak at 17.9° 2θ decreases only a little, meanwhile a minor peak corresponding to Eu(Nap)₂AA crystalline state appears at 9.8° 2θ. The same phenomenon is also true when the PS system is concerned. XRD results suggested that Eu(Nap)₂AA

moiety is much more uniformly dispersed in the polymer complexes than in Eu(Nap)₂AA-doped polymers. Both the long range and relative short range periodic arrangement of atoms and atomic groups are disturbed by introducing Eu(Nap)₂AA moiety into polymer chains. As to Eu(Nap)₂AA-doped PMMA or PS systems, only the long range regularity is disturbed, the formation of aggregates is also detectable at an Eu content 2.2 wt.%. The copolymers are likely to adopt conformation and tacticity that less favour the ligand interaction and exciton migration and as a result a much great part of the excitation is transferred to Eu³⁺ under UV radiation. The special conformation is just the driving force that causes the highly fluorescent property.

4. Conclusion

Eu–polymer complexes containing naphthoate ligand, prepared by this novel and simple method, turned out to be excellent fluorescent materials. In Eu(Nap)₂AA complex, the strong π–π stacking interaction between aromatic rings caused very efficient ligand excitation migration quenching. In the polymer complex, ligand exciton migration was hindered due to the large distance between Eu(Nap)₂AA moieties, and as a result the fluorescent intensity was greatly enhanced. The polymer complexes have advantages over Eu(Nap)₂AA-doped polymers in that: (a) the polymer complexes exhibit more intense Eu typical fluorescence (b) in polymer complexes, Eu(Nap)₂AA moiety is dispersed much more uniformly, which is very important in optical applications.

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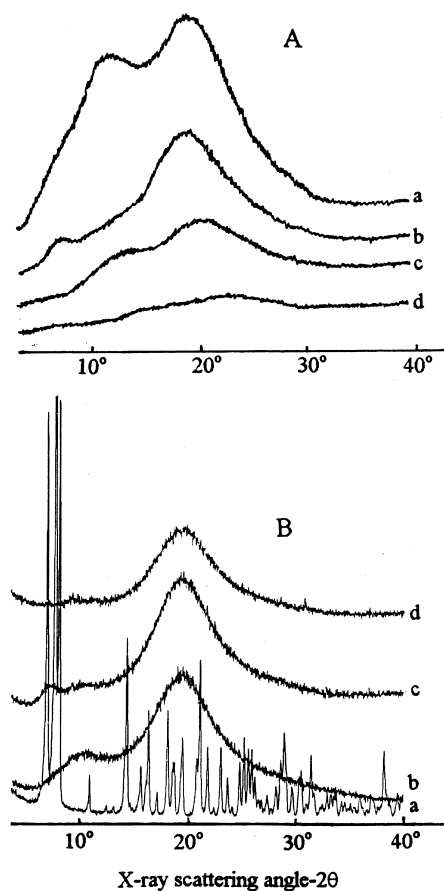


Fig. 4. X-ray diffraction patterns from (A): (a) PMMA, (b) 2.8% Eu(Nap)₂AA-doped-PMMA, (c) 1.8% PMM/AAEu(Nap)₂, (d) 2.8% PMM/AAEu(Nap)₂; and (B): (a) Eu(Nap)₂AA, (b) PS, (c) 2.2% Eu(Nap)₂AA-doped-PS, (d) 2.2% PS/AAEu(Nap)₂.

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