

GREEN SYNTHESIS AND CHARACTERIZATION OF TERPOLYMER RESIN DERIVED FROM ANTHRANILIC ACID, SALICYLIC ACID AND FORMALDEHYDE

Amit M. Surjushe^{1,*} and Arun B. Patil²

¹Department of Chemistry, Smt. Vatasalabai Naik Mahila Mahavidyalaya,
Pusad, Maharashtra, India.

²Department of Chemistry, Phulsingh Naik Mahavidyalaya,
Pusad, Maharashtra, India.

*E-mail: amitsurjushe99@gmail.com

ABSTRACT

This paper presents the green synthesis of a terpolymer resin by using the microwave assisted synthesis. The ASF terpolymer resin have been prepared from anthranilic acid (A), salicylic acid (S) and formaldehyde (F) in DMF media at 132 ± 2 °C using 1:1:2 molar proportions of the reacting monomers in 114 second. The synthesized terpolymer resin was purified and then characterized by different spectral methods like Proton NMR, FT-IR, XRD and TEM the structure of the obtained ASF resin.

Keywords: Green synthesis, microwave irradiation, structure, spectral analysis, ASF.

©2015 RASĀYAN. All rights reserved

INTRODUCTION

Terpolymer resin find very useful applications as adhesives, high temperature flame resistant fibers, coating materials, semiconductors, catalysts, and ion-exchange resins¹⁻⁵. Ion-exchange resins have attracted much interest in the recent years due to their application in waste water treatment, metal recovery and for the identification of specific metal ions^{6,7}. Ion-exchangers are widely used for the treatment of radioactive wastes from nuclear power stations^{8,9}. The chelation ion-exchange is haviour of poly (2-hydroxy-4-acryloyloxybenzophenone) resin towards the divalent metal ions were studied by batch equilibration method as a function of contact time and pH¹⁰. A cross-linked styrene / maleic acid chelating matrix has been reported for its higher ability to remove the metal ions¹¹ such as Cr^{3+} , Fe^{3+} , Ni^{2+} , Cu^{2+} and Pb^{2+} . Acidic polymers such as poly (methacrylic acid) and poly (acrylic acid) have the tendency to remove the metal ions, e.g., Ag^+ , Cu^{2+} , Co^{2+} , Ni^{2+} and Cr^{3+} at different pH and polymer/metal ion ratios¹². Salicylic acid and melamine with formaldehyde terpolymer found to have higher selectivity for Fe^{3+} , Cu^{2+} and Ni^{2+} ions rather than Co^{2+} , Zn^{2+} , Cd^{2+} and Pb^{2+} ions¹³.

Resins synthesized by condensation of mixtures of phenol or hydroxybenzoic acid with formaldehyde and various amines have also been reported¹⁴. The metal ion uptake capacity increases with increasing mole proportions of the terpolymer synthesized from substituted benzoic acid¹⁵. o-nitrophenol and thiourea with paraformaldehyde terpolymer was identified as an excellent cation exchanger for Zn^{2+} and Co^{2+} ions¹⁶. Salicylic acid/formaldehyde/resorcinol resin has been synthesized and explored its use for the removal and separation of heavy metal ions from their binary mixtures.¹⁷

Microwave assisted synthesis of the chelating resin was introduced first by Mondal who modified chloromethylated polystyrene DVB (2%) with o-aminothiophenol S-acetic acid under a microwave irradiation for 45 min at 180 W power levels¹⁸ instead of classical 40 h refluxing. The resin thus obtained was compared with resin obtained by classical heating in terms of yield, IR and elemental analyses and it was found that the products are identical. By using the same technique, an adenine anchored polystyrene DVB (2%) was also synthesized by the same group of workers¹⁹. Microwave assisted synthesis is a green,

ecofriendly and a short-time process. The present work deals with the synthesis and characterization of anthranilic acid- salicylic acid- formaldehyde (ASF) terpolymer resin by microwave irradiation in dimethylformamide medium (DMF). The synthesized terpolymer resin was characterized by Proton NMR, FT-IR, X-RD, TEM.

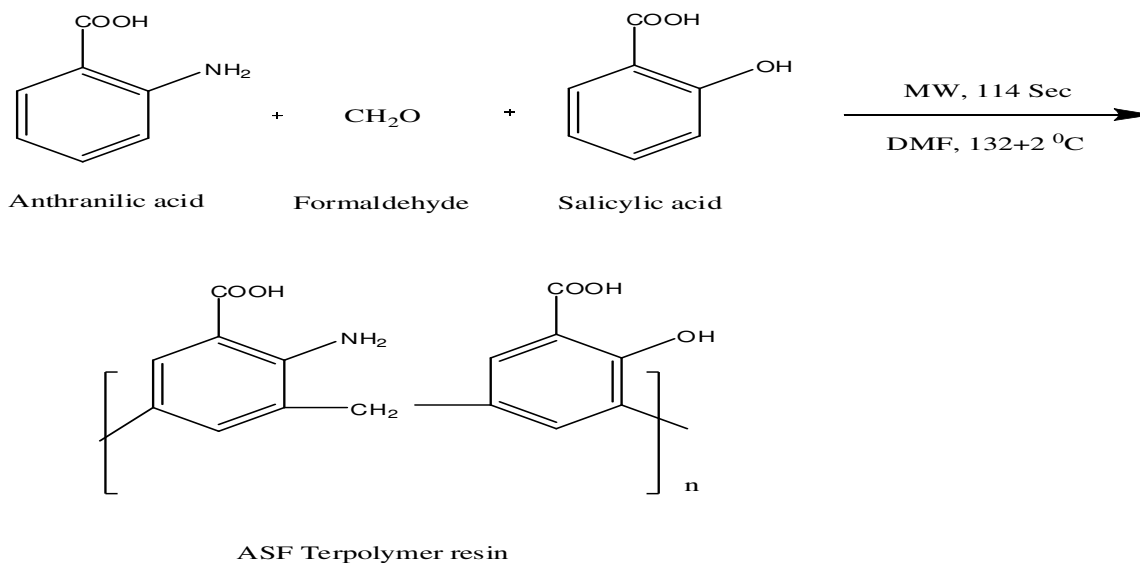
EXPERIMENTAL

Materials

Anthranilic acid (Loba, Mumbai), Formaldehyde (37%) (S. D. Fine Chemicals, Mumbai) was used as received. Salicylic acid (Thomas Baker, Mumbai) was used as received. The solvents and monomers were purified by the conventional methods.

Green synthesis of ASF terpolymer resin

The ASF terpolymer resin was synthesized by microwave assisted synthesis using monomer Anthranilic acid (A) (0.02 mol) and salicylic acid (S) (0.02 mol) with formaldehyde (F) (0.2 mol) in the presence of DMF medium at $132 \pm 2^\circ\text{C}$ for 114 second using a microwave system at 180 W. The reaction mixture was then cooled, poured into crushed ice with constant stirring and left overnight. The yellow colored terpolymer resin obtained was then washed with warm water and methanol to remove unreacted materials. The terpolymer resin was purified by dissolution in 8% NaOH and re-precipitated by drop-wise addition of 1:1 (v/v) of 2 M HCl. The precipitated product was filtered off, washed with warm water, and dried in vacuum desiccators over anhydrous calcium chloride. The reaction route is shown in Scheme-1 (Melting point = $238\text{--}245^\circ\text{C}$. Yield = 7.9 gm).



Scheme-1: Synthesis of ASF terpolymer resin

Spectral Analysis

A Shimadzu spectrometer was used for recording the FT-IR spectrum of the ASF resin to identify the linkages and functional groups. The proton NMR spectrum of the ASF terpolymer resin was recorded in DMSO solvent using an FT-NMR spectrometer model Avance-II Bruker at 400 MHz.

RESULTS AND DISCUSSION

The terpolymer resin ASF is yellow in color, insoluble in cold and hot water, chloroform, carbon tetrachloride but completely soluble in acetone, 1,4-dioxane, *N,N*-dimethyl formamide, dimethyl sulfoxide, pyridine.

FT-IR Spectroscopy

The FT-IR spectrum provides useful information about the linkages and the functional group present in the terpolymer. The FT-IR spectrum of the ASF terpolymer resin is shown in Figure-1.

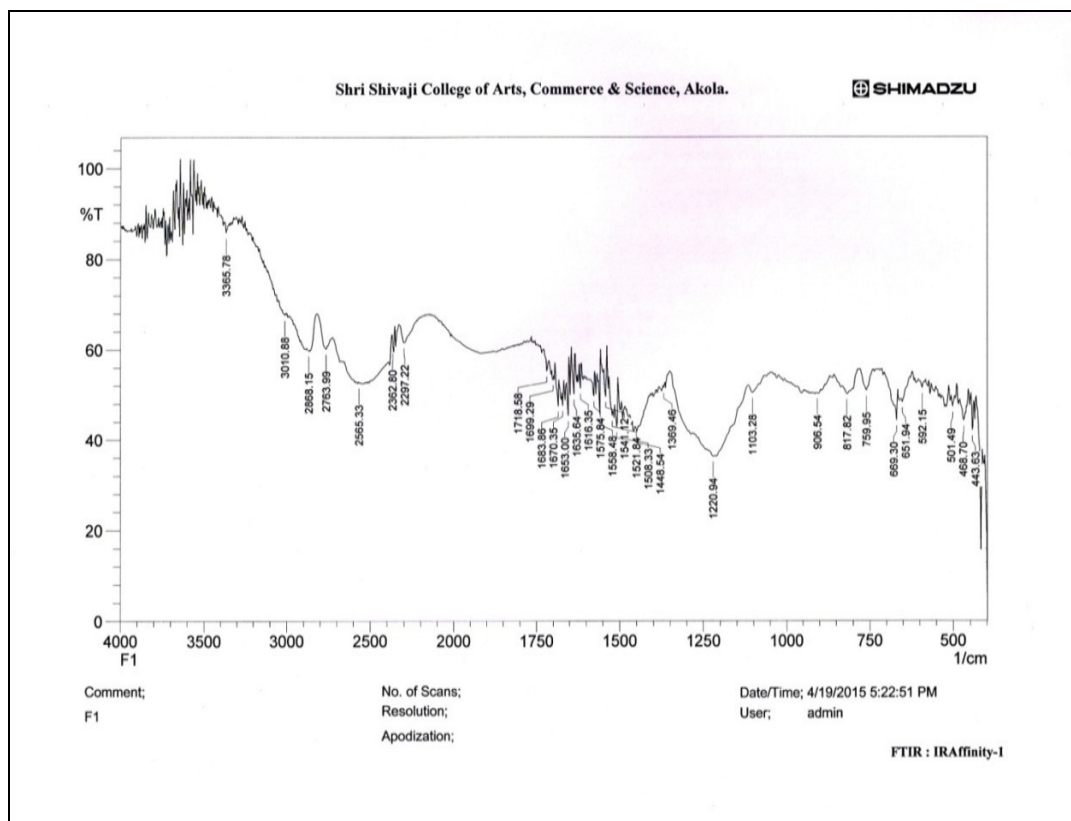


Fig.-1: FT-IR spectrum of the ASF terpolymer resin.

The spectrum shows a broad band at 3365.78 cm^{-1} due to the (O-H) stretching vibration of Ar-OH involved in the intra-molecular hydrogen bonding with Ar-COOH. The strong band appeared at 1220.94 cm^{-1} is due to (C-N) stretching vibration¹⁹ of Ar-NH₂. The strong band at 1653 cm^{-1} may be assigned to (C=O) stretching vibration of the carboxyl group present in the resin molecule²⁰. The band appeared at 3365.78 cm^{-1} is due to NH-stretching vibration of amino group.²¹ This band seems to be merged with a broad band of -OH group of -COOH groups. The tetra-substitution in the benzene ring is established by the presence of the medium bands at 1103.28 cm^{-1} and 906.54 cm^{-1} which are attributed to (C-H) bending vibration²¹. The weak band at 2888.15 cm^{-1} is due to the (C-H) stretching vibration of methylene group¹⁹.

Proton NMR Spectra

The Proton NMR spectrum of ASF terpolymer resin is depicted in Figure-2. The proton NMR spectrum reveals that the signals around 2.8-4.3 ppm are due to the methylene proton of the Ar-CH₂-Ar linkage. The multiplet signals observed in the range of 6.8-7.9 ppm are indication of the presence of aromatic protons. The signal displayed at 8.2 ppm may be due to the carboxylic proton of Ar-COOH. The signal in the region of 9.8 ppm is assigned to the -OH group of Ar-COOH involved in the intramolecular hydrogen bonding with proton of -OH in Ar-OH. A weak signal appeared in the region of 1.2 ppm is assigned to the -NH₂ protons of Ar-NH₂ group in the terpolymer resin.

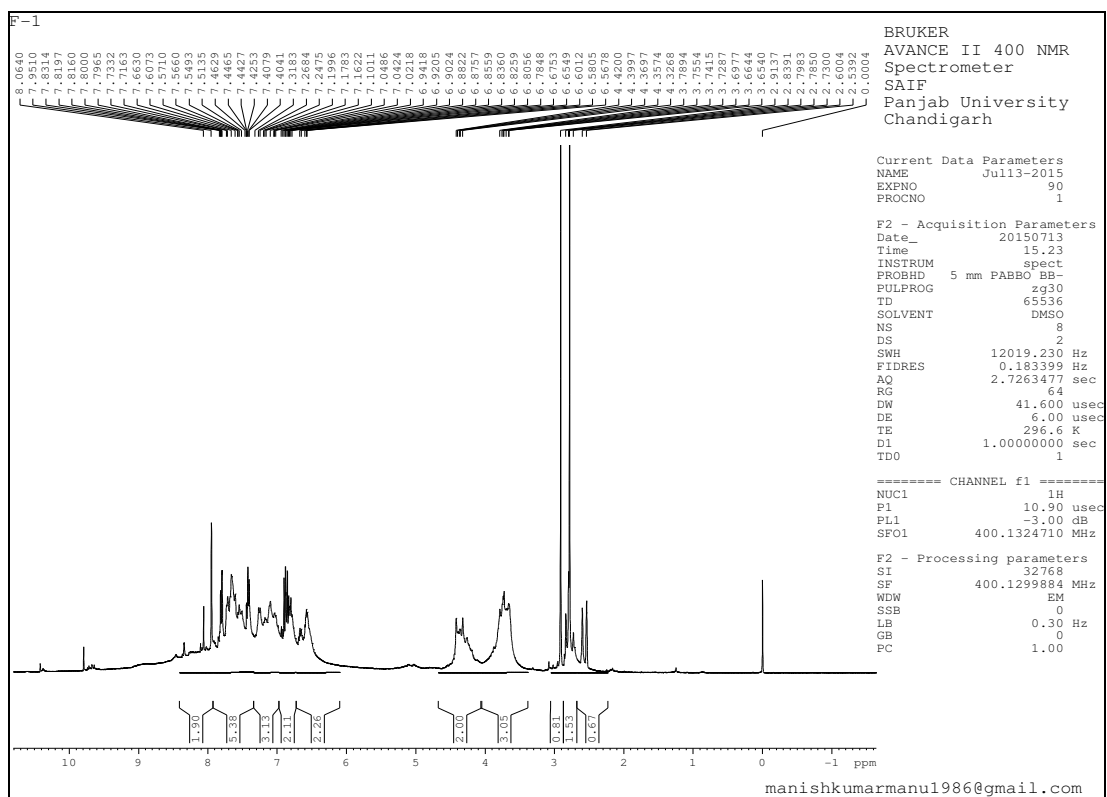


Fig.-2: Proton NMR spectra of ASF terpolymer resin.

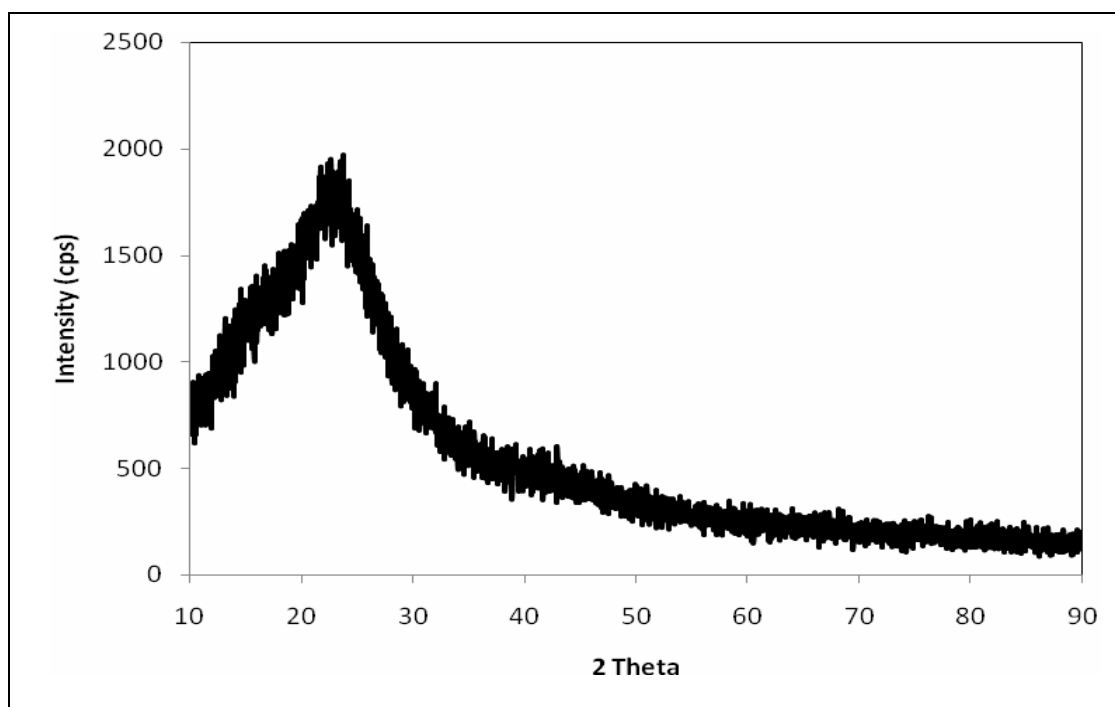


Fig.-3: X-RD of ASF terpolymer resin

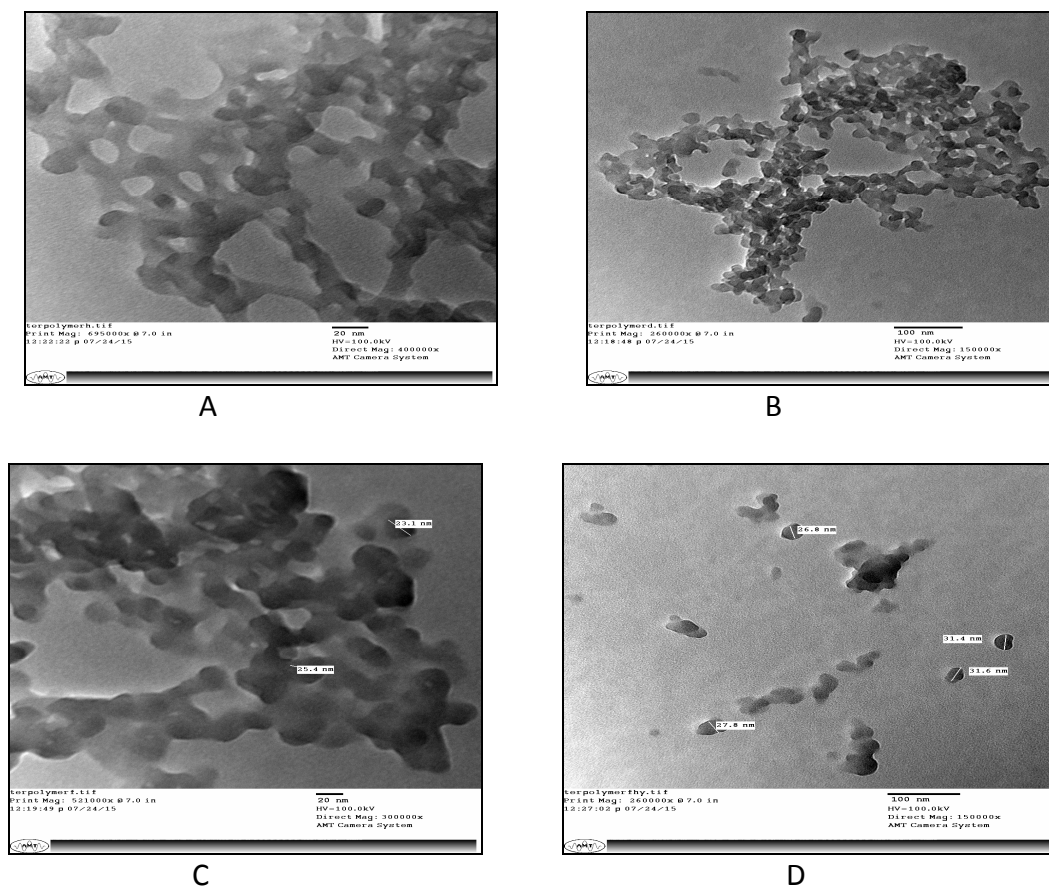


Fig.-4: Transmission Electron micrographs (TEM) of ASF terpolymer resin

X-Ray diffraction

The x-ray diffraction diagram of the polymer displayed the main characteristic peak and a broad shoulder in the range of $2\theta^{22-23}$. In view of the relative half value width, it may be concluded that the polymer is partially crystalline. The broad characteristic peak indicates the amorphous nature of the polymer which can also be explained by TEM study. The XRD spectrum was used to calculate crystallite size of ASF terpolymer resin using Scherer's formula of Cullity.

$$d = \frac{0.9 \lambda}{B \cdot \cos \theta_B}$$

Where λ is x-ray wavelength (1.54056 Å), θ_B is Bragg's diffraction angle and B is reflection broadening as full width at half maximum intensity. The particle size of ASF terpolymer resin has been calculated which is found to be at around 28.21 nm. The polymer under study is a terpolymer hence it is very difficult to assign its exact structure. However on the basis of the nature and relative position of the monomers, elemental analysis, IR, NMR, TEM and XRD spectral studies and taking into consideration the most probable structure has been proposed for ASF terpolymer resin (Scheme-1).

Morphological studies

The morphology of the synthesized and purified terpolymer resins under investigation has been reported by transmission electron micrographs at magnifications 150000 X and 300000 X are shown in Figure-4.

The size of terpolymer resin is approximately 23.1 nm to 31.6 nm. The image of copolymer clearly indicates a less close packed structure with high porosity or voids. The voids present in the copolymer may be responsible for the swelling behavior and the reactivity of the active sites buried in the polymer matrix. The image also showed a transition state between amorphous and crystalline state. The crystalline form in the copolymer may be due to the acidic nature of monomers. However, more predominantly the copolymer is amorphous and this change of crystalline into amorphous is due to the polycondensation. At different magnification the resin shows more amorphous character with less closed packed surface having deep pits.

CONCLUSIONS

The terpolymer resin ASF was synthesized by the microwave assisted synthesis of anthranilic acid-salicylic acid-formaldehyde (ASF) terpolymer resin in the presence of DMF. This method is energy-saving as well as time-saving as compared to the conventional method which requires 5 hours for the completion of the reaction. The resin is yellow in color, insoluble in cold and hot water, chloroform, carbon tetrachloride but completely soluble in acetone, 1,4-dioxane, *N,N*-dimethyl formamide, dimethyl sulfoxide, pyridine. Through FT-IR, proton NMR, X-RD, TEM the proposed structure of the ASF terpolymer resin was confirmed.

ACKNOWLEDGEMENT

The authors are thankful to the Principal, Phulsingh Naik Mahavidyalaya, and Pusad for providing laboratory facilities. We are also grateful to Director, SAIF Punjab University, Chandigarh, for spectral analysis, Principal, Shri Shivaji College of Arts Commerce & Science, Akola for IR.

REFERENCES

1. O. Szabadka, E. Varga, L. Nagy, *Talanta*, **59**, 1081(2003).
2. S. S. Katkamwar, A. B. Zade, S. S. Rahangdale, W. B. Gurnule, *J. Appl. Polym. Sci.*, **113**, 3330(2009).
3. Li. X. Gui, H. H. Rong, Y. Yang, *Polymer*, **42**, 4099(2001).
4. J. Y. Wang, C. Yuan, *Huaxue Yu Nianhe*, **1**, 20(2002).
5. A. N. Egorov, Y. I. Sukhorukov, G. V. Plotnikova, A. K. Khaliullin, *Rus. J. Appl. Chem.*, **75**, 152(2002).
6. L. K. Orazzhanova, M. G. Yashkarova, L. A. Bimendina, S. D. Kudaibergenov, *J. Appl. Polym. Sci.*, **87**, 759(2003).
7. A. A. Atia, A.M. Donia, K. Z. Elwakeel, *React. Funct. Polym.*, **65**, 267(2005).
8. R. A. Beauvais, S. D. Alexandratos, *React. Funct. Polym.*, **36**, 113(1998).
9. S. A. Patel, B. S. Shah, R. M. Patel, P. M. Patel, *Iran Polym. J.*, **13**, 445(2004).
10. R. M. Zalloum, S. M. Mubarak, *J. Appl. Polym. Sci.*, **109**, 3180(2008)
11. P. K. Roy, A. S. Rawat, Choudhary, P. K. Rai, *J. Appl. Polym. Sci.*, **94**, 1771(2004).
12. B. L. Rivas, E. D. Pereira, P. Gallegos, K. E. Geckeler, *Polym. Adv. Technol.*, **13**, 1000(2002).
13. W. B. Gurnule, H. D. Juneja, L. J. Paliwal, *React. Funct. Polym.*, **50**, 95(2002).
14. W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal, R. B. Kharat, *Synth. React. Inorg. Met-Org. Chem.*, **33**, 1187(2003).
15. M. Karunakaran, A. Burkanudeen, *Orient. J. Chem.*, **19**, 225(2003).
16. A. Burkanudeen, M. Karunakaran, *Orient. J. Chem.*, **18**, 65(2002).
17. B. A. Shah, A. V. Shah, P. M. Shah, *Iran Polym. J.*, **16**, 173(2006).
18. B. C. Mondal, A. K. Das, *React. Funct. Polym.*, **53**, 45(2003).
19. B. C. Mondal A. K. Das, *Ind. J. Chem. Technol.*, **10**, 489(2003).
20. B. A. Shah, A. V. Shah, R. R. Bhatt, *Iran Polym. J.*, **16**, 173(2007).
21. W. B. Gurnule, J. V. Khobragade and M. Ahamed, *Der. Pharma. Chem.*, **6**, 334 (2014).
22. A. N. Gupta, V. V. Hiwase, A. B. Kalambe, *Chemical Science Transactions*, **3**, 19(2014).
23. S. D. Kukade, R. R. Naik, S. V. Bawankar, *Orbital: The Electronic Journal of Chemistry* **6**, 601(2014)

[RJC-1301/2015]