

# Synthesis and characterization of Poly ( $\epsilon$ -caprolactone)/ $\text{Fe}_3\text{O}_4$ -Safranin nanocomposites

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## ABSTRACT

Magnetic nanohybrid consists of nanosized ferrite and a dye safranin was prepared and characterized by various analytical methods. The HRTEM confirmed the size of the synthesized nanohybrid. The surface catalytic effect of nanohybrid towards the ring opening polymerization (ROP) of  $\epsilon$ -caprolactone (CL) was analyzed. ROP of CL was carried out under different  $[M/I]$  such as 10, 50, 100, 200 and 400 and the  $[M/C]=1000$  was maintained throughout the experimentation. Thus obtained PCL/nanocomposites were characterized by FTIR spectroscopy, UV-visible spectroscopy, Fluorescence spectroscopy, X-ray photoelectron spectroscopy, HRTEM etc. The binding constants were determined by using UV-visible and fluorescence spectra. This type of materials is very useful in the MRI field as a bio-imaging agent.

**Keywords:** ring opening polymerization, nanohybrid, synthesis, characterization

## I. INTRODUCTION

ROP of aliphatic cyclic esters are of great interest due to their wide applications in bio-medical field as a drug carrier, suture etc., Among the polyesters, PCL occupies the first because of its bio-compatibility with less cytotoxicity. ROP of  $\epsilon$ -CL can be done either by anionic or by cationic mechanism. For this purpose various chemical initiators are used. For example NaOH initiated ROP of  $\epsilon$ -CL was carried out by Monsalve et al(1). The hydroxyl group of carmine involved in the ROP of  $\epsilon$ -CL in the presence of stannous octoate as a catalyst(2). Hydroxyl vinyl butyl ether initiated ROP of  $\epsilon$ -CL was reported in the year 2010(3). Mesoporous PCL was obtained via the ROP in the presence of tartaric acid as an initiator (4). Other initiators were also used for the ROP of  $\epsilon$ -CL (5-8). By thorough literature survey we could not find out any report based on the safranin functionalized  $\text{Fe}_3\text{O}_4$  as a chemical initiator for the ROP  $\epsilon$ -CL. The novelty of the present investigation is fluorescent, amino functionalized, magnetic PCL was

synthesized by a one step eco-friendly bulk polymerization method.

## II. EXPERIMENTAL

### 1. Materials

Ferric chloride, Ferrous sulphate, Sodium hydroxide and safranin were purchased from nice chemicals, India. Double distilled water (DD water) was used for making solutions.  $\epsilon$ -caprolactone, stannous octoate were purchased from sigma Aldrich, USA and used as received. Chloroform and diethyl ether were purchased from spectra chemicals, India.

### 2. Synthesis of Safranin Functionalized $\text{Fe}_3\text{O}_4$

10g of ferric chloride was dissolved in 100mL DD water. 5g ferrous sulphate was dissolved in separate in 100mL DD water. Now this two solutions were mixed at room temperature under vigorous stirring conditions. After the Vigorous stirring for 5mins, Sodium hydroxide solution was added in a drop wise manner (100g NaOH dissolved in 100mL DD water). The addition process was continued for the next 2hrs. The  $\text{Fe}_3\text{O}_4$  formation was confirmed by the dark color precipitated. At the end of reaction, the reactants in a 500mL beaker was put on to a magnetic bar and kept in to for 5mins. The black color precipitated were settled down and the remaining supernatant solution were pipetted out. 50mL of fresh DD water was added to the  $\text{Fe}_3\text{O}_4$  nano crystals, stirred well and kept on the magnetic bar for 5 mins. In such a way the purification process was continued for 3 times. The excess NaOH,  $\text{FeSO}_4$  and  $\text{FeCl}_2$  were removed and dried at  $110^\circ\text{C}$  for 8 hrs. Thus obtained fine black powder is known as Ferrite. Thus obtained  $\text{Fe}_3\text{O}_4$  nano crystals were gained and stored in a Zipper lock cover. In the case of Safranin functionalized  $\text{Fe}_3\text{O}_4$  synthesis, the above said procedure was followed in the presence of 5g of Safranin Powder in 100 mL DD water. The end product has a dark brown coloration and this is known as Safranin functionalized  $\text{Fe}_3\text{O}_4$  nano hybrid system.

### 3. Synthesis of Safranin end capped PCI

The main aim of present investigation is find out a suitable application of synthesized nano hybrid system. In the present investigation, the catalytic activity of nano hybrid towards the ring opening polymerization of Caprolactone was tested. The procedure in brief is mentioned here. 1g of CL was accurately weighed in a 25mL capacity round bottomed flask. 0.001g of stannous octoate catalyst was added with the round bottomed flask. Required amount of nano hybrid was accurately weighed and mixed with the caprolactone. The ROP of CL was carried out at 5 different [M/I] such as 10, 50, 100, 200, 400. Here the [M/C] was maintained at 1000, after the physical mixing the round bottomed flask was kept in oil bath at 160°C. The round bottomed flask was heated under N<sub>2</sub> atmosphere at 160°C for 2 hrs. During the course of a reaction, the color of nano hybrid was changed became a highly viscous mass. Even though the ROP of CL was carried out by bulk polymerization method. It was further purified by reprecipitation method. The highly viscous mass was dissolved in 25mL Chloroform and reprecipitated by 250mL of diethyl ether. The total content was transferred into a 500mL beaker and evaporated to dryness and fumehood. After the evaporation, the aerial drying process a dark brown color product was obtained. This is again weighed and stored in a zipper lock cover. This product is known as Safranin end capped PCL.

### III. CHARACTERIZATIONS

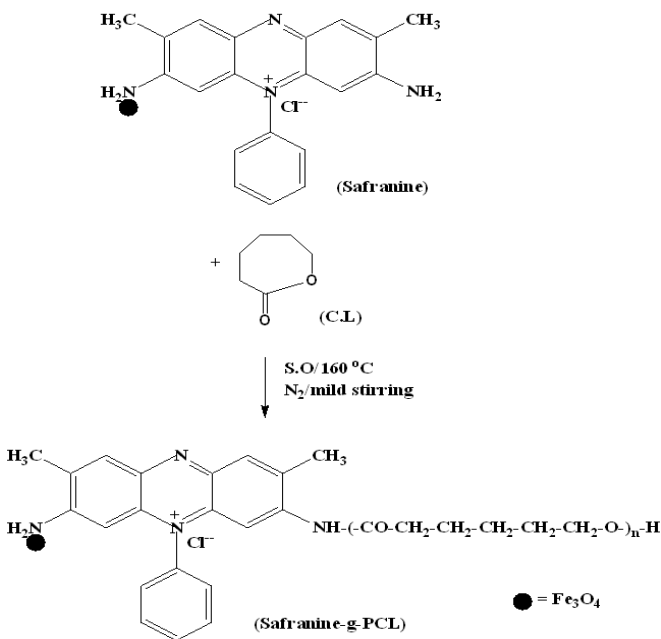
FTIR spectra were recorded with the help of Shimadzu 8400 S, Japan model instrument by KBr pelletization method from 400–4000 cm<sup>-1</sup>. 3 mg of polymer was ground with 200 mg of spectral grade KBr and made into a disc under the pressure of 7 tons. UV-visible spectrum was measured by dissolving the sample in chloroform solvent. The instrument used here is thermofisher Heliyas α (USA) from 200–800 nm. The same sample solution was subjected to fluorescence emission measurement from 350 to 700 nm by using Elico SL174 (India) Instrument. The melting temperature (T<sub>m</sub>) of the polymer samples were determined by using a Dupont Thermal Analyst 2000 Differential Scanning Calorimeter 910 S, USA model instrument. All the measurements were done under N<sub>2</sub> atmosphere in a temperature range of RT to 100 °C with 10 °C min<sup>-1</sup> heating rate. Field emission scanning electron microscopy (FESEM) was used to examine morphological behaviour of copolymer with the help of an FESEM, Hitachi S4800 Japan, instrument. Magnetic measurements were carried out with a superconducting quantum interference device magnetometer (Lakesore-7410-VSM, USA) with magnetic fields up to 7 T at 32 °C. The binding energy of the samples was determined by XPS(XPS, Thermo Scientific, Theta Probe, UK).

### IV. RESULTS AND DISCUSSION

#### 1. Characterization of Safranin Functionalized Fe<sub>3</sub>O<sub>4</sub>

Figure 1 a indicates the FTIR spectrum of pristine Fe<sub>3</sub>O<sub>4</sub>. A broad peak around 3500cm<sup>-1</sup> is due to the OH stretching. This is due to the water molecules intercalated with the Fe<sub>3</sub>O<sub>4</sub>. A doublet peak around 620 cm<sup>-1</sup> is attributed to the metal oxide stretching. Figure 1b explains the FTIR spectrum of pristine safranin molecules. The peaks at 3173 and 3324 cm<sup>-1</sup> are corresponding the aromatic C-H symmetric and anti symmetric stretching respectively.

A hump at 3395 cm<sup>-1</sup> explains the NH stretching of safranin. The C-N stretching of safranin is confirmed by noting a peak at 1330 cm<sup>-1</sup>. The chloride iron stretching is appeared at 440 cm<sup>-1</sup>. The aromatic CH bending vibration can be seen at 834, 874 and 945 cm<sup>-1</sup>. The benzenoid stretching of safranin is appeared at 1605 cm<sup>-1</sup>. Fig 1c represents the ferrite-safranin hybrid system. Here also one can see peaks corresponding to aromatic and aliphatic CH stretching, metal oxide stretching, C-N stretching and chloride iron stretching.



Scheme-1. Synthesis of Safranin-g-PCL

Appearance of these peaks confirmed that the hybrid formation is simply a surface adsorption process.

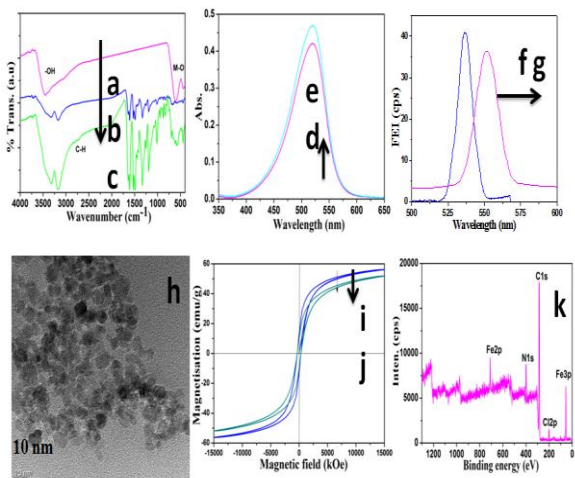


Fig. 1: FTIR spectrum of (a) Fe<sub>3</sub>O<sub>4</sub>, (b) Fe<sub>3</sub>O<sub>4</sub>-Safranine, (c) Safranine, UV-visible spectrum of (d) Safranine, (e) Fe<sub>3</sub>O<sub>4</sub>-Safranine, Fluorescence emission spectrum of (f) Safranine, (g) Fe<sub>3</sub>O<sub>4</sub>-Safranine, (h) HRTEM of Fe<sub>3</sub>O<sub>4</sub>, VSM of (i) Fe<sub>3</sub>O<sub>4</sub>, (j) Fe<sub>3</sub>O<sub>4</sub>-Safranine, XPS of (k) Fe<sub>3</sub>O<sub>4</sub>-Safranine.

The UV-visible spectrum of safranine before and after hybrid formation is shown in figure 1 as d,e respectively. Safranine shows one peak at 520nm. After the hybrid formation (fig 1e) Safranine exhibits the peak at 520nm. The results indicate that even after the hybrid formation the absorbance peak position is not shifted. This confirmed the surface functionalization of ferrite by the Safranine moieties. Generally the metaloxide surface functionalization accord through the physisorption process. In the present investigation the amino group of Safranine must be physically adhered on the Fe<sub>3</sub>O<sub>4</sub> surface. Figure 1 f, g indicates the fluorescence emission spectrum of Safranine before and after hybridization. The pristine Safranine exhibits and emission peak at 536.6nm whereas the hybrid exhibits and emission peak at 551.7nm. The red shift in the emission peak confirmed the surface functionalization of Fe<sub>3</sub>O<sub>4</sub> by the Safranine molecules. Figure 1h represents the HRTEM of Safranine functionalized Fe<sub>3</sub>O<sub>4</sub> molecules. The size of the Fe<sub>3</sub>O<sub>4</sub> determined as 10-15nm. The image also indicates the partly agglomerated structure of Safranine functionalized Fe<sub>3</sub>O<sub>4</sub>. The VSM group of Fe<sub>3</sub>O<sub>4</sub> before and after functionalization with Safranine is shown in fig 1 i,j respectively. The pure Fe<sub>3</sub>O<sub>4</sub> shows the VSM value of 56.4emu/g whereas the hybrid exhibits VSM value of 51.7emu/g. the decrease in VSM value confirmed the surface functionalization

Fe<sub>3</sub>O<sub>4</sub> by safranine molecules. Figure 1k represents the XPS of Safranine functionalized Fe<sub>3</sub>O<sub>4</sub>. The XPS indicates the Fe2p(212.5), N1s(399.7), C1s(284.3), C2p(201.1) and Fe3p(52.7)eV. The appearance of N1s, C1s, C2p confirmed the functionalization of Fe<sub>3</sub>O<sub>4</sub> by Safranine molecules.

## 2. characterization of safranine functionalized fe<sub>3</sub>o<sub>4</sub> end capped pcl

The PCL/Fe<sub>3</sub>O<sub>4</sub>-safranine nano composites were characterized by various analytical techniques. The forthcoming session narrates the discussion on the PCL nano composite system.

### 2.1 FTIR study

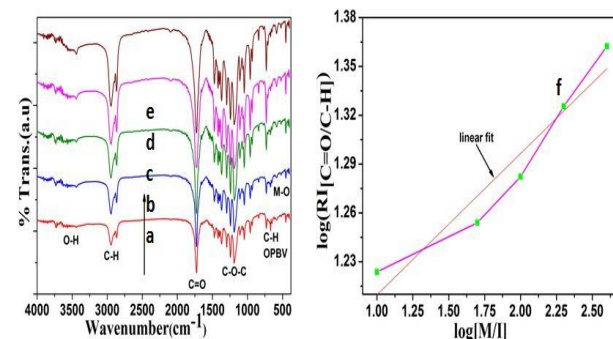


Fig. 2: FTIR spectrum of PCL synthesized at various [M/I] of (a) 10, (b) 50, (c) 100, (d) 200, (e) 400, (f) plot of log[M/I] versus log(RI[C=O/C-H]).

Figure 2 represents the FTIR spectrum of PCL synthesized at various [M/I]. The [M/I] was varied between 10 to 400 (Fig. 2 a-e). The other experimental conditions were kept constant. The important peaks are characterized below a small peak at 3452 cm<sup>-1</sup> is due to the OH stretching of PCL. The CH symmetric and anti symmetric stretchings are observed at 2865 and 2951 cm<sup>-1</sup> respectively. The C=O stretching of PCL is appeared at 1724 cm<sup>-1</sup>. The ester C-O-C linkage of PCL is appeared at 1189 cm<sup>-1</sup>. The CH OPBV is appeared at 729 cm<sup>-1</sup>. The Fe-O stretching is appeared at 455 cm<sup>-1</sup>. the C-N stretching of safranine is appeared at 1366 cm<sup>-1</sup>. Thus the FTIR spectrum confirmed the functionalities present in the PCL nano composite system. The important point noted here is while increasing the [M/I] the corrected peak area of C=O stretching is linearly increased. Further the CH OPBV is also linearly increased while increasing the [M/I]. This is due to the decrease in initiator concentration and hence the availability of initiating sites are less. As a result of decrease in initiator concentration the molecular weight of PCL should be increased. Our previous publication

confirmed the order of same (JPR). In order to confirm the order of ROP of CL in the presents of hybrid system as an initiator the plot of  $\log[M/I]$  Vs  $\log RI_{[C=O/C-H]}$  (fig 2f) was made and the slope value was noted as 0.09. This indicates that in order to form 1 mole of PCL less than 0.1 mole of initiator was required. This confirmed the catalytic activity of  $Fe_3O_4$  and initiating capability of safranin molecules.

## 2.2 UV-visible spectroscopy

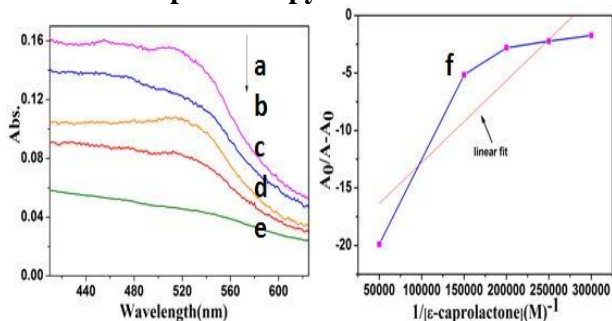


Fig. 3: UV-visible spectrum of PCL synthesized at various  $[M]$  of (a) 0.50 g, (b) 1.50 g, (c) 2.0 g, (d) 2.5 g, (e) 3.0 g, (f) plot of  $(1/\text{weight of monomer})$  versus  $[A_0/A-A_0]$ .

In order to find out the interaction between the initiator and polymer UV-visible study was carried out (i.e) binding constant was determined at various  $[M]$ . Here the  $[M]$  was varied between 0.5 to 3.0g while keeping the other experimental conditions were constant. While increasing the  $[M]$  the absorbance value of UV-visible spectrum at 526nm (fig. 3 a-e) was found to be decreased. This is due to the sharing initiator by more and more polymer chains. In order to find out the binding constant the plot of  $1/\text{weight of CL}$  Vs  $A_0/A_0-A$  (fig 3.f). The slope value was determined as  $1.13 \times 10^{-6}$ . This binding constant value explained the interaction between nano hybrid PCL chains.

## 2.3 Fluorescence spectroscopy

Figure 4 a-e represents the fluorescence spectrum of PCL nano composite synthesized at various  $[M]$  by keeping the other experimental conditions were constant. The system produced an emission peak at 604.7nm. While increasing the  $[M]$  the FEI of PCL nano composite were found to be reduced. This is due to the quenching effect of CL and also the sharing of initiator by more number of polymer chains. In order to find out the binding constant the plot of  $\log(\text{weight of CL})$  Vs  $\log I_0-I/I$  fig 4.f were drawn. The plot shows two regions. While increasing the  $\log$  weight of CL the  $\log I_0-I/I$  value was slowly increased up to 3.3 thereafter the Y

axis value was steeply increased. In order to find out the slope value linear fit was made and the slope value was determined as 0.54 as a binding constant. From the intercept value the number of binding site were determined as 1.5. We know that safranin contains two amino groups. Hence this two amino groups must be involved in the ROP of CL. The final product will have a safranin bridged PCL. It means both the amino groups of safranin were attached with the PCL chains.

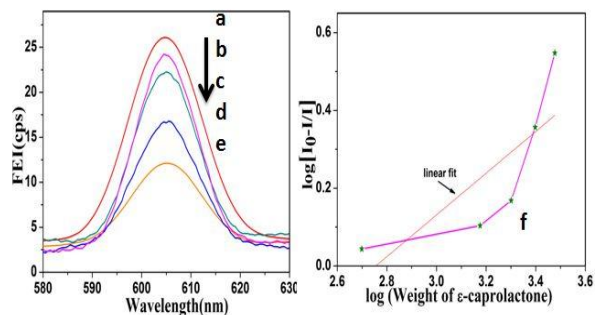


Fig. 4: Fluorescence emission spectrum of PCL synthesized at various  $[M]$  of (a) 0.50 g, (b) 1.50 g, (c) 2.0 g, (d) 2.5 g, (e) 3.0 g, (f) plot of  $\log(\text{weight of monomer})$  versus  $\log(I_0-I/I)$ .

## 2.4 DSC study

The role of nano hybrid initiating system on the melt transition behavior of PCL was studied and indicates in fig 5(a-e). It was found that while increase in the  $M/I$  the  $T_m$  value of PCL was slowly increased from 58 to 64°C.

And also the melt transition peaks informed that at higher  $M/I$  the crystallinity of PCL was reduced. The increase in  $T_m$  value of PCL can be ascribed to the increase in molecular weight of PCL. It means that the weight average molecular weight of the polymer was increased when the initiator molecules are less.

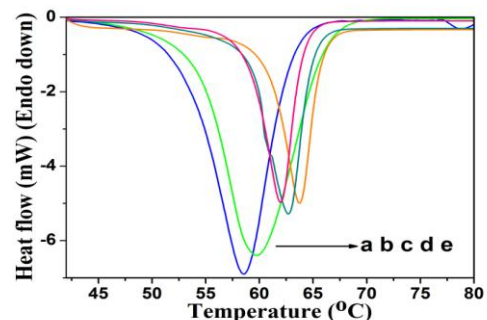


Fig. 5: DSC of PCL synthesized at various  $[M/I]$  of (a) 10, (b) 50, (c) 100, (d) 200, (e) 400

## 2.5 HRTEM, VSM and XPS study



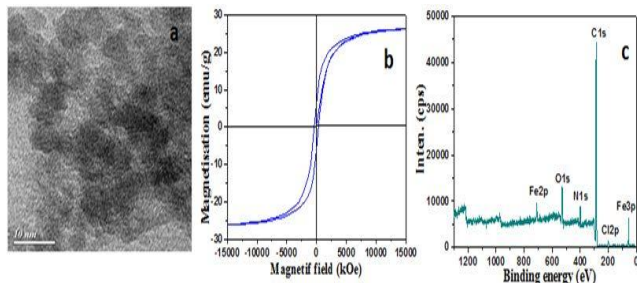


Fig. 6: (a) HRTEM of PCL, (b) VSM of PCL, (c) XPS of PCL nano composite

Figure 6 a indicates the HRTEM of PCL nano composite synthesized at  $M/I=100$ . The size of the ferrite nano particle was determined as less than 10nm. Figure 6 b indicates the VSM loop of PCL nano composite system synthesized at  $M/I=100$ . The magnetization value was determined at 25.4 emu/g. This is definitely lower than that of pristine ferrite and its hybrid. The encapsulation effect is responsible for such a low magnetization value. Figure 6 c represents the XPS of PCL nano composite system synthesized at  $M/I=100$ . The XPS is similar to that of XPS of hybrid system. The important point noted here is the intensity of C1s at 287.9eV was increased due to the PCL chains. Thus the XPS confirmed the PCL nano composite formation.

## V. CONCLUSIONS

The niche points are summarized here as conclusions. A peak at  $1605\text{ cm}^{-1}$  corresponding to the benzenoid structure of safranin confirmed the nano hybrid formation. The UV-Visible spectrum declared the surface functionalization of  $\text{Fe}_3\text{O}_4$  by safranin through the amino group of safranin. The nano hybrid exhibited the particle size of 10 – 15 nm with agglomerated structure. The decreasing VSM value from 56.4 to 51.7 emu/g confirmed the surface functionalization of  $\text{Fe}_3\text{O}_4$  by safranin. The binding constant value ( $1.13 \times 10^{-3}$ ) was determined from the UV – visible spectroscopy for the polymer nano composite system. The fluorescence emission spectrum informed the number of binding sites at 1.5. The DSC study confirmed the polymer formation

through the  $T_m$  value. The HR-TEM determined the  $\text{Fe}_3\text{O}_4$  particle size as less than 10 nm. The encapsulation of  $\text{Fe}_3\text{O}_4$  by PCL further confirmed by VSM measurement and the value was determined as 25.4 emu/g.

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