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Research Article

A STUDY ON FORMATION OF SALYCILIC ACID FORMALDEHYDE POLYMER SAMPLE

KRUNAL M DARJI*

Prempur Primary School, HMT.SK-Gujrat

*Corresponding Author

Abstract

Condensation of salicylic acid (0.02 mole) with formaldehyde (0.016 mole) in presence of aqueous 40% H₂SO₄.

Keywords: pipette, thermometer, spectro-photometer, conical flask, water bath.

Introduction

General characteristics of polymer samples

The polymer sample obtained by each of above methods was light brown in colour. It was a light weight powder. The solubility behavior of all the polymer samples have been studied. The salicylic acid – formaldehyde polymer is soluble in acetone while p-hydroxy benzoic acid – formaldehyde solution is not completely soluble in acetone. The polymer samples were found to be completely soluble in other solvents like, ethanol, Dioxane, tetrahydrofuran, Di methyl formamide and di methyl sulfoxide. All the solvents gave reddish brown colored polymer solutions.

The polymer samples are soluble in aqueous alkali. These polymer samples dissolve in aqueous bicarbonate liberating carbon dioxide. The solution of the sodium salt of polymer in water affords violet-blue precipitates with aqueous ferric chloride solution. From the solution in aqueous alkali the product almost completely separated on acidification.

Formation of salicylic acid formaldehyde (1:1 conc . Hcl –water)-oxalic acid mixture polymer sample

A mixture of salicylic acid (0.25 mole), 37% formaldehyde solution (0.25 mole), 375 ml of 1:1 HCl solution mixture and 6.25 gm oxalic acid was refluxed with good stirring at 125-130°C for 6 hours. During this

time, the solid polymer was formed. The solid was filtered, washed with a large amount of water and then with boiling water. The air-dried polymer sample was Soxhlet-extracted with benzene to remove unreacted monomer. The polymer sample was dissolved in 1:1 mixture of acetone and ethanol and reprecipitated as a pasty mass by adding distilled water. The pasty mass was washed by decantation and collected. The mass was dissolved in dilute alkali and reprecipitated by gradual addition of 1:1 conc. HCl – water mixture with stirring. The polymer sample did not melt upto 360°C. The yield was 18.5 gm. About 10 gm polymer sample was fractionated.

Analysis	%C	%H
Found	64.08	4.06
Required for repeat unit C ₈ H ₆ O ₃	64.00	4.00

Formation of 4-hydroxy benzoic acid (1:1 conc . hcl –water)-oxalic acid mixture polymer sample

A mixture of 4-hydroxy benzoic acid (0.25 mole), 37% formaldehyde solution (0.25 mole), 500 ml of 1:1 HCl solution mixture and 8.5 gm oxalic acid was refluxed with

good stirring at 125-130^oC for 6 hours. During this time, the solid polymer was formed. The solid was filtered, washed with a large amount of water and then with boiling water. The air-dried polymer sample was Soxhlet-extracted with benzene to remove unreacted monomer. The polymer sample was dissolved in 1:1 mixture of acetone and ethanol and reprecipitated as a pasty mass by adding distilled water. The pasty mass was washed by decantation and collected. The mass was dissolved in dilute alkali and reprecipitated by gradual addition of 1:1 conc. HCl – water mixture with stirring. The polymer sample did not melt upto 360^oC. The yield was 25 gm. About 10 gm polymer sample was fractionated.

Analysis	%C	%H
Found	64.05	4.03
Required for repeat unit C ₈ H ₆ O ₃	64.00	4.00

Formation of resorcylic acid (1:1 conc .Hcl – water)-oxolic acid mixture polymer sample

A mixture of Resorcylic acid (0.25 mole), 37% formaldehyde solution (0.25 mole), 500 ml of 1:1 HCl solution mixture and 8.5 gm oxolic acid was refluxed with good stirring at 125-130^oC for 6 hours. During this time, the solid polymer was formed. The solid was filtered, washed with a large amount of water and then with boiling water. The air-dried polymer sample was Soxhlet-extracted with benzene to remove unreacted monomer. The polymer sample was dissolved in 1:1 mixture of acetone and ethanol and reprecipitated as a pasty mass by adding distilled water. The pasty mass was washed by decantation and collected. The mass was dissolved in dilute alkali and reprecipitated by gradual addition of 1:1 conc. HCl – water mixture with stirring. The polymer sample did not melt upto 360^oC. The yield was 25 gm. About 10 gm polymer sample was fractionated.

Analysis	%C	%H
Found	57.83	3.66
Required for repeat unit C ₈ H ₆ O ₄	57.83	3.61

Infrared spectral characteristics

General

This method has been widely employed in the study of structure of the phenol-formaldehyde polymers. The spectral study has furnished useful information about the structure of polymers [22-24]. The presence of CH₂ bridge is clearly established by this study [25,26]. The type of substitution of the phenol monomer has been indicated by the spectrum [22-26]. In a PF polymer the nature of substitution of the phenol moiety in the middle of the polymer chain will be different from the substitution of the phenol moiety forming the end-

group [27]. If the spectrum is very well resolved the band characteristics of these two types of phenol moieties will be discernible. The intensity of band characteristic of the end group has been employed to estimate molecular mass of PF polymers [25]. The salicylic acid condensation is reported to yield methylene-di-salicylic acid. The analysis of its IR spectrum revealed that in MDSA the union is mostly as shown below. Structure of salicylic acid formaldehyde polymer has also been suggested on the basis of IR spectral study [28].

In the spectrum of hydroxybenzoic acid – formaldehyde polymer, one searches for the presence of bands characteristics of the structural features. A list of these bands is presented below along with the range in which one may find the characteristic band [29].

Table 2.1 Anticipated spectral features

Group	IR characteristic cm ⁻¹
OH group	
Phenolic OH stretching (Free)	3612-3593 cm ⁻¹
Carboxylate OH stretching (Free)	3560-3500 cm ⁻¹
O-H bending (in plane)	1200 cm ⁻¹
C-O stretching	1410 – 1310 cm ⁻¹
OH deformation	950-900 cm ⁻¹
-CH₂- Bridge	
CH stretching	2870-2845 cm ⁻¹
CH bending	1465 ±20 cm ⁻¹
Aromatic CH	
C-H stretching	3030 cm ⁻¹
C-H bending	1225 – 950 cm ⁻¹
C=O vibration	
Internal hydrogen bonding	1680-1650 cm ⁻¹

Experimental and results

The spectra of the polymers described in this chapter have been taken in KBr pellet. Carefully purified KBr was used for the purpose. Absence of KBr was checked by examining IR spectrum of pure KBr pellet. The pellet for the IR study was prepared by mixing 2.0 mg of polymer sample with 1.0 gm of pure KBr in a mini-ball mill and compressing this mixture in a disc at a pressure of 20000 psi under vacuum. The disc thus prepared was transparent and very lightly colored. The spectrum of pellet was taken on IR-5 spectrophotometer. IR spectrum of salicylic acid – formaldehyde, 4-hydroxy benzoic acid – formaldehyde and Resorcylic acid – formaldehyde polymers samples

prepared from them have been taken by this method. The positions of all bands have been noted and presented in tables 2.2 and 2.3. The spectra are presented in figure 2.1 to 2.3.

Results and Discussion

The examination of all the three IR spectra of three type of polymers reveals that:

•All the spectra are identical in all the aspects.

- The bond from 3600 to 2500 with the inflexion due to –OH of COOH and phenolic OH group.
- The inflexion at 2850 and 2920 cm^{-1} are due to CH_2 bridge.
- The strong band at 1680 cm^{-1} is due to –COOH group.
- Other bands are appeared at their respectable position.

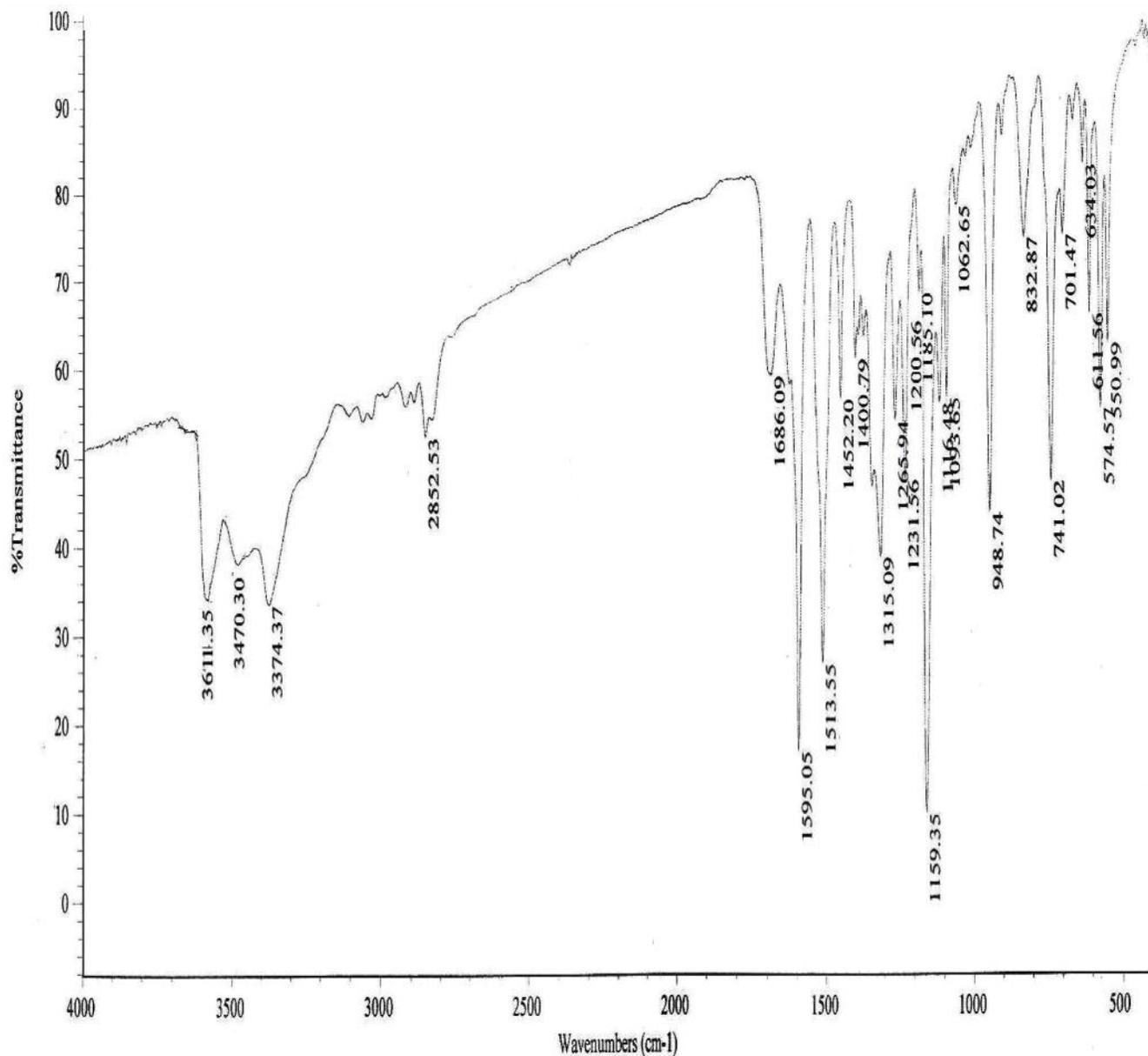


Figure 2.1 IR spectrum of Salicylic acid – formaldehyde oligomers

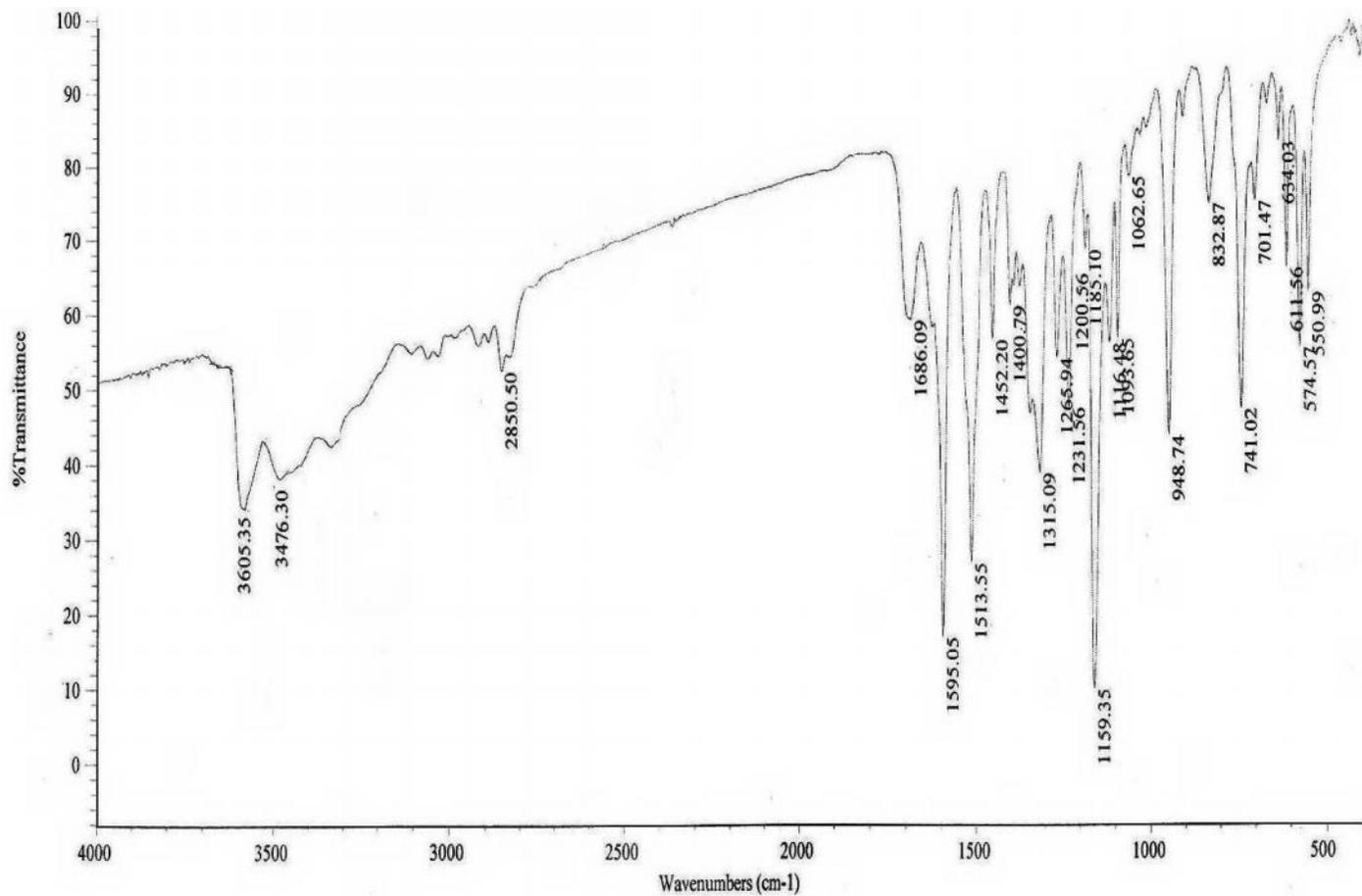


Figure 2.2 IR spectrum of p-hydroxy benzoic acid – formaldehyde oligomers

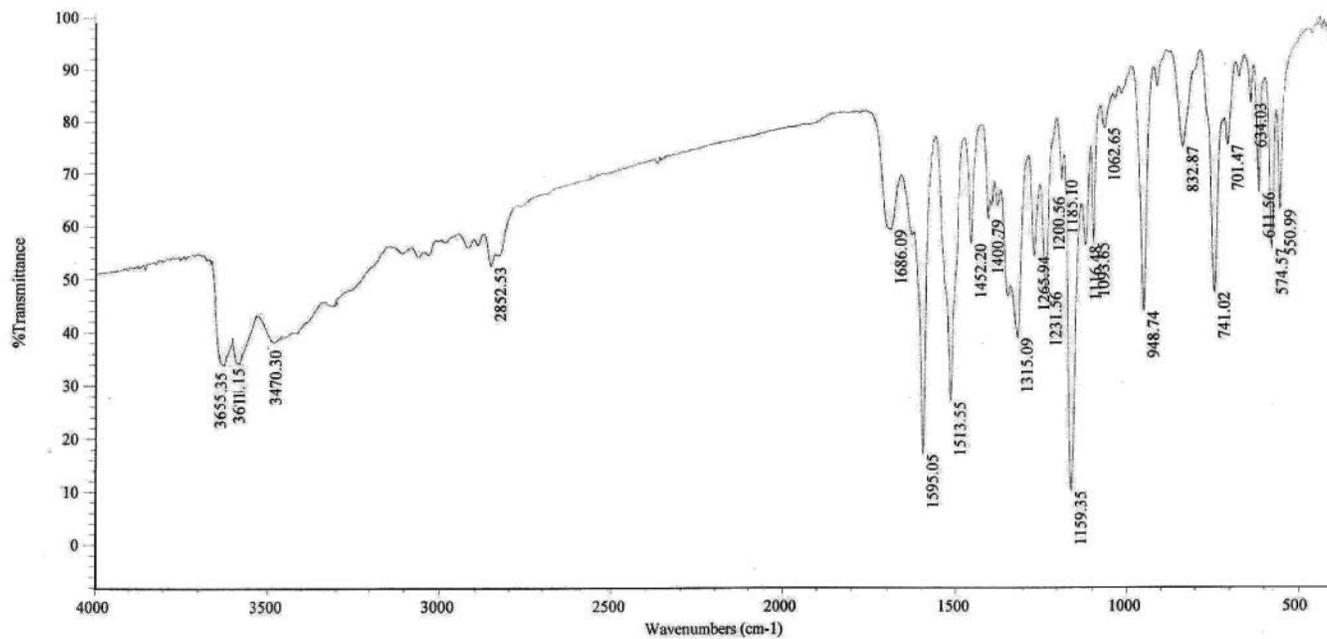


Figure 2.3 IR spectrum of Resorcilic acid – formaldehyde oligomers

Table 2.2 Anticipated spectral features of prepared oligomers

Sr. No.	Group	Salicylic acid - Formaldehyde Oligomer cm^{-1}	p-OH Benzoic acid- Formaldehyde Oligomer cm^{-1}	Resorcilic acid-formaldehyde oligomer cm^{-1}
1	Phenolic OH stretching (Free)	3611.35	3605.35	3655.35, 3611.15
2	Carboxylate OH stretching (Free)	3470.30	3476.30	3470.30
3	O-H bending (in plane)	1200.56	1200.56	1200.56
4	C-O stretching	1315.09	1315.09	1315.09
5	OH deformation	948.74	948.74	948.74
6	CH stretching	2852.53	2850.50	2852.53
7	CH bending	1452.20	1452.20	1452.20
8	Aromatic C-H stretching	3374.37	3374.35	3374.30
9	Aromatic C-H bending	1159.35	1159.35	1159.35
10	C=O stretching	1686.09	1686.09	1686.09

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