



SYNTHESIS, CHARACTERIZATION AND THERMAL DEGRADATION STUDIES OF COPOLYMER DERIVED FROM SALLICYLADEHYDE, MELAMINE AND FORMALDEHYDE

WASUDEO B. GURNULE* and SONALI S. DHOTE^a

Department of Chemistry, Kamla Nehru Mahavidyalaya, Sakkardara, NAGPUR – 440009 (M.S.) INDIA

^aDepartment of Chemistry, Laxminarayan Institute of Technology, Rashtasant Tukdoji Maharaj Nagpur University, NAGPUR – 440010 (M.S.) INDIA

(Received : 21.02.2012; Revised : 15.03.2012; Accepted : 21.03.2012)

ABSTRACT

Copolymer (SMF) has been synthesized using the monomers salicylaldehyde, melamine and formaldehyde in 1 : 1 : 3 molar proportions. The structure of SMF copolymer has been elucidated on the basis of elemental analysis and various physicochemical techniques, i.e. UV-Visible, FT-IR and ¹H-NMR spectroscopy. Detailed thermal degradation study of the new copolymer has been carried out to ascertain its thermal stability. Thermal degradation curve is discussed which shows three decomposition steps. The activation energy (E_a) and thermal stability calculated by using the Sharp-Wentworth, Freeman-Carroll and Freidman's methods. Thermodynamic parameters such as entropy change (ΔS), apparent entropy change (S^*) and frequency factor (z) have also been evaluated on the basis of the data of Freeman-Carroll method. The order of reaction (n) is found out to be 0.99.

Key words: Thermal degradation, Copolymer, Salicylaldehyde, Melamine, Formaldehyde.

INTRODUCTON

A large amount of work has been reported from these laboratories on the synthesis, characterization, structure and thermal studies of several polymers¹⁻³. The Freeman-Carroll⁴ and Sharp-Wentworth⁵ methods have been used to evaluate various kinetic parameters for these copolymers. The method for estimating kinetic parameters from dynamic TG studies suffers from the difficulty that the two parameters, temperature and time can not be continuously changed. This problem is eliminated in Freeman-Carroll method where the parameters of temperature and time can be varied. Methods for estimating kinetic parameters from dynamic TG studies⁶⁻⁹ are mostly based on the assumptions that the Arrhenius equation is valid and that the thermal and diffusion barriers are negligible.

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 process ability, thermal stability, versatile characteristics and cost effectiveness. W. Tang and coworkers¹⁰ studied the

thermal decomposition kinetics of thermotropic copolyesters made from trans-p-hydrocinnamic acid and p-hydrobenzoic acid. 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. Michael et al. studied synthesis, characterization and thermal degradation of 8-hydroxyquinoline-guanidine-formaldehyde terpolymer¹¹. Rahangdale and coworkers studied thermal degradation of polymers derived from 2, 4-dihydroxy-acetophenone, dithioamide and formaldehyde^{12,13}.

Terpolymer resins are derived from 2,4-dihydroxypropiophenone, biuret, and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation^{14,15}. Thermal degradation of p-nitroaniline, p-chloroaniline and p-aminophenol has been studied by Dash *et al.*¹⁶ and 2-hydroxyacetophenone, oxamide and formaldehyde¹⁷. S. L. Oswal et al synthesized and studied thermal properties of copoly (maleimide-methylmethacrylate), terpoly (maleimide-methylmethacrylate-acrylic acid), and terpoly-(maleimide-methylmethacrylatemethylacrylic acid). The thermal behaviour was studied by TG and DSC techniques¹⁸. Thermoanalysis and rheological behavior of copolymers of methyl methacrylate, N-phenylmaleimide and styrene studied by G. Jungang et al.¹⁹. In order to synthesize polymers having numerous practical applications, there is a need to investigate the effect of heat on the polymers in order to establish their thermal stability. It must be pointed out that all the methods proposed have been developed by assuming that both activation energy and kinetic model do not change along the process. However, it has concluded from free- model kinetic methods of analysis that the activation energy is a function of the reacted fraction²⁰⁻²⁴.

However, the literature studies have revealed that no copolymer has been synthesized using the monomer salicylaldehyde, melamine and formaldehyde. Therefore, in the present communication we report the synthesis, structural characterization and thermal degradation studies of SMF copolymer.

EXPERIMENTAL

Synthesis of SMF copolymer resin

The SMF copolymer was prepared by condensing salicylaldehyde (0.1 mol) and melamine (0.1 mol) with formaldehyde (0.3mol) in the presence of 2M HCl as a catalyst at 126 ± 2 °C in an oil bath for 5 hr .

The brown colored solid product obtained was immediately removed and extracted with diethyl ether to remove excess of salicylaldehyde -formaldehyde copolymer, which might be present along with the SMF copolymer. It was further purified by dissolving in 8 % NaOH and then filtered. The copolymer was then reprecipitated by drop wise addition of 1 : 1 (v/v) conc. HCl / water with constant stirring and filtered. The process was repeated twice. The resulting copolymer sample was washed with boiling water and dried in a vacuum at room temperature. The purified copolymer resin was finely ground to pass through 300-mesh size sieve and kept in a vacuum over silica gel. The yield of the copolymer was found to be about 80-83%.

The elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyzer instrument. The UV-Visible studies were out carried using Hitachi 330 UV-VIS-NIR Spectrometer in the range 200-850 nm. The Infrared spectrum was recorded in the region of 500-4000 cm^{-1} on Perkin Elmer Spectrum RX1 FT-IR Spectrometer. *H NMR studied using Bruker Avance-II FT-NMR Spectrometer in DMSO- d_6 solvent. All the analytical and spectral studies for the newly synthesized copolymer were carried out at Sophisticated Analytical Instrumentation Facility (SAIF), Punjab University, Chandigarh.

The nonisothermal thermogravimetric analysis was performed in air atmosphere with heating rate of $10^{\circ}\text{C. min}^{-1}$ using 5 - 6 mg of samples in platinum crucible from temperature of 40°C to 800°C and

thermograms are recorded for SMF sample at SICART, Vallabhvidyanagar, Gujrat. 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.

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, Freeman- Carroll and Freidman.gives a straight line from which slop we obtained energy of activation (E_a)and intercept on Y-axis as order of reaction (n). The change in entropy (ΔS), frequency factor (z), apparent entropy (S^*) can also be calculated by further calculations.

RESULTS AND DISCUSSION

The newly synthesized SMF copolymer resin was found to be brown 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 this copolymer was determined by using electrically heated melting point apparatus and is found to be 425K.

The UV-visible spectra of SMF copolymer resin in pure DMSO was recorded in the region 200-600 nm. The spectra of these copolymer exhibit to absorption maxima in the regions of 220-240 and 290-330 nm. The bands at 220-240 nm indicate the presence of a C = O group containing a carbon-oxygen double bond in conjugation with the aromatic nucleus, and this is characteristic of the $\pi \rightarrow \pi^*$ transition. The later band indicates $\pi \rightarrow \pi^*$ transition. The bathochromic shift (the shift toward a longer wavelength) from the basic values (257 nm and 320 nm) may be due to the combined effect of conjugation and the phenolic hydroxyl group (auxochrome).

In IR spectra a broad absorption band appeared in the region 3400 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding.[28] A sharp strong peak at 1600 cm^{-1} may be ascribed to aromatic skeletal ring. The bands obtained at 1272 cm^{-1} and 1420 cm^{-1} suggest the presence of methylene (-CH₂-) bridge.[29] The 1,2,3,5 substitution of aromatic benzene ring recognized by the sharp, medium / weak absorption bands appeared at 903 cm^{-1} , 1050 cm^{-1} , 1105 cm^{-1} and 1218 cm^{-1} . The presence of sharp and strong band at 3102 cm^{-1} indicates the presence of -NH bridge. This band seems to be merged with very broad band of phenolic hydroxyl group.

The NMR spectrum of SMF copolymer was scanned in DMSO-d₆ solvent. The chemical shift (δ) ppm observed is assigned on the basis of data available in literature.[30] The singlet signal obtained at 3.9 (δ) ppm may be due to the methylene proton of Ar-CH₂-N moiety. The singlet at 1.35 (δ) ppm is due to the methylene proton of Ar-CH₂-Ar moiety. The singlet at 2.61(δ) ppm is due to methylene proton of Ar-CH₂ moiety. The singlet at 3.47(δ) ppm may be due to methylene proton of Ar- CH₂-N moiety. The singlet at 4.25(δ) ppm may be attributed to proton of Ar-NH₂- group. The weak multiplied signals (unsymmetrical pattern) in the region 6.74-6.82(δ) ppm may be due to aromatic proton (Ar-H). The signal at 8.52(δ) ppm may be due to phenolic hydroxyl groups. The much downfield chemical shift for phenolic -OH indicates clearly the intramolecular hydrogen bonding on -OH group. The polymers under study are copolymer and hence, it is diffiucult to assign their exact structures.

Thermogravimetric analysis of the copolymer

The thermal stability of copolymer is evaluated by dynamic thermo-gravimetric analysis in air atmosphere with heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$.

Thermogram of TG of SMF copolymer is shown in Fig. 1 Thermogram of copolymer depicts four steps decomposition after loss of water molecule in the temperature range 40°C – 750°C. The first step decomposition takes place between 40 °C - 100°C corresponds to 6.66 % loss which may attributed to loss of a water molecule against calculated 7.01% present per repeat unit of the polymer. The second step decomposition starts from 100°C - 135°C which represents degradation of -OH group and -NH groups attached to the aromatic ring (14.66 % experimental and 14.64 % calculated). The third step which is start from 135°C - 300°C corresponding to loss of aromatic rings (35.76% experimental and 35.29% calculated). The fourth step decomposition starts from 300°C - 750°C leaving behind melamine moiety (81.99% experimental and 81.82% calculated).

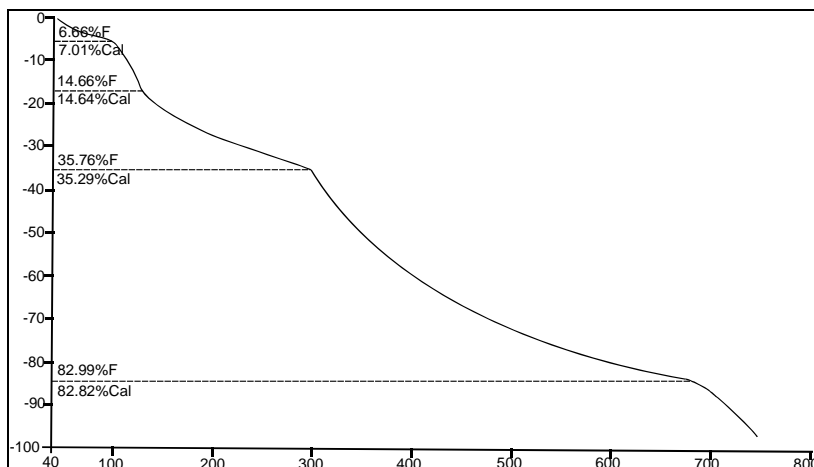


Fig. 1: T. G. Degradation of SMF polymer

Thermo-analytical data

A plot of percentage mass loss versus temperature is shown in the Fig. 1 for a representative SMF copolymer. To obtain the relative thermal stability of the copolymer, the method described by Sharp-Wentworth, Freeman-Carroll and Freidman was adopted. 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.

By using thermal decomposition data and then applying above methods the activation energy (E_a) is calculated which are not perfectly in agreement with each other. But the 'average E_a ' calculated by Freeman-Carroll and Freidman is nearly same and 'average E_a ' by Sharp-Wentworth is nearly double than both methods. However the error in activation energies obtained from the Sharp-Wentworth isoconversional method is significant and largely increases as far as conversion increases. On the other hand, it has been considered of interest to analyze the behavior of the process constitute by two competitive reactions that would lead to an apparent dependence between E_a and α when analyzed by isoconversional method, in spite such dependence is not real³¹.

A representative thermal activation energy plot of Sharp-Wentworth (Fig. 2), Freeman-Carroll (Fig. 3) and Freidman method for the copolymer has been shown. Thermodynamic parameters such as entropy change (ΔS), frequency factor (z), apparent entropy change (S^*) calculated on the basis of thermal activation energy (E_a). These values are given in (Table 1).

The abnormally low value of frequency factor, it may be concluded that decomposition reaction of SMF copolymer can be classed as a 'slow' reaction. There is no other obvious reason^{32,33}. Fairly good

straight-line plots are obtained using the two methods. This is expected since the decomposition of copolymer is known not to obey first order kinetic perfectly^{34,35}.

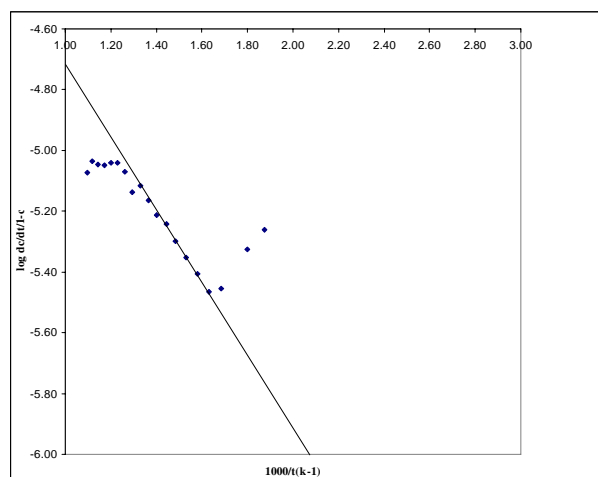


Fig. 2: Activation energy plot by Sharp-Wentworth plot for SMF polymer

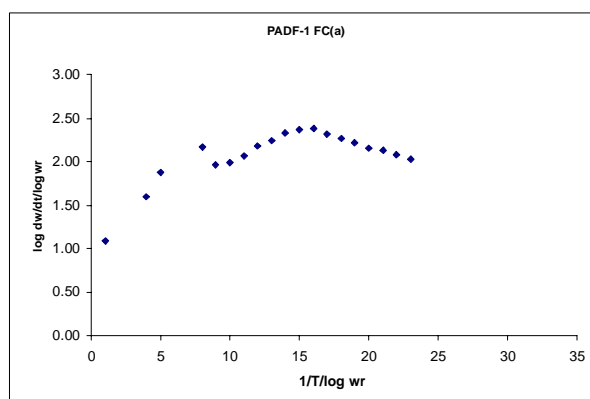


Fig 3: Activation energy plot by Freeman-Carroll plot for SMF polymer

CONCLUSION

The SMF copolymer based on the condensation polymerization of para amino phenol and dithiooxamide with formaldehyde in the presence of acid catalyst has been prepared. From the elemental analysis, UV-visible, FT-IR and ^1H NMR spectral studies the proposed structure of the SMF copolymer has been determined. Freeman-Carroll and Freidman provide accurate values of activation energy while Sharp-Wentworth would lead to important error in determination of activation energy.

ACKNOWLEDGEMENT

Authors thanks 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 H Patel, M Patel, K Patel, R Patel, E-polymers, **125**, 1-11 (2007).
- 2 M. M.Jadhao, L. J.Paliwal, N. S. Bhav, Ind. J. Chem., **44A**, 1-5 (2005).

- 3 P. E. P Michael, J. M.Barbe, H. D.Juneja, L. J. Paliwal, Euro. Polym. J., **43(12)**, 4995-5000 (2007).
- 4 E. S. Freeman and B. Carroll, J. Phys. Chem., **62**, 394 (1958).
- 5 J. B. Sharp and S. A. Wentworth, Anal. Chem., **41**, 2060 (1969).
- 6 A. W. Coats and J. P. Redfern, Nature (London) **208**, 68 (1964).
- 7 H. L.Friedman, J. Polym. Sci., Polym. Symp., **183** (1963).
- 8 T.Ozawa, J. Thermal Anal., **7** 601(1985).
- 9 H. H. Horowitz and G. Metzger, Anal. Chem., **35**, 1464 (1963).
- 10 W. Tang, X G. Li, D. Yan, J. App. Polym. Sci., **91**, 445 (2004).
- 11 P. E. P. Michael, J. M. Barbe, H. D. Juneja, L. J. Paliwal, Eur. Polym. J., **43**, 4995 (2007).
- 12 S. S. Rahangdale, A. B. Zade, W. B. Gurnule, J. Appl Polym Sci.,**108(2)**, 747 (2008).
- 13 S. S. Rahangdale, A. B. Zade, W. B. Gurnule, J. Ultra Sci., **19(2)**, 213 (2007).
- 14 M. V. Tarase, A. B. Zade, W. B. Gurnule, J. Ultra. Sci., **3(1)**, 41 (2007).
- 15 M. V. Tarase, A. B. Zade, W. B. Gurnule, J. Appl Polym Sci., **108(2)**, 738 (2008).
- 16 D. K. Dash, S. K. Sahu, P. L. Nayak, J. Therm. Anal. Cal., **86**, 517 (2006).
- 17 W. B. Gurnule, H. D. Juneja, L. J. Paliwal, J. Prog. Cryst. Growth Char. Mater., **45**, 155 (2002).
- 18 S. L. Oswal, N. S. Sarkar, V. K. Bhandari, H. B. Oza, C. B. Patel, Iran Polym. J., **13(4)**, 297 (2004).
- 19 G. Jungang, L. Guodong, Y. Liting, Z. Liucheng, Polym. Engg. Sci., **40(5)**, 1226 (2000).
- 20 H. Chen, N. Liu, W. Fang, Polym Degrad Stab., **91**, 1726 (2006).
- 21 T. Vlase, G. Vlase, N. Birta, N. Doca, J Therm Anal Cal., **88**, 631 (2007).
- 22 A. Khawam, D. R. Flanagan, Thermichin Acta, **429**, 93 (2005).
- 23 A. A. Joraid, Themochim Acta, **456**, 1 (2007).
- 24 P. E. P. Michael, P. S. Lingala, H. D. Juneja, L. J. Paliwal, J. App. Polym. Sci., **92(4)**, 2278 (2004).
- 25 E. S. Freeman, B. Carroll, J. Chem Rev., **62**, 394 (1958)
- 26 H. L. Freidman J. Polym Sci., **C6**, 183 (1964).
- 27 J. B. Sharp, S. A. Wentworth, Anal Chem., **41**, 2060 (1969).
- 28 J. M. Patel, M. G. Patel, H. J. Patel, K. H. Patel, R. M. Patel, J. Mac. Mol. Sci., **45**, 281 (2008).
- 29 W. B. Gurnule, P. K. Rahangdale, L. J. Paliwal, R. B. Kharat, Synth React. Inorg. Met. Org. Chem., **33**, 1187 (2003).
- 30 B. A. Shah, A. V. Shah, R. R. Bhatt, Iran J. Polym, **16**, 173 (2007).
- 31 J. M. Criado, P. E. Sanchez-Jimenez, L. A. Perez-Maqueda, J. Them. Anal. Cal, **92**, 199 (2008).
- 32 Y. Tonbul, Yardakoc K. Turk, J. Chem., **25**, 332 (2001).
- 33 H. Zhao, Y. Z. Wang, D. Y. Wang, B. Wang, B. Wu, D. Q. Chen, Polym Degrad Stab., **80**, 135 (2003).
- 34 R. N. Singru, A. B. Zade, W. B. Gurnule, J. App Polym Sci., **109(2)**, 859 (2008).
- 35 M. M. Jadhav, L. J. Paliwal, N. S. Bhave, J. App Polym Sci., **101(1)**, 227(2006).