

## Synthesis and Characterization of Terpolymer

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*para*-Hydroxy benzoic acid, thiourea and *para*-formaldehyde terpolymer resin was synthesized with different molar ratio of monomers in presence of the catalyst 2 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl. The resin was characterized by IR and UV spectral analysis. Molecular weight of the terpolymer was determination using gel permeation chromatography and thermal stability of the terpolymer was determined by thermogravimetric analysis.

**Key Words:** Synthesis, Characterization, Terpolymer.

### INTRODUCTION

Terpolymers find very useful applications<sup>1-3</sup> as adhesives, high temperature flame resistant fibers, coating materials, semiconductors and catalyst and ion exchange resins. Ion exchange resins have attracted much interest in recent years due to their application in wastewater treatment. A variety of polymers resulting from the polycondensation of multifunctional monomers lead to copolymers were synthesized already. Salicylic acid formaldehyde has many applications. The terpolymer of hydroxybenzoic acid, urea/thiourea and trioxide has been widely investigated because of their numerous applications<sup>4</sup>. However, a literature survey revealed that no polymers have been synthesized from *p*-hydroxybenzoic acid, thiourea and *para*-formaldehyde. Kanti and Pancholi synthesized a terpolymer by condensation of salicylic acid, dithioxamate with trioxane in presence of acid catalyst<sup>5,6</sup>. By the same method a terpolymer of *p*-hydroxybenzoic acid, thiourea with *para*-formaldehyde was synthesized and characterized in this present work.

### EXPERIMENTAL

The entire reagents used were of AR grade. The acid catalysts were of LR grade and double distilled water is used for the experiments. *p*-Hydroxy benzoic acid (2.76 g), thiourea (1.52 g) and *para*-formaldehyde (1.76 g) were taken in the round bottom flask and refluxed for 4 h in oil bath in presence of 2 M H<sub>2</sub>SO<sub>4</sub> (100 mL) as catalyst. After the completion of refluxing, over the given time period the content of the flask was poured on ice cold water. The pale yellow coloured resin

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was separated and washed thoroughly with cold water and then with hot water. The resin sample was air dried, powdered well and extracted with solvent to remove unreacted monomers. The resin thus obtained was purified twice by dissolving in 10 % NaOH and reprecipitating in 1:1 HCl. The colourless resin was filtered off and washed finally with hot water to keep it free from chloride and then dried. The resin was powdered well. The yield of the resin was 3 g. Other resins of the same series with different ratio of monomer and catalyst were also be synthesized which is given in the Table-1.

TABLE-1  
MOLAR RATIO OF MONOMERS AND CATALYST  
TAKEN FOR SYNTHESIS OF RESINS

Name of the polymer	Weight of 4-hydroxybenzoic acid (g)	Weight of thiourea (g)	Weight of <i>para</i> -formaldehyde (g)	Catalyst (100 mL)	Yield of polymer (g)
HTP-1	2.76	1.52	1.76	2M H <sub>2</sub> SO <sub>4</sub>	3.0
HTP-2	2.76	2.28	4.40	2M H <sub>2</sub> SO <sub>4</sub>	2.6
HTP-3	2.76	1.52	1.76	2M HCl	3.2
HTP-4	2.76	2.28	4.40	2M HCl	4.4

## RESULTS AND DISCUSSION

All the resins synthesized above methods were colourless and light powders. They are soluble in the solvent such as NaOH, KOH, pyridine and DMF give yellow coloured resin solution. They are insoluble in the solvent such as HCl, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>O, benzene, toluene, acetone, carbon tetrachloride, chloroform, ether, dichloromethane, petroleum and ethanol.

**Spectral study:** IR spectra of the resins synthesized by condensation of *p*-hydroxy benzoic acid, thiourea with *para*-formaldehyde is shown in Fig. 1. A strong band near 2972 cm<sup>-1</sup> is due to presence of aromatic ring stretching vibration<sup>6,7</sup>. The peaks near 800, 1200 and 3200 cm<sup>-1</sup> indicate 1,3,4,5-substituted aromatic ring. A broad band near 3436 cm<sup>-1</sup> may be due to the presence of -OH stretching vibration of -COOH group<sup>6</sup>. A sharp band near 1650 cm<sup>-1</sup> is due to -CO stretching of carboxylic group. A sharp band near 3316 cm<sup>-1</sup> may be due to the -NH stretching. Finally a band near 2972 cm<sup>-1</sup> may be -CH<sub>2</sub> group involved in bridging and aromatic ring<sup>7</sup>. UV spectrum of the above polymer shows (Fig. 2) a weak R band ( $\epsilon_{\max} < 30$ ) may be due to loosely held n electron of thionyl group electron transferred to  $\pi^*$  orbital.

**Molecular weight determination:** Molecular weight of the terpolymer was determined by using gel permeation chromatography with refractive index detector and polystyrene column and 100 % THF as solvent, which is shown in the Table-2. Molecular weight of the resin synthesized by above methods is found to have a value closer to 5000. Polymer synthesized using 2 M H<sub>2</sub>SO<sub>4</sub> has marginally higher molecular mass than the polymer obtained by condensation in presence of 2 M HCl.

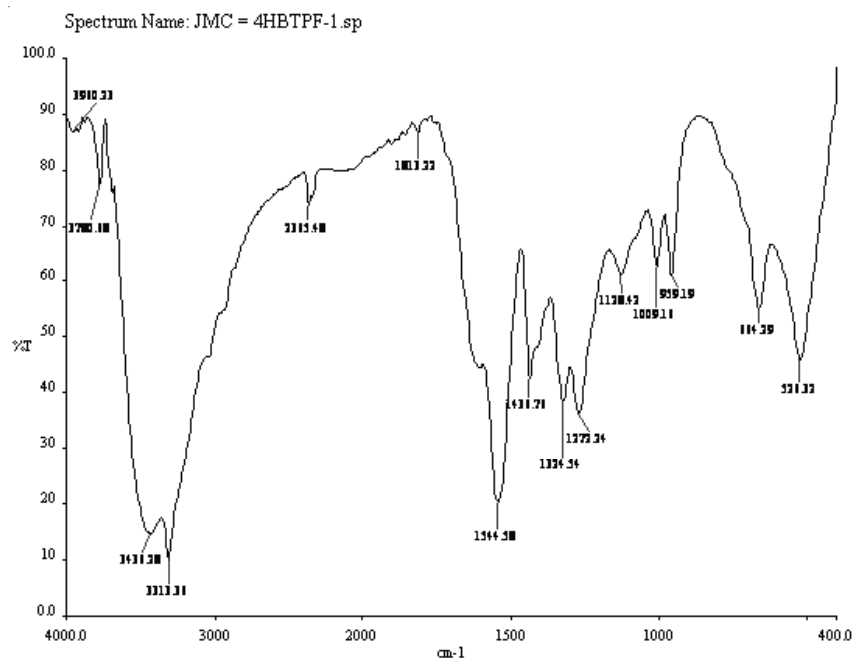


Fig. 1. IR spectrum of *p*-hydroxybenzoic acid, thiourea and para-formaldehyde terpolymer

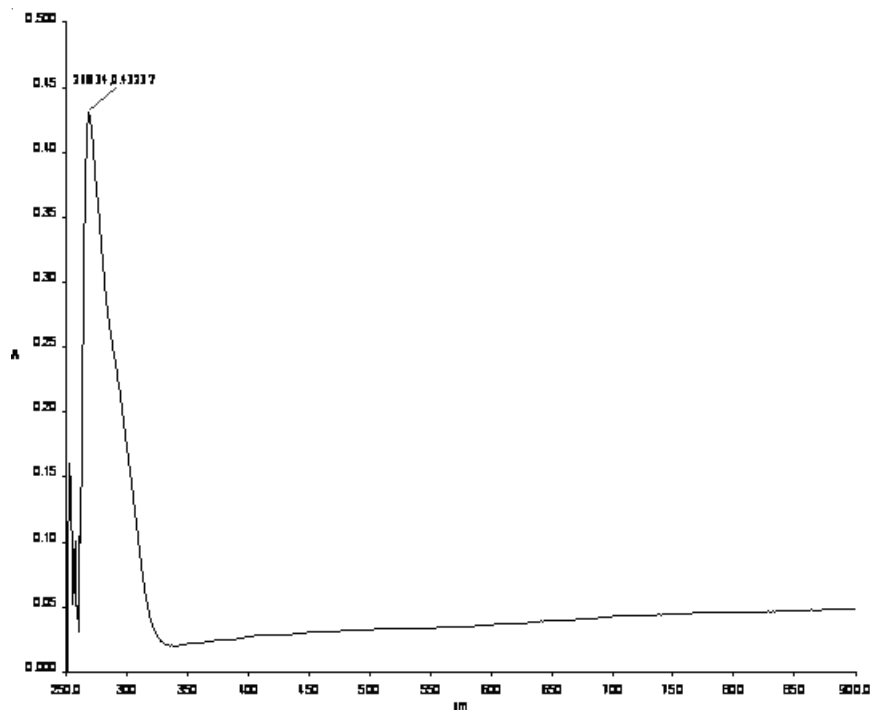


Fig. 2. UV spectrum of *p*-hydroxybenzoic acid, thiourea and para-formaldehyde terpolymer

TABLE-2  
MOLECULAR WEIGHT OF THE POLYMER MADE  
FROM GCP FOR VARIOUS MOLE RATIOS

Sample name	M <sub>n</sub>	M <sub>w</sub>	M <sub>z</sub>	M <sub>n</sub> / M <sub>w</sub>	M <sub>z</sub> /M <sub>n</sub>
HTP-1	4466	5129	5660	1.1485	1.2672
HTP-2	4579	5247	5762	1.1458	1.2582
HTP-3	4441	5124	5662	1.1538	1.2748
HTP-4	4501	5160	5670	1.1452	1.2584

**Thermogravimetric analysis:** Thermo gravimetric analysis is found to be a very useful method to assess the thermal stability of a polymer resin<sup>8</sup>. TGA and DTA data of the polymer is presented in the Tables 3 and 4. The thermogram recorded is shown in the Fig. 3. The resin exhibits a three stage decomposition process. The first decomposition start at 175 °C and extended up to 215 °C with the weight loss of 8 % of the resin. This is due to the decomposition of carboxylic groups present in the terpolymer. The second stage of weight decomposition started at 271 °C which is extended up to 341 °C which is due to loss of side chains of the polymer. The third stage of weight loss started from 498 °C and at 545 °C complete decomposition of the terpolymer takes place. The polymer under study are terpolymers and the most probable structure of the polymer is linear or sparse-branched linear structure.

TABLE-3  
THERMOGRAVIMETRIC ANALYSIS (TGA)

Temperature (°C)	Percentage of undegraded polymer
158.28	99.86
215.58	93.86
271.27	53.50
341.49	16.23
423.49	13.88
545.68	3.896

TABLE-4  
DIFFERENTIAL THERMAL ANALYSIS (DTA)

Decomposition point	Temperature (°C)
1	175.23
2	315.68
3	498.06

## Conclusion

Thermogravimetric analysis of the resin shows low percentage of moisture content of the ring which indicates high degree of cross linking in the polymer and from the thermogram it could be seen the thermal stability of the polymer. The spectral study of terpolymer shows the presence of more number of chelating ability of functional groups in the terpolymer. Hence studies have been initiated with respect to this polymer in connection the removal of toxic trace inorganics from aqueous system.

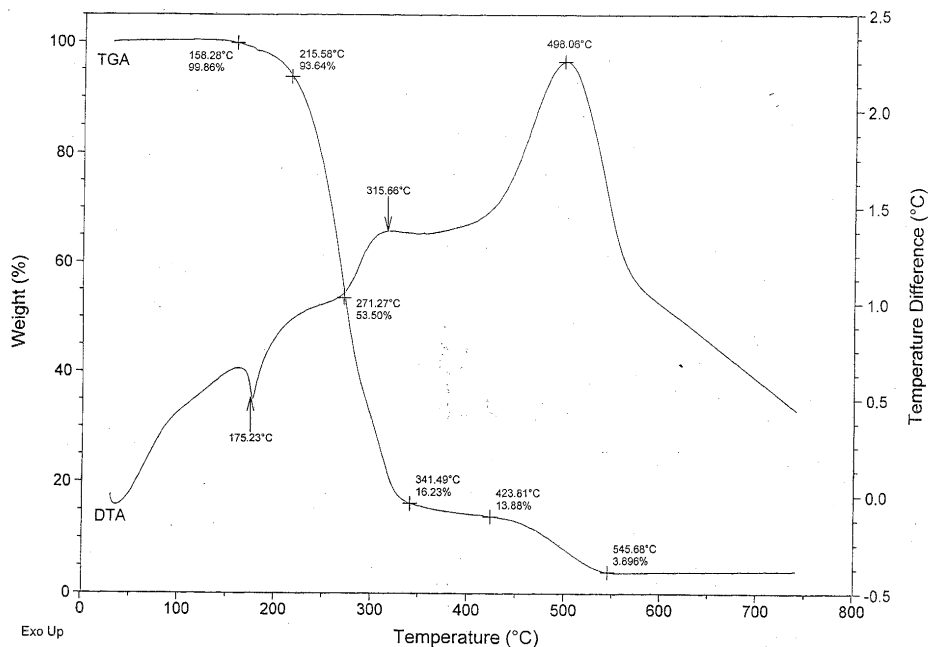


Fig. 3. TGA and DTA of *p*-hydroxybenzoic acid, thiourea and para-formaldehyde terpolymer

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