Synthesis and spectral study of 2, 4-Diaminophenol based copolymer

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Abstract. A copolymer resin was synthesized by condensation polymerization reaction of 2,4-diaminophenol, Oxamide and formaldehyde with 2N NaOH as a catalyst. The purification of copolymer was carried out by precipitation technique and column chromatography. The purified copolymer resins were confirmed by Infra-red, \textsuperscript{1}H and \textsuperscript{13}C-NMR spectroscopy. Further formation of copolymer has been confirmed by Mass Spectrometry. The surface morphology of copolymers was established by Scanning Electron Microscopy (SEM). Degradation of synthesized copolymer were performed by Thermogravimetric Analysis (TGA). The stability is observed as up to 473 K and complete mass loss was observed up to 1173 K.

Keywords. Condensation polymerization, Characterization, Thermogravimetry.

1. Introduction

In recent year tremendous scientific development of polymer is due to their applicability in numerous filed like epoxy binder, coating material, water softening, environmental remediation, bimolecular separation, hydrometallurgy and medical equipment’s. Synthesized copolymer has ionic functional groups with suitable physical and chemical properties further it is applicable especially as cation exchanger. Cation exchange or chelate ion exchange properties for various alkali and alkaline earth metals ions implement adsorption and desorption by activated carbon and batch ion exchange method were together discussed in order to confirm the presence of metal ion uptake selectivity. It involves the measurements of distribution of a metal ion between the two parts, shaking time and in media of different ion concentration. The weakly acidic ion exchangers i.e. carboxylate -COOH, basic ion exchanger i.e tertiary and secondary amine –NR\textsubscript{3} and -NR\textsubscript{2} with extreme absorption capacity at pH >7.0. Copolymers of aniline and 3-nitroaniline are ideally use in conduction it has other applications in numerous field of optoelectronic as well as energy storage devices due to conjugated system in organic synthesized polymers.

A versatile synthetic copolymer derived from hydroxyphenol and amino group containing compounds were studied due to their tremendous use as anion exchanger, thermal stabilizer, electrical conductor, photographic binder [1-5] etc. Copolymers that is manufacture from 8-hydroxyquinoline using the linkage of formaldehyde have been reported extensively. [6,7,8] Polymer derived from hexamine and m-cresol and polymer ion exchange resin of phenolic compounds with amines and amide with formaldehyde and their properties such as thermal stability [9] electrical conductivity, and ion exchange properties for toxic metal ions were studied. [10] Synthesis and Characterization of
Pyrogallol-Formaldehyde have been studied and used as an adsorbent material for the recovery of rhodium(III) [11]. Biobased Phenol Formaldehyde polymer synthesized and characterized by Yong Zhao and et.al [12]. Substituted carbamide and 2, 2-dihydroxy biphenyl were used to synthesized novel polymers having good properties like ion-exchange, binder and well thermal stability [13-15]. However, the literature studies have publicized that no copolymer were synthesized using the monomer 2,4-diaminophenol having strong ion exchangeable groups, oxamide and formaldehyde as a condensing material. Hence, in the present research we discuss the synthesis, spectral characterization and degradation studies of 2,4-DAPOF copolymer.

2. Preparation method of copolymer (2,4-DAPOF)

The synthesis of 2,4-diaminophenol-Oxamide-Formaldehyde (2,4-DAPOF) copolymer is as follows: 200 mL of 2 N NaOH solution containing a mixture of 2,4-diaminophenol (0.1 mol), oxamide (0.1 mol), and formaldehyde (0.3 mol) were transfer to a 500-ml round-bottom flask armed with a mechanical stirrer. The round bottom flask kept in oil bath and heated at 414 K for 7 h. The reaction scheme is represented in figure 1. Purification of synthesized polymer was carried out by transferred it in to ether all the impurities that dissolved in to the ether has been removed and then it subjected to the column chromatography using the solvent Dimethyl sulphoxide (DMSO) and Hexane in the different proportion. The purity of final polymer was check by the thin layer chromatographic (TLC) technique. The purified polymer was concentrated from DMSO. The finished product, brown powder was kept in oven for about 2 hours at 90 °C.

![Figure 1. Reaction of 2, 4-DAPOF copolymer](image)

3. Spectral and thermal studies

IR spectrum were recorded in Fourier Transform Infrared Spectrophotometer (FT-IR) in between of 500-4000 cm⁻¹. Hydrogen-NMR spectrum were recorded in DMSO-d₆ used as solvent on 400 MHz
Bruker Advance-II spectrophotometers & $^{13}$C-NMR spectrum was recorded using Bruker 100 MHz Spectrophotometer. Scanning Electron Microscopy (SEM) analysis was carried out in Diya labs, Mumbai. Degradation pattern of copolymer were studied on Electron Impact-Mass Spectrometry (EI-MS). The thermogravimetric study were performed in oxygen atmosphere at 10 °C.min$^{-1}$ heating flow on Pyris1 Thermogravimetric Analyzer (Perkin Elmer) up to 1000 °C.

4. Thermo gravimetric analysis

Thermo gravimetric analysis (TGA) is very valuable tools to regulate the stability of polymer in certain temperature and also provide information regarding degradation pattern of polymer. Normally, in TGA at starting evaporation of volatile matter and moisture content could determine. Moisture content means the water molecule that are associated with the polymeric material that is called water of crystallization. After the removal of water content from the polymer some functional group has been degraded those containing ester and ether linkages and some other groups containing oxygen is in the back bone of that polymeric material. With continuation of functional groups, the branching attached to the aromatic ring has been degraded. At the end of degradation, the heavy materials like benzene ring and remaining moiety has been finished. TGA technique mostly used for polymeric material including elastomer, thermoplastic, thermosetting, fibers, coating material, paints and composite material. [16,17]

5. Results and discussion

5.1. FT-IR analysis

The FT-IR analysis is used to identify the functional group of the synthesized material [28]. The FTIR-spectra of 2,4-DAPOF copolymer spectral data is mentioned in Table 1 and characterized in Figure 2. From the figure it appears that, 3291.4 cm$^{-1}$, a broad and strong band which might be due to phenolic – OH, stretching vibration of showing intermolecular hydrogen bonding. [18] The presence of -NH-stretch in oxamide moiety may be ascribed as weak band at 3400 cm$^{-1}$. [18] The strong and sharp signals at 1518.4 cm$^{-1}$ has been assigned due to the presence of –NH stretching in aromatic amine. [18] A medium band displayed, 1417.6 cm$^{-1}$ may be caused by stretching vibration of carbon-carbon bond in aromatic ring. >C=O stretch in oxamide moiety is represented by a broad band appeared at 1690 cm$^{-1}$. A medium band at 1208.3 cm$^{-1}$ may be due to carbon oxygen stretching in phenol. The trisubstitution of benzene ring is acknowledged from the small bands observed at 864.1 and 1089.2 cm$^{-1}$. [18] Methylene group obtained at 2770.3 cm$^{-1}$. Results obtained in these studies are in well arrangement with those reported in literature. [18]

Table 1. FT-IR Spectral data of 2,4-DAPOF copolymer

| Observed Wavenumber (cm$^{-1}$) | Assignment                      |
|--------------------------------|--------------------------------|
| 2,4-DAP-O-F                    |                                |
| 3291.4 b, st                   | –OH (phenolic)                 |
| 34,000 st, w                   | >NH stretch (amino)            |
| 2970.3 m, st                   | methylene –CH$_2$ stretch      |
| 1417.6 m                       | >C=C< stretch in aromatics     |
| 1690.0 st                      | >C=O stretch in amino          |
| 1518.4 st                      | Ar-NH (Amine)                  |
| 1208.3 sh, m                   | >C-O stretch in phenol         |
1089.2 sh
864.1 sh

Tri substituted benzene ring

Figure 2. Infrared spectra of 2,4-DAPOF copolymer

5.2. $^1$H- NMR analysis

$^1$H-NMR spectrum of 2,4-DAPOF is given in Figure 3. A Phenolic -OH group proton detected at δ 5.1 ppm, is caused by deuterated proton exchange reaction [19,20]. Singlet is observed at δ 6.0 & 7.5 ppm and is owing to aromatic protons of phenol. In oxamide moiety, amino proton of –CH$_2$-NH-CO- linkage appeared as medium singlet signal at δ 6.5 ppm. Singlet signal for methylene protons of NH-CH$_2$-NH-linkage looked at δ 4.2 ppm. Another singlet seemed at δ 4.0 ppm may be credited to amino proton of Ar-NH. One singlet signal observed at 2.71 ppm might be recognized for methyl protons of HN-CH$_2$ moiety [19, 20].

Figure 3. $^1$H- NMR spectra of 2,4-DAPOF copolymer
5.3. $^{13}$C-NMR analysis.

The $^{13}$C-NMR graph of 2,4-DAPOF copolymer is displayed in Figure 4 and chemical shift values of particular carbon reported according to standard books [23, 24]. The Carbon first to Carbon six of the aromatic ring indications the peaks at 134.2, 114.2, 120.6, 137.8, 103.9 and 136.7 ppm respectively. The peak observed at 35.3 ppm is given to the CH$_2$ carbon of Ar-CH$_2$-NH. [21, 22]. The peaks observed at 26.3 ppm is caused by the CH$_2$ carbon of NH-CH$_2$ group and at 162.7 ppm caused by -C=O carbon of oxamide moiety of copolymer. [25]

![Figure 4. $^{13}$C - NMR spectra of 2,4-DAPOF copolymer](image4.png)

5.4. EI- MS analysis

The EI- MS spectrum of 2,4-DAPOF copolymer is shown in Figure 5 and peaks observed at m/z 250, 136, 114, 85 and 56. Following is the fragmentation mechanism to account for the MS peaks are mentioned in figure 6. [26].

![Figure 5. EI- MS spectra of 2,4-DAPOF copolymer](image5.png)
5.5. SEM Analysis
SEM analysis was performed on 2,4-DAPOF and shown in Figure 7. The SEM image displays porous structure with surface integrity. The SEM photograph at 2,000 and 1,500 magnifications is clearly revealing of porous structure with high sponginess or cavities. The swelling behavior and active sites on polymer surface appeared due to sponginess present in the copolymer. The image also showed an amorphous and crystalline structure of polymer. Predominantly condensation polymerization reaction is responsible for amorphous nature of copolymer. [21,27]
5.6. *Thermo gravimetric Analysis*

TGA analysis of 2,4-DAPOF synthesized copolymer shows in Figure 8. The plot depicted the percent mass verses temperature in an air atmosphere, approximately 10 mg of sample was heated at a rate of 10 °C/min with air as an atmosphere. The TGA results show that the 2,4-DAPOF polymer undergoes thermal degradation beginning at 200 °C with a total mass loss of 90.14 % and residue remaining about (10.0%). [16,17] Polymers absorb a small amount of moisture as a water of crystallization which can be determine the percentage of water present with polymer by TGA graph. The newly synthesized polymer degraded in three stages with initial loss of water molecule which is shown in Table 2.

**Table 2. Degradation pattern of 2,4-DAPOF copolymer with temperature range**

| Temperature | Loss of materials                                      | Percentage loss |
|-------------|-------------------------------------------------------|-----------------|
| 0-200 °C    | Moisture (May be water molecule)                      | 7.15 %          |
| 200-800 °C  | Loss of Benzene ring with one –OH and two –NH groups and one –CH₂ | 55.29 %         |
| 800-1000 °C | Two –CONH and two –CH₂                                  | 90.14 %         |

**Figure 7.** SEM Micrographs of 2,4-DAPOF copolymer

**Figure 8.** Thermal degradation thermogram of 2,4-DAPOF copolymer

6. **Conclusion**

2,4-DAPOF newly synthesized copolymer has confirmed and is checked by the results got by the TLC and spectral technique like Infra-red, $^1$H and $^{13}$C-NMR spectroscopy. Further formation of copolymer and its degradation pattern has been confirmed by mass spectrometry. TGA Monograph has shown three degradation phases, first indicating evaporation of water molecule associated with the polymer, second
shows deduction of benzene ring with one –OH, two –NH and one –CH₂ groups and third step represents lasting molecule. The synthesized polymer is very suitable as coating material because of its stability was observed as up to 473 K. The surface of the copolymer was observed to be more sponginess or cavities. The swelling behavior and active sites on polymer surface appeared due to sponginess present in the copolymer, clearly showing the appropriateness of the synthesized polymeric resin for ion-exchange properties.

7. References

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