Synthesis and characterizations of novel acid functionalized and fluorescent poly(ε-caprolactone)

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Abstract ε-Caprolactone (CL) was subjected to ring opening polymerization (ROP) under inert (nitrogen) atmosphere at 413 K for 1 h in the presence of stannous octoate (SO) as a catalyst and Eosin Y, a xanthenes type dye as a novel chemical initiator. The ROP was carried out at two different experimental conditions, namely at various concentrations of initiator and monomer, to get more scientific information from the resultant product. Thus, obtained Eosin Y conjugated poly(ε-caprolactone) (PCL) was characterized by different analytical tools like FTIR spectroscopy, NMR spectroscopy, gel permeation chromatography (GPC), UV–Visible spectroscopy, photoluminescence (PL) spectroscopy, X-ray photoelectron spectroscopy (XPS), and differential scanning calorimetry (DSC). Finally, the morphology of the Eosin Y conjugated PCL was studied by scanning electron microscopy (SEM). The binding constant (K) was determined from both UV–Visible spectroscopy and PL spectroscopy, and the static quenching mechanism was proposed. The number of binding site (n) was also determined from PL spectroscopy and the results were compared with the FTIR-RI method.

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Introduction

The current research and development in the polymeric drug delivery systems is timely with the advances in understanding the disease related mechanisms. This relies on the development of novel polymeric architectures and appropriate synthetic methodologies to tailor their physicochemical properties. However, even if synthetic polymer-based drug delivery systems have been applied in drug delivery for the last 50 years, there are few examples of these macromolecules being used successfully in clinics and it is worth to have a look on them and persevere investigating their production by cleaner, more efficient, and less expensive ways without environmental pollution issues. The use of ε-caprolactone (CL) as a polymerization monomer offers the potential to produce biodegradable polymers in a reaction that proceeds under mild catalytic conditions. The absence of a need for purification and desiccation steps for the monomers and catalyst is a great benefit in terms of reducing the process energy required for this catalytic system. Poly(ε-caprolactone) (PCL) is one of the most attractive aliphatic polyesters, because of its widely recognized biodegradability and unique compatibility with a large range of polymers. PCL can be easily subjected to ring opening polymerization from CL by heating in the presence of a suitable catalyst. Wang et al. [1] reported about the ring opening polymerization (ROP) of CL with yttrium triflate catalyst in the presence of different initiators and they analyzed the efficiency of initiators towards % yield, molecular weight of polymer and polydispersity. In 2002, Schenk et al. [2] compared the initiating efficiency of Sn(IV) and Al(III) initiators toward the ROP of lactones and lactides. Hydrolytic polymerization of CL by triphenyl tin acetate was carried out and zero order kinetics with respect to monomer and first order

kinetics with respect to catalyst was evaluated [3]. Bulk polymerization of CL with rare earth phenyl initiators were carried out with high yield and higher molecular weight and the products were analyzed by FTIR and H^1-NMR spectra [4]. Report on the bulk polymerization of CL with different initiating systems is available in the literature [5–11].

Recently, fluorescent polymers have attracted considerable attention because of their potential applications in different fields [12–15] particularly in bio-imaging [16]. Among the commercially available dyes, we are very much interested in xanthenes type dyes particularly Eosin Y, because of its moderate electronic excited state (E_s 53.16 kcal/mol) [17, 18]. Generally, the fluorescent polymers are synthesized in three steps [19] namely, (1) synthesis of polymers, (2) functionalization of polymer chain ends, and (3) conjugation of dyes with polymer chain end. This consumes a lot of time, toxic solvents, and not an economically cheaper one. Moreover, the dye molecules are made up by complicated fused aromatic rings, difficult to bio-degradation process. Recently, Zhang et al. [20] reported about the synthesis of fluorescent PCL by difluoroboron dibenzoylmethane initiator. Further, the fluorescent polymer was characterized by UV–visible spectroscopy, PL spectroscopy, and NMR spectroscopy. Even then, after the synthesis of fluorescent polymer, there was no functional group for further structural modification. Moreover, the binding constant and number of binding sites were not determined.

In order to solve the above mentioned problems, the present investigation was undertaken, i.e., one step synthesis of fluorescent acid functionalized polymer without environmental pollution. The present work was undertaken to study the polymerization of CL in the presence SO as the catalyst and Eosin Y dye as an initiator by bulk polymerization method under nitrogen atmosphere, resulting in a fully bio-degradable and acid functionalized fluorescent polymer, for the first time. The molecular weight and molecular weight distribution of the polymer samples were investigated. This type of material is suitable for cancer treatment.
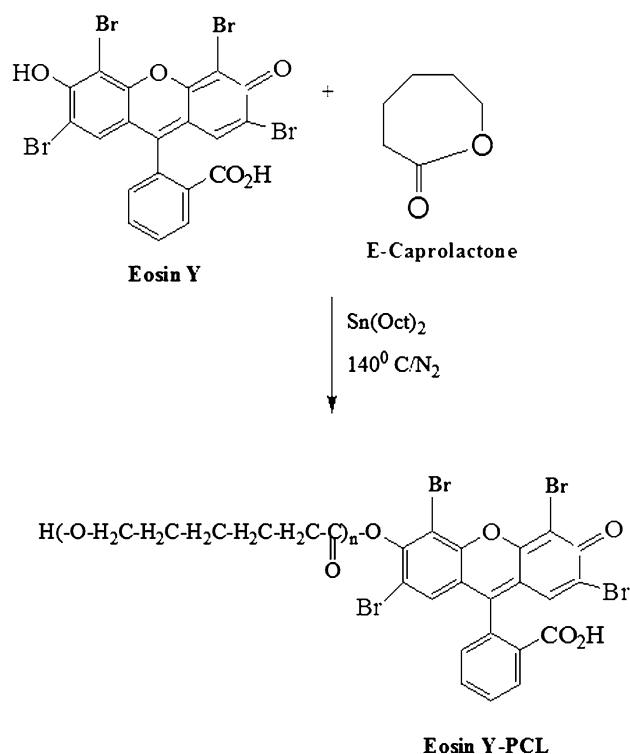
Experimental

Materials

Stannous(II)-2-ethyl hexanoate (SO, Across Chemicals, USA), ε-Caprolactone (CL, Across Chemicals), 2-(2,4, 5,7-tetrabromo-6-hydroxy-3-oxo-3*H*-xanthen-9-yl) benzoic acid (Eosin Y, Aldrich Chemicals, USA) were freshly purchased and used as such. $CHCl_3$ solvent was purchased from Aldrich Chemicals. Dietylether, non-solvent, was purchased from Aldrich Chemicals and used as received.

Synthesis of Eosin Y tagged PCL

Eosin Y tagged PCL was synthesized by bulk polymerization method. A typical polymerization procedure is as follows: 0.10 mM of SO (catalyst) was taken in a 25 mL capacity two necked round bottom flask and 100 mM of CL (monomer) and 0.02 g of Eosin Y (initiator) were charged and mixed well for 120 s. After mixing, the temperature was raised to 413 K for bulk polymerization under nitrogen purging. After 3600 s of ROP, highly viscous liquid was obtained. Now the liquid was cooled, dissolved in chloroform, and re-precipitated by the addition of diethylether. Further, the sample was washed with de-ionized water to remove the un-reacted dye molecules and the water washing was repeated for three or more times till the filtrate became colorless, if the un-reacted dye molecules are present. The polymer samples were subjected to freezing and dried under freeze drier. The dried samples were collected, weighed, and stored in a vial. The ROP of ε-CL was carried out with five different Eosin Y concentrations as follows: the monomer/initiator $[M_0/I_0] = 10$, 50, 100, 200, and 400. The monomer/catalyst $= 1000$. The reactions are mentioned in Scheme 1. In order to calculate the binding constant (K) and number of initiating sites (n),

Scheme 1 Ring opening polymerization of caprolactone of Eosin Y

the ROP of ε-CL was carried out at five different monomer concentration variations.

Characterization

FTIR spectra for the samples were recorded with the help of Perkin Elmer Spectrum 100 series instrument by KBr pelletization method from 400 to 4000 cm^{-1}. 3 mg of Eosin Y tagged PCL sample was grinded with 200 mg of spectral grade KBr and made into a disk under the pressure of 7 tons. After proper baseline corrections the corrected area of the peaks corresponding to carbonyl stretching (1726 cm^{-1}) and C–H out of plane bending vibration (730 cm^{-1}) were determined and the relative intensity (RI) was calculated as below.

$$\text{RI of } [\text{C=O/C-H}] = A_{1726}/A_{730} \tag{1}$$

Jasco V-570 instrument was used for the UV–Visible spectrum measurement. 2 mg of Eosin Y tagged PCL sample was dissolved in 10 mL of acetone under ultrasonic irradiation for 10 min and subjected to UV–Visible spectral measurements. H^1 and C^{13} nuclear magnetic resonance (NMR) (500 MHz) spectra were obtained using an NMR apparatus (Varian, Unity Inova- 500 NMR) at room temperature in CDCl$_3$ solvent. DSC was measured by using Universal V4.4A TA Instruments under nitrogen atmosphere at the heating rate of 10 K/min from room temperature to 373 K. The second heating scan of the sample was considered in order to delete the previous thermal history of the sample. Photoluminescence spectrum was measured with the help of PL, Jasco Model FP-6000, Japan, instrument from 400 to 700 nm. The samples prepared for the above said UV–Visible spectral measurements were subjected to PL spectrum too. A Waters 2690 gel permeation chromatography (GPC) instrument was used to determine the M_n and M_w of the polymer samples by using tetrahydrofuran (THF) as an eluent at room temperature at the flow rate of 1 mL min^{-1} against polystyrene (PS) standards. Scanning electron microscope (SEM) of Eosin Y conjugated PCL sample was recorded with the help of JSM 6300 instrument, a Jeol product. The shorter wavelength UV-lamp was purchased from Spectroline UV-lamp, Japan. The binding energy of Eosin Y–PCL system was determined by XPS, (XPS, Thermo Scientific, Theta Probe, UK).

Results and discussion

FTIR study

Eosin Y initiated ROP of CL was carried out in the presence of SO under nitrogen atmosphere at 413 K with mild

stirring condition by bulk polymerization method. Eosin Y has two types of functional groups such as –OH and –COOH, in which the –OH group is involved in the ROP of CL and the –COOH group is present as a functional group for further structural modification like drug loading. In the present investigation, the ROP of CL was carried out at five different $[M_0/I_0]$ ratios such as 10, 50, 100, 200, and 400.

The FTIR spectrum of Eosin Y initiated ROP of CL is given in Fig. 1. Figure 1a indicates the FTIR spectrum of PCL–Eosin Y with the $[M_0/I_0]$ = 10. The OH chain end or carboxyl group of Eosin Y was appeared as a broad peak around 3500 cm^{-1}. The C–H symmetric and anti-symmetric stretching was appeared at 2859 and 2942 cm^{-1}, respectively. The ester carbonyl stretching was observed at 1726 cm^{-1}. A peak at 1042 cm^{-1} explained an ester C–O–C linkage [2]. The C–H out of plane bending vibration was observed at 730 cm^{-1}. Br from Eosin Y unit was seen at 583 cm^{-1}. The FTIR spectra of PCL–Eosin Y with $[M_0/I_0]$ values of 50, 100, 200, and 400 are mentioned in Fig. 1b–e, respectively. For the sake of convenience, the FTIR spectrum of Eosin Y is given in supporting information as Fig. S1. The important point noted here is while increasing the $[M_0/I_0]$ value, the relative intensity of the ester carbonyl peak is also increased simultaneously and which suggests the increase in PCL chain length with molecular weight.

Figure 2 indicates the log–log plot of $[M_0/I_0]$ versus $\text{RI}_{[\text{C=O/C–H}]}$. While increasing the $[M_0/I_0]$ values, the RI of [C=O/C–H] was increased linearly (Table 1). This is due to the following reasons: while increasing the $[M_0/I_0]$ ratios, the concentration of initiator was decreased and the active site available for the initiation of ROP of CL was reduced. Availability of less initiating species activated the chain growth and resulted with the increase in molecular weight of PCL. As a result of increase in molecular weight, the
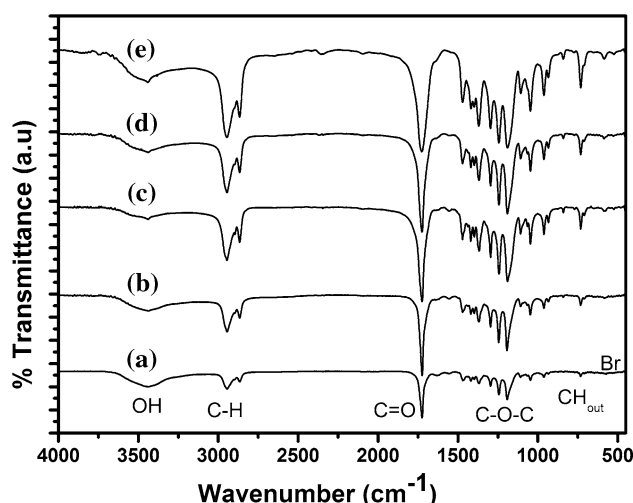

Fig. 1 FTIR spectrum of Eosin Y tagged PCL with the $[M_0/I_0]$ ratio of (a) 10, (b) 50, (c) 100, (d) 200, (e) 400

$RI_{[C=O/C–H]}$ was increased. In order to find out the order of ROP reaction, the above said log–log plot was made and the slope value was determined as 0.45 which indicated the 0.50 order of ROP of CL. $R_{ROP} \alpha [M_0/I_0]^{0.45}$, where the R_{ROP} is the rate of ROP reaction. It indicates that 0.50 mol of Eosin Y is required to initiate 1 mol of CL. The increase in $RI_{[C=O/C–H]}$ with the increase in $[M_0/I_0]$ ratios confirmed the increase of degree of polymerization (D_P) of PCL with simultaneous increase in molecular weight. Recently, Anbarasan and co-workers utilized the FTIR-RI method to calculate the order of functionalization reaction in polyolefins [21–23], order of ketone, and olefin formation reactions in poly(vinyl alcohol) during an aqueous treatment [24–26] and % amino and % imino forms in poly(aniline)s [27–29]. Based on these reports, we applied the FTIR-RI method to the present investigation to determine the order of ROP reaction for the first time.

NMR analysis

The H^1-NMR spectrum of Eosin Y initiated ROP of CL is shown in Fig. 3a. The structure of **3** is confirmed by the NMR signals as mentioned in Fig. 3a. The data is mentioned below: 1.38 ppm (m, 3-CH$_2$), 1.65 (m, 2-CH$_2$ + 4-CH$_2$), 2.31 (t, 5-CH$_2$), 3.65 (t, 6-OH), 4.02 (t, 1-CH$_2$), 6.86 (t, 8-CH), 7.08 (s, 9-CH), 7.45(d, 7-CH). Appearance of an aromatic proton signal confirmed the presence of Eosin Y at the chain end of PCL (**3**). Further, the structure was confirmed through C^{13}-NMR spectrum. Figure 3b represents the C^{13}-NMR spectrum of **3**. Appearance of a peak at 62.64 ppm confirmed the chemical conjugation of Eosin with PCL chain. The data is given below: **1** 64.14, **2** 28.34, **3** 24.56, **4** 25.52, **5** 34.11, **6** 173.56, and **7** 62.64 ppm. Thus, the H^1-NMR and C^{13}-NMR spectra

confirmed the chemical conjugation of Eosin Y at the chain end of PCL. As mentioned in Table 1, the % conversion of CL was quantitatively calculated from H^1-NMR spectrum for all samples (**1–5**). The results indicated that 79–100% conversion of CL was observed while varying the $[M_0/I_0]$ from 400 to 10. This proves that Eosin Y is an efficient initiator for the ROP of CL even at lower concentration. Moreover, the initiator efficiency values (Table 1) are increased with the increase of $[M_0/I_0]$ values. This concluded that at lower concentration of Eosin Y, with minimum number of initiating species, it exhibited the maximum efficiency with the increase in molecular weight of PCL. The increase in weight average molecular weight with the increase of $[M_0/I_0]$ value is shown in Table 1. Zhang et al. [30] reported about the calcium methoxide initiated ROP of ε-caprolactone and L-lactide. Bulk polymerization of ε-caprolactone at 393 K showed that the initiator efficiency increased with the M_n with the simultaneous increase in $[M_0/I_0]$ for per unit of calcium atom. In the present investigation also the initiator efficiency increased with the increase in $[M_0/I_0]$ values with simultaneous increase of both M_n and M_w.

GPC measurement

The effect of $[M_0/I_0]$ ratios on the molecular weight of PCL was studied by using poly(styrene) as a standard. While increasing the $[M_0/I_0]$ ratios, both the M_n and M_w were increased (Table 1). The increase in molecular weight is due to the decrease in the initiating sites, which co-ordinates the ROP of CL in an ordered manner. While varying the $[M_0/I_0]$ ratios from 10 to 400 (**1–5**), the M_w was varied from 3.1×10^3 to 12.3×10^3 g/mol. The GPC traces of **1–5** are indicated in Fig. 4a–e. This indicates that at lower concentration of initiator only we can get higher molecular weight of PCL. In the present investigation, the polydispersity (PD) value was varied between 1.14 and 1.23 while varying the $[M_0/I_0]$ values and this confirmed the narrow molecular weight of Eosin Y initiated ROP of CL. While increasing the $[M_0/I_0]$ ratios, the M_w is increased. This confirmed the increase in chain length of PCL with simultaneous increase of M_w. While increasing the $[M_0/I_0]$ values, the D_P value is also increased. When the $[M_0/I_0]$ value is 10, the D_P value is 21 whereas the D_P value is 102 when the $[M_0/I_0]$ value is 400. This confirmed the efficient initiating nature of Eosin Y for the ROP of CL by bulk polymerization method. Currently, Yan et al. [31] reported about the M_w of amino functionalized PCL and its copolymers. They reported about high molecular weight polymer for longer reaction time (12 h). In the present investigation, moderate molecular weight PCL was obtained with acid functionalization within 2 h of ROP reaction.
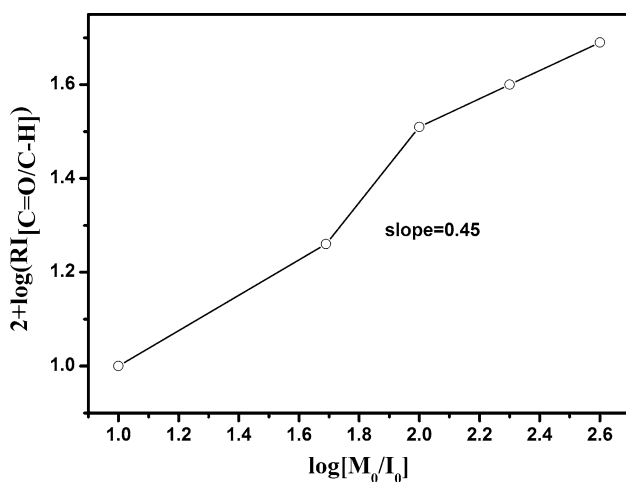

Fig. 2 Effect of $[M_0/I_0]$ on the $RI_{[C=O/C–H]}$

Table 1 Effect of $[M_0/I_0]$ on the % conversion, FTIR-RI, molecular weight, and T_m of Eosin Y tagged PCL

$[M_0]/[I]_0$	Code	Conversion (%)[a]	IE[b]	RI[c]$_{[C=O/C–H]}$	$M_n^d \times 10^{-3}$	$M_w^d \times 10^{-3}$	M_w/M_n^d	DP[e]	T_m (°C)[f]
10	**1**	100	43.8	0.10	2.6	3.1	1.17	21.1	54.3
50	**2**	97	136.3	0.18	3.7	4.2	1.14	31.8	55.6
100	**3**	91	147.8	0.32	7.6	8.9	1.17	72.8	56.9
200	**4**	85	231.6	0.39	8.3	10.2	1.23	84.6	57.8
400	**5**	79	361.8	0.48	9.9	12.3	1.23	102.1	60.9

[a] Monomer conversion: $\{([M]_0 - [M])/[M]_0\} \times 100$, determined from H^1-NMR spectrum

[b] Initiator efficiency $= M_{n(cal)}/M_{n(exp)}$; $M_{n(cal)} = [MW_{CL}] \times [M/I] \times$ (% conversion)

[c] Relative Intensity: determined from FTIR spectrum (A_{1726}/A_{730})

[d] GPC data

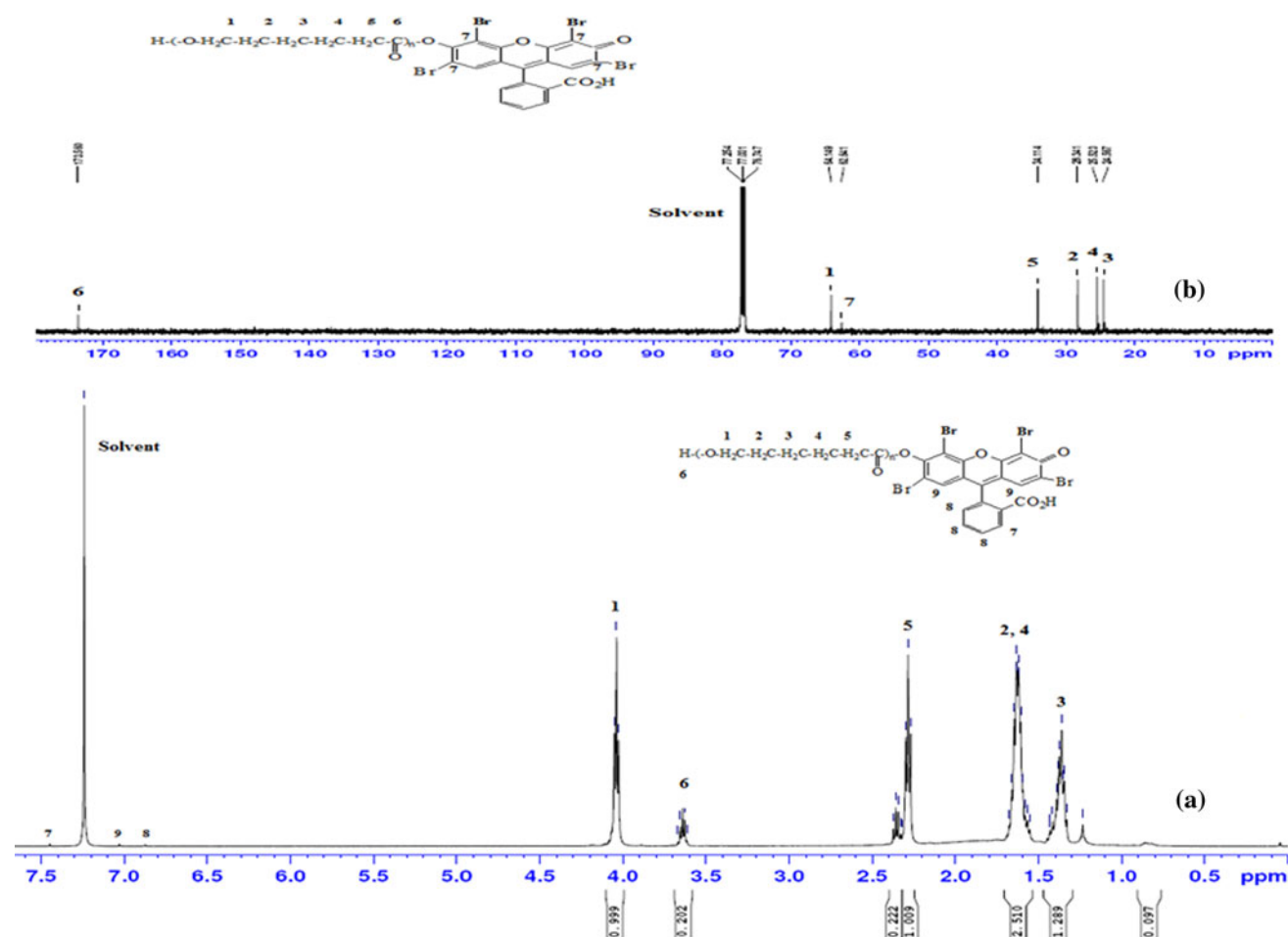[e] DP $= M_w$ of PCL/weight of CL

[f] T_m determined from DSC experiment

Fig. 3 a H^1-NMR and **b** C^{13}-NMR spectrum of PCL–Eosin Y with $[M_0/I_0] = 100$

DSC profile

The melting temperature (T_m) of Eosin Y initiated ROP of CL was determined by DSC method. Figure 5 indicates the DSC thermograms of **1–5**. Figure 5a represents the DSC thermogram of **1** with the T_m of 327.15 K. Figure 5b–e shows the DSC thermogram of **2**, **3**, **4**, and **5**, respectively. While increasing the $[M_0/I_0]$ values the T_m values are increased. This can be explained as below: (1) while increasing the $[M_0/I_0]$ values, the concentration of initiator
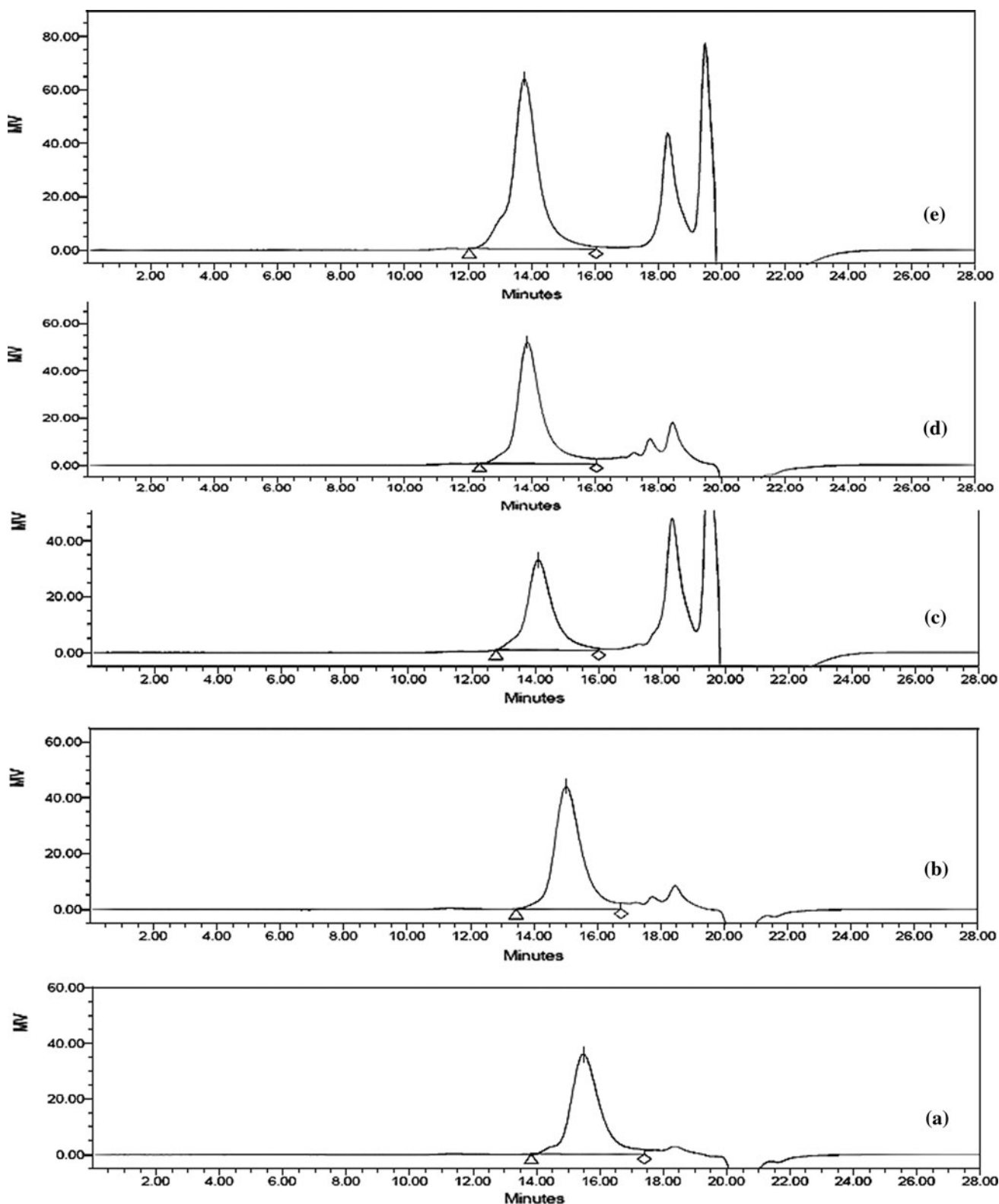
Fig. 4 GPC of PCL with the $[M_0/I_0]$ value of (a) 10, (b) 50, (c) 100, (d) 200, (e) 400

(Eosin Y) was decreased. As a result of decrease in initiator concentration, the number of initiating sites or species is decreased and increase of molecular weight of the polymer.

(2) The increase in molecular weight of the polymer was responsible for the increase in T_m value. The increase in M_w with the increase in $[M_0/I_0]$ was confirmed already by
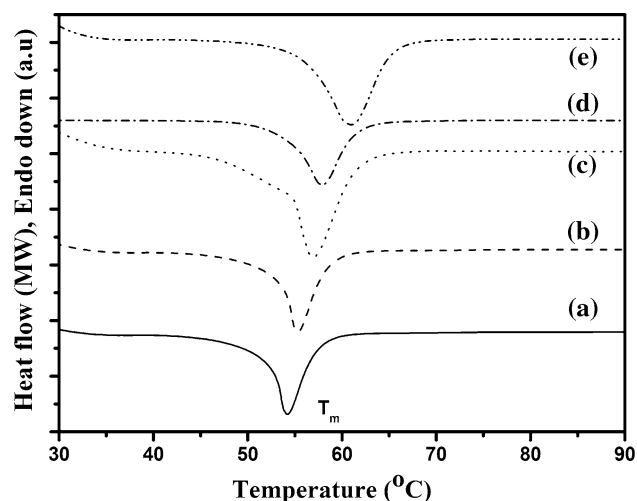
Fig. 5 DSC heating scan of PCL–Eosin Y with the $[M_0/I_0]$ value (*a*) 10, (*b*) 50, (*c*) 100, (*d*) 200, (*e*) 400

the GPC method. The final conclusion from the DSC analysis is while increasing the $[M_0/I_0]$ values the corresponding T_m values are increased due to the decrease in the number of initiating sites. Table 1 shows the data. Currently, Lin et al. [32] reported about the T_m of hetero-nucleo-base functionalized PCL. Our report coincides with their report.

XPS history

Figure 6a exhibits the XPS of pristine Eosin Y. The spectrum showed many peaks among which we are very much interested in C1*s*, O1*s*, and Br3*d* binding level of Eosin Y. Peaks corresponding to the above said level are observed at 281.9, 530.8, and 91.9 eV, respectively. Appearance of these three peaks confirmed the chemical compositions of Eosin Y, the other peaks are corresponding to the metal oxides present in the Eosin Y. Figure 6b
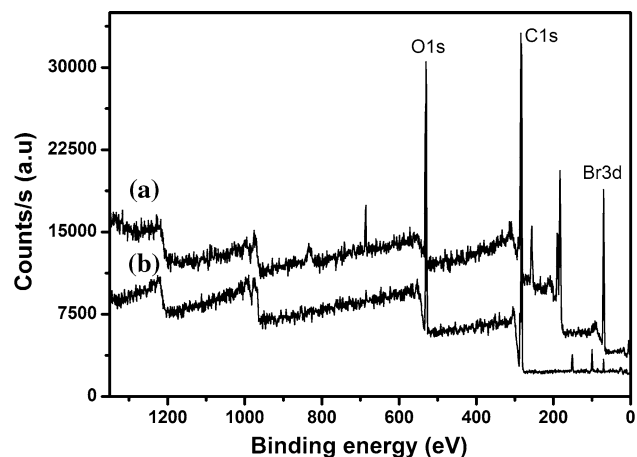

Fig. 6 XPS of (*a*) Eosin Y, (*b*) PCL–Eosin Y with $[M_0/I_0] = 100$

indicates the XPS of **3**. Here also the above said peaks are observed without any change in the binding energy level. This confirmed the Eosin Y tagged PCL structure. While comparing the % content of Br in the pristine Eosin Y (28.11%) and **3** (3.71%), the later one exhibited lower % of Br due to the lower concentration of Eosin Y used for the initiation of ROP of CL.

SEM report

Figure 7 indicates the surface morphology of Eosin Y tagged PCL (**3**). Figure 7a–d indicates the dried leaf like morphology with micro pores. Generally, the micro pores containing compounds are used as a drug carrier [33]. The SEM surface analysis indicates that PCL–Eosin Y system is a suitable candidate for the drug carrier applications. The poly(ethylene glycol) macro initiator initiated ROP of CL showed a porous PCL with coarser like structure [34]. This concluded that the surface morphology of PCL depends on the nature and molecular weight of an initiator used for the ROP of CL.

UV–Visible study

At 140 °C, the Eosin Y initiated ROP of CL in the presence of SO was carried out at various concentrations of CL through the co-ordination-insertion mechanism. At the end of the ROP of CL, one end of PCL chain is occupied with the Eosin Y whereas the other end is occupied by OH group. In this situation it is necessary to find out the binding constant and the number of binding sites required for the ROP of CL. This can be done with the aid of two helping tools, namely UV–Visible spectroscopy and PL spectroscopy. Figure 8 represents the UV–Visible spectrum of Eosin Y-PCL systems synthesized at various concentrations of CL. Figure 8b–f indicates the UV–Visible spectrum of PCL–Eosin Y systems synthesized at various [CL]. The absorbance value at 540.7 nm was decreased with the increase of [CL]. In this experiment, the $[M_0/I_0]$ value was maintained at 100. For the sake of comparison, the UV–Visible spectrum of pristine Eosin Y is represented in Fig. 8a with the high absorbance value at 516.7 nm. After the ROP of CL in the presence of Eosin Y by bulk method, the absorbance peak was red shifted to 540.7 nm with the decrease in absorbance value. The red shifting and decrease in absorbance value of Eosin Y confirmed the existence of sigma bond between Eosin Y and PCL chain.

The binding nature of Eosin Y with CL through ROP can be determined based on the Benesi–Hildebrand approach [35] based on the UV–visible spectroscopy. The plot of reciprocal of the differences in the absorbance spectra at 566 nm elicited by CL addition versus the
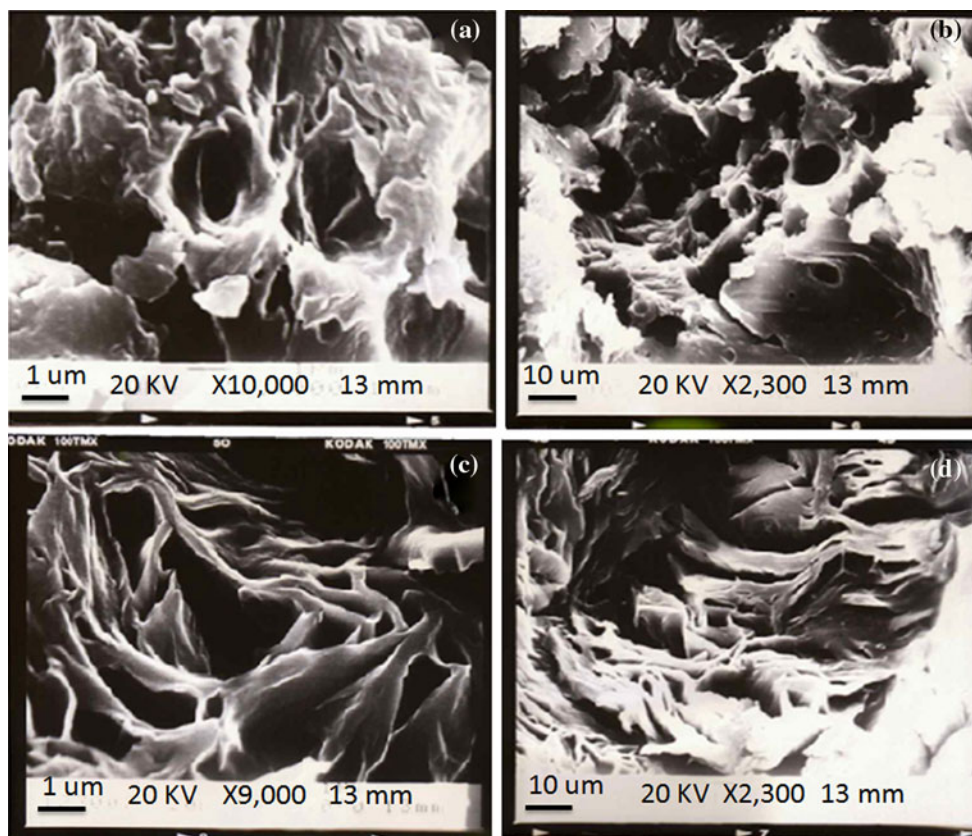
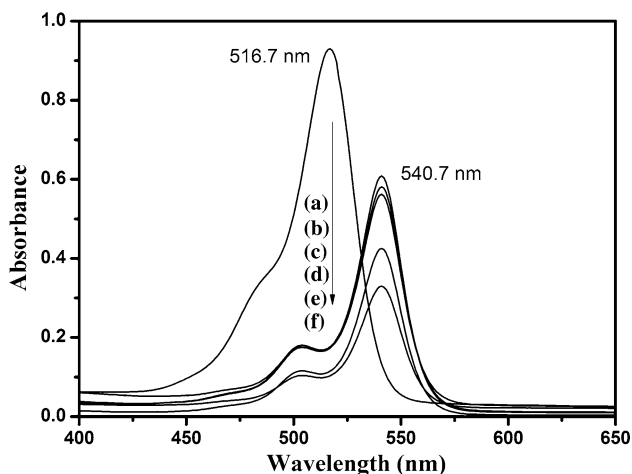**Fig. 7** SEM of PCL–Eosin Y with the $[M_0/I_0] = 100$

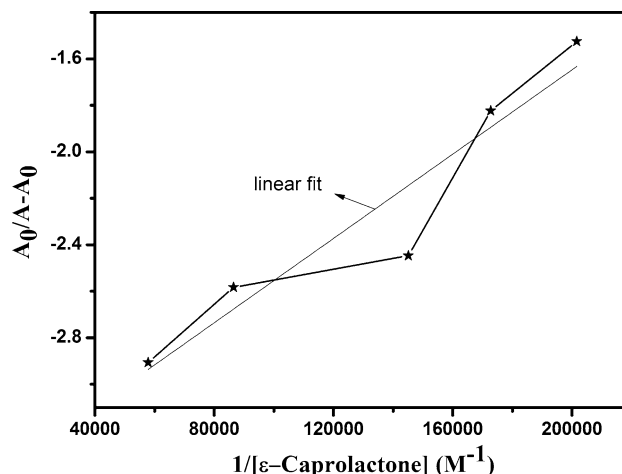**Fig. 8** UV–Visible spectrum of Eosin Y tagged PCL at different [CL]

Fig. 9 Plot of effect of [CL] on UV–Visible absorbance at 540.7 nm

reciprocal of the [CL]. From the ratio between the intercept and the slope of the plot (Fig. 9) the value of K was obtained as 3.8×10^5 M^{-1}. In 2009, Hajian et al. [36] studied the interaction between doxorubicin dye and DNA. They reported that while increasing the concentration of DNA, the absorbance of doxorubicin was decreased

continuously. The binding constant, K, was determined as 3.2×10^4 L/mol. In the present investigation, the K-value was determined as 3.8×10^5 M^{-1} and this high value is due to the bulk polymerization method. The higher K-value confirmed the existence of strong chemical interaction between PCL and Eosin Y, i.e., existence of a sigma bond between them.

PL characterization

Figure 10 indicates the PL spectrum of PCL–Eosin Y system, while varying the [CL]. The spectrum showed that while increasing the [CL], the PL intensity was decreased. Figure 10a–e indicates the same. For the sake of comparison the PL spectrum of pristine Eosin Y at the same concentration of PCL–Eosin Y system is shown in the inset. Eosin Y after binding with PCL, the emission peak was red shifted to 558.5 nm with decrease in PL intensity. The high difference in the intensity confirmed the existence of strong sigma bond interaction between Eosin Y and PCL. The decrease in PL intensity can be explained on the basis of static quenching mechanism [35]. The static mechanism is supported by the following evidences: (i) PCL was synthesized at higher temperature by bulk polymerization method and hence absence of a new complex formation peak in the UV–Visible spectrum, (ii) a bathochromic shift in the UV–Visible spectrum strongly supported the static quenching rather than the dynamic quenching.

The left inset of Fig. 10 indicates the photograph of UV irradiated PCL–Eosin Y samples synthesized at different $[M_0/I_0]$. Sample **1** with higher Eosin Y concentration exhibited the more brightness under UV irradiation whereas the sample with lower concentration of Eosin Y (**5**) exhibited less brightness due to the lower concentration of Eosin Y as well as the quenching effect of PCL. The color is also changed from yellow to green. It is true that the PCL is not a fluorescent polymer by nature. After conjugation with a dye (Eosin Y), the PCL becomes fluorescent. In the present investigation, the non-fluorescent PCL is converted into a fluorescent PCL by simple ROP method in the presence of Eosin Y. While increasing the $[M_0/I_0]$, the color of PCL was varied from yellow to green. This can be
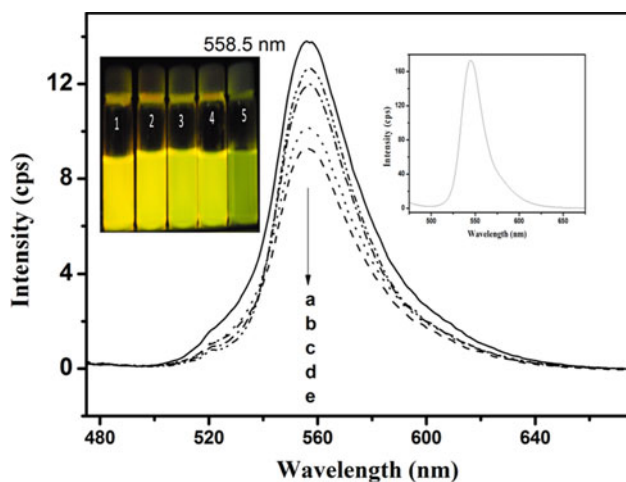
explained by two factors, namely (i) concentration of Eosin Y and (ii) molecular weight of PCL. While decreasing the concentration of Eosin Y, the color becomes pale (VIBG-YOR concept) and appears like a greenish one. Moreover, while reducing the concentration of Eosin Y, the number of initiating species is reduced and resulting with high molecular weight PCL. This concept was proved by GPC results. The high molecular weight PCL is acting as a quencher and decreases the intensity of yellow light. The intensity of yellow light was decreased step by step while increasing the $[M_0/I_0]$ and finally it formed a greenish color.

In order to determine the binding constant and number of binding sites, the modified Stern–Volmer equation was utilized for this purpose based on the PL spectroscopy. The equation is mentioned below

$$\log[(F_0 - F)/F] = \log K - n\log[Q] \qquad (2)$$

where F and F_0 are the fluorescence intensities with and without CL (quencher Q), K is binding constant, and n is number of biding sites. These two parameters can be determined from plotting $\log[(F_0 - F)/F]$ vs. $\log[Q]$ (Fig. 11). The slope and intercept values yielded the number of binding sites and binding constant, respectively, by linear fit method. The K-value was determined as 80×10^{-2} and the n value was calculated as 0.32 ($\sim$0.50).

Eosin Y contains one free hydroxyl group and one carboxyl group. The free hydroxyl group has the capability of initiating the ROP of CL. In the present investigation, the OH group was involved in the ROP of CL. This concept was already confirmed by FTIR, UV–Visible, PL, GPC, NMR, and DSC experiments. The FTIR-RI method indicated that 0.50 mol of Eosin Y is required to initiate 1 mol of CL. The same is supported by the n value ($\sim$0.50). This again confirmed that the free OH group only involved in the ROP of CL and the one end of PCL chain was occupied

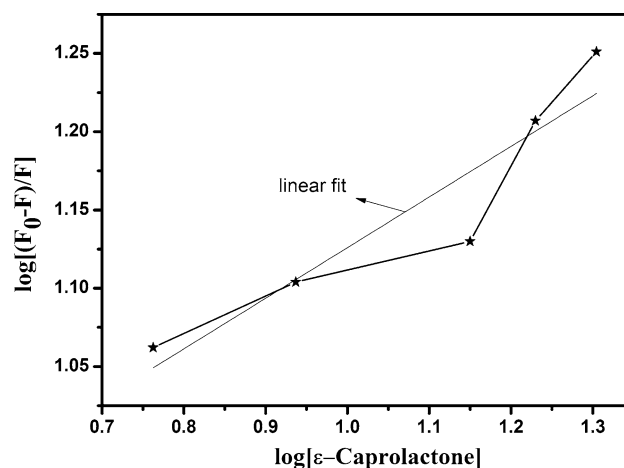**Fig. 10** PL spectrum of Eosin Y tagged PCL at different [CL]

Fig. 11 Plot of effect of [CL] on PL intensity of Eosin Y tagged PCL

with Eosin Y unit whereas the other end of PCL was caped with OH group. This concluded that the carboxyl group of Eosin Y was as such and available for further structural modification. In such a way this method is an economically cheaper one rather than the conventional three-step method for the synthesis of acid functionalized PCL.

Conclusions

In conclusion, poly(ε-caprolactone) was synthesized by bulk polymerization method in the presence of SO and Eosin Y at 413 K under nitrogen atmosphere at different $[M_0/I_0]$ values. The FTIR spectrum confirmed the functional groups like ester (1042 cm^{-1}), carboxyl ketone (1726 cm^{-1}), and Br (583 cm^{-1}) in the samples **1–5**. Both the H^1 and C^{13} NMR spectra confirmed the chemical structure of Eosin Y conjugated PCL. The molecular weight was increased with the increase in $[M_0/I_0]$ values from 10 to 400 and the corresponding weight average molecular weight was increased from 3050 to 12285 g/mol. When the $[M_0/I_0]$ value was 400, the corresponding T_m was determined as 333.9 K from the DSC analysis. The UV–visible spectrum showed the blue shifting for the samples **1–5** due to the chemical sigma binding of Eosin Y at the chain end of PCL. The PL spectrum informed the decrease in intensity for the **1–5** systems. XPS confirmed the decrease in Br % content in the sample **3** than in the pristine Eosin Y. The SEM morphology confirmed the micro pores structure of Eosin Y conjugated PCL. The binding constant, K, was determined as 80×10^{-2} and the number of binding site was calculated as 0.50 from the PL spectrum by modified Stern–Volmer equation and supported by the FTIR-RI method.

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