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Synthesis and Optical Properties of Eu@ AcPEG Polymer

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Abstract

This paper summarizes structural and optical properties of rare-earth (Eu^{3+}) doped terminally Acetyl Polyethylene Glycol *(Eu@AcPEG)* polymeric materials. The attention is drawn toward Eu@*AcPEG a* derived polymer in terms of their unique luminescence, photostability and non-toxicity. *Eu@AcPEG* polymeric material was synthesised by conventional solution casting technique. The monomer modification was confirmed by ^{1}H-NMR. Eu^{3+} ion has been doped in the matrix of AcPEG to improve the luminescence properties. Then the doped polymer was characterized by SEM, TG-DTA, Fourier transform infrared (FTIR), UV-Visible (UV-Vis) and Photo-luminescent (PL) spectroscopy. AcPEG derived polymer exhibits strong emission in the UV-A (345 nm). Besides it, the polymer fluorescence intensity decreased as the Eu^{3+} concentration increases due to the complex formation. In addition, Eu@AcPEG sample exhibits violet and red emission attributed to the Eu^{2+} ($4f_6\,5^1–^4f^7$) and Eu^{3+} ($^5D_o–^7F_J$) dopant spices respectively. Present work offers a novel face of PEG with great potential in a variety of emerging applications, in particular, as photonic devices area.

Keywords: Poly(ethylene glycol), PEG, Acetyl Poly(ethylene glycol) AcPEG, Fluorescent emission, Cluster formation, Metal ion.

1. Introduction

Organic and inorganic fluorescent materials have contributed greatly to the development of modern era. The current generation of inorganic phosphors used in most lighting and display applications based on near-ultraviolet (nUV) or blue LED chip emission into a broad spectrum of white light or specific colors for display applications [1].

For this purpose the optical properties of polymers have been investigated intensively because of their wide applications in electronic and optical devices, such as chromic display and optoelectronic devices [2]. Across the world, a large community of researcher havebeen make constantly efforts to developing new materials to be used in photonic and optoelectronic devices, such as light-emittingdiodes (LEDs), organic photovoltaic devices and polymer lasers [3].

Poly(ethylene glycol) (PEG), among widely used in biomedical fields for a long time owing to its solubility, nontoxicity, non-immunogenicity and good compatibility with the environment [4,5,6]. Further PEG and its derivatives used extensively in bio sensing, food industries, textile industries and cosmetics. PEG exhibited fluorescence hardly in general [7-13], however oxidise PEG, its derived polymers, composite form with inorganic and doped with transition/rare earth metal emit a strong fluorescence. Polyethylene glycol (PEG) molecule generally has two hydroxyl groups (-OH) at its both ends, and the -OH groups are highly reactive to many small molecules, which provide versatile options for chemical modification of PEG.

In the present work, we attempt alteration the optical properties of PEG by transforming the -OH end groups by a functional groups dichloromethane (CH_2Cl_2) through the chemical reactions. Acetylation of PEG can be done facilely in a simple laboratory by using very cheap raw materials. Then, Acetyl Polyethylene Glycol (AcPEG) doped with lanthanide metal (Eu^{3+}) ions. The chemical structure, morphology, thermal and optical properties of a novel Eu@AcPEG polymer samples are analysed and discussed.

2. Experimental

Material and Method

Analytical grade reagents and solvents were used in this work without further purification. polyethylene glycol-2000 **(PEG-2000) was** purchased from TCI chemicals, India and (dimethylamino)pyridine (DMAP) was purchased from Sigma Aldrich, dichloromethane from SDF chemicals Ltd, acetic anhydride was purchased from Thomas Bakers Chemicals PVT. Ltd. and impurity salt $EuCl_3.6H_2O$ (CDH, 99.5 %).

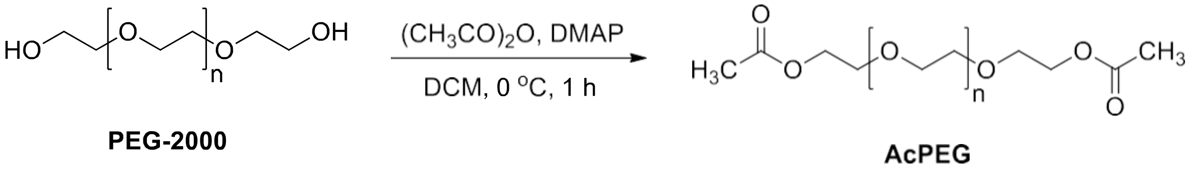
Instrument and Measurement

^1H and ^{13}C NMR spectra of the synthesized AcPEG were recorded on Jeol Delta 400 and 100.6 MHz spectrometers, respectively using tetramethylsilane (TMS) as an internal standard. Field emission scanning electron microscopy (FESEM) and energy dispersive spectroscopy (EDS) analysed using Hitachi S-3700 M microscope. Thermo gravimetric/differential thermal analysis (TG/DTA) of the homogenized reagent mixtures was also carried out using (Perkin-Elmer Diamond) system from room temperature to 1273 K at a heating rate of 10 K. UV-Vis. spectra were recorded on Perkin-Elmer Spectrometer Lambda 45 at 10^{-4} molar concentrations. Conventional excitation and emission spectra of the powder samples wererecorded using (Horiba Jobin–YvonFluorolog) modular spectrofluorimeter at room temperature using a Xenon lampas continuous source. Fluorescence decay curves were alsotaken on (Horiba Jobin–YvonFluoroCube) single photoncounting system.

Synthesis

Synthesis of Acetyl Polyethylene Glycol (AcPEG) polymer:

A solution of polyethylene glycol-2000 **(PEG-2000)** (5 g, 2.5 mmol) and 4 (dimethylamono)pyridine (DMAP) (76.25 mg, 0.625 mmol) in dichloromethane (50 mL), acetic anhydride (709 µL, 7.5 mmol) was added drop wise at 0ºC temperature with continuous stirring. After complete addition of acetic anhydride, the reaction mixture was stirred further for 1 h and completion of the reaction was monitored using thin layer chromatography (tlc). After completion of the reaction, solvent was evaporated over a rotary evaporator to obtain a thick gel. The crude product thus obtained was purified by column chromatography using 2% methanol in chloroform as eluent to afford pure acetyl polyethylene glycol (**AcPEG**). It was obtained as a white solid in 89% yield. **M.pt.**: 72-74 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 2.078 (s, 6H, $OCOCH_3$), 3.62 (d, 191H, J = 6.0 Hz, OCH_2O), 3.63-3.70 (m, 4H, OCH_2O), 4.20 (m, 4H, OCH_2O); **^{13}C NMR** (100.6 MHz, $CDCl_3$): δ 21.0 (CH_3), 63.6, 69.1, 70.5, 171.1 (C=O); **IR** (KBr, cm^{-1}): 3005, 2879, 1736 (C=O), 1454, 1352, 1292, 1243, 1093 (C-O), 947, 850, 748, 664 [14,15].

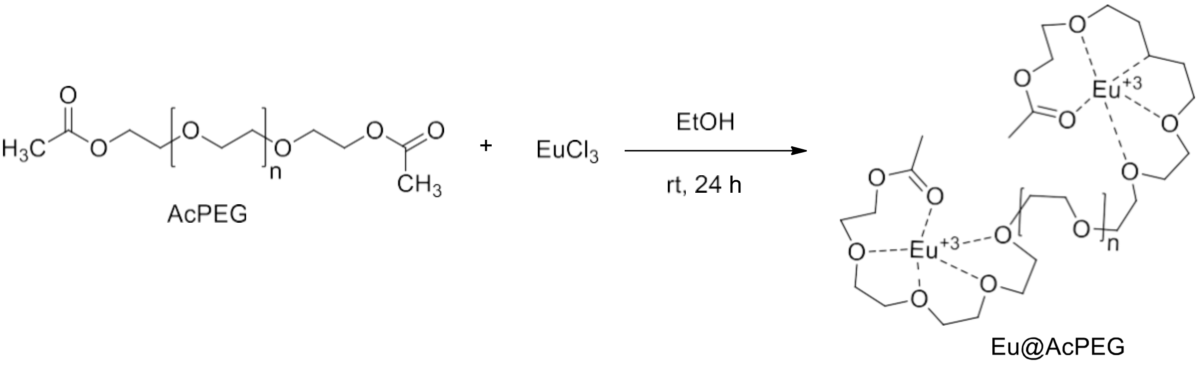


Scheme 1: Synthesis of acetyl polyethylene glycol (**AcPEG**)

In ^1H NMR spectra of AcPEG characteristic peak for six methyl protons was observed at δ 2.07 ppm and in ^{13}C-NMR spectra peaks for methyl and carbonyl groups were appeared at 21.0 and 171.1 ppm respectively.

Preparation of Eu-dopped acetyl polyethylene glycol (Eu@AcPEG) polymer:

A mixture of $EuCl_3$ and acetyl polyethylene glycol (0.5 – 6% w/w) in ethanol was stirred for 24 h at room temperature. Thereafter solvent was evaporated over a rotary evaporator to obtained a semi-solid **Eu@AcPEG**materials with different weight/weight (w/w) compositions ranging 0.5-6% (Scheme 2) [15].

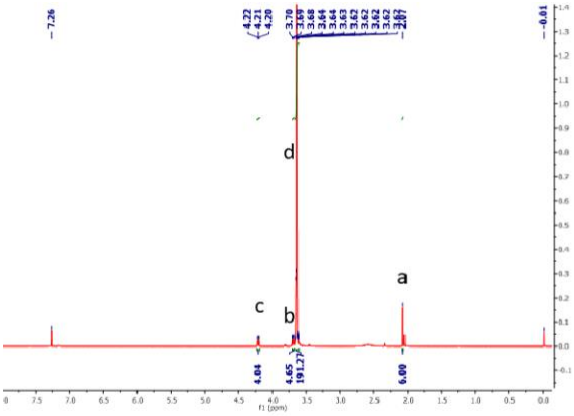


Scheme 2: Preparation of Eu-dopped acetyl polyethylene glycol (**Eu@AcPEG**)

3. Result and Discussion

Structural and Morphological properties of Eu@AcPEG

Present study was started from the synthesis of terminally acetyl polyethylene glycol (**AcPEG**) from polyethylene glycol (**PEG-2000**) by acetylation process using acetic anhydride in dichloromethane solvent at 0 ºC temperature. To analyse molecular structure and morphology of the product NMR spectra and SEM were taken of Eu@AcPEG as shown in figure 1-2 and figure 3-4 respectively. In ^{1}H NMR spectra of AcPEG characteristic peak for six methyl protons was observed at δ 2.07 ppm and in ^{13}C-NMR spectra peaks for methyl and carbonyl groups were appeared at 21.0 and 171.1 ppm respectively. In Fig. 1(A, b and c), SEM image, scanned area for EDX and EDX spectra respectively. Corn flex like irregular structure of AcPEG and Eu@AcPEG was observed. In EDX spectra the presence of Eu clearly observed in Eu@acPEG sample however there is no signal observed in AcPEG. Elemental (C, O and Eu) weight % of the samples are given in the inset table of figure 3c and 4c.



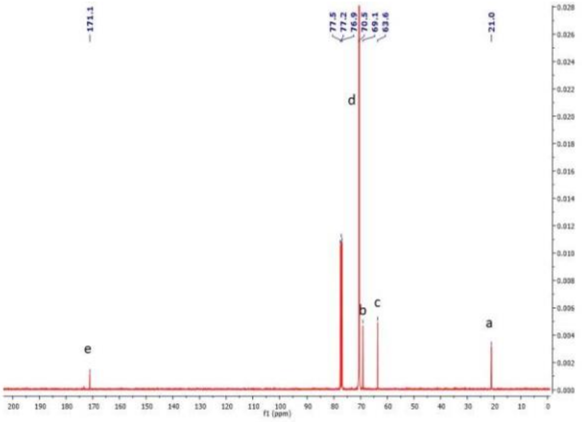
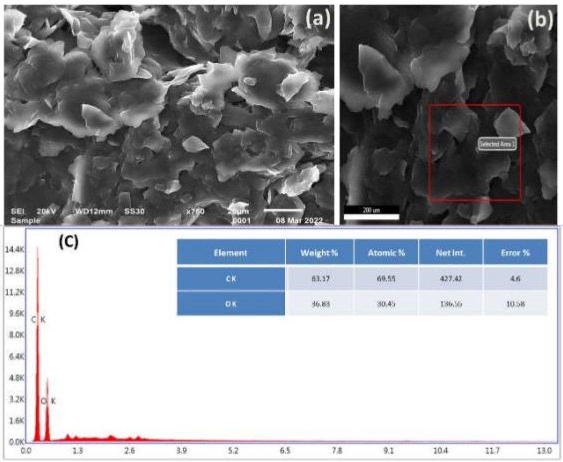
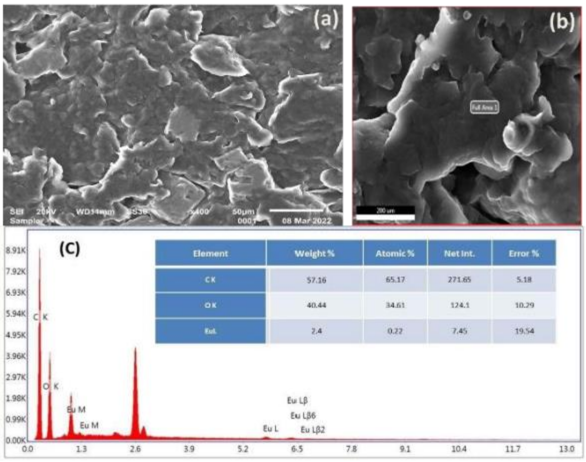


Figure 1: 1H NMR spectra of P8k in D2O at different concentrations (A) and those at 50 mg/mL under varied pH values

Figure 2: 1H NMR spectra of P8k in D2O at different concentrations (A) and those at 50 mg/mL under varied pH values



Element	Weight %	Atomic %	Net Int.	Error %
C K	63.17	69.55	427.42	4.6
O K	36.83	30.45	136.55	10.58



Element	Weight %	Atomic %	Net Int.	Error %
C K	57.16	65.17	271.65	5.18
O K	40.44	34.61	124.1	10.29
EuL	2.4	0.22	7.45	19.54

Figure 3: (a) SEM images of AcPEG (b) Scanned area for EDX spectra (c) EDX spectra with elements wt%

Figure 4: (a) SEM images of Eu@AcPEG (b) Scanned area for EDX spectra (c) EDX spectra with elements amount (wt%)

Thermal stability of Eu@AcPEG

Fig. 3 shows the TG/DTA curves of Eu@AcPEG recorded from temperature range 20-700 ºC in nitrogen environment. It is observed that the sample shows an endothermic peak for DTA at around 65 ºC, which is consistent with little weight loss (about 5%) in the same temperature range. The weight loss and heat absorbed by the sample is attributed to evaporation of absorbed water. Basically the decomposition of PEG began at around 395 ºC [Preparation and characterization of polyethylene glycol/poly(L-lactic acid) blends [16 Ioanna-Georgia Athanasoulia and Petroula A. Tarantili Pure Appl. Chem. 2017; 89(1): 141–152], however the decomposition of AcPEG at higher temperature than PEG. Based on the experimental result the onset temperature (T_{onset}) fount 335 ºC and the temperature of maximum thermal degradation rate (T_{peak}) at 420 ºCwere evaluated. It may be cause by the modification of two hydroxyl groups (-OH) at its both ends by the CH_2 group.

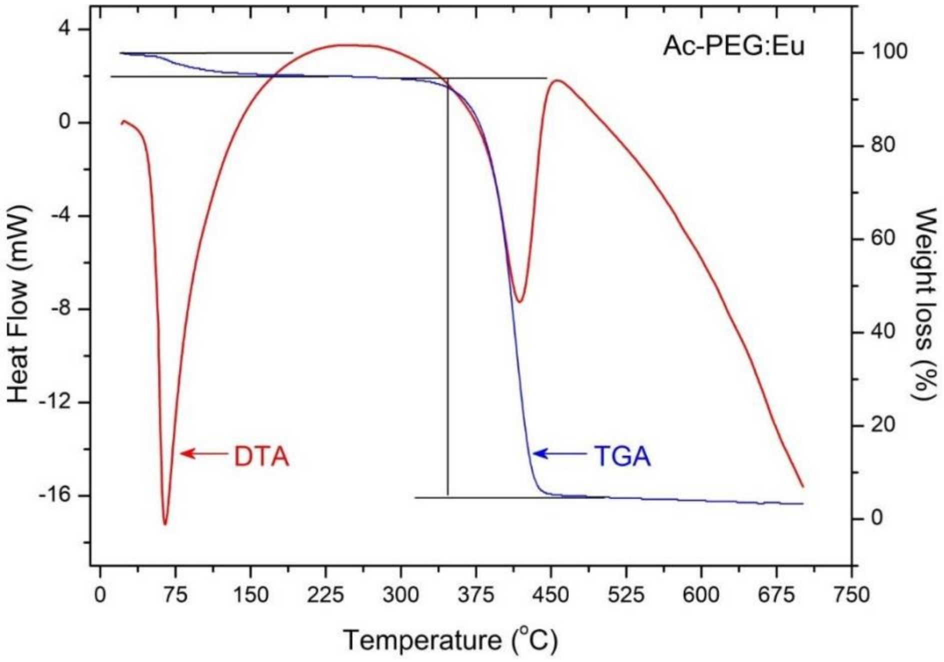


Figure 5: TG/DTA curves Eu@AcPEG derived polymer in nitrogen atmosphere.

UV-Visible properties

PEG, AcPEG and Eu@AcPEG samples were examined under the UV-Visible characterisation to explore the effect of Eu ions in the matrix AcPEG and acetylation of PEG. UV-visible spectroscopy, detect surface plasmon resonance (SPR) bands. Generally, the SPR bands are influenced by the size, shape, morphology, composition and dielectric environment of the material [17,18.]. In the present study acetyled PEG (AcPEG) shows three absorption bands at around 254, 284 and 235 nm as shown in figure 4. Despite various molecular modifications (acryloyl chloride, acetyl chloride, diacrylate, and thionyl chloride) not much change can be seen in pi-pi transition except for red or blue shift, however, on the higher wavelength side the absorption takes place according to the terminal modification. [19,20]. In the present study AcPEG shows 254 and 285 nm absorption band attributed to π-π* (CC) and n-π* () transition respectively. On adding Eu metal in AcPEG and PEG blue shift was observed in 254 nm peak while there is no shift observed in 285 nm peak. Eu@AcPEG exhibits a sharp absorption band at 227 nm and another at 285 nm.

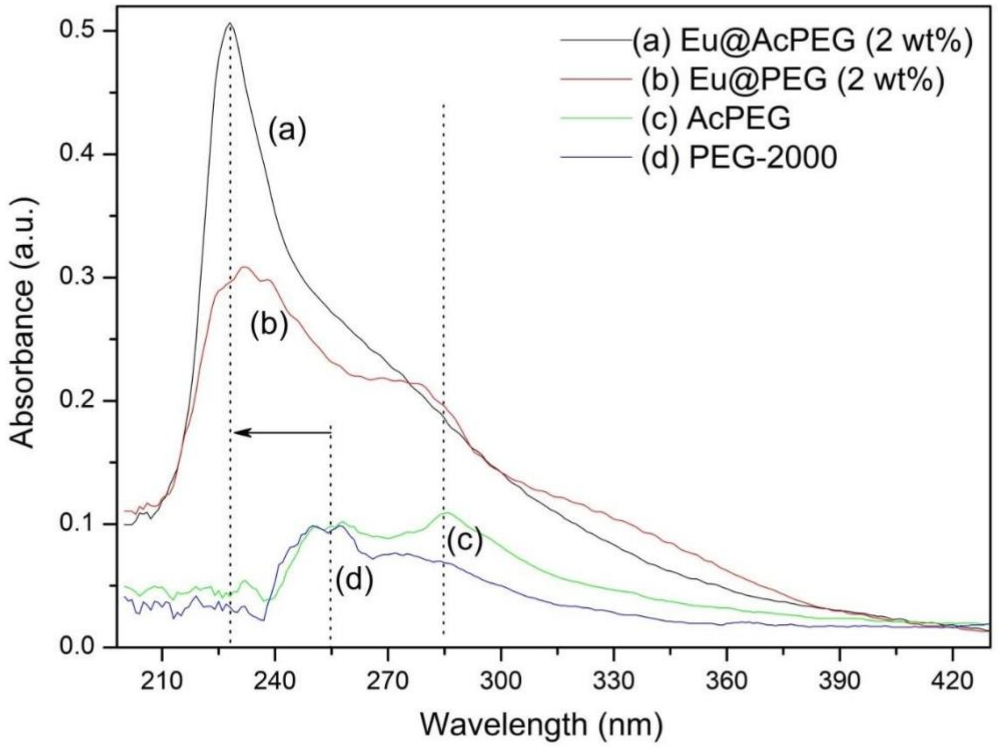


Figure 6: UV-Vis spectra of PEG, AcPEG, Eu@PEG and Eu@AcPEG

Photoluminescence properties of PEG/Ac-PEG@ Eu^{3+} Polymer

PEG exhibited fluorescence hardly in general, however oxidise PEG, composite form with inorganic and doped with transition/rare earth metal emit a strong emission [7-13]. The principal cause for the fluorescence is the oxidation improves the density of oxygen-contained group that creates probabilities for the crosslink of PEG chain. In this series, AcPEG a derived polymer from PEG was grown through end group (OH^-) of PEG modify by a functional groups dichloromethane (CH_2Cl_2). Samples of sufficient concentration in ethanol (150 mg/ml) of AcPEG and Eu@AcPEG were under fluorescence spectroscopy to check the effect on emission of Eu^{3+} metal ions. AcPEG sample exhibits two semi resolved emission peaks at 330 and 345 nm can be attributed most likely to the well-known CTE mechanism. Under this process the formation of clusters or a certain type of aggregation of the heteroatoms of the polymer chain [21-25]. Beside, in figure 4 can be seen that on adding Eu^{3+} metal ions sample Eu@AcPEG under excitation at 294 nm displays three bands in the ranges of 345nm, 405 nm and 570–730 nm corresponding to wide range UV-A , violet and deep red emissions, respectively. On the increasing the concentration of Eu^{3+} metal ions (from 0.5-6.0 wt%) the intensity of emission peak centred at 330 and 345 nm constantly decreased. Such type of emission quenching of PEG, between nontraditional intrinsic luminogens (NTIP) polymer and metal ions has been often considered as a static process, even though different mechanisms have been proposed [26-28]. On the other hand a new violet emission peak at 405 nm grows which increases exponentially as doping concentration increases while the emission at red region remain almost content. Thus, the violet emission band ascribed to the transition of $4f_6\,5^1$–$^4f^7$ of Eu^{2+} ion and the peaks of red emission in the range 570-730 nm is ascribed to the transition ^5D_o–^7F_J (J = 0, 1, 2, 3) of Eu^{3+} ion. Thus, in the Eu@AcPEG sample both species (Eu^{3+} and Eu^{2+}) are present due to the reduction of Eu^{3+} into Eu^{2+} ion. The larger charge/radius ratio is assumed to be responsible to donate them with a stronger electron-withdrawing ability among all the tested ions [29-31]

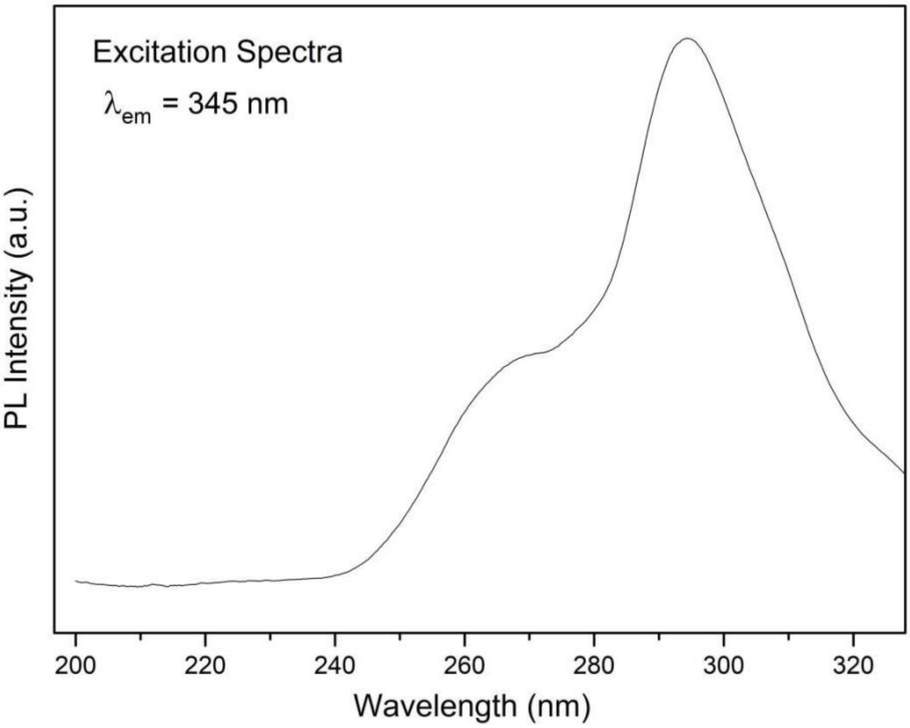


Figure 7: Excitation spectra of Eu@AcPEG (2.0 wt%) at emission 345 nm at room temperature.

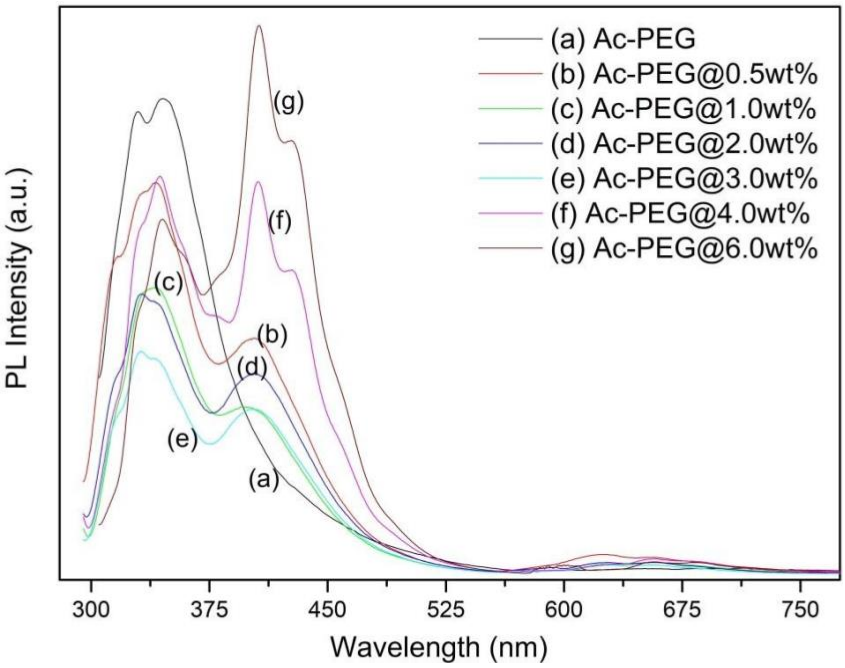


Figure 8: Emission spectra of Eu@AcPEG p (0-6.0 wt%) polymer at excitation wavelength 295 nm nm at room temperature

Thus the UV emission decreases and violet emission increases continuously with increasing the concentration of Eu^{3+} ions in AcPEG sample. The pattern profile of UV (345 nm) and violet (405 nm) emission and their ratio (violet/uv) shown in figure 7, it observed that the emission ratio of these two increases exponentially.

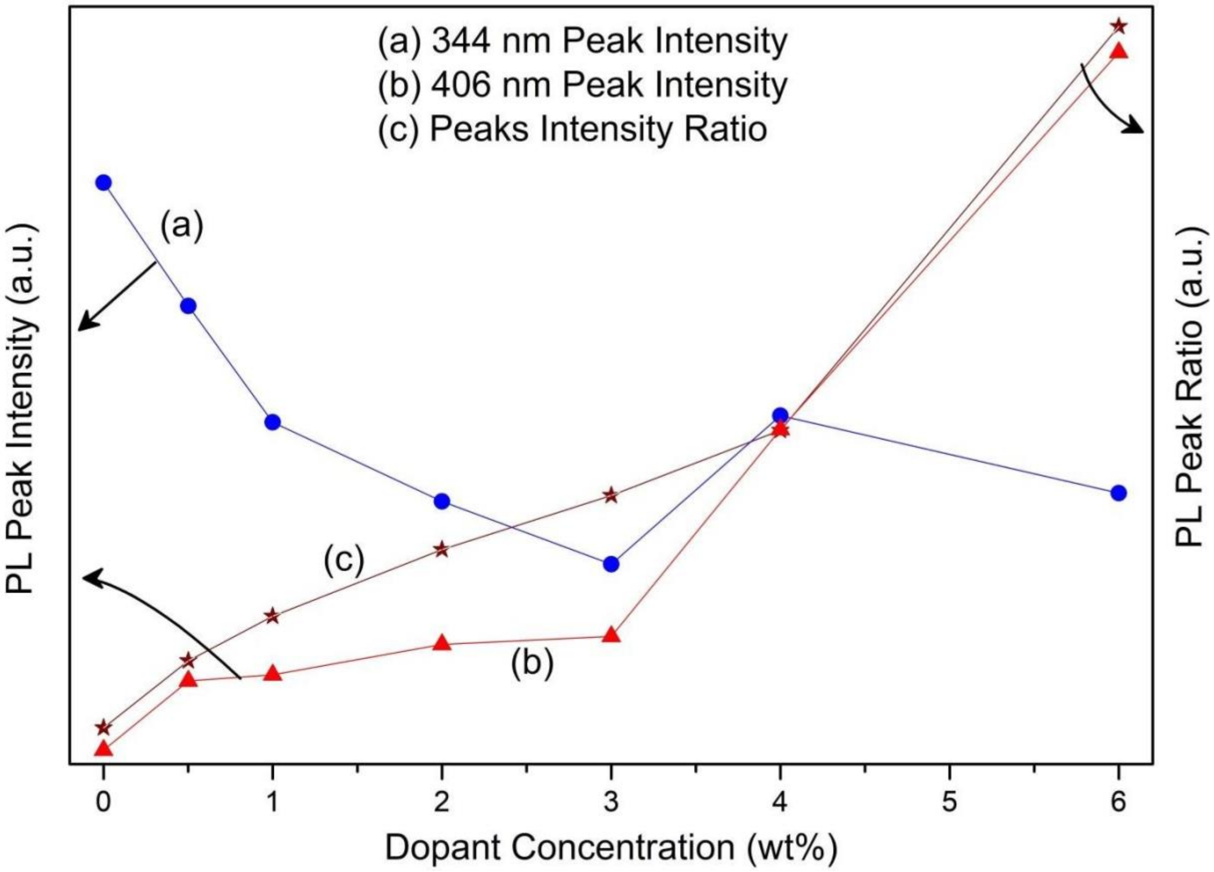


Figure 9: Emission intensity variation of UV-A (345 nm) and violet (405 nm) and their ratio

4. Conclusion

Acetyled PEG (AcPEG), a derived polymer from PEG was developed through a simple acetylation process. Terminal group (-OH) modification was confirmed by ^{1}H NMR spectra of AcPEG characteristic peak for six methyl protons was observed at δ 2.07 ppm and in ^{13}C-NMR spectra peaks for methyl and carbonyl groups were appeared at 21.0 and 171.1 ppm respectively. The optical absorption band of the PEG and AcPEG sample becomes wide on Eu metal incorporation. AcPEG sample exhibits strong emission in UV region. Eu@AcPEG sample shows an additional violet emission peak with UV emission. However, on increasing the Eu concentration, the UV emission starts decreasing and the violet emission starts increasing. Concluding, after acetylation fluorescence centres can be developed in PEG. Also the fluorescence properties of AcPEG can be tailored by adding the rare earth metal. Therefore, easy modification of the end group, solubility, nontoxicity, non-immunogenicity, economically cheap, and good compatibility with the environment make it a good candidate for photonics application. Rare investigated AcPEG needs more studiesto elaborate on its properties and applications

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