

THERMOANALYTICAL STUDIES AND KINETICS OF NEWLY SYNTHESIZED COPOLYMER DERIVED FROM *p*-HYDROXYBENZOIC ACID, AND SEMICARBAZIDE

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ABSTRACT

The Copolymer (p-HBSF) was synthesized by condensation of *p*-hydroxybenzoic acid and semicarbazide with formaldehyde in the presence of 2M HCL as a catalyst at 126 ± 2 °C for 5 hrs. with molar proportion of reactants. The synthesized copolymer resin has been characterized by different physico-chemical techniques. Thermogravimetric analysis of all copolymer resins in present study have been carried out by non-isothermal thermogravimetric analysis technique in which sample is subjected to condition of continuous increase in temperature at linear rate. Thermal study of the resins was carried out to determine their mode of decomposition and relative thermal stabilities. The copolymer (p-HBSF) was characterized by FT-IR, ¹H-NMR Spectroscopy. The thermal decomposition behavior of copolymer was studied by using TGA in static nitrogen atmosphere at a heating rate of 10⁰C/min. The advantage of Freeman-Carroll method is to calculate both the order of reaction (n) and energy of activation in one single stage by keeping heating rate constant. Thermal activation energy (E_a) calculated with above two mentioned methods are in close agreement. Freeman Carroll and Sharp-Wentworth methods were used to calculate the thermal activation energy (E_a), the order of reaction (n), entropy Change (ΔS), free energy change (ΔF), apperent entropy change (ΔS), and frequency factor (Z). The thermal activation energy determined with the help of these method was in good agreement with each other.

Keywords: Synthesis, condensation, thermogravimetric analysis, activation energy, decomposition, resins.

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INTRODUCTION

Thermogravimetric analysis has been widely used to investigate the decomposition characteristics of polymeric matter. Copolymers, very special classes of polymers, are known for their versatile uses and are found to be amorphous, crystalline or resinous in nature. Phenolic resins have been the workhorse as matrix resins in composites for structural and thermal applications in aerospace because of their ease of processability, thermal stability, versatile characteristics and cost effectiveness. W. Tang and coworkers studied the thermal decomposition kinetics of thermotropic copolyesters made from trans-*p*-hydrocinnamic acid and *p*-hydrobenzoic acid^{1,2}. Copolymers occupy an intermediate position between organic and inorganic compounds and it is hoped that the study of copolymers will lead to the production of polymer, which are both thermally stable and useful as fabricating materials. P. E. P. Michael *et al.* studied synthesis, characterization and thermal degradation of 8-hydroxyquinolineguanidine-formaldehyde copolymer³. Rahangdale and coworkers studied thermal degradation of copolymers derived from 2, 4-dihydroxyacetophenone, dithioamide and formaldehyde⁴. Copolymers can be used as high energy material, ion-exchanger, semiconductors, antioxidants, fire proofing agent, optical storage data, binders, molding materials *etc.* Copolymers were applied in various fields of research as ion-exchangers, high thermal resistance materials, and electrical appliances⁵. The study of thermal behaviour of copolymers in air at different temperature provides information about the nature of species produced at various temperatures due to degradation. Copolymers having good thermal stability and catalytic activity have enhanced the development of polymeric materials. Copolymer resins are derived from 2,4-

dihydroxypropiophenone, biuret and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation⁶⁻⁸. Terpolymers of salicylic acid, thiourea with trioxane and phydroxybenzoic acid, thiourea with trioxane have been reported in the literature⁹⁻¹².

The present paper deals with the synthesis, structural characterization of p-HBSF copolymeric resin by various physicochemical studies Thermal analysis of the newly synthesized resin of p-hydroxybenzoic acid, thiosemicarbazide with formaldehyde (F), by applying the Sharp-Wentworth and Freeman-Carroll methods. Energy of activation (E_a), thermodynamic parameters viz. Z , ΔS , ΔF , S^* , and order of reaction/ (n) were determined by applying Freeman-Carroll Method¹³⁻¹⁵.

EXPERIMENTAL

Materials

The entire chemical used in the synthesis of various new copolymer resins were procured from the market and were analar or Fluka or chemically pure grade. Whenever required they were further purified by standard methods like thin layer chromatography, reprecipitation and crystallization which are generally used for the analytical purification purpose.

Synthesis of p-HBSF copolymer resins

The new copolymer resin p-HBSF was synthesized by condensing p-hydroxybenzoic acid (0.1 mol) and semicarbazide (0.1 mol) with formaldehyde (0.2 mol) in a mol ratio of 1:1:2 in the presence of 2 M 200 ml HCl as a catalyst at $126 \pm 2^\circ \text{C}$ for 5h, in an oil bath with occasional shaking, to ensure thorough mixing. The separated copolymer was washed with hot water and methanol to remove unreacted starting materials and acid monomers. The properly washed resin was dried, powdered and then extracted with diethyl ether and then with petroleum ether to remove salicylic acid- semicarbazide formaldehyde copolymer which might be present along with p-HBSF copolymer. The yellow color resinous product was immediately removed from the flask as soon as reaction period was over and then purified. The reaction and suggested structure of p-HBSF is shown in Fig.-1.

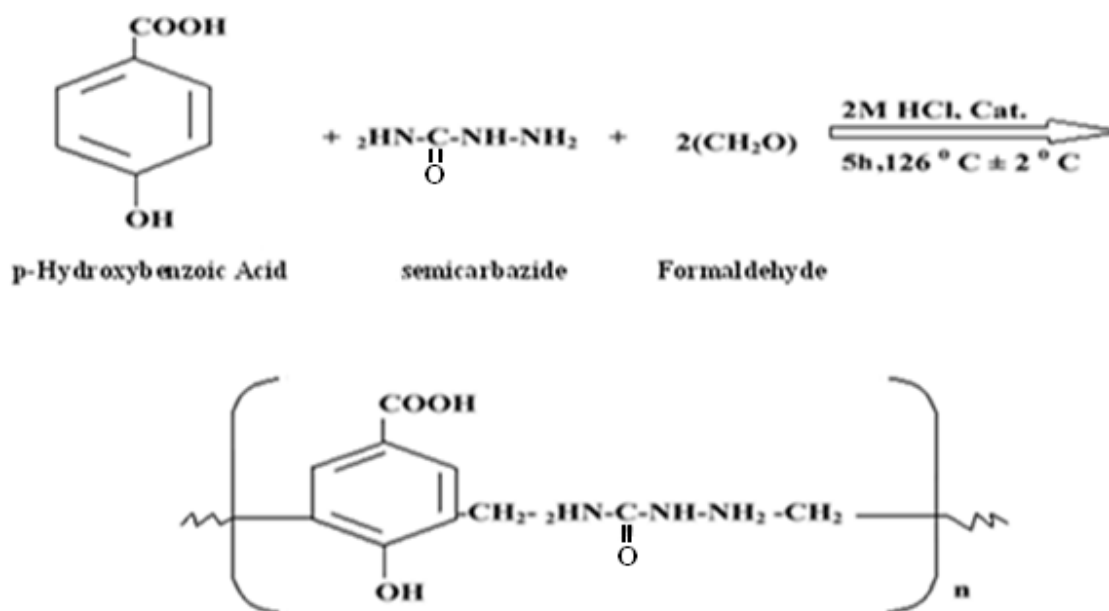


Fig.-1: Synthesis of p-HBSF copolymer resin.

The copolymer was purified by dissolving in 10% aqueous sodium hydroxide solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated hydrochloric acid / distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated twice. The copolymer sample p-HBSF thus obtained was filtered, washed several times with hot water, dried in air, powdered and kept in vacuum desiccator over silica gel.

Thermoanalytical Study

The non-isothermal thermogravimetric analysis was performed in air atmosphere with heating rate of $10^{\circ}\text{C}.\text{min}^{-1}$ from temperature range of 50°C to 600°C using Perkin Elmer Diamond TGA analyzer in argon environment. The thermograms were recorded at Sophisticated Instrumentation

Centre for Applied Research and Testing (SICART), Vallabh Vidyanagar, Gujarat. The thermal stability of copolymer, based on the initial decomposition temperature, has also been used here to define their relative thermal stability, neglecting the degree of decomposition. A plot of percentage mass loss versus temperature is shown in the Fig. 4 for a representative p-HBSF copolymer. From the TG curves, the thermoanalytical data and the decomposition temperatures were determined for different stages. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth and Freeman-Carroll adopted.

RESULTS AND DISCUSSION

The newly synthesized purified p-HBSF copolymer resin was found to be yellow in color. The copolymer is soluble in solvents such as DMF, DMSO and THF while insoluble in almost all other organic solvents. The melting point of p-HBSF copolymer resin is 188°C and the yield of the copolymer resin was found to be 87 %.

FT-IR Spectra

A broad band appeared in the region $3500\text{--}3200\text{ cm}^{-1}$ may be assigned to the stretching vibrations of phenolic hydroxy (-OH) groups exhibiting intermolecular hydrogen bonding. The presence of -NH in thiosemicarbazide moiety may be assigned due to sharp band at $2800\text{--}3200\text{ cm}^{-1}$. The sharp band displayed at $1700\text{--}1682\text{ cm}^{-1}$ may be due to the stretching vibrations of carbonyl group (C=O). The bands obtained at $1400\text{--}1200\text{ cm}^{-1}$ suggest the presence of methylene bridges in the polymer chain. The weak band appearing at $750\text{--}780\text{ cm}^{-1}$ is assigned to C - OH bond. 1, 2, 4, substitution of aromatic ring is recognized from the bands appearing at 1281, 1207, 1199 cm^{-1} respectively



Fig.-2: FT-IR Spectra of p-HBSF copolymer

NMR Spectra

Weak signal in the range of 7.2 ppm is attributed to phenolic -OH proton. The NMR spectra of p-HBSF copolymer resins show a weak multiplet signal (unsymmetrical pattern) in the region 6.8 (δ) ppm which is due aromatic protons. A medium singlet peak appeared at 3.7 (δ) ppm may be assigned to methyl protons of Ar-CH₂-NH group. Intense signal appeared in the region 2.3 (δ) ppm may be due to Ar-CH₂-NH. Triplet signal appeared in the region 3.35 (δ) ppm can be assigned to amido proton of -CH₂-NH-CO- linkage.

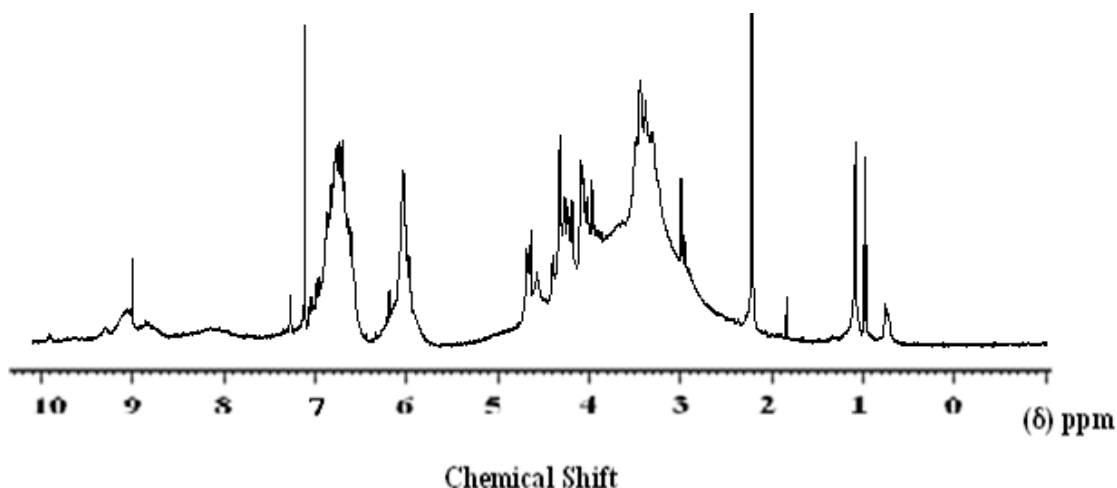


Fig.-3: NMR Spectra of p-HBSF copolymer

Thermogravimetry

The thermogravimetric data provide information regarding the thermal stability of a polymer. The thermograms were obtained by heating resin sample in air at 10⁰ C/min. The results of percentage weight loss of the copolymer resins depicts three steps decomposition in the temperature range 140-600°C and are furnished in Figure 4. The slow decomposition between 0-195°C corresponds to 6.8 % loss which may be attributed to *loss of water molecule* against calculated 7.0 % present per repeat unit of the polymer. The first step decomposition start from 195-265°C which represents *loss of hydroxyl group and acid group* (32.00 % found and 31.53 % cal.). The second step decomposition start from 265-440°C corresponding to 66.54% removal of *aromatic nucleus and methylene bridge* against calculated 66.54%. The third step decomposition side chain from 440-600°C corresponding to removal of *Semicarbazide moiety* (100.00% found and 100.00% cal.).

With the help of thermogravimetric data the thermal activation energies (*E_a*) and order of reaction (*n*) calculated. Also other thermodynamic parameters such as entropy change (*ΔS*), apparent entropy change (*S**) and frequency factor (*Z*) are determined and reported in the Table 1 & 2. To provide further evidence regarding the degradation system of analyzed compounds, we derived the TG curves by applying an analytical method proposed by Sharp-Wentworth and Freeman-Carroll. The 'average *E_a*' calculated by Freeman-Carroll (23.55 KJ/mole) and 'average *E_a*' by Sharp- Wentworth (23.77 KJ/mole) is nearly same.

Sharp -Wentworth method

Using the equation derived by Sharp and Wentworth,

$$\log [(dc/dT)/(1-c)] = \log (A/\beta) - [E_a/2.303R] \cdot 1/T \quad (1)$$

Where,

dc/dT = rate of change of fraction of weight with change in temperature

β = linear heating rate *dT/dt*.

By plotting the graph between $(\log dc/dt)/(1-c)$ vs $1/T$ we obtained the straight line which give energy of activation (E_a) from its slope. Where β is the conversion at time t , R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and T is the absolute temperature. The plots (Fig.-2) give the activation energies at different stages of degradation reaction take place.

Freeman-Carroll method

The straight-line equation derived by Freeman and Carroll, which is in the form of n

$$[\Delta \log (dw / dt)] / \Delta \log W_r = (-E / 2.303R) \cdot \Delta (1/T) / \Delta \log W_r + n \quad (2)$$

Where,

dw/dt = rate of change of weight with time.

$W_r = W_c - W$

W_c = weight loss at completion of reaction.

W = fraction of weight loss at time t .

E_a = energy of activation., n = order of reaction.

The plot between the terms $[\Delta \log (dw/dt)] / \Delta \log W_r$ Vs $\Delta (1/T) / \Delta \log W_r$ gives a straight line from which slope we obtained energy of activation (E_a) and intercept on Y-axis as order of reaction (n). The change in entropy (S), frequency factor (z), apparent entropy (S^*) can also be calculated by further calculations.

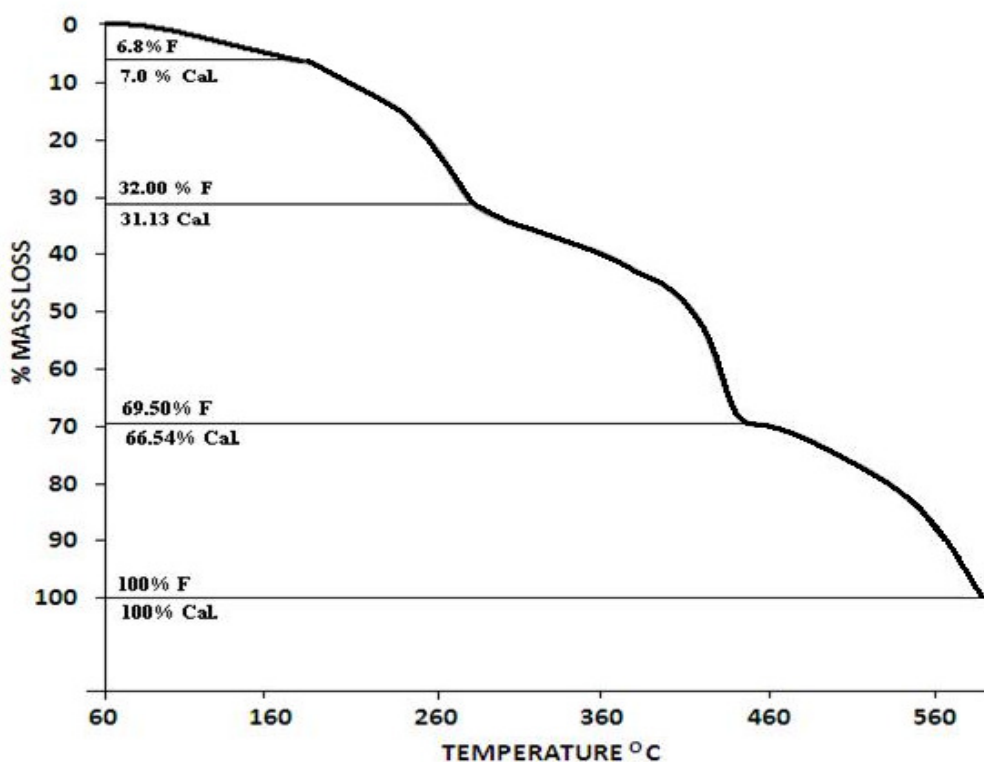


Fig.-4: Decomposition Pattern of p-HBSF copolymer Resin.

Table-1: Results of Thermogravimetric Analysis of p-HBSF copolymer

Copolymer	Half Decomposition Temp. T^*K	Activation Energy (kJ/mol)	
		Freeman Carroll	Sharp Wenwoth
p-HBSF	683	23.55	23.77

Table.2: Kinetic Parameters of p-HBSF copolymer

Copolymer	Entropy Change $-\Delta S(J)$	Free Energy Change $\Delta F(kJ)$	Frequency factor $Z(S^{-1})$	Apparent Entropy Change (S^*)	Order of reaction (n)
p-HBSF	-299.55	206.95	644	-23.82	0.98

CONCLUSION

From the FT-IR and 1H NMR spectral studies the proposed structure of the p-HBSF copolymer has been determined. A copolymer, p-HBSF based on the condensation reaction of p-hydroxybenzoic acid semicarbazide formaldehyde in the presence of acid catalyst was prepared. In TGA the energy of activation evaluated from the Sharp-Wentworth and Freeman-Carroll methods are found to be nearly equal and the kinetic parameters obtained from Freeman-Carroll method are found to be similar, indicating the common reaction mode. However, it is difficult to draw any unique conclusion regarding the decomposition mechanism. Low values of collision frequency factor (Z) may be concluded that the decomposition reaction of p-hydroxybenzoic acid, semicarbazide, formaldehyde copolymer can be classified as 'slow reaction'. The decomposition reaction was started at higher temperature, indicating a copolymer p-HBSF is thermally stable at higher temperature.

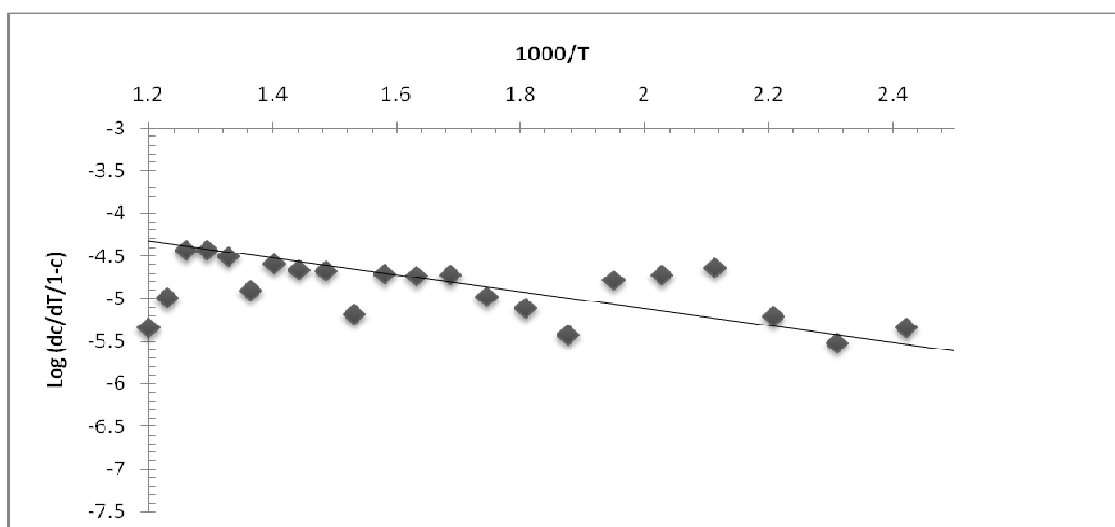


Fig.-5: Sharp-Wentworth plot of p-HBSF copolymer

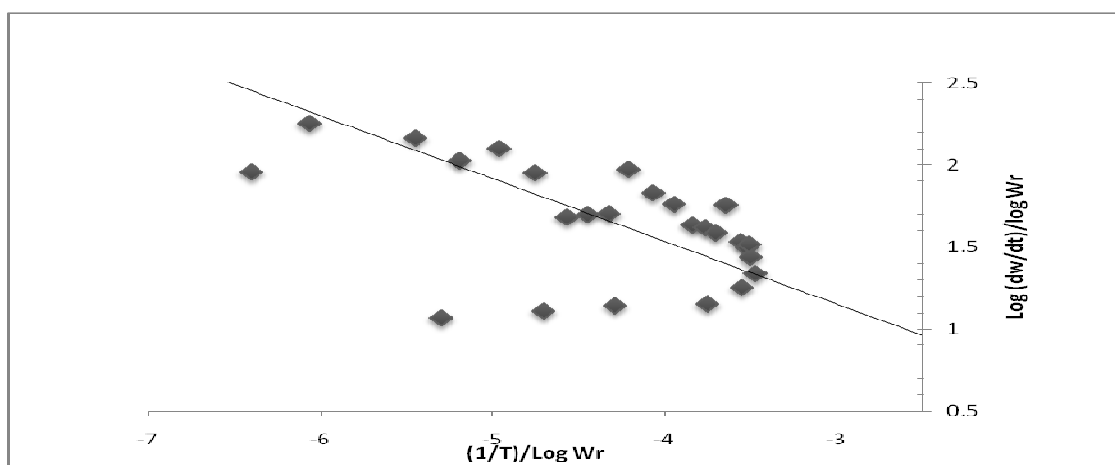


Fig.-6: Thermal activation energy plot of p-HBSF copolymer

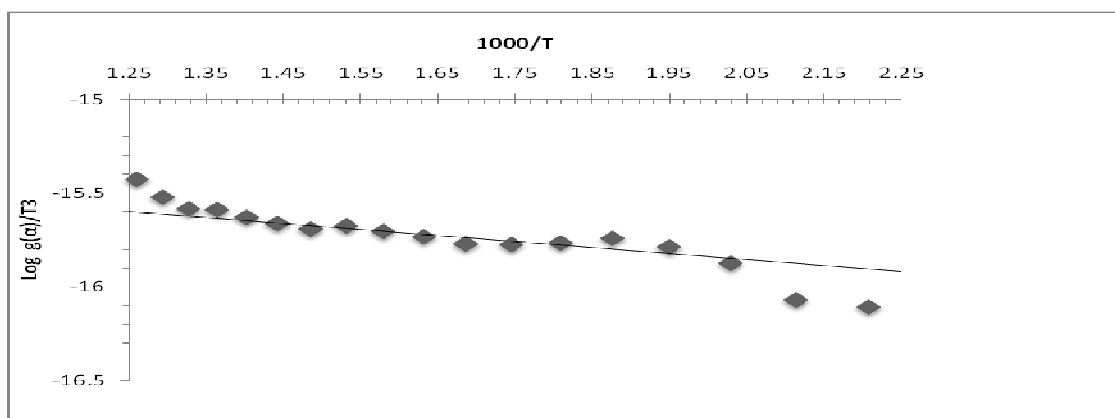


Fig.-7: Freeman-Carroll plot of p-HBSF copolymer

ACKNOWLEDGEMENTS

Authors are thankful to the SAIF, Punjab University, Chandigarh for carried out spectral analysis, and also to the SICART, Vallabhvidyanagar, Gujrat for carried out the thermal analysis.

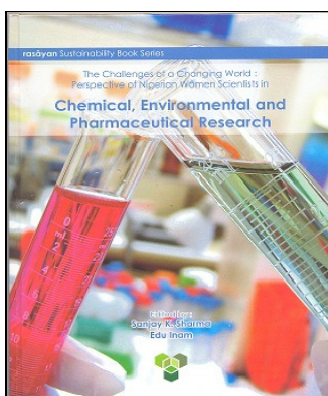
REFERENCES

1. D. Bilba, D. Bijan, and L. Tofan, *Croa. Chem. Acta*, **71(1)**, 155(1998).
2. Kimura Hajime, Murata Youchi, Matsumoto Akihiro, Hasegawa Kiichi, Ohtsuka Keido and Fulkuda Akinori, *J. Appl. Polym. Sci.*, **74(9)**, 2266(1999).
3. O.D. Bonner, C.F. Jumper and O.C. Rogers, *J. Phys. Chem.*, **62**, 250(1958).
4. P.K. Rahangdale, W.B. Gurnule, L.J. Paliwal and R.B. Kharat, *Synth. React. Inorg. Met. Org. Chem.*, **33(7)**, 187(2003).
5. W.B. Gurnule, H.D. Juneja and L.J. Paliwal, *Indian J. Chem.*, **39(A)**, 1110(2000).
6. S. Narayan, S.B. Bhavne and R.B. Kharat, *J. Indian Chem. Soc.*, **58**, 1194(1981).
7. N. Malthy and Roop Singh *Indian J. Sci. Tech.*, **(5)**, 2302(2012)
8. B.A. Shah; A.V. Shah, R.R. Bhatt, *Iran. Polym. J.*, **16(3)**, 173(2007).
9. R.K. Samal and B.K. Senapati, *J. Appl. Polym. Sci.*, **62**, 655(1996).
10. R.C. DeGeiso, L.G. Donaruma and E.A. Tomic., *Anal. Chem.*, **34**, 845(1962).
11. P.E. Michael, P.S. Lingala, H.D. Juneja and L.J. Paliwal, *J. Appl. Polym. Sci.*, **92**, 2278(2004).
12. A.R. Burkanudeen, M. Karunakaran, M.A. Riswan Ahamed, *Orient J. Chem.*, **18**, 65(2002)
13. R.N. Singru, A.B. Zade, W.B. Gurnule, *J. Appl. Polym. Sci.*, **109**, 859(2008).
14. T.B. Mostafa, *J. Am. Sci.*, **6(8)**, 512(2010).
15. M.V. Patel, M.B. Dolia, J.N. Patel, and R.M. Patel, *React. Funct. Polym.*, **65(3)**, 195(2005).
16. Arun Sing, Sanjaykumar Saraf, *Int. J. Polym. Mat. Sci.*, **58**, 499(2009).
17. W.B. Gurnule, K.A. Nandekar, J.R. Dontulwar, *Inter. J. Know. Engg.*, **3(1)**, 151(2012).
18. J.N. Patel, M.B. Dolia, M.B. Patel, and R.M. Patel, *J. Appl. Polym. Sci.*, **100(1)**, 437(2006).
19. M. Porter; *Handbook of Industrial Membrane Technology*, Noyes, Pork Ridge, New York, (1990).
20. Walter de Gruyter, *Ion Exchangers*, (K. Dorfner, ed.), Berlin, (1991).
21. W. Kemp, *Organic Spectroscopy*, Macmillan, Hong Kong, (1975).
22. C.E. Harland, *Ion exchange: Theory and Practice*, The Royal Society of Chemistry, Cambridge, (1994).

23. B.S. Furniss, A.J. Hannaford, P.W.G. Smith, A.R. Tatchell. *Vogel's Text Book of Practical Organic Chemistry*. Addison Wesley Longman Ltd, England, (1998).
24. A.R. Burkanudeen, R.S. Azarudeen, M.A. Riswan Ahamed, *Proc. Int. Conf. Chem. Eng. Applic. (CCEA 2010)*, Singapore, **26-28**, 282 (2010).
25. W.B. Gurnule, H.D. Juneja and L.J. Paliwal, *Asian J. Chem.*, **11(3)**, 767 (1999).
26. M.V. Tarase, A.B. Zade and W.B. Gurnule, *J. Ultra Sci.*, **3(1)**, 41(2007)
27. R.N. Singru, V.A. Khati, W.B. Gurnule, A.B. Zade, J.R. Dontulwar, *Anal. Bioanal. Electrochem.*, **3(1)**, 67 (2011).
28. P.U. Singare, R.S. Lokhande and T.S. Prabhavalkar, *Bull. Chem. Soc. Ethiop.*, **22**, 415(2008).
29. M.M. Patel, M.A. Kapadia, G.P. Patel, J.D. Joshi, *J. Appl. Polym. Sci.* **106 (2)**, 1307(2007).
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