

Synthesis, spectral characterization and application of Triazine based Schiff base and its Cu-complex

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ABSTRACT

A schiff base (SB) between salicylaldehyde and 2,4-diamino-6-phenyl-1,3,5-triazine was prepared. Thus synthesised SB is characterised by various analytical techniques like Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy. The initiating efficiency of SB towards the ring opening polymerization (ROP) of Caprolactone (CL) was carried out. The poly(caprolactone) (PCL) formation was confirmed by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) measurements. The scanning electron microscopy confirmed the surface morphology of PCL.

Keywords: Schiffbase · Ring opening polymerization · Characterization

I. INTRODUCTION

The SB compounds are considered as privileged ligands because of their versatile electronic properties and antimicrobial activities [1,2]. In 2011, Uysal et al [3] reported about the synthesis and characterization of star shaped metal complexes of amino substituted triazine cored SB. Salicylaldehyde based SB and its metal complexes were reported by Abdel and co-workers [4]. Acyclic SB Gadolinium(III) complex report is available in the literature [5]. Fluorescent complex of SB was studied by Rao and research team [6]. Other authors also studied about the SB-metal complexes [7,8]. Few reports are available on the triazine based SB. In the present investigation we are going to report about the triazine SB. PCL is a bio compatible plastic material with wide range of applications in biomedical field as a drug carrier [9,10]. Such a nice bio-medical polymer candidate can be synthesized through ROP by using different initiators [11-16]. Various functional groups such as –OH, -NH₂, -SH, -CO₂H were used for the initiation purpose. Recently, the SB and their metal complexes are used as an initiator for the ROP of CL. For example, Zhang et al [17] synthesis of Nd based SB complex for the ROP of CL. Other authors also reported about the ROP of CL by using SB and its

complex as an initiator [18-21]. By thorough literature survey, we could not find any report based on the triazine SB as an initiator for the ROP of CL.

II. EXPERIMENTAL

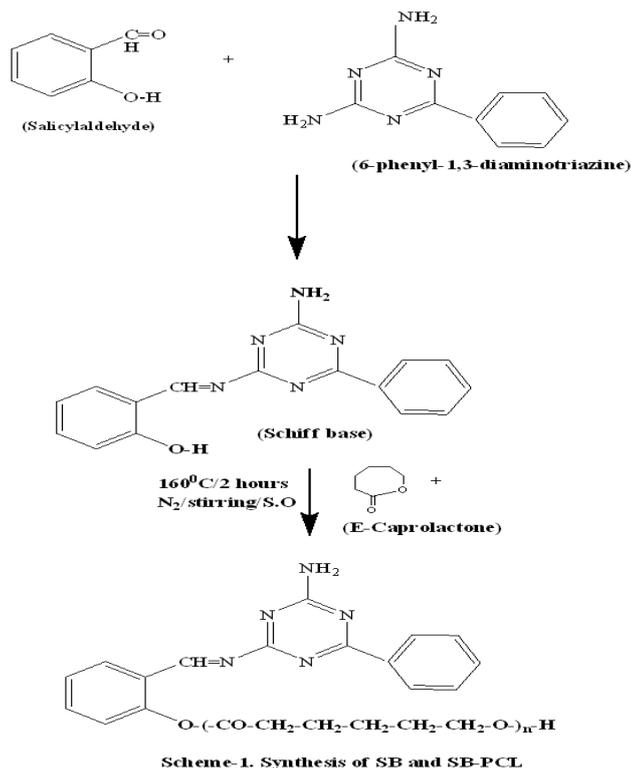
1. Materials

Salicylaldehyde (SD fine, India), Triazine (2,4-diamino-6-phenyl-1,3,5-triazine, Sigma Aldrich, India), ε-caprolactone (CL, Sigma Aldrich), chloroform (SD fine), diethylether (SD fine chemicals) were purchased and used as received. Stannous octoate (S.O, Sigma Aldrich), dimethylsulphoxide (DMSO, spectrum chemicals, India) were purchased and used as received. Double distilled (dd) water was used for solution preparation work.

2. Synthesis of PCL by using SB

A two way necked 25 mL capacity round bottom (RB) flask was taken and dried well. One neck acts as a sulphur free N₂ inlet, whereas the second one acts as a N₂ outlet. 1g CL was charged in the above said two way necked RB flask. With this 0.001g SO, as a catalyst was charged. Here the [M/C]=1000. ROP of CL was carried out at various [M/I] ratio. Required amount of SB is accurately weighed and mixed with the two way necked RB flask. The contents were mixed for 10 min under N₂ purging at room temperature.

After the thorough mixing the two ways necked RB flask was kept in an oil bath. The temperature of the oil bath was maintained at 160°C. The ROP was allowed for next 2 hrs under mild stirring condition. At the end of the reaction the N₂ purging was stopped and the highly viscous liquid was dissolved in the 25 mL chloroform solvent. Thus obtained polymer was purified by the re-precipitation with diethylether, as a non solvent [14,15]. After the drying process for 6 hrs, the SB end capped PCL was obtained as a white crystalline powder. Thus obtained white crystalline powder was weighed and stored in a zipper lock cover. The ROP of CL was carried out at various [M/I] of 10, 50, 100, 200 and 400. Further the samples were subjected to analytical characterizations.



III. CHARACTERIZATION

FTIR spectra were recorded with the help of Shimadzu 8400 S, Japan model instrument by KBr pelletization method from 400 – 4000 cm^{-1} . 3 mg of polymer was ground with 200 mg of spectral grade KBr and made into disc under the pressure of 7 tons. Surface morphology of the sample was measured by JSM 6300, Jeol product, SEM instrument. $^1\text{H-NMR}$ spectra of the SB was recorded by using Bruker Biospin High Resolution Digital 300 MHz NMR Spectrometer, USA. Dueterated chloroform (CDCl_3) was used as the solvent, and tetramethyl silane (TMS) served as the internal standard. Thermal stability of the polymer sample was measured by Dupont 951 thermogravimetric analyzer, USA. Thermograms were recorded under air atmosphere in a temperature range of 30 to 800 $^\circ\text{C}$ at the heating rate of 10 $^\circ\text{C}/\text{min}$. A Waters 2690 GPC instrument was used to determine the M_w of the polymer samples using THF as an eluent at room temperature at the flow rate of 1 mL min^{-1} against polystyrene (PS) standards. The melting temperature (T_m) of the polymer samples were determined by using Dupont Thermal Analyst 2000 Differential Scanning Calorimeter 910S, USA model instrument. All the measurements were done under N_2 atmosphere in a temperature range of RT to 100 $^\circ\text{C}$ with 10 $^\circ\text{C}/\text{min}$ heating rate.

IV. RESULTS AND DISCUSSION

1. Characterization of SB

1.1 FTIR Study

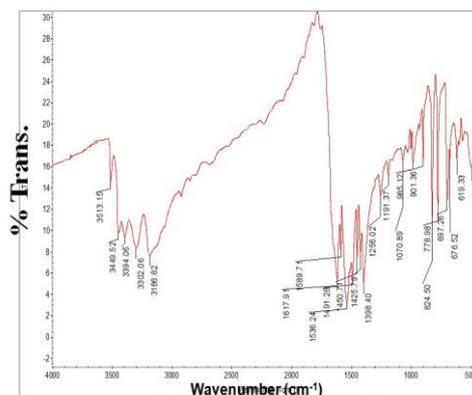


Fig. 1: FTIR spectrum of SB

The functional groups present in the SB can be identified by the FTIR spectrum (Fig.1). The aromatic $-\text{OH}$ stretching is appeared at 3449 cm^{-1} . The $-\text{CH}=\text{N}$ is appearing at 1617 cm^{-1} [20]. The free $-\text{NH}$ stretching is appeared at 3302 cm^{-1} . The aromatic $-\text{C}=\text{N}$ appeared at 1256 cm^{-1} . The aromatic $-\text{CH}$ out of plane bending vibration can be seen at 824 cm^{-1} . The above stretching confirmed the SB formation.

1.2 NMR Study

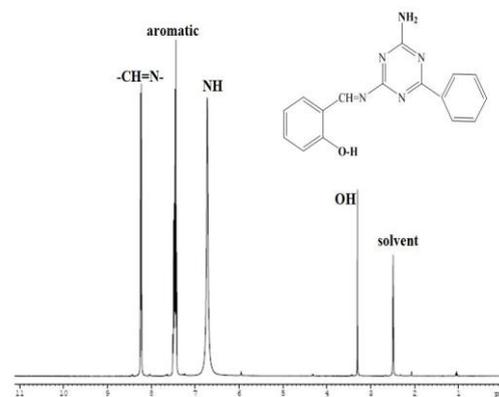


Fig. 2: $^1\text{H-NMR}$ spectrum of SB

Figure 2 represents the $^1\text{H-NMR}$ spectrum of SB. A peak corresponding to duet rated solvent DMSO is appeared at 2-3 ppm (Fig. 2). The free $-\text{OH}$ is appeared at 3.305 ppm (the normal expectation is that the free $-\text{OH}$ group should appear in the region between 5-6 ppm). In the SB, the $-\text{OH}$ proton is highly shielded, therefore instead of position 5-6 ppm, got the $-\text{OH}$ signal at 3.30 ppm. The $-\text{NH}_2$ proton is appeared at 6.725 ppm. Peak between 7.421 to 6.725 ppm is due to aromatic phenyl ring. Peak at 8.225-8.245 ppm is due to $-\text{CH}=\text{N}$ proton.

2. Characterization of SB-PCL

2.1. FTIR Study

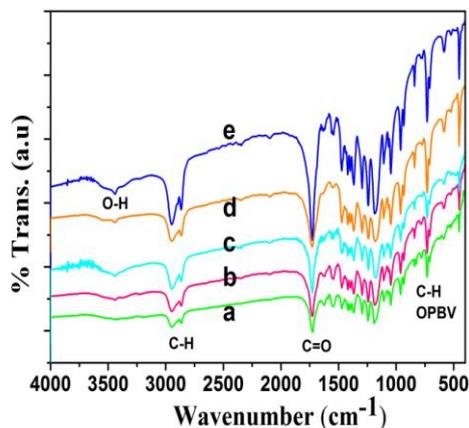


Fig. 3. FTIR spectrum of SB-PCL synthesized at various [M/I] ratio of (a)10, (b)50, (c)100, (d)200, (e)400

The FTIR spectrum of PCL prepared in the presence of SB as an initiator at various [M/I] (Fig.3) ratio is as follows. The -OH stretching of PCL attached at the chain end is appeared at 3422 cm^{-1} . The -CH symmetric and antisymmetric stretching are appeared at 2879 and 2953 cm^{-1} respectively. The -NH stretching of SB appeared at 3368 cm^{-1} . The -C=O stretching of PCL is identified at 1724 cm^{-1} [14-16]. The -CH out of plane bending vibration can be seen at 729 cm^{-1} . The -CH bending vibration of PCL is appeared at 1472 cm^{-1} . The -CH stretching of SB is appeared at 1370 cm^{-1} . The important point noted here is while increasing the [M/I] ratio, the corrected peak area of carbonyl group is also increased linearly. This is due to the decrease of initiating species while increasing the [M/I] ratio. The decrease in initiating species increased the molecular weight of the PCL. Recently, Meenarathi et al [15] reported similar type results. Our results are coinciding with their report.

2.2. SEM analysis

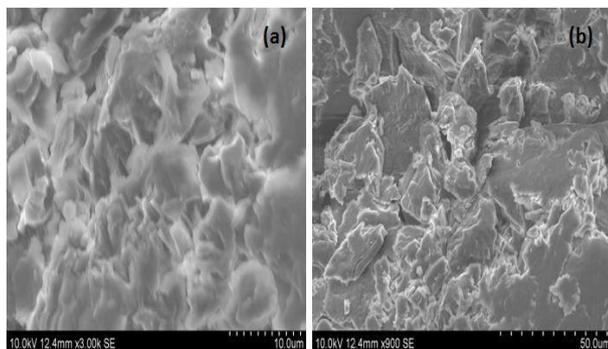


Fig. 4: SEM images of SB-PCL system (a,b)

Figure 4 (a, b) indicates the surface morphology of SB initiated ROP of CL. The morphology indicated the presence of micro voids on the surface of PCL. The peculiar morphology of PCL is the broken stone like shape. The presence of micro voids and broken stone like morphology confirmed the presence of PCL [14-16].

2.3. DSC Study

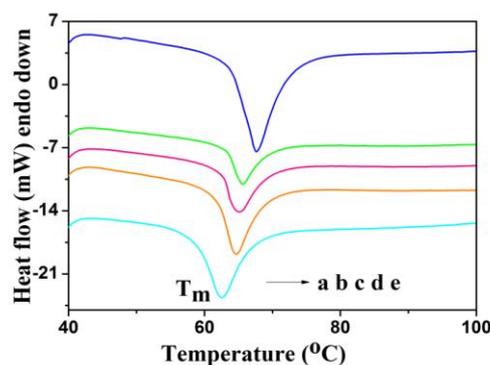


Fig. 5: DSC thermograms of SB-PCL system synthesized at various [M/I] ratio of (a)10, (b)50, (c)100, (d)200, (e)400

The DSC thermogram of PCL synthesised at various [M/I] ratio is given in Fig. 5 (a-e). The thermogram exhibits one sharp endothermic peak associated with the T_m of PCL. The important point noted here is while increasing the [M/I] ratio, the T_m value of PCL is also increased. The T_m is varied from $62 - 64.8\text{ }^{\circ}\text{C}$ while increasing the [M/I] ratio from 10-400. This can be explained as follows. At higher [M/I] initiator ratio, the availability of initiating species was found to be low and hence the increase of M_w of PCL. As a result of increase in M_w the T_m of PCL was increased. This is in accordance with the literature report [16].

2.4. TGA Study

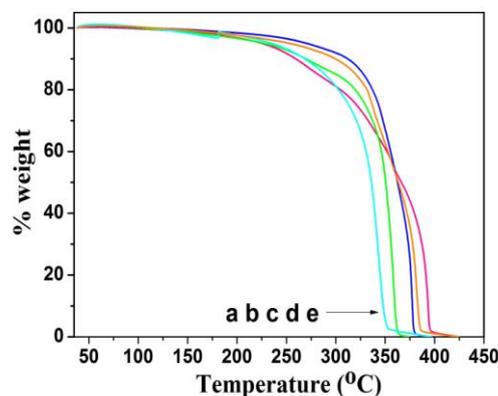


Fig. 6: TGA thermograms of SB-PCL system synthesized at various [M/I] ratio of (a)10,(b)50, (c)100, (d)200, (e)400

Figure 6 represents the TGA thermogram of PCL synthesised at various [M/I] ratios. The thermogram exhibits a two step degradation process at lower [M/I] ratio, whereas at higher [M/I] ratio, the thermo gram exhibits a single step degradation process. The first minor degradation step around 334.7 °C is due to the breaking of the linkage between the SB and the PCL. The second major weight loss around 380 °C is associated with the degradation of PCL backbone [14-16]. While increasing the [M/I] ratio the PCL backbone degradation temperature was found to be reduced. At the same time, the first minor weight loss step slowly disappeared. This can be explained as follows. At lower [M/I] ratio, there are lot of initiating species are available and resulting with the low M_w polymer. But at higher [M/I] ratio few initiating species are available and hence the increase of M_w and hence separate degradation step for breaking of SB from PCL chain was not observed. Moreover, due to the presence of number of PCL chains, the degradation of SB from PCL is negligible.

2.5. GPC analysis

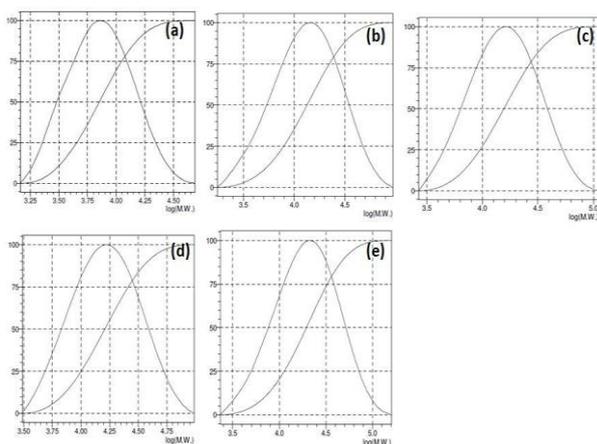


Fig.7. GPC of SB-PCL system synthesized at various [M/I] ratio of (a)10, (b)50, (c)100, (d)200, (e)400

In order to confirm the initiating efficiency of SB towards the ROP of CL GPC measurements were carried out. While increasing the [M/I] ratio from 10-400, both the M_n and M_w were increased from 5934 – 14454 g/mole respectively. The polydispersity (P.D) of PCL was varied between 1.47 and 1.74, this concludes that PCL has a narrow M_w without any cross linking [15]. Figure 7 (a-e) represents the GPC of PCL synthesised at various [M/I] ratios.

V. CONCLUSIONS

From the above simple study the following points were emerged out as conclusion: FTIR study declared that the $-\text{CH}=\text{N}$ stretching was appeared at 1617cm^{-1} for the SB. The presence of $-\text{CH}=\text{N}$ present in the SB was confirmed by $^1\text{H-NMR}$ spectroscopy. The GPC results

confirmed that the $-\text{OH}$ group from SB effectively involved in the ROP of CL. The SB-PCL system exhibited broken stone like morphology. Polymers synthesised at higher [M/I] ratio exhibited the higher thermal stability due to higher M_w of PCL.

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