Synthesis of fluorescent diblock copolymer nanoparticle supported catalyst for the reduction of Cr(VI), p-nitrophenol and rhodamine 6G dye: a comparative study

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Abstract. A fluorescent diblock copolymer nanocomposite (DBCNC) was synthesized by ring opening polymerization (ROP) method using rhodamine 6G (R6G) dye as an initiator through bulk polymerization technique. ROP of caprolactone was carried out at 160°C for 2 h under nitrogen atmosphere in the presence of stannous octoate ($\text{Sn}(\text{Oct})_2$) as a catalyst followed by the ROP of tetrahydrofuran in the presence of phthalicanhydride as a co-monomer. Thus, synthesized fluorescent DBCNC was characterized by various analytical tools such as FTIR spectroscopy, UV–visible spectroscopy fluorescence emission spectroscopy, DSC, TGA and FESEM. The catalytic reduction of p-nitrophenol (NiP), Cr(VI) and R6G was carried out in the presence of DBCNC as a catalyst with the help of UV–visible spectrophotometer. The apparent rate constant (k_{app}) and induction time (T_i) were determined from the UV–visible spectral data. The nanosized V_2O_5 was prepared by a simple chemical reduction of bulk-sized V_2O_5 by using sodium borohydride (NaBH_4) as a reducing agent. During the DBC formation, 0.01 g of nanosized V_2O_5 was added. This type of polymer supports the catalyst which is very much useful in the catalysis industry because of its easy separation and recyclable property.

Keywords. Synthesis; diblock copolymer; characterization; catalytic reduction; Cr(VI).

1. Introduction

Poly(ϵ -caprolactone) (PCL) is one of the most important bio-medical polymers and is used as a drug-carrier material because of its bio-compatibility and bio-degradability [1,2]. The applications of PCL are restricted to some extent due to its water insoluble nature. To increase its water solubility, it is block copolymerized with some water miscible monomers by using different techniques. The diblock copolymer (DBC) of PCL is reviewed in this paper. In 2005, PCL-based liquid crystalline DBC was synthesized and characterized thoroughly [3]. A RAFT technique was adopted for the synthesis of PCL-based DBC [4]. A DBC between PCL and MMA was prepared by living ring opening polymerization (ROP) method [5].

A coupled RAFT and ROP was carried out for the preparation of DBC between vinyl pyrrolidone and caprolactone (CL) one pot synthesis [6]. Wu *et al* [7] reported the synthesis of lipase catalysed oxidation responsive PEG-based PCL-DBC. Yan and co-workers [8] synthesized a DBC between PCL and PEG. Similarly, the other DBC systems such as methoxyPEG [9], poly(N-isopropylacrylamide)-b-PCL [10], PCL-PEG [11], MeO-Peg-NH-L-GlyA-PCL [12], PCL-PDMAEMA [13], PE-PCL [14], PEG-PCL-PU [15], chitosan-PCL [16], PCL-collagen [17], PCL-poly(oxanorbornene) [18], PCL-PS [19] and PCL-piperazine-PU [20] were synthesized for bio-medical applications. In 2016, Murugesan and research team [21] synthesized

poly(sulphanilic acid)-PCL triblock copolymer for humidity sensor and drug-release application. PCL-PTHF-DBC was prepared by Kailash and co-workers [22] for effective drug release purpose.

Nowadays, the environment is being polluted by the effluents of various industries such as pharmaceutical, dyes, tannery and metal plating industries. Among these, hexavalent chromium, rhodamine-based dyes and p-nitrophenol (NiP) are playing vital role in water pollution. Various methodologies like adsorption, catalytic reduction and photocatalytic reduction are widely used. Adsorption technique is the cheapest one, but it has its own limitation like maximum adsorption capability. Moreover, photo-catalytic reduction is less usable during the winter season. Hence, catalytic reduction is the best one due to its high efficiency and number of recyclability. Recently, the polymer scientists turned their attention towards the synthesis and application of polymer-supported nanocatalyst for the catalytic reduction purpose, because the isolation of the catalyst is very easy after the reaction is completed. Rhodamine 6G (R6G) is a xanthenes type, economically cheaper cationic dye and is used for laser application. R6G contains one extended double bond and is very easy for degradation via reduction after its utilization. NiP plays a vital role in pharmaceutical industry as a building block material. The effluents from pharmaceutical industry is discharged into the water bodies, the quality of water is disturbed and hence, unfit for the domestic

application. Hexavalent chromium is a hazardous one, but it has wide applications in chemistry and chemical engineering field as a catalyst. The Cr(III) is less toxic when compared to Cr(VI) and it is necessary to reduce hexavalent into trivalent chromium. To solve the above said problems, various methodologies are followed in the literature. The photo-degradation of rhodamine dye was carried out in the presence of copolymer encapsulated mesoporous TiO_2 [23]. Photocatalytic degradation of chlorophenol was carried out with the aid of TiO_2 immobilized bio-degradable polymer [24]. Photo-degradation of chlorophenol and methyl orange dye was successfully done with TiO_2 and Fe_2O_3 immobilized low cost PE [25]. Catalytic reduction of NiP was carried out in the presence of hierarchical structured polystyrene/polyaniline@Au nanostructure [26]. Photo-catalytic degradation of polycyclic aromatic hydrocarbon dye was done in the presence of poly(acrylonitrile) [27]. Catalytic reduction of R6G dye is carried out with the help of $\text{Ag@Fe}_3\text{O}_4$ core-shell nanostructure system [28]. In 2013, Ghorai *et al* [29] reported about the photo-degradation of R6G in the presence of TiO_2 nanospheres. In 2006, Priya and co-workers [30] reported the kinetics of photo-catalytic degradation of mixture of phenolic derivatives. Similarly, the catalytic reduction of Cr(VI) into Cr(III) in the presence of a catalyst was reported by various research teams [31,32]. By thorough literature survey, we found that few reports are available on the catalytic reduction of R6G, Cr(VI) and NiP by using DBCNC. This motivated us to do the present investigation. The literature review indicated that the DBC of PCL has been used in the bio-medical engineering alone. In the present investigation, we would like to extend the application of PCL-based DBC to the catalysis field. The advantages are lesser amount of polymer is required, and after the reaction, the polymer catalyst can be easily isolated by the addition of diethylether (non-solvent). This is the novelty of the present investigation.

2. Experimental

2.1 Materials used

ϵ -Caprolactone (CL) and stannous octoate ($\text{Sn}(\text{Oct})_2$) were purchased from Sigma Aldrich, India and used as received. Tetrahydrofuran (THF) and potassiumdichromate (PDC) were purchased from Spectrum Chemicals, India. Rhodamine 6G (R6G), p-nitrophenol (NiP), vanadium-pentoxide (V_2O_5), chloroform, diethylether were purchased from s.d. Fine Chemicals, India. Double-distilled (DD) water was used for solution preparation.

2.2 Reduction of V_2O_5

One gram of bulk-sized V_2O_5 was dissolved in 50 ml DD water taken in a 200 ml beaker. For this beaker, 1 g of NaBH_4 was added under stirring condition. The stirring was allowed

to continue for 2 h. At the end of the reaction, the nanosized brown red product was filtered and dried at 100°C for 8 h. Then, the dried sample is weighed and stored in a air tight cover under nitrogen atmosphere.

2.3 Synthesis of DBCNC

In a 25 ml capacity round bottomed flask (RBF), 1 g of CL monomer, 0.10 g R6G (initiator) and 0.001 g $\text{Sn}(\text{Oct})_2$ (ROP catalyst) were added. These contents were stirred well at room temperature for 10 min. The content is transferred to an oil bath maintained at 160°C . The mild stirring is continued for 2 h. At the end of this reaction, a highly viscous solution is formed inside the RBF. The viscous solution is diluted with 10 ml chloroform solvent and re-precipitated with 200 ml diethylether [33]. A pink coloured mass was generated, which is R6G end-capped PCL (scheme 1). The mass was dried under fume hood for 8 h. Thus, obtained powder product is a homo PCL. Here, $[\text{M}/\text{I}] = 10$ and $[\text{M}/\text{C}] = 1000$ ratios were maintained. The imino group of R6G involved in the ROP of CL. One gram of homo PCL was dissolved in 25 ml THF and heated at 85°C for 24 h in the presence of 0.001 g of PAH (comonomer). Under nitrogen atmosphere 0.010 g of nanosized V_2O_5 was added and stirred. At the end of the reaction, the contents get evaporated to dryness. Again, a pink coloured product was obtained [34]. The product was weighed and stored in a air tight cover. Thus, obtained polymer is a fluorescent DBCNC.

2.4 Characterization

The UV-visible spectrum (Shimadzu 3600 NIR, Japan) for samples were recorded in an aqueous medium from 250 to 700 nm. The Fourier transform infrared (FTIR) spectrum for the samples were measured by using Shimadzu 8400S, Japan model instrument by KBr pelletization method from 400 to 4000 cm^{-1} . Differential scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) were measured using Universal V4.4A TA Instruments under nitrogen atmosphere at the heating rate of $10^\circ\text{C min}^{-1}$ from room temperature to 800°C . In DSC, the second heating scan of the sample was considered to delete the previous thermal history of the sample. Fluorescence emission spectral measurement was carried out with the help of an instrument, Elico SL 172, India. The surface morphology and particle sizes of the grafted samples were determined by field emission scanning electron microscope (FESEM) method using Hitachi S4800 Japan model instrument.

2.5 Catalytic reduction study

Catalytic reduction study was quantitatively followed with the help of UV-visible spectrophotometer. The catalytic reduction procedure is briefly explained. A standard solution of PDC or NiP with the concentration of $1.10 \times 10^{-5}\text{ M}$ was prepared from 2 ml of sample taken in a 5 ml nanoreactor for

Scheme 1. Synthesis of fluorescent DBCNC.

UV-visible spectral measurement [35]. Excess amount (15 mg) of NaBH_4 was added and 1 mg of the DBCNC sample was added into the nanoreactor. The reactor was shaken well and UV-visible spectrum was recorded at 1 min interval of time.

3. Results and discussion

FTIR spectrum of DBCNC is given in figure 1. The important peaks are characterized below: The -OH stretching observed at 3569 cm^{-1} . The C-H symmetric and anti-symmetric stretchings were observed at 2851 and 2928 cm^{-1} , respectively. The C=O stretching of PCL appeared at 1735 cm^{-1}

[33]. Apart from these, the C-N (1367 cm^{-1}), C-O-C (1018 cm^{-1}), aromatic C-H deformations (670 and 804 cm^{-1}) and metal-oxide (537 cm^{-1}) stretching were observed. A peak at 1653 cm^{-1} confirmed the formation of tetrahydrofuranium ion [22]. Appearance of C=O stretching (1735 cm^{-1}), tetrahydrofuranium ion stretching (1653 cm^{-1}), C-N stretching (1367 cm^{-1}) and aromatic C-H deformations (670 , 804 cm^{-1}) confirmed the formation of DBCNC.

UV-visible spectrum of pristine R6G is given in figure 2a. The spectrum exhibits two absorbance peaks at 545 and 508 nm corresponding to the monomer and dimeric structure of the dye [36]. After the nanocomposite formation, the absorbance peak was red shifted to 582 and 547 nm (figure 2b). The red shift in the peak confirmed the chemical linkage between

Figure 1. FTIR spectrum of DBCNC.

Figure 3. Fluorescence emission spectrum of (a) R6G and (b) DBCNC.

Figure 2. UV-visible spectrum of (a) R6G and (b) DBCNC.

Figure 4. DSC thermogram of DBCNC.

the R6G and DBC. The fluorescence emission is the peculiar property of the R6G dye molecule. The pristine R6G exhibited an emission peak at 564 nm (figure 3a). Figure 3b indicates the emission spectrum of DBCNC system. The spectrum exhibits an emission peak at 597 nm. The emission peak position of the DBCNC exhibited the red shift and this confirmed the chemical linkage between the R6G and the DBC. This is in accordance with the literature report but with red shift due to chemical conjugation [36].

DSC thermogram of DBCNC is given in figure 4. The thermogram exhibits an endothermic peak at 60.8°C corresponding to the T_m of the DBCNC. Appearance of single T_m confirmed the formation of diblock copolymer without any individual homopolymer formation. In 2016, Kailash and co-workers [22] reported the DSC of PCL-PTHF DBC. Our result

coincides with their report. The thermal stability of DBCNC was tested by TGA. The TGA thermogram (figure 5) exhibited a multistep degradation process. The first minor weight loss below 200°C is associated with the removal of moisture and loosely bound solvent molecules. The second major weight loss around 300°C is corresponding to the degradation of PTHF segments [22]. The third major degradation step around 450°C is associated with the degradation of PCL backbone [37]. Above 650°C, the system exhibited remaining 21.2% weight residue. This confirmed the presence of nanosized V_2O_5 .

FESEM image of the DBCNC is given in figure 6. The surface of the DBC is covered by the nanoparticle with the size of <35 nm. Here, one can see both the agglomerated and non-agglomerated nanoparticles. Moreover, the interphase region

Figure 5. TGA thermogram of DBCNC.

Figure 6. FESEM image of DBCNC.

between hydrophilic PTHF and hydrophobic PCL leads to the formation of nanoparticles [38]. Hence, the nanoparticles appeared are due to the nanosized V_2O_5 and polymer nanoparticles.

Main aim of the present investigation is to study the catalytic activity of the DBCNC towards the reduction of Cr(VI), NiP and R6G. Let us do study one by one. In figure 7, we studied the effect of weight of DBCNC on the reduction of Cr(VI). One milligram of DBCNC is mixed with 2 ml of PDC solution and 15 mg of $NaBH_4$. The catalytic activity is studied in terms of reduction of Cr(VI) into Cr(III). The Cr(VI) ion is appeared at 373 nm in the UV-visible spectrum. During the course of the reduction, the peak at 373 nm is decreased. This confirmed the catalytic reduction of Cr(VI) into Cr(III) [39]. The catalytic reduction of Cr(VI) is quantitatively studied by the UV-visible spectroscopy. Figure 7a–i indicates the UV-visible spectrum of Cr(VI) taken at 1 min time interval. It was

found that while increasing the reaction time, the absorbance at 373 nm is rapidly decreased. Within 9 min, 99% of Cr(VI) was reduced. To determine the apparent rate constant (k_{app}), the plot of time vs. $\ln(A/A_0)$ (figure 7j) was drawn. The plot was found to be in a straight line with the decreasing trend. From the slope value, the k_{app} value was determined as $8.38 \times 10^{-3} s^{-1}$. This coincides with the literature report [39]. The intercept value is considered as an induction time (T_i) as 1.97 s.

Further, we study the effect of higher concentration of catalyst on the catalytic reduction of Cr(VI). Hence, 5 mg of DBCNC is taken, whereas the other experimental conditions were kept as constant. The UV-visible spectrum is shown in figure 8a–e. The spectrum indicates that within 3 min, 85% of Cr(VI) was reduced. The k_{app} value was determined from the slope of the plot of time vs. $\ln(A/A_0)$ (figure 8f) as $1.54 \times 10^{-2} s^{-1}$. The T_i value was noted as 2.52 s. By comparing the k_{app} values one can come to the conclusion that while increasing the weight of polymer that supports catalyst, the k_{app} value is also increased, it means the reaction is more and more activated [39]. While increasing the weight of catalyst, the T_i value is increased. This can be explained as follows. It is well known that while increasing the time, the solute–solute interaction breaks and solute–solvent interaction is formed. In the present investigation, the DBC is acting as a carrier. The DBC nanoparticle and nanosized V_2O_5 are acting as a real catalyst. Moreover, the polymer is amphiphilic in nature. Under aqueous medium, it gets dissolved and distributed throughout the reaction medium. Hence while increasing the weight of DBC, the T_i value also increased. Here, two materials are playing vital role in the reduction of Cr(VI). Before the complete dissolution of the DBC in the medium, the nanosized V_2O_5 distributed on the surface of the DBC which is acting as a heterogeneous catalyst. After the dissolution, the DBC nanoparticles start to act as a homogeneous catalyst. So, after the addition of DBCNC, the k_{app} value is 1.86 times increased. The catalytic reduction of Cr(VI) by using AC-Pd [39] and CNT-Pd [40] lead to the k_{app} value of 3.3×10^{-3} and $5.85 \times 10^{-5} s^{-1}$ respectively. When compared with the literature value, the present investigation yielded good results.

The ultimate aim is to test the catalytic activity of DBCNC towards the reduction of NiP into amino phenol. The catalytic reduction of NiP follows the pseudo-first order kinetics. Under similar experimental conditions, as used for the reduction of Cr(VI), the reduction of NiP was carried out. The NiP shows one absorbance peak at 405 nm (figure 9a) [30]. While increasing the time, the absorbance at 405 nm is steadily decreased (figure 9a–i). In this case also within 9 min, 99% of NiP was reduced. The k_{app} value was determined by plotting time against $\ln(A/A_0)$ (figure 9j). The k_{app} value was calculated as $1.56 \times 10^{-2} s^{-1}$. The T_i value is noted from the intercept as 5.02 s. The k_{app} value declares that in the presence of a catalyst, the reduction of NiP into amino phenol was greatly enhanced. The interesting point is the k_{app} value for the NiP system is higher than that of the Cr(VI) system, by using the same catalyst. This concludes that k_{app} value depends on

Figure 7. UV-visible spectrum of Cr(VI) (a-i) taken at 1 min time interval and (j) plot of time vs. $\ln(A/A_0)$, for 1 mg of catalyst system.

Figure 8. UV-visible spectrum of Cr(VI) (a-i) taken at 1 min time interval and (j) plot of time vs. $\ln(A/A_0)$, for 5 mg of catalyst system.

Figure 9. UV-visible spectrum of NiP (a-i) taken at 1 min time interval and (j) plot of time vs. $\ln(A/A_0)$.

Figure 10. UV-visible spectrum of R6G (a–f) taken at 1 min time interval and (g) plot of time vs. $\ln(A/A_0)$.

the nature of the material to be reduced. In the previous system, the hazardous inorganic metal ion was reduced from +6 oxidation state to +3 oxidation state, the less-pollution state [39]. In the later system, the organic nitro group is chemically reduced into amino group. Above all, under identical experimental conditions, the T_i value is calculated for inorganic and organic systems. For 1 mg of DBC, the Cr(VI) system consumed 1.97 s, whereas the NiP system consumed 5.02 s. This is 2.5 times greater than the Cr(VI) system. On thorough analysis, one can come to a conclusion that the T_i value depends not only on the weight of polymer supported catalyst used, but also depends on the charges present on the material to be reduced. In the case of Cr(VI), six electrons to be transferred, but in the case of NiP, both $+(NO_2^+)$ and $-(phenolate)$ ions are present. This leads to the resonance stabilization effect. As a result, the NiP consumes higher T_i . While using nano-TiO₂ [41] and Pt₉₂Bi₈ [42] as a catalyst for the reduction of NiP, the k_{app} values were determined as 3.0×10^{-3} and $4.16 \times 10^{-4} \text{ s}^{-1}$, respectively. When compared with the literature value, the present system yielded the highest k_{app} value of $1.56 \times 10^{-2} \text{ s}^{-1}$.

Next, we analyse the influence of catalyst on the catalytic reduction of mixture of Cr(VI), NiP and R6G. When the catalyst comes to the practical application, then only it will have a real value i.e., utilization of DBCNC for the reduction of industrial effluents containing a mixture of component to be reduced. By keeping this concept in mind, equal volume of Cr(VI) and NiP was mixed (1:1 ratio). After thorough mixing, 2 ml of the aliquot was taken for the reduction reaction. Here also, 1 mg of DBCNC was used as a catalyst. Fifteen milligram of NaBH₄ was used as a reducing agent. The R6G is considered as a dye effluent (derived from the DBCNC itself). Again the reduction reaction was quantitatively followed with the help of UV-visible spectrophotometer. Figure 10a–f indicates the same. The mixture of components exhibits a peak at 400 nm. As usual within 3 min, 99% of the mixture of components was reduced. But one can see an absorbance peak at 522 nm corresponding to the R6G [43]. Hence, the

reduction of NiP and Cr(VI) is ruled out for the time being. An absorbance peak at 522 nm is slowly reduced, while increasing the reduction time. To find out the k_{app} value for the reduction of R6G, the plot of time vs. $\ln(A/A_0)$ (figure 10g) was made. In this case, the extended double bond of R6G is reduced. From the plot, the k_{app} value was calculated as $1.32 \times 10^{-2} \text{ s}^{-1}$. This shows that the chemical reduction is faster than the photo-chemical reactions [43]. The T_i value was directly taken from the intercept as 2.08 s. For the reduction of R6G, Ag/ZnO [44] and Ag/Fe₃O₄ [28] like catalysts were used and the k_{app} values were determined as 1.83×10^{-3} and $1.89 \times 10^{-3} \text{ s}^{-1}$, respectively. Photo-chemical reduction of R6G was thoroughly studied by Prof. Giridhar and co-workers with different catalyst systems like CS–TiO₂ [45], CeAl₂O₃ [46] and Ce_{0.90}Fe_{0.01}VO₄ [47] with the corresponding k_{app} values of 5.55×10^{-3} , 2.8×10^{-4} and $1.86 \times 10^{-3} \text{ s}^{-1}$. When compared with chemical as well as photo-chemical reduction values, the present investigation yielded the highest k_{app} value of $1.32 \times 10^{-2} \text{ s}^{-1}$ and this accounted the role of DBC in the catalytic reduction reaction. The chemical reduction yielded better results when compared with the photo-chemical reduction of R6G.

In overall comparison, the Cr(VI) produced lower k_{app} value, whereas the NiP system produced the higher k_{app} value. In the case of T_i value, again the Cr(VI) system consumed the lowest T_i . In fact, the lowest T_i value should produce the highest k_{app} value. The case is not true here. Because in the case of polymer-supported catalyst system, the solubility of polymer and exposure of DBC nanoparticles plays a vital role. In all aspects, the polymer-supported nanocomposite catalyst is a suitable one because of its easy recoverable and reusable nature.

4. Conclusions

From the above kinetic study, the important points are collected and presented here as conclusions. The FTIR

spectrum confirmed the various functional groups present in the DBCNC. The red shift in the UV–visible spectrum confirmed the presence of chemical conjugation between DBCNC and R6G. The fluorescence emission spectrum cosupported the UV–visible spectrum. Appearance of single melting peak at 60.8°C confirmed the DBCNC formation. The TGA study declared that the PTHF segments degraded earlier to PCL degradation. The FESEM study indicated the formation of DBC nanoparticle with the size of <40 nm. The catalytic reduction study showed that the increase of weight of the polymer-supported nanocatalyst lead to the increase in k_{app} value. The catalytic reduction of Cr(VI) is faster than that of the NiP and R6G systems. The T_i value depends on the size, resonance effect and nature of the material to be reduced.

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