# Dimedone and Phenylazo Dimedone Chelates of Europium as Emitters in Polymers

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**ABSTRACT:** Transparent polymers when incorporated with strongly fluorescent europium chelates were found to be responding to excitation with UV radiation. In this work, two novel europium chelates have been synthesized using the β-diketones dimedone and phenylazo dimedone along with 1,10-phenanthroline. These chelates were characterized by elemental analyses, magnetic susceptibility measurements, UV, IR, and ESI mass spectral techniques. The chelates synthesized with metal : β-diketone : 1,10-phenanthroline ratio 1 : 3 : 1 were incorporated into polymer matrices. Four polymers, polyethylene vinyl acetate or acetate (EVA), polystyrene (PS), poly methyl methacryalate (PMMA), and polyethylene glycol (PEG) were used for the studies. All these, except the liquid oligomer PEG were cast into thin films. PEG was used as such for the studies. The photoluminescence spectra of the plain polymers were found to be having peaks very close to the absorption peaks of the polymers doped with europium chelate. This observation can be used in optical devices. Thermal analyses like TG/DTG/DTA of the polymer films were conducted to ascertain the thermal stability of the material. The SEM analyses of the films indicated a smooth surface with uniform distribution of the doped chelate. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 696–701, 2011

**Key words:** dyes; films; photophysics; europium chelates; SEM

## INTRODUCTION

Polymers and glasses were found[1,2] to accommodate organic and inorganic molecules into their matrices without affecting the photophysical properties of the guest compounds. A polymer when excited can transfer its energy to the neighboring chromophore non-radiatively if its emission band overlaps the absorption band of the acceptor. The distance between the donor and acceptor must also be less than 10 nm. This property of the chelate-polymer system is exploited in this work, where polymer donor transfers energy to the embedded europium which in turn emits radiation at ∼ 613 nm. The ligand of the chelate is excited to higher energy state by the ultraviolet light. Next, by intersystem crossing, energy is transferred to the triplet state and from there to the excited state of the lanthanide ion. In the case of europium, the excited state is $^5$D. Therefore, when the metal returns to the ground state $^7$F, fluorescence is emitted.[3] Lanthanide chelates stay at excited state for about $10^5$ times longer than other fluorophores and hence significantly enhance sensitivity and also dramatically reduce back ground fluorescence. These chelates have wider stokes shift (about 200–300 nm) than other fluorophores and have sharp emission peaks, which are independent of the structure of the ligand and are stable upto 7 years. Lanthanides also possess the unique property of emission, which is independent of the matrix into which they are embedded. While synthesizing lanthanide chelates for optical applications, one part of the ligand is usually designed to bind strongly and shield, (Fig. 1) the lanthanide ion against quenching. β-diketones, cryptands, calixarenes, cyclodextrins, crown ethers, etc, are used for the purpose. In addition to such molecules, organic chromophores like N-heterocycles are also used to complex with the lanthanide ions. These light harvesting moieties enhance absorption cross section of $Ln^{3+}$ absorption bands which are otherwise narrow ($\Delta\lambda < 1$ nm) and weak ($\varepsilon < 1$ $M^{-1}$ $cm^{-1}$) and serve as antennae molecules to transfer energy toward the central metal ion.[4] Pyridines, bipyridine, 1,10-phenanthroline, etc., are some examples for antennae molecules. This work is focused on complexes of europium in which β-diketones act as shielding ligand and 1, 10-phenanthroline act as antenna ligand. The luminescence phenomenon in the visible region is not disturbed by vibrational C—H overtone absorptions of the matrix. Moreover, for the same reason, polymers have their low loss windows in the spectral region ∼ 600 nm, which is also one of the standard wavelengths[5] in optical telecommunications. Therefore, europium, one of the strongest emitters
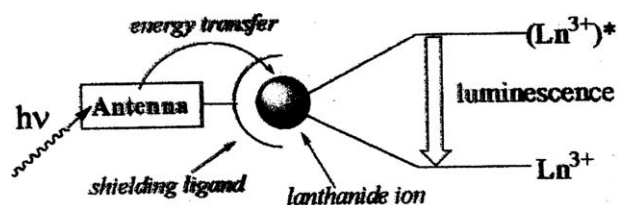
**Figure 1** Pictorial representation of lanthanide chelates in photophysical phenomenon.

among the lanthanides which emits fluorescence at 613 nm, is chosen for the study. The high quantum yield of europium chelates when compared with the weak fluorescent group also rationalizes the choice of the metal ion. There has been plenty of work[6–10] in the field of optical and electrical properties of lanthanide β-diketones and the antennae ligands incorporated into glass, silica, or polymer matrices like PMMA, PS, and perfluorocyclobutyl polymer. When the luminescence peak of plain polymers show proximity to the absorption peaks of the complexes in films, these polymers work well[11] to become hosts for europium complexes to be used as active material in polymer optical fibre amplifier (POFA) and organic light-emitting diode (OLED). The doping in many of the works referred here is done by adding the chelate to the monomer and then polymerization is initiated. However, doping in this study is carried out by adding the chelate as such into the polymer solution so that the chelate to polymer ratio could be adjusted which is not quite possible when polymerization is initiated from a monomer. Even though a few reports[12] are available for using azo β-diketones, not much work has been done with these ligands. These organic dyes have the additional advantage of wide absorption cross sections, which extend the absorption-emission overlap region. A comparative study of the photophysical properties of dimedone and phenylazo dimedone chelates when incorporated in four polymers, EVA, PS, PMMA, and PEG, are presented here. It has been found that PMMA acts as the best host polymer that allows maximum intensity in fluorescent emissions.

## EXPERIMENTAL

### Materials

The chemicals used, the β-diketones dimedone (loba) and thenoyl trifluoroacetone (E Merck), *o*-phenanthroline (Merck), and $EuCl_3$ (Alfa Aeser) were of standard AnalaR grade. Phenylazo dimedone was synthesized by diazo coupling aniline with dimedone. The solvents methanol and chloroform used were from E Merck and were used as received. Ethanol was purified by distillation. Polymers like EVA, PS, and PMMA used here were of synthetic grade

(E Merck, PDI 1.2–1.3). The liquid olegomer PEG was purchased from E Merck. PEG 400 was used, which has a molecular weight in the range 380–420.

### Measurements

Metal (Eu) percentage was obtained by standard method[13] after igniting the chelates to oxide, digesting with conc. HCl, diluting to known volume, and estimating by complexometry method using EDTA as titrant and xylenol orange as indicator which changes color from purple to pale-yellow at the end point. C, H, N percentages were obtained by microanalyses using Elementar Vario EL III CHNS analyzer. UV–visible spectra were taken on Jasco UV/vis spectrophotometer V-550. PL spectra on Elico SL 174 spectro fluorometer were measured in methanolic solution for quantum yield studies, and thin film strips were used for the doped polymer. FTIR spectra were obtained by compressing into KBr discs for characterization of chelates, and circular film strips were used for doped polymers on a Jasco FTIR spectrophotometer–4100. ESI mass spectra were obtained from Micromass Quattro II triple quadrapole mass spectrometer with samples dissolved in methanol and ESI capillary at 3.5 kV, cone voltage 40 V. Magnetic moments were determined at room temperature $\sim 26°C$ using Magway magnetic susceptibility instrument of Sherwood Scientific, calibrated[14] using $Hg[Co(NCS)_4]$. SEM micrographs were taken with SEM JEOL-JSM-6300 electron microscope operating at accelerating voltage 20–30 kV using polymer films (1 cm × 1 cm) sputtered with a thin layer of gold. Thermal analyses were carried out on Perkin Elmer, Diamond TG/DTA instrument in inert ($N_2$) atmosphere at heating rate of 10°C/min.

### Synthesis of ligands and complexes

#### Ligands

The ligands used in this investigation were dimedone (D), phenylazo dimedone (AD), and 1, 10-phenoantharoline (phen). Dimedone and 1,10-phenanthroline were used as purchased. Phenylazo derivative of dimedone was synthesized (yield = 85%; mp = 120°C) and characterized by elemental analysis, IR, UV, NMR and mass spectral and single crystal XRD techniques as described elsewhere.[15]

#### Complexes

*Europium complex [Eu(AD)₃phen].* To a 2*M* solution of sodium hydroxide in 5 mL ethanol, 0.005 mol of phenylazodimedone was added followed by 0.002 mol of 1,10-phenanthroline, and the solution was stirred until complete dissolution. Europium (III) chloride (0.002 mol ) in ethanol was added drop wise when a

deep-pink precipitate separated out. Stirring was continued for 4–5 h, and the precipitated chelate was filtered, washed with ethanol, and dried over $MgSO_4$ in vacuum desiccator and recrystallized from methanol. (yield = 45%; mp = 145°C)

*Europium complex [Eu(D)₃phen].* This chelate was synthesized exactly in the same method as above except that dimedone was used instead of phenylazo dimedone. The recrystallization and drying conditions were also the same as described above, (yield = 41%; mp = 240°C).

## RESULTS AND DISCUSSION

### Characterization of complexes

Elemental analysis data confirmed the molecular formula $EuC_{54}N_8O_6H_{56}$ for the chelate [Eu(AD)₃phen] and $EuC_{36}N_2O_6H_{44}$ for the chelate [Eu(D)₃phen] with 1 : 3 : 1 stoichiometry of metal:β-diketone/azo β-diketone:*o* phen. The paramagnetic nature and magnetic susceptibility values at room temperature were typical[16] of europium complexes. The elemental percentages of the complexes were found(calc.) [Eu(AD)₃phen]; C 60.36(60.90), H 5.70(5.20), N 10.11 (10.50), Eu 14.13 (14.23) and [Eu(D)₃phen]; C 56.36(56.40), H 5.59(5.80), N 3.46(3.72), Eu 20.67 (20.21) The IR stretching bands consisted of all the expected values as follows [Eu(AD)₃phen]:1658(free C=O), 1547(chelated C=O),1615(C=N),582 (M-N),447 (M-O). [Eu(D)₃phen]: 1659(free C=O), 1547 (chelated C=O),604 (M-N),439 (M-O).$\nu$C=N band was observed only for [Eu(AD)₃phen] which further confirmed the hydrazono β-diketone moiety. The electron spray ionization (ESI) mass spectra of the complexes were having very prominent M + 1 peaks at 1065 for [Eu(AD)₃phen] and at 753 for [Eu(D)₃phen] together with M + 2 peaks. This strongly confirms the molecular formula. Moreover, the peaks at $m/z$ 959 ($M^+$-$C_6H_5N_2$), 839 B.P ($M^+$-($C_6H_5 \times 2 + CH_3$), 691 ($M^+$-(*o*-phen + $C_6H_5 N_2 + CH_3 \times 6$-2H) for [Eu(AD)₃phen] confirms the stoichiometry of 1 : 3 : 1 w.r.t Eu:phenylazodimedone:*o*-phenanthroline.

### Fluorescence quantum yield studies

Fluorescence quantum yield is one of the most important optical properties used to express the fluorescent characteristics. The standard chosen in this work was europium thenoyltrifluoro acetonate, $[Eu(TTA)_3(H_2O)_2]$ which has been synthesized solely for this purpose. The synthesis was done as per reported[17] procedure and the chelate was characterized: (mp 163°C, Eu percentage-16.89 (found) 17.85 calc.).The quantum yield of $[Eu(TTA)_3(H_2O)_2]$ is taken[18] as 0.19 for a $10^{-3}M$ solution in ethanol at 25°C. The following equation was made use of for calculation of quantum yield,
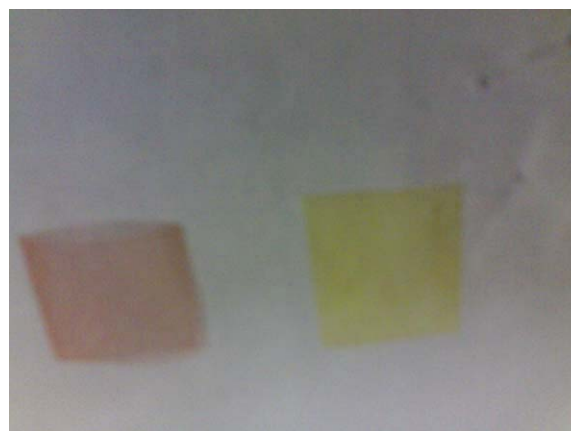
**Figure 2** Photograph of polymer films doped with the chelates (a)Eu(AD)₃phen/PS (pink) and (b)Eu(D)₃phen/ EVA (yellow). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\phi_{sample} = A_{sample} \in_{st} c_{st}\phi_{st}/A_{st} \in_{sample} c_{sample}$$

where $\phi$, $A$, $c$, and $\in$ represent quantum yield, area of fluorescence peak of europium complex at 613 nm, concentration of the solution, and molar absorption coefficient, respectively. Subscript "st" refers to standard. The $\phi$ values for the complexes were obtained as 0.2754 and 0.2543 for [Eu(AD)₃phen] and [Eu(D)₃phen], respectively. This shows that both are having appreciable quantum yield with values higher than that of $[Eu(TTA)_3(H_2O)_2]$. Therefore, both chelates are suitable for optical applications in POFA/OLED.

### Polymer films and optical studies

Casting

The polymers EVA, PS, and PMMA were made into thin films, (Fig. 2) after dissolving in $CHCl_3$, by stirring at a temperature of $\sim$ 50°C, and allowing to evaporate on shallow dishes at room temperature. The chelate was incorporated by dissolving it in methanol and adding to a solution of the polymer in $CHCl_3$. While preparing the polymer solution, stirring was carried out for 1 h to confirm homogeneity. The chelate to polymer ratio was 1 : 5 by weight. The films were kept in separate polythene sheets in a desiccator. The liquid oligomer PEG-400 was used as such, and doping was done by directly dissolving the chelate in PEG with stirring for 1 h.

Absorption spectral analyses

From the IR spectra of plain and the doped polymers, it was obvious that the original peaks of polymers are retained in more or less the same way in the doped ones showing that there are no strong forces of attraction between the polymer and the chelate. This
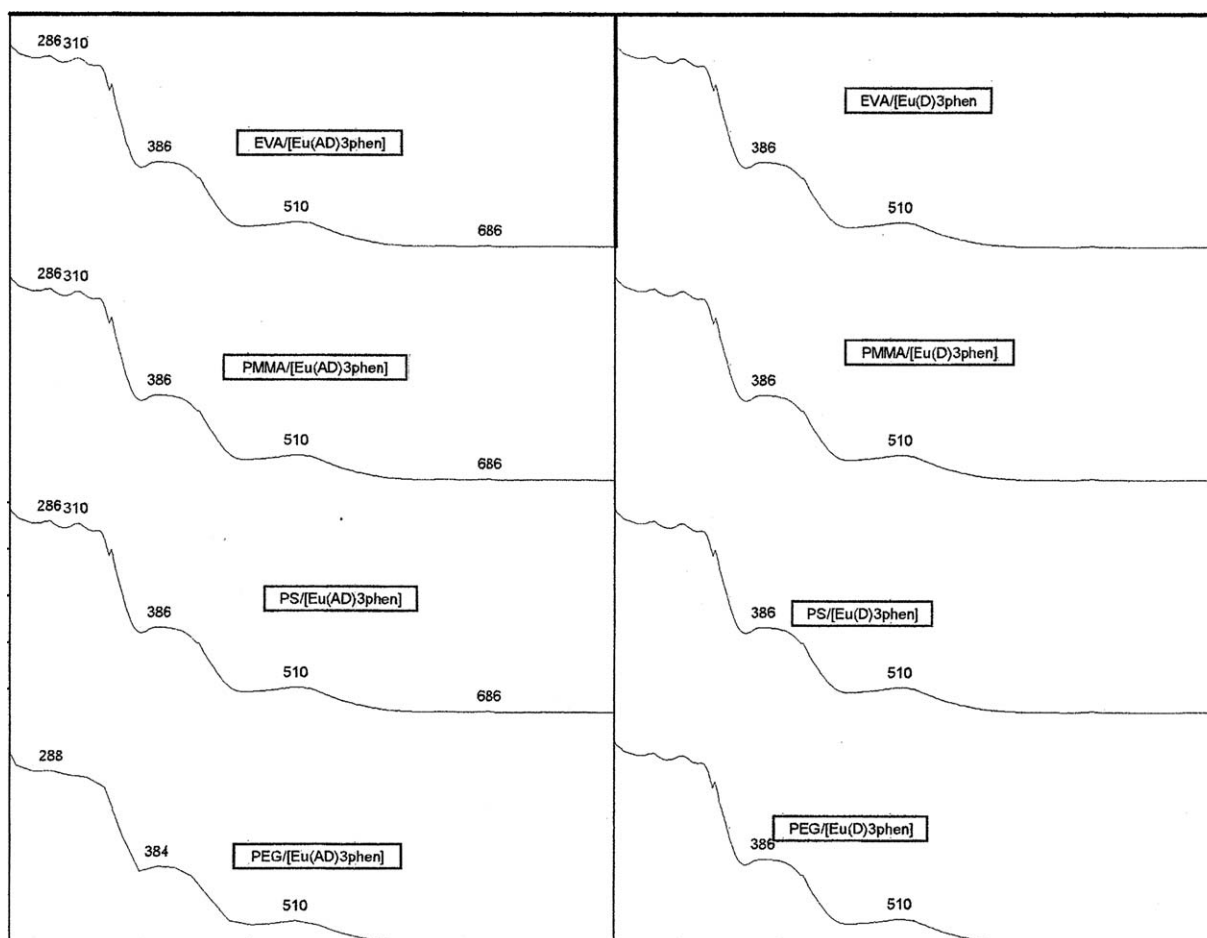
**Figure 3** UV–visible spectra of doped polymers.

observation also reaffirms the fact that the fluorescent property of the chelate is not affected by the doping process. The UV–visible spectra (Fig. 3) of the doped polymers showed the $\lambda_{max}$ at ∼ 350 which is characteristic of europium β-diketonate complexes.

Scanning election microscopy
of doped polymer films

Scanning election microscopy (SEM) is mainly aimed at observing the surface morphology of materials. SEM micrograph of a sample doped polymer film is presented here—one with [Eu(D)$_3$phen ] doped in EVA, (Fig. 4).The single films of size 1 cm × 1 cm sputtered with Au paste were used as sample and data acquired over ∼ 5–10 min. The SEM micrograph clearly indicates a flat surface. The surface roughness and film thickness were almost approximated to <10 run and ∼ 200 nm, respectively. The pictures show a uniform distribution of the doped material which is a clear indication of how well these layers can perform if used in POFA or OLEDS which require uniform emission. The SEM analyses were done after 5–6 months of storage of the films which showed the keeping qualities of the films.

Thermal analyses of doped polymers

The simultaneous thermo gravimetric (TG/DTG) and differential thermal analyses (Table I) of the three polymers, EVA, PS, and PMMA, each doped
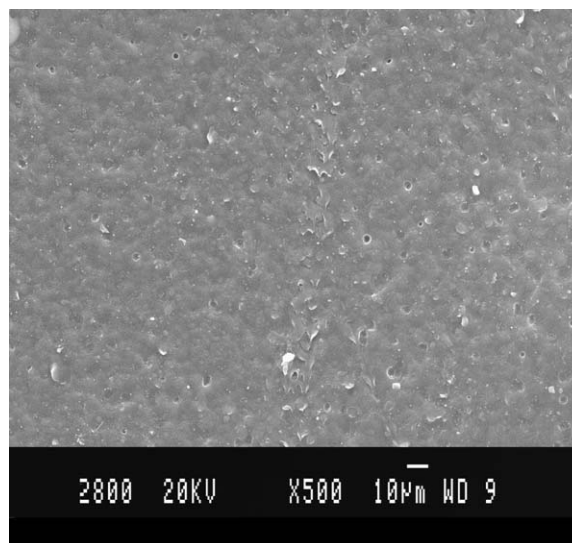


**Figure 4** SEM Micrgoraph of EVA/[Eu(D)$_3$ phen].

**TABLE I**
**Comparison of the Stability of the Plain and Doped Polymers Based on TG/DTG/DTA Analysis**

| | Stage 1 | | Stage 2 | | | Stage 3 | | |
|---|---|---|---|---|---|---|---|---|
| Material | $T_1$ (°C) | $T_{max1}$ (°C) | $T_2$ (°C) | Residual weight (%) | $T_{max2}$ (°C) | $T_3$ (°C) | Residual weight (%) | DTA peak (°C) |
| EVA | 290 | 335 | 405 | 82 | 470 | 490 | 15 | nil |
| EVA/[Eu(AD)₃phen | 290 | 370 | 424 | 81 | 469 | 492 | 3 | 472(endo) |
| EVA/[Eu(D)₃phen | 291 | 363 | 429 | 74 | 470 | 482 | 1 | 358(endo) |
| PS | 275 | 398 | 430 | 15 | nil | nil | nil | 410(endo) |
| PS/[Eu(AD)₃phen | 310 | 414 | 432 | 13 | nil | nil | nil | 383(endo), 414(endo) |
| PS/[Eu(D)₃phen | 270 | 415 | 440 | 8 | nil | nil | nil | 415(endo) |
| PMMA | 250 | 310 | 320 | 86 | 380 | 400 | nil | 320(endo), 430(exo) |
| PMMA/[Eu(AD)₃phen | 260 | 314 | 321 | 87 | 378 | 411 | 15 | 373(endo) |
| PMMA/[Eu(D)₃phen | 252 | 316 | 320 | 85 | 360 | 407 | 12 | 359(endo) |

with [Eu(AD)₃phen] and [Eu(D)₃phen], were carried out. The thermal analysis of the oligomer PEG could not be conducted because it was in the liquid form. All analyses had been done in inert atmosphere (N₂) as the presence of oxidants may accelerate the decomposition process. The decomposition data of undoped polymers were taken from published literature.[19–21] The thermal stabilities of the doped polymers showed that the temperature withstanding capacities of the host polymer were retained. $T_{max1}$ of the doped polymers are 30–40° higher than that of plain EVA. This was a clear indication of the deceleration of heating rate and hence the slow response of the doped polymers toward temperature changes. It is clear that the thermal stabilities of the doped polymers are comparable to the undoped host polymer PS. The initial degradation temperature of the polymer when doped with [Eu(AD)₃phen] is higher. The temperature at which maximum weight loss occurs, $T_{max}$ is also high for the doped polymers. The above data clearly indicate that the thermal stability of the undoped polymer PMMA is retained, in the doped ones. The initial degradation temperatures of PMMA/[Eu(AD)₃phen] are higher than the host polymer. The thermal studies were conducted to have an idea of the stability of the doped polymers when used in optical devices. It has been found that the polymers, despite hosting a hygroscopic complex show good thermal stability and do not absorb moisture even when kept air exposed.

**TABLE II**
**Analysis of PL Peak of Plain Polymers with Absorption Peaks of Doped Polymers**

| | | Absorption max (nm) with embedded chelate | |
|---|---|---|---|
| Polymer | PL peak (nm) | [Eu(AD)₃phen] | [Eu(D)₃phen] |
| EVA | 346.5 | 386 | 386 |
| PS | 339.0 | 386 | 386 |
| PMMA | 357.0 | 386 | 386 |
| PEG | 306.5 | 384 | 386 |

**Optical studies**

The photoluminescence spectra of plain polymers exhibited peaks which were close to the absorption peaks of the complexes doped in different polymers, (Table II) clearly indicate how these doped polymers may work well with POFA or OLEDS. The chelates doped in the polymer films were excited at their $\lambda_{max}$. Of the four polymers chosen, PMMA gave the best result with the PL peak showing more proximity to absorption peaks which were constant at 386 nm. The PL peaks of the doped polymers are shown in Figures 5 and 6. All show the peak at ∼ 618 nm which is characteristic of europium irrespective of the matrix into which it is incorporated. Here also,
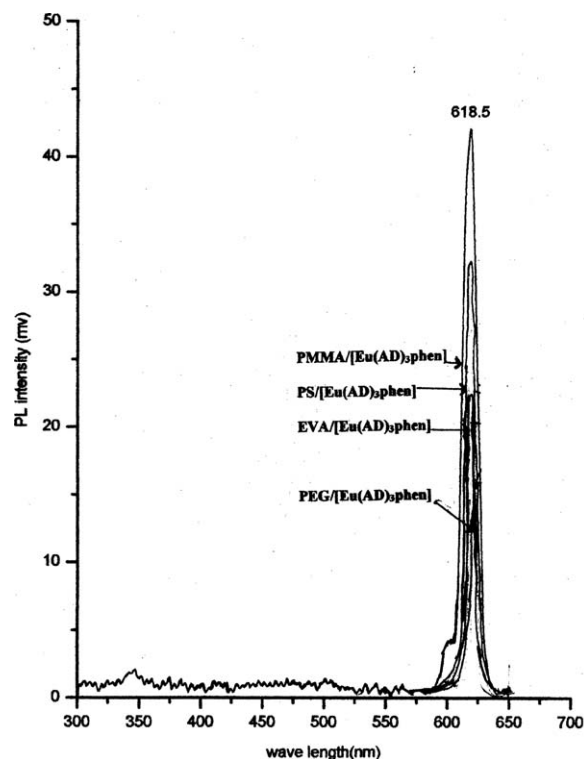


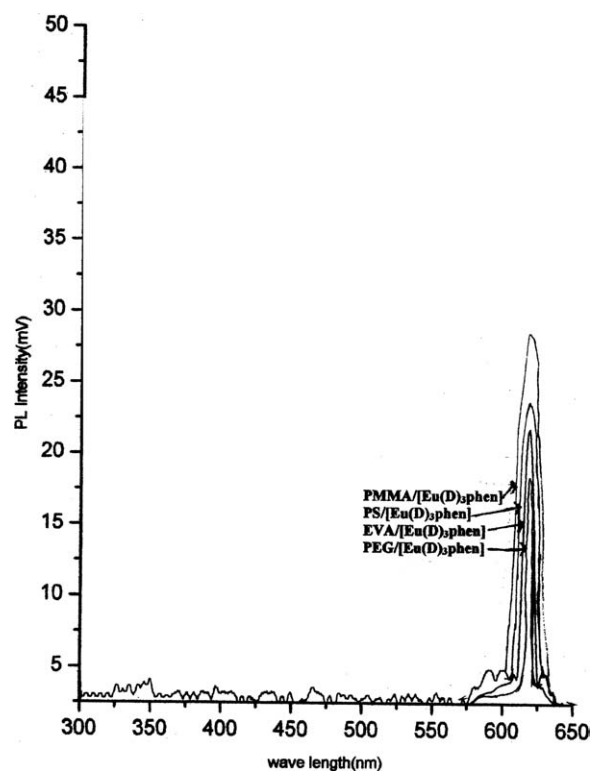**Figure 5** Photoluminescence spectra of polymers doped with [Eu(AD)₃ phen].

**Figure 6** Photoluminescence spectra of polymers doped with [Eu(D)$_3$ phen].

the polymer PMMA is found to be the best host allowing a high intensity fluorescence emission, whereas in others, there is a considerable amount of intensity decrease. The complex [Eu(AD)$_3$phen] shows more intensity than [Eu(D)$_3$phen] which may be due to the presence of azo group in the former.

## CONCLUSIONS

This work shows the possibility of using rare earth chelates doped as such into polymer host for applications like POFA/OLEDS. The use of EVA for this purpose has not been reported earlier. This polymer does not perform as well as the modern per fluori-nated or deuterated polymers which are very costly. However, structural alterations in the polymer can be attempted to satiate the present demands of photophysics. This method can be extended to other azo beta diketones or other rare earths and the applicability can be checked by fabricating POFA, wave guides or OLEDS.

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