



3D Architected polyazomethine gel synthesis: its self-assembled intercalating complexation with nitro aromatic acceptor

D S RAGHUVANSHI^{1,*}, N B SHIRSATH¹, P P MAHULIKAR¹ and J S MESHARAM²

¹School of Chemical Sciences, North Maharashtra University, Jalgaon 425 001, India

²Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur 440 033, India

*Author for correspondence (devendrar2@gmail.com)

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Abstract. Azomethine is the key linkage in all Schiff base reactions. The present context has efficiently emphasized on the utilization of Schiff base strategy effectively in the synthesis of polyazomethine polymer gel materials. The synthesized polymer gel is characterized by different physical techniques for testing its proper existence such as FESEM analysis, thermal gravimetric analysis, differential scanning calorimeter analysis, FTIR analysis and electron dispersive X-ray scattering analysis. The morphological study has revealed that the material is having 3D lamellar-layered architecture, i.e., layer-by-layer array of polymer chains. The synthesis governs several advantages, such as executing without using any catalyst and water as a green solvent. The present study also checked its complexation ability with nitro aromatic acceptors. The intercalation of nitro aromatic molecule between the two straight chains of the polymer gel is the beautiful peculiarity of these red-coloured complexes.

Keywords. Azomethine; Schiff base; complexion ability; green solvent.

1. Introduction

Schiff's base reactions are well-known organic reactions that are the main source of several versatile organic moieties and the reaction intermediates responsible for enormous applications in the diversified fields as pharmacy [1], agriculture [2,3], biosciences [4], physical sciences [5], chemical sciences [6], etc. By virtue of its virtual applicability, Schiff bases have attracted great attention in the past few decades [7] and they are very prominent in the research related to organic compounds. The application of Schiff bases in polymer sciences is less as compared to other research areas [8].

Studies on Schiff polymers have been conducted by few research groups and a great diversity of structures is obtained [9]. It is obviously known that aromatic schiff base polymers are high performance polymers presenting high thermal stability, good mechanical strength and semi-conducting properties [9,10]. However, poor solubility of high-molecular-weight polymers makes it difficult to versatile applications and the determination of their structural and macromolecular features. Generally, the transition temperatures of conjugated polyazomethines remains over the decomposition limit and their technical applications are strongly limited by their sensitivity to acidic hydrolysis and thermal exchange reactions between different azomethine groups [9].

Hydrogels are generally prepared through covalent or noncovalent cross-linking between polymer chains [10,11].

Since non-covalent gel phase materials are formed through weak and transient interactions, such as the van der Waals force, hydrophobic interaction, electrostatic interaction and hydrogen bonding. These 3D networks can simply undergo sol-gel phase transitions in response to a variety of external stimuli and thus are injectable, smarter and appropriate for different applications [12]. A number of strategies have been useful for the synthesis of novel supramolecular polymeric gels based on dynamic covalent chemistry [13]. In the field of supramolecular chemistry, the host-guest interactions and self-organizations are very frequent, which induces first harnessed pre-organization for the design of tailor-made molecular receptors effecting molecular recognition from metal ions to anions and chiral molecular substrates [14–16]. The identification of neutral guests has attracted much attention due to their great biological and environmental relevance [17–19]. However, few examples, which rely on colour change [20–22], have been reported so far. They represent a convenient visual detection method in classical chemical analysis, in particular, rapid detection of explosives such as trinitrotoluene. Most of the available sensors are composed of polymers, nanomaterials, etc [23]. Surprisingly, less attention has been paid to picric acid (2,4,6-trinitrophenol, TNP) [24,25], although its explosive power is somewhat superior to that of trinitrotoluene (TNT) and it is also widely used in the manufacture of rocket fuels, fireworks, matches and so on [10,15]. In addition, TNP has been recognized as an environmental contaminant and is harmful to wildlife and humans [26–28]. Therefore, the development of fast, convenient

and specific analytical methods for TNP is highly desirable [29–31].

The present context is mainly focusing on synthesis of aliphatic 3D-structured azomethine polymer synthesis. The reactions are optimized at elevated temperature conditions, which shows the polymer gelation achieved efficiently at 0–5°C temperature without the use of any catalyst or solvent. In this way, it utilizes green approach for the synthesis. Moreover, the synthesized polymer readily forms intercalating red-coloured complexes with nitro aromatic acceptors such as picric acid, which can be used as visible detecting agents for those notorious compounds.

2. Experimental

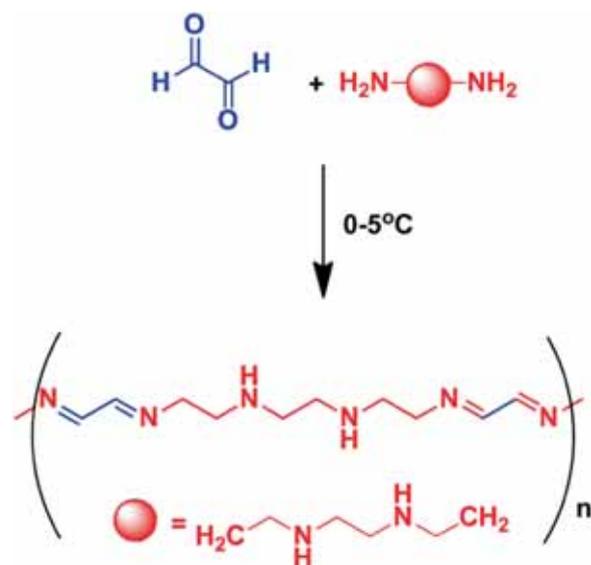
2.1 Methods

Glyoxal (40%) is purchased from Sigma Aldrich Chemicals. Triethylenetetramine (TETA) is purchased from Sisco Laboratory, Mumbai, India. Picric acid, 2,4-dinitrophenol (2,4 DNP), 2,4-dinitrophenyl hydrazine (2,4 DNPH) and 2,4-dinitrobenzene (2,4 DNB) are purchased from SD Fine Chemicals, Mumbai, India. Thermal gravimetric analysis (TGA) is executed on TGA-4000 (Perkin Elmer) with the Nitrogen flow rate of 20 ml min⁻¹ and temperature increment rate of 15°C min⁻¹. Differential scanning calorimetric analysis is executed on DSC-4000 (Perkin Elmer) with the nitrogen flow rate of 20 ml min⁻¹ and temperature increment rate of 10°C min⁻¹. Field emission scanning electron microscope images are taken on Hitachi S4800 instrument after gold plating applied with the help of Hitachi Ion Sputter E1010 instrument. The phase identification of the synthesized product was obtained by X-ray diffraction (D8 Advance, Bruker AXS). Fourier transform infrared (FTIR) analysis is done on Shimadzu FTIR Affinity-1 using KBr pellets. The UV–Vis absorption study was performed at room temperature in the wavelength range of 200–800 nm on a UV–Vis spectrometer (Shimadzu UV-1700). Samples for UV–Vis studies were placed in cuvettes before the polymerization was complete in aqueous ethanol as a solvent (i.e., within 10 min of the initiation of polymerization) and were allowed to equilibrate for 1.5 h or more before spectra were obtained.

2.2 Reaction scheme

2.2a Scheme 1. Synthesis of polymer gel

Procedure 10 mmol of glyoxal (40%) is subjected to slow stirring using a magnetic stirrer. Its temperature is brought down to 0–5°C. The slow addition of 10 mmol of TETA into chilled glyoxal is executed through an addition funnel. During addition, exothermic reaction occurs; so, the rate is adjusted such that the reaction temperature must not reach above the 5°C otherwise the product gets degraded.



Scheme 1. Synthesis of polymer gel.

2.2b Scheme 2. Intercalation of picric acid into the polymer gel sheets

Procedure The procedure is same as mentioned in scheme 1; the change is only the addition of picric acid (10 mmol) before the slow addition of TETA into chilled glyoxal (figure 1).

3. Results and discussion

The colour of a synthesized polymer gel is pale yellow; while the π - π^* and n - π^* stacking provides a deep red colour to the complex (figure 2). The picric acid binds to straight chain polymer by inter-hydrogen bonding and finds the interstitial location of each polymeric chain forming lamellar layer architecture in the morphology of the synthesized polymer gel. Therefore, the gel can be used as a trapping agent in the picric acid contaminant industrial waste to trap and separate it.

3.1 Electron dispersive X-ray scattering analysis

From the EDXS analysis (figure 3), it is clear that the synthesized polymer is non-conducting and contains carbon and nitrogen as major elements in the composition, which proves that the synthesized polymer is polyazomethine, i.e., consists of C=N as a key repeating unit [32].

3.2 Thermal gravimetric analysis

Thermal gravimetric analysis is showing a three-step degradation of polyazomethine polymer comprising TETA as a repeating unit. The first step in the degradation process starts from 60 upto ~200°C (figure 4) due to the entrapped moisture

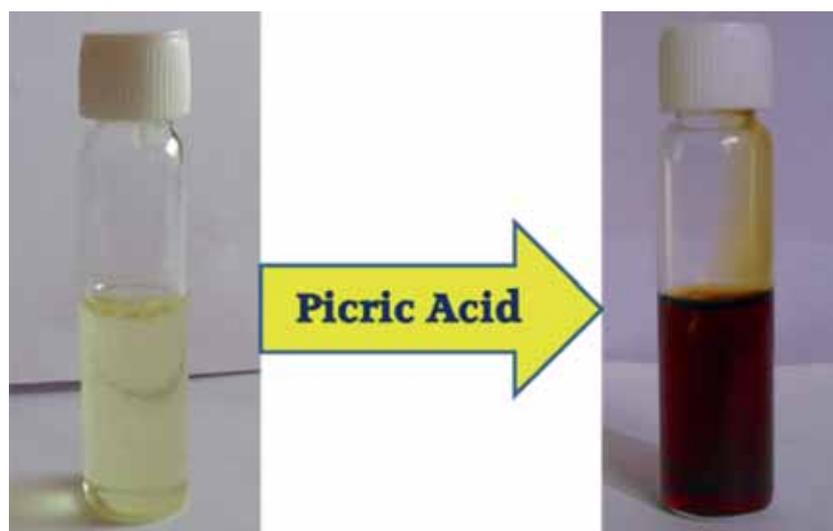


Figure 2. Visual detection of polymer picrate formation.

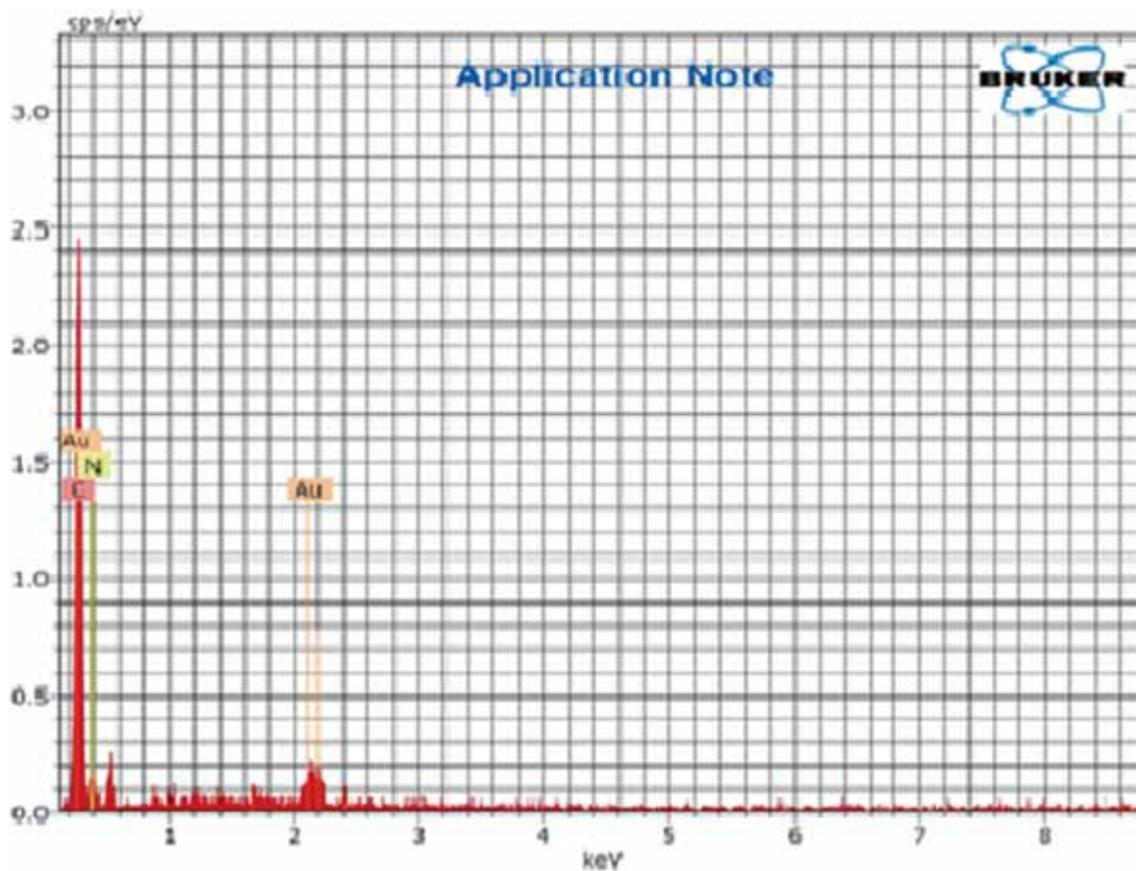


Figure 3. EDXS plot for element detection.

3.5 Ultra-visible spectroscopic analysis

The UV-visible spectroscopic evaluation is executed to check the complex formation with nitro aromatic acceptor. The

UV titrations of polymer gel with nitro aromatic compound is done by taking separate peaks and then series of peaks with increasing concentration of nitro aromatic compound into polymer gel solution. These titrations show that the

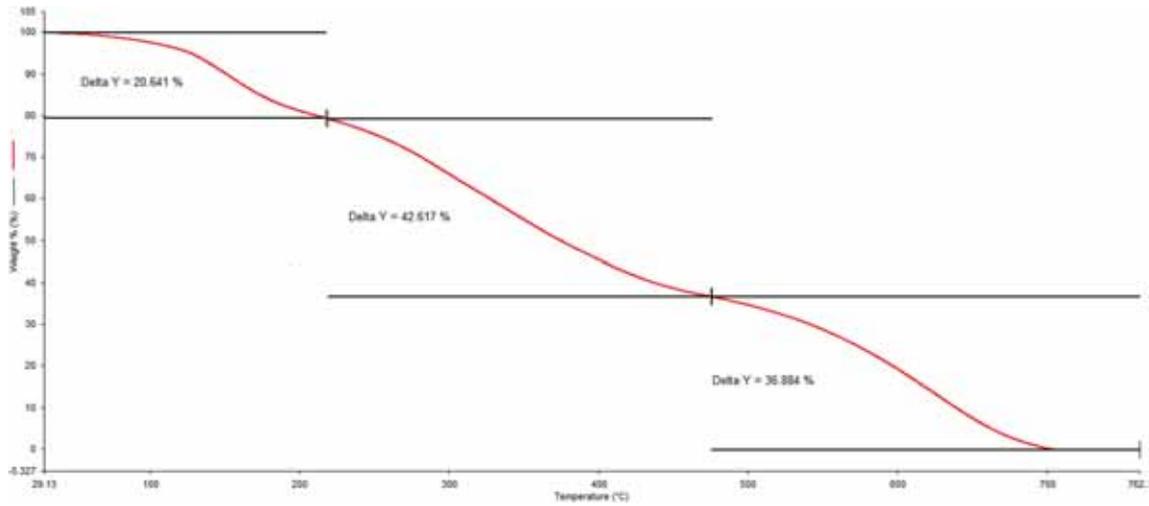


Figure 4. TGA graph for thermal decomposition study.

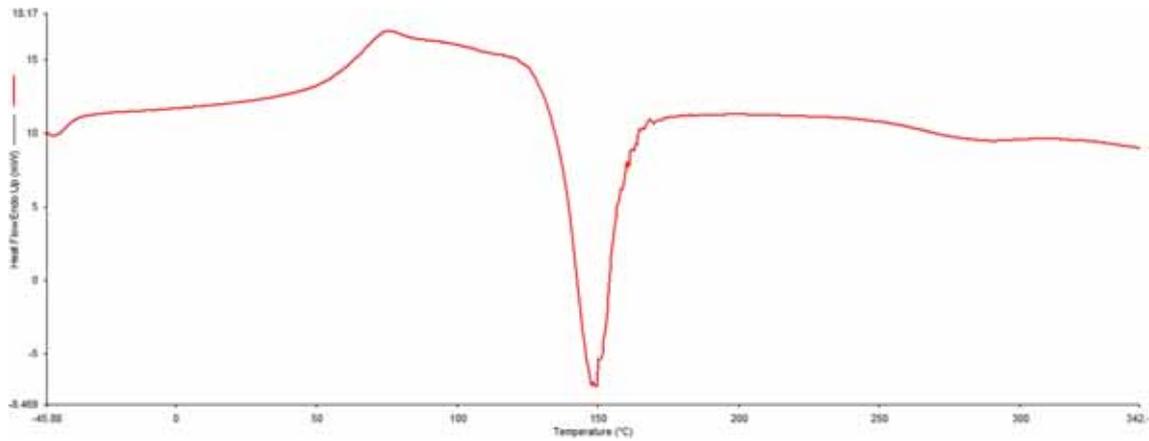


Figure 5. DSC graph to identify the mode of reaction and the transition temperatures of the polymer.

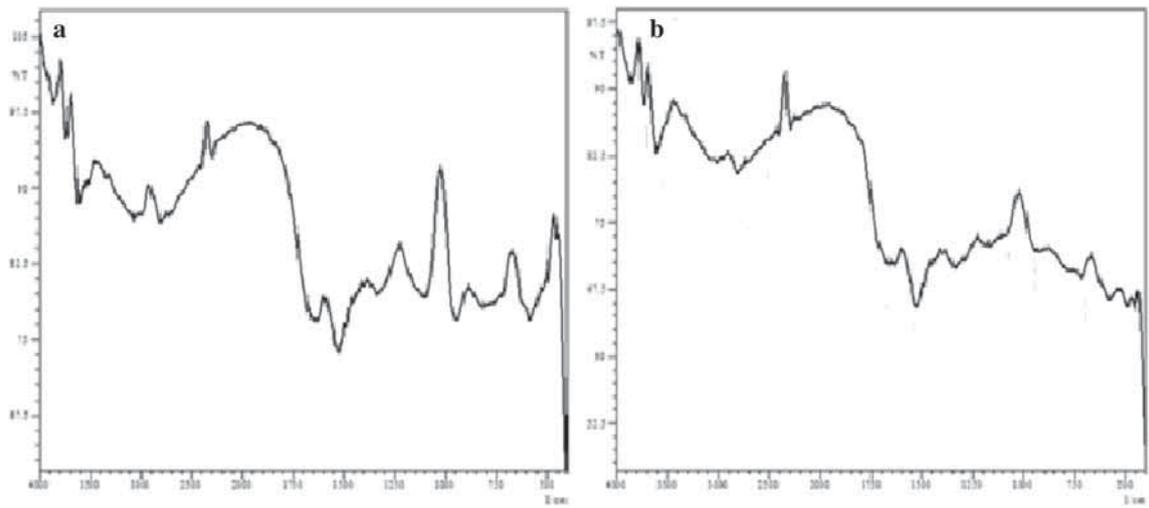


Figure 6. FTIR analysis: (a) graphs of synthesized polymer gel material and (b) picrate of polymer gel material.

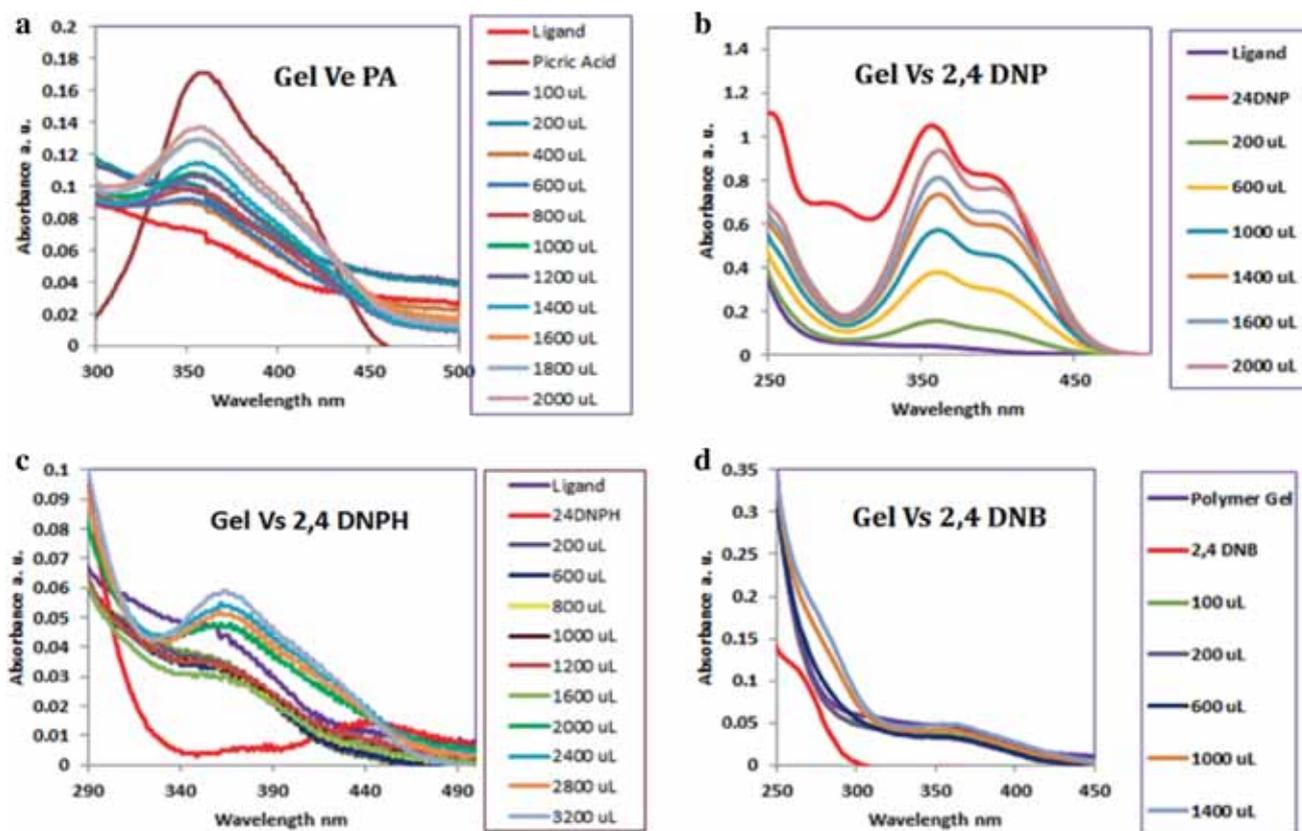


Figure 7. UV-visible spectroscopic analysis. UV plot of polymer gel and increasing amounts of (a) picric acid, (b) 2,4-dinitrophenol, (c) 2,4-dinitrophenyl hydrazine and (d) 2,4-dinitobenzene into it.

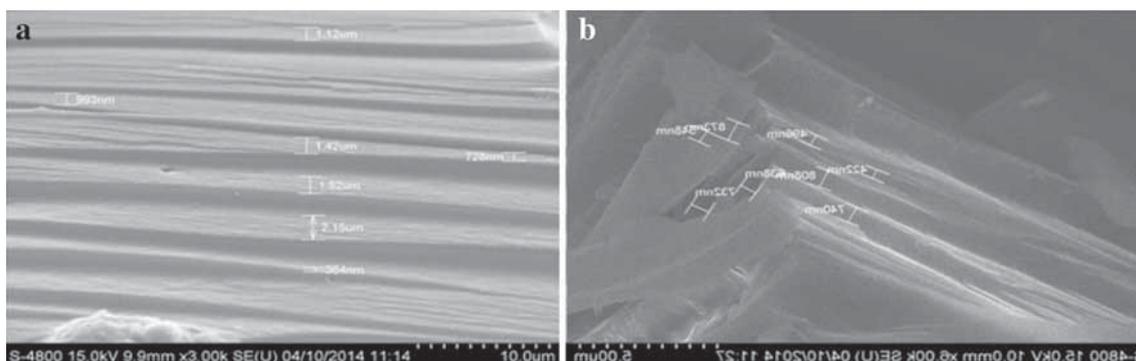


Figure 8. FESEM analysis: (a) surface morphology of polymer gel, (b) separated layer observed in side cut of polymer sheet.

gels readily bind with picric acid (figure 7a) and 2,4 DNPH (figure 7c) and gives blue shift with respect to parent nitro compound. However, it shows red shift in case of 2,4 DNB (figure 7d). It does not show any shift in case of 2,4 DNP (figure 7b) [36–38].

3.6 FESEM analysis

The morphological sample is studied with the help of SEM images (figure 8). FESEM images are showing sheet like structures; which are separated by an average distance of

1.5 μm . Thus, it is evident that the polymer is having a three-dimensional lamellar layered-like morphology. The layers can be easily observed in figure 7. It may be concluded that the chains grow straight without any kind of branching in it [39,40].

4. Conclusion

In this study, we have achieved the synthesis of 3D architecture polyazomethine gel material with stability. The main

difficulty of oxidization at room temperature is overcome by synthesizing the gel at ambient temperature conditions, i.e., 0–5°C. Owing to enlarged stability period, we have optimized its several physical parameters that are clearly revealing that the synthesized polymer gel has the lamellar layer architecture. The TGA graph also shows the presence of water of crystallization in the pore voids or interlayer surfaces of gel; so, it is the hydrogel material, which absorbs water. It can be applied as picric acid trapping agent as it readily forms red-coloured complexes with the nitro aromatic compounds. The picric acid occupies space between the two sheets of lamellar layers in polymer morphology.

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