



SYNTHESIS AND CHARACTERIZATION OF HIGH PERFORMANCE TERPOLYMER RESIN DERIVED FROM P-CHLOROPHENOL, BIURET AND FORMALDEHYDE

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Abstract- The terpolymer (p-CPBF) was synthesized by the condensation of p-Chlorophenol, Biurete with Formaldehyde in the presence of 2M HCl catalyst and using various molar proportion of the reacting monomers. The synthesized terpolymer then characterized by different and spectral studies like UV-Visible, IR and ¹H MMR. The morphology of synthesized terpolymer was studied by scanning electron 26 microscopy (SEM). The crystalline and amorphous nature of the polymer was studied by XRD spectra. Thermal studies of resin was carried out to determine their mode of decomposition, apperent activation energy. The kinetic parameters of the thermal degradation of the terpolymer samples were evaluated from the thermograms using Sharp-Wentworths method . The order of thermal stabilities of terpolymers were determined by using TGA.

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Introduction

In recent year there have been of growing intrest in design and synthesis of terpolymers due to their special properties and potential applications in sorption, waste water treatmeants, organic synthesis, hydrometallurgy, catalysis and recovery of trace metal element. [1-4] Terpolymer can also be synthesized by the condensation ofr mixture of phenols or hydroxybenzoic acid, various amines and formaldehyde [5-7]. A literature survey reveals that ion-exchange terpolymer resins have been synthesized from salicylic acid, thiourea and trioxane and also from p-hydroxybenzoic acid , urea and formaldehyde [8-9]. Ion-exchanges are widely used in analytical chemistry, hydrometallurgy, antibiotic purification and separation of radioisotopes and in a large scale water treatment and pollution control [10]. In an earlier communication [10-11] from this department a number of such terpolymer have been reported. However, no work has been carried out on the syntesis , characterization and structural studies of the terpolymer resin from p-Chlorophenol, Biurete and Formaldehyde

Experimental

Synthesis of Terpolymer (p-CPBF) Resin

A mixture of p-chlorophenol (1.71 gm. 0.1 mole), biuret (1.43 gm, 0.1 mole) and formaldehyde (7.5 ml 0.2 mole) and 2M hydrochloric acid (200 ml) was taken in a RB flask fitted with water condenser and heated in an oil bath at 126°C ± 2°C for 5 hours with occasional shaking [75]. The temperature of electrically heated oil bath was controlled with the help of dimmerstat. The resinous solid product obtained was immediately removed from the flask as soon as the reaction period was over and then purified.

The resinous product so obtained was repeatedly washed with cold distilled water dried in the air and powdered with the help of agate and pestle. The powder was washed many times with hot water to remove unreacted monomers. The air dried powder then extracted with diethyl ether and then with petroleum ether to remove p-chlorophenol-formaldehyde copolymer which might be present along with p-CPBF terpolymer. It was further purified by dissolving in 8% sodium hydroxide solution, filtered and reprecipitated by gradual dropwise addition of ice cold 1 : 1 (v/v) concen-

trated hydrochloric acid/distilled water with constant and rapid stirring to avoid lump formation. The process of reprecipitation was repeated thrice. The p-CPBF terpolymer resin so obtained was filtered, washed several times with hot water, dried in air powdered and kept in vacuum desiccator over silica gel.

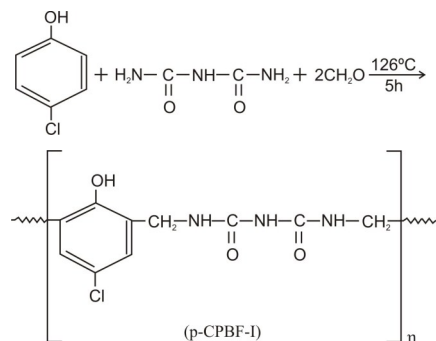


Fig.1- Preparation of p-CPBF-I Terpolymer

Results and Discussion

The terpolymer were soluble in DMF, DMSO, THF, etc. However it is insoluble in common organic solvent. The Composition of the polymeric unit was assigned on the basis of a detailed study of the elemental analysis of the polymer, UV- visible, IR and NMR spectral studies. The elemental analysis of the terpolymer was performed to determine the composition of polymeric unit.

The UV-Visible spectra of p-CPBF terpolymer gave rise to two characteristic bands at 260-280 nm and 297 nm. These observed positions of the absorption bands indicates the presence of carbonyl group (ketonic) possessing double bond which is in conjugation with the aromatic nucleus. The appearance of former band (more Intense) can be accounted for $\pi \rightarrow \pi^*$ transition while the latter band (less intense) may be due to $n \rightarrow \pi^*$ electronic transition.

The IR spectral studies of p-CPBF resin revealed that all these terpolymers give rise to nearly similar pattern of spectra. The assignment of vibrational frequencies is mainly based on the data available in the literature, A broad band appeared in the region $3700-3300\text{cm}^{-1}$ may be assigned to the stretching vibrations of phenolic hydroxy (-OH) groups exhibiting intermolecular hydrogen bonding [11]. The sharp band displayed at 1625cm^{-1} may be due to the stretching vibrations of carbonyl group (C=O) of both ketonic as well as biuret moiety [11]. The presence of -NH in biuret moiety may be assigned due to sharp band at $3005-3020\text{cm}^{-1}$ [11]. A strong sharp peak at $1528-1539\text{cm}^{-1}$ may be ascribed to aromatic skeletal ring [12]. The bands obtained at $1337 - 1355\text{cm}^{-1}$ suggest the presence of methylene bridges [13] in the polymer chain. The weak band appearing at $737 - 749\text{cm}^{-1}$ is assigned to C - Cl bond. 1,2,4,6 -tetrasubstitution of aromatic ring is recognized from the bands appearing at $953, 1081, 1112$ and 1236cm^{-1} respectively [12-14].

Weak signal in the range of 7.00 to 7.47 (d) ppm is attributed to phenolic -OH proton. The NMR spectra of p-CPBF terpolymer resins show a weak multiplet signal (unsymmetrical pattern) in the region 6.8 to 7.11(d) ppm which is due aromatic protons. The singlet signal appearing at 5.31 - 5.40 (d) ppm may be due to imido proton of -CO-NH-CO- linkage [13]. Intense signal appeared in the region 4.83 - 4.86 (d) ppm may be due to protons of methylenic bridges (CH_2) of polymer chain. Triplet signal appeared in

the region 3.42 - 4.84 (d) ppm can be assigned to amido proton of $-\text{CH}_2\text{-NH-CO-}$ linkage. A medium singlet peak appeared at 2.5 - 3.0 (d) ppm may be assigned to methyl protons of $\text{Ar-CH}_2\text{-NH}$ group. Except p-CPBF-I, p-CPBF-II terpolymer, all the remaining two terpolymers viz. p-CPBF-III and p-CPBF-IV terpolymer resins exhibit signals in the region 3.8 - 4.8 which may be due to methylene bridges of $\text{Ar-CH}_2\text{-Ar}$ linkage [14]

Scanning electron micrographs of the p-CPBF terpolymer resin has been recorded at 1500X and 3000X magnification. The SEM micrographs of p-CPBF terpolymer resin sample exhibits spherulites with deep corrugation. The spherulites are typical crystalline formation and they grow in high viscous and concentrated solution. In the present case, the spherulites are complex polycrystalline. The crystals are smaller in surface area with less closely packed structure. The spherulites morphology of resin exhibit crystalline structure with deep corrugation which is clearly visible in SEM photographs of resin. These evidences indicate that more or less the resin shows amorphous character with less close packed surface having deep pits. The resin thus possesses amorphous nature and showing higher exchange capacity for metal ions [15]. Thus SEM study shows that the p-CPBF terpolymer resin has crystalline and some amorphous characters. Thus it has the transition structure between crystalline and amorphous.

Thermogram of the terpolymer resins depicts three steps decomposition in the temperature range $180-600^\circ\text{C}$. The slow decomposition between $0-180^\circ\text{C}$ corresponds to 7.0% loss which may be attributed to loss of water molecule against calculated 7.05% present per repeat unit of the polymer. The first step decomposition start from $180-320^\circ\text{C}$ which represents loss of hydroxyl group and chloro group (26.00% found and 26.15% cal.). The second step decomposition start from $320-520^\circ\text{C}$ corresponding to 63.83% removal of aromatic nucleus and methylene bridge against calculated 64.00%. The third step decomposition side chain from $520-600^\circ\text{C}$ corresponding to removal of biuret moiety (100.00% found and 100.00% cal.).

Conclusion

Terpolymer based on the condensation reaction of p-chlorophenol, and biuret with formaldehyde in the presence of acid catalyst has been prepared..

The kinetic parameters like energy of activation, order of reaction etc. have been calculated from the Isothermal TG data using the methods which are widely used for finding the kinetic parameters in the thermal degradation of organic polymers and Hence these methods which are familiar amongst organic polymers, may also be used in obtaining the kinetic parameters for the, thermal degradation of terpolymers.

References

- [1] Kaliyappan T., Kannan P. (2000) *Prog. Polym. Sci.*, 25,343.
- [2] Finn R.C., Zubieta (2001) *J. Inorg. Chem.*, 40,2466.
- [3] Antipuly C.K., Katragadda S., Cow A., Gesser H.D. (1990) *Talanta.*, 491.
- [4] Akelah A., Sherrington D.C. (1981) *Chem. Rev.*, 81, 557.
- [5] Patel B.K., Patel M.M. (1988) *J. Ind. Chem. Soc.*, LXV, 651.
- [6] Patel B.K., Patel M.M. (1988) *J. Ind. Acad. Sci.*, 100, 405.
- [7] Patel B.K., Patel M.M. (1988) *J. Ind. Chem. Soc.*, 65,651-654.
- [8] Patel H.S., Patel S.R. (1984) *J. Macromol. Soc. Chem.*, A21

(3), 343-352.

- [9] Joshi R.M., Patel M.M. (1983) *J. Chem.*, 22A, 390-394.
- [10] M. M. Patel, R. Manavalan; *J. Indian Chem. Soc.* 61(1984) 490
- [11] Kunnin R. (1958) *Ion-Exchange Resins*, 3rd Ed., Willey, 12, 68.
- [12] Gurnule W.B., Juneja H.D., Paliwal L.J. (2001) *Ultra Sci.*, 13 (3), 333-339.
- [13] Gurnule W.B., Juneja H.D., Paliwal L.J. (2002) *React. Funct. Polym.* 50(1), 95-100.
- [14] Dyer J.R. (1971) *Application of Absorption Spectroscopy of Organic Compounds*, 32.
- [15] Vogel A.L. (1961) *Quantitative Inorganic Analysis* Longman Group Limited.
- [16] Suzuki E.J. (2002) *Microscopy.*, 208,157.