

Synthesis of 4,4 Dihydroxybiphenyl-Carbohydrazide-Formaldehyde Copolymer and Its Characterization

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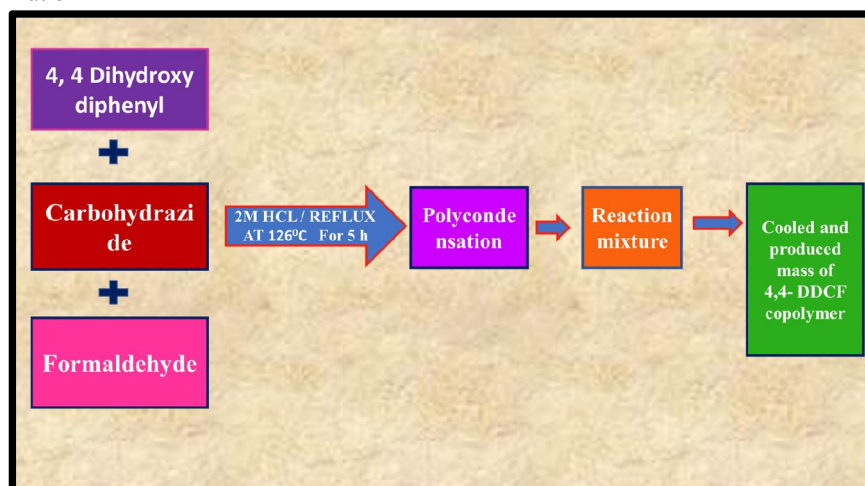
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Abstract: The novel copolymer 4,4'-DDCF was synthesized by the condensation of 4,4'-dihydroxydiphenyl, carbohydrazide, and formaldehyde in the presence of acid catalyst with using 1:1:2 molar ratio of reacting monomers. Copolymer composition has been determined on the basis of their elemental analysis and no. average molecular weight of copolymer was determined by gel permeation chromatography method. The viscosity of the copolymer in dimethyl sulfoxide (DMSO) was measured to determine its unique functions and constants. The structure of the copolymer was determined by examining its infrared spectra. Further examination of 4,4 DDCF was carried out using techniques such as nuclear magnetic resonance (NMR) spectroscopy, ultraviolet-visible (UV-Vis) spectroscopy, and atomic analysis. Scanning electron microscopy was also used by researchers to examine the morphology of the copolymer.

Keywords: Polycondensation, Copolymer, Dihydroxydiphenyl, Carbohydrazide, Synthesis, Characterization



Schematic representation of Synthesis of copolymer 4,4 DDCF

I. INTRODUCTION

Copolymers have high molecular weights and are made up of small repeating units held together by strong covalent bonds. Copolymer synthesis is an important subject of study in polymer science because it allows for the tailoring of polymers for specific purposes. Polymers are becoming increasingly popular because to their versatility and uniqueness.



Copolymers are suitable for packaging, adhesives, and coatings in electrical sensors and semiconductors due to their thermal stability and ability to produce materials.

C. Kohod and coworker prepared a yellow colour copolymer which was synthesized from 8-HQ5-SAHMDAF blended by gathering (0.2 mol) 8-hydroxyquinoline5-sulfonic acid, (0.1 mol) hexamethylenediamine and (0.3 mol) formaldehyde at 124°C in an oil bath for 5 hrs [1]. Megha Rangari and et.al. had done thermal degradation studies of high-performance copolymer resin of 8-HQAF derived from 8-hydroxyquinoline, acrylamide and furfural with 2M HCl in the molar ratio in an oil bath at a temperature of 122 °C also they made composite from synthesized copolymer.[2] Applications of ion chelation exchange capability and antibacterial properties had been studied of synthesized copolymer derived from o-cresol-formaldehyde-catechol by Jayathilake and coworkers [3]

By condensing 2 amino 6-nitrobenzothiazole, formaldehyde, and melamine in the presence of 2M HCl as a catalyst at 122°C in an oil bath for 5 hours, Gupta and colleagues created BMF-IV copolymer. A yellow solid product was sorted out.[4] The copolymer 8-HQ-5-SAGF, or 8-Hydroxyquinoline-5-sulphonic acid-guanidine-formaldehyde copolymer, was described by Rathod and his colleague using the polycondensation process in a 1:1:2 molar ratio. This 8-HQ-5-SAGF copolymer resin was examined using a Perkin Elmer TGA/DTA thermal analyzer. This copolymer was subjected to elemental analysis using the Perkin Elmer 789N QP-2010 device.[5] By polycondensation in a melt of guanidine hydrochloride and hexamethylene diamine at a specific temperature, Okladnikova and colleagues synthesized Polyhexamethylene guanidine hydrochloride (PHMGhch). PHMGhch's superior antibacterial activity and gelation properties make it a promising polymer for medical applications.[6]

Y. U. Rathode and colleagues investigated the photoluminescence of a copolymer and its copolymer/carbon composite utilizing phthalic acid and formaldehyde in combination with 8-hydroxyquinoline5-sulphonic acid.[7] Akshay and colleagues studied a multifunctional copolymer made by a controlled polycondensation technique that combined formaldehyde, acrylamide, and 8-hydroxyquinoline. Fourier-transform infrared (FT-IR) spectroscopy, UV-visible spectroscopy, and proton nuclear magnetic resonance were used to characterize the structure and confirm that all functional moieties were successfully integrated into the polymer framework.[8] The copolymer resin 4-HBAF was created by combining 4-hydroxybenzoic acid, adipamide and formaldehyde in molar ratio with hydrochloric acid as a catalyst reported by Thakare and Gurnule[9]

Using HCl as a catalyst to eliminate hexavalent chromium ions, Vilayatkar and Sudip Mondal created a polymer resin from 8-hydroxy quinoline (8-HQ), thiourea, and formaldehyde in a 1:1:2 mol ratio[10]. Wasudeo B. Gurnule and Yashpal U. Rathod evaluated thermal properties of terpolymer (8-HQ-5-SAAF) synthesized using 8 hydroxyquinoline-5-sulphonic acid, anthranilic acid and formaldehyde via the poly condensation method[11]. The thermal decomposition behavior of HMBPDANF-II has been synthesized by condensation of 2-hydroxy, 4-methoxybenzophenone and 1, 5 diamino naphthalene with formaldehyde in the presence of hydrochloric acid as a catalyst in molar proportion of reactants. This copolymer had been carried out by using TGA in static nitrogen atmosphere at a heating rate of 10 0C/min.[12]

Using benzoyl peroxide (BP) as an initiator, Yousef Wadouh and coworkers synthesized a co-polymer (styrene/allyl-2.3.4.6-tetra-O-acetyl-β-D-glucopyranoside) from glucose in four steps by addition polymerization in accordance with the radical process. Allyl-2.3.4.6-tetra-O-acetyl-β-D-glucopyranoside monomer was first synthesized in three steps and the reaction was monitored by HPLC, FT-IR, and TLC. In the fourth step, the monomer was polymerized with styrene, and FT-IR and NMR spectroscopy were used to determine its structure [13-15]. Using the polycondensation process, Nandekar and Gurnule created p-HBSF-I copolymer from p-hydroxybenzoic acid, semicarbazide, and formaldehyde. Using an agar well diffusion method, p-HBSF-I copolymer was employed for antibacterial and antifungal investigations.[16-18]

This communication describes the synthesis and characterization of a novel copolymer produced from 4,4'-dihydroxybiphenyl, carbonylhydrazide, and formaldehyde (4,4-DBCF) using polycondensation. Characterization incorporates spectral investigations, scanning electron microscopy, and X-Ray Diffraction to analyze surface characteristics of copolymers.



Experimental

Materials

Central Scientific Company, Nagpur supplied 4,4'-dihydroxybiphenyl, carbohydrazide, and formaldehyde. Solvents, including hydrochloric acid and dimethyl sulfoxide, were also obtained from Central Scientific Company in Nagpur. All chemicals used were of analytical grade and utilized exactly as received.

Synthesis of novel copolymer

The novel copolymer was manufactured using polycondensation of monomers such as 4,4 dihydroxydiphenyl, carbohydrazide, and formaldehyde in 1:1:2 molar ratios using 2M HCL and refluxed for five hours at 126°C. The reaction mixture was then cooled and rinsed with warm water and ethanol before being filtered to remove unreacted monomers and contaminants. Finally, the copolymer was dried in the air. The proposed reaction scheme is given in figure 1.

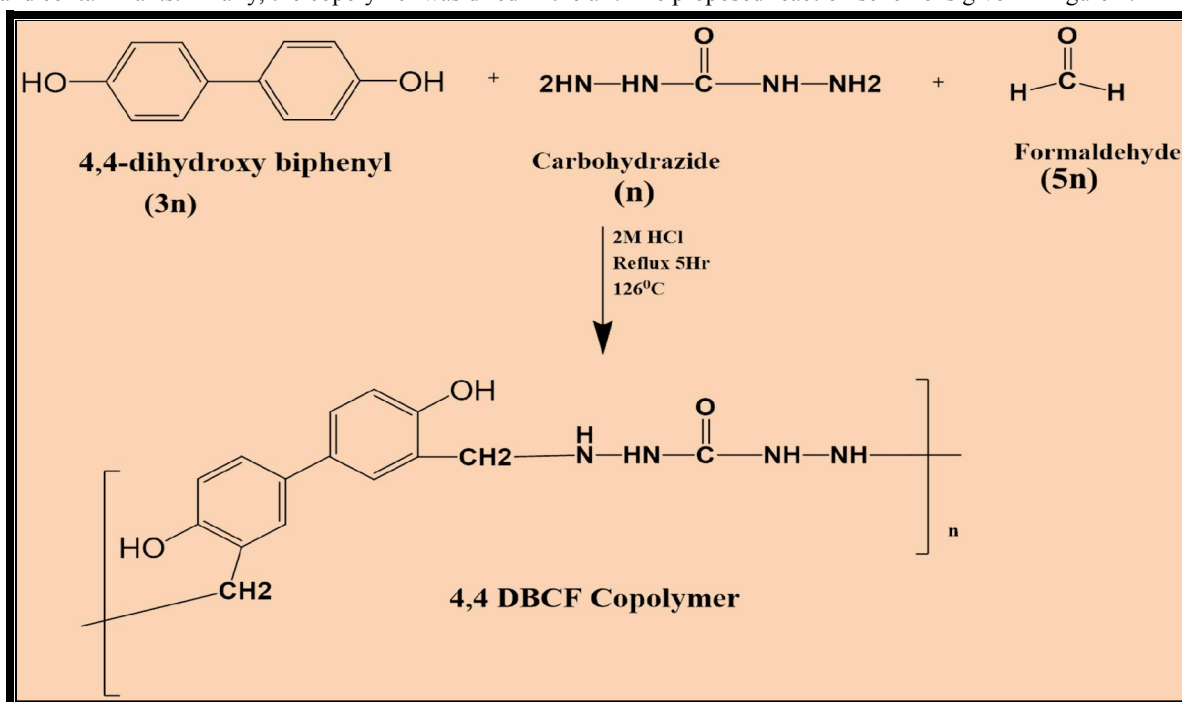


Fig.1: Synthesis of 4,4 DBCF copolymer

Characterization

Using a twin beam spectrophotometer equipped with an automatic pen chart recorder, the UV-visible spectra were recorded at room temperature in dimethylsulphoxide between 190 and 850 nm. The Cary 630 Agilent Technology FT-IR Spectrophotometer was used to perform FT-IR spectra in the 4000-650 cm⁻¹ range. Using DMSO as a solvent, the copolymer's 1H-NMR spectrum was captured using a Varian 400 MHz NMR Spectrophotometer. All of the analytical and spectral investigations for the produced copolymer resin were documented at Sprint Testing Solutions, Parel, Mumbai, India.

II. RESULTS AND DISCUSSIONS

It was discovered that the produced copolymer had a yellowish colour. The copolymer is insoluble all other inorganic and organic solvents, but soluble in solvents like dimethyl sulphoxide (DMSO), dimethylformamide (DMF), and partially soluble in tetrahydrofuran (THF).



FT-IR Spectra

The FTIR spectra of 4,4 DBCF copolymer is shown in the figure. The broad band appeared at 3202 cm^{-1} and 3023 cm^{-1} may be due to O-H stretching of phenolic group and N-H stretching of hydrazide group exhibiting intermolecular hydrogen bonding. [19] The peak appeared at 1607 cm^{-1} due to C=O stretching or C=N stretching indicate amide linkage from carbohydrazide. The strong peak at 1467 cm^{-1} indicate C-H stretching confirmed presence of aromatic ring. The medium band at 1347 cm^{-1} suggested -NH-NH- the hydrazide linkage of carbohydrazide. The strong band observed at 1202 cm^{-1} indicate C-O stretching phenolic -OH group. The peak observed at 1110 cm^{-1} suggested presence of methylene bridge -(CH₂)- in the copolymer chain. [20,21]

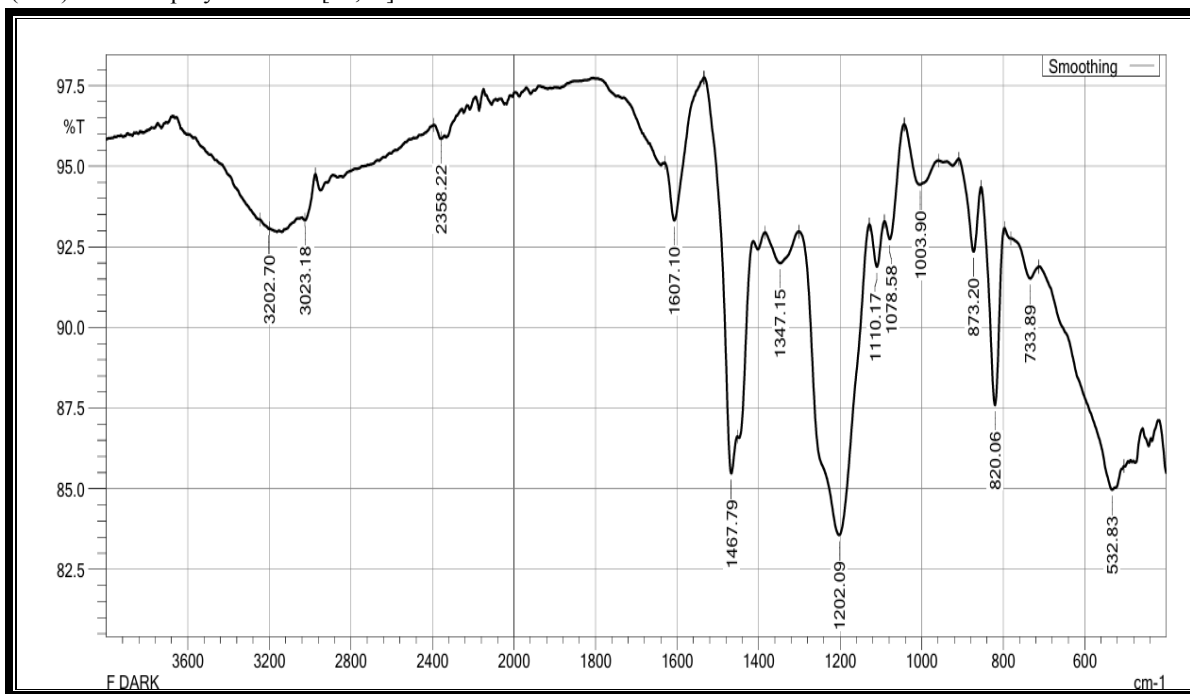


Fig. 2:-FT-IR Spectra of 4,4 DBCF copolymer

¹H-NMR

The ¹H NMR of copolymer 4,4 DBCF is introduced in the figure 3. NMR Spectra shows the presence of methylene proton of the Ar-CH₂-NH bridge has attributed to singlet signal in the region of 3.32 ppm. [22-24] A Singlet proton in the region 2.50 ppm might be because of proton near to -NH-CO- hydrazide environment due to high degree of polymerization there is absence of aromatic proton which is generally appears at 6.7 -8 ppm region. Also due to strong intermolecular hydrogen bonding there is missing of OH and NH proton. [25,26]



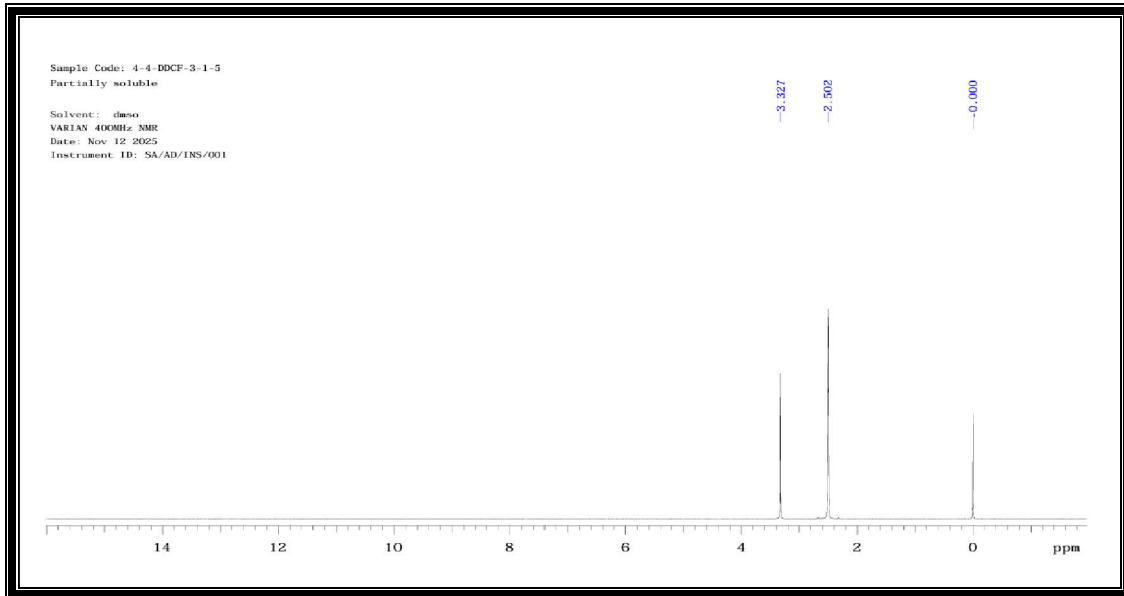


Fig 3: Proton NMR of Copolymer 4, 4 DBCF

X-Ray Diffraction

The X-ray diffraction pattern of 4,4 DBCF copolymer shows an amorphous material's characteristic broad diffuse peak centered around $2\theta = 18-22^\circ$. The copolymer's lack of long-range crystalline organization is indicated by the absence of distinct and strong Bragg reflections. This wide halo indicates that the substance is non-crystalline and is caused by the copolymer chains' jumbled arrangement.

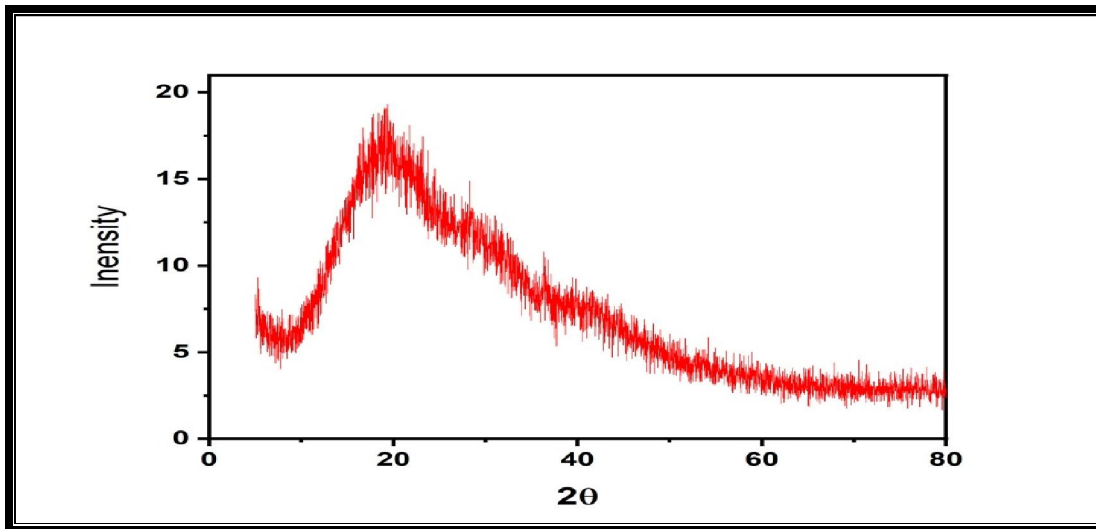


Fig 4: X-Ray diffraction of 4,4 DBCF copolymer

Scanning Electron Microscopy of 4,4 DBCF copolymer

The SEM analysis has greatly aided in material characterization, surface property recognition, and particle size determination.[27-28] Scanning electron microscopy was used to analyze the morphology of the copolymer 4,4 DBCF, as seen in Fig. 5. The copolymer was discovered to be more amorphous than crystalline based on the photos. The copolymer exhibits a more amorphous character with a close-packed surface having deep pits and the reactivity of active



sites buried in the copolymer matrix [29-30] The absence of regular structures and clearly defined grain boundaries suggests that the material lacks long-range molecular order. This morphological characteristic implies that the copolymer is amorphous. Additionally, the creation of a strongly crosslinked polymer network is supported by the fused and randomly distributed structure. These findings align with X-ray diffraction data, which further validate the copolymer's amorphous nature.

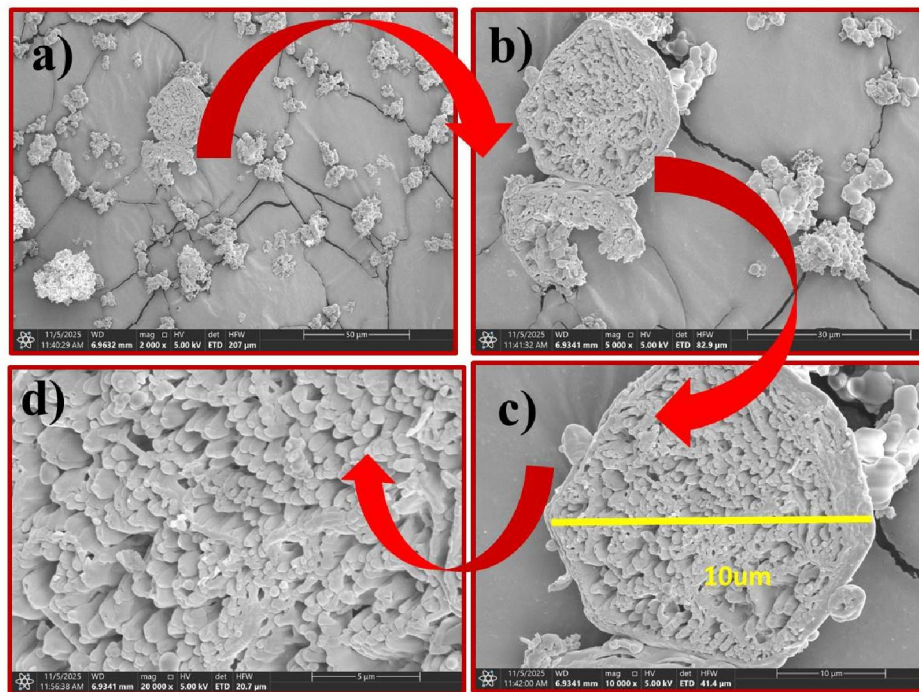


Fig. 5: Scanning electron microscopy Micrograph of 4,4 DBCF copolymer

III. CONCLUSION

The copolymer synthesized from 4,4 Dihydroxy biphenyl, Carbohydrazide and formaldehyde in 3:1:5 ratio using 2 M HCl as catalyst in an oil bath at 120°C. The structure of copolymer 4,4 DBCF was confirmed by FT-IR 1H-NMR spectral studies. Scanning electron microscopy shows the morphology of copolymer that the copolymer was more amorphous in nature than crystalline. This amorphous nature also confirmed by X-ray diffraction study. These all are confirmed that these new monomer prepared a novel copolymer.

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