Synthesis and Characterization of 2-Hydroxy, 4-Methoxy, Benzophenone - Melamine - Formaldehyde (2-H,4-M, Bphn-M-F) Copolymer Resins.

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Abstract

Copolymer resin (2-H, 4-M, Bph-M-F) was synthesized by using monomers 2-Hydroxy, 4-Methoxy, Benzophenone and melamine was condensed with formaldehyde at different proportion in a round bottom flask in presence of acetic acid as a catalyst. Compositions of copolymer resin have been determined on the basis of their elemental analysis and the number average molecular weights were determined by conductometric titration in non-aqueous medium. For ascertaining the some characteristic, functions and constants viscometric measurements in dimethyl formamide (DMF) have been carried out. The UV-visible, FTIR and proton nuclear magnetic resonance (H$^+$ NMR) spectra were studied to elucidate the structure.
Keywords: Synthesis, polycondensation, resin, structure, degree of polymerization, Characterization

Introduction

Melamine containing copolymer much research work has being carried out on the synthesis and characterization. Gurnule et al [1] synthesized copolymer derived from substituted 2-Hydroxy, 4-Methoxy formaldehyde resin shows improved ion-exchange properties, thermal resistance property, coordinating property and good storage stability etc. Melamine formaldehyde copolymer is good fire retardant properties are due to release of nitrogen gas when burn. Phenolic resins have more application in ion exchanger, semiconductor, adhesive materials because of chemical and high resistance. Melamine formaldehyde resins are harder and stronger than phenolic resins but have lower moisture and heat resistance thus it can be molded into product. Khobragade et al have synthesized pthalic acid melamine formaldehyde resins are widely used as complexing agents in various applications due to their good complex forming ability[2]. Kapse et al. synthesized copolymer by polycondensation of p-Hydroxyacetophenone, Quinhydrone and Melamine in presence of Poly-Phosphoric acid (PPA)[3]. Chelating ion- exchange properties studied for Cu2+, Mg2+, Pb2+ and Bi3+ by batch equilibrium method. PAQM resins are more selective Cu2+> Mg2+> Pb2+. Shah and coworkers have prepared terpolymers from 8-hydroxyquinoline-formaldehyde-catechol terpolymer were reported [4]. The resin was characterized by FTIR, NMR, UV-visible spectroscopy and elemental analysis. The morphology of the synthesized resin was studied by scanning electron microscopy (SEM). The present work describes the synthesis and characterization of copolymer derived from 2-Hydroxy, 4-Methoxy, Benzophenone and melamine was and formaldehyde.

Materials

The entire chemicals were of A. R. grade. Solvents like N, N-dimethylformamide (DMF), dimethyl sulphoxide (DMSO), ethanol and diethyl ether etc. were of also analytical grade and were purified by known method prior to their use in various physico-chemical studies (Merck, India) and used after distillation. 2-Hydroxy, 4-Methoxy, Benzophenone, melamine, formaldehyde, glacial acetic acid using these monomers formation of copolymer.

Synthesis of 2-H,4-M, Bphn-M-F Copolymer Resins

　　　　The proportionate mixture of 2-Hydroxy, 4-Methoxy, Benzophenone (0.1 mol) and melamine (0.1 mol) was condensed with formaldehyde (0.3 mol) in a proportion of 1:1:3 in a round bottom flask in presence of 2M acetic acid as a catalyst. This mixture was heated for 5 to 6 hrs at 126 ± 2 ^{0}C in an oil bath with occasional stirring (5-7). Excellent yield of copolymer resin can be obtained by this reaction. The powdered sample was washed many times with boiling water and ethanol to remove unreacted monomers.The air dried powdered then extracted with diethyl ether and then with petroleum ether to remove 2-Hydroxy, 4-Methoxy, Benzophenone - Melamine - Formaldehyde copolymer which might be present along with 2-H,4-M, Bphn-M-F copolymer resin. It was further purified by dissolving in 8% NaOH solution, filtered and reprecipitated by gradual drop wise addition of ice cold 1:1 (v/v) concentrated HCl/distill water. The yield of the copolymer resin was found to be 83%.The reaction is shown as follows.
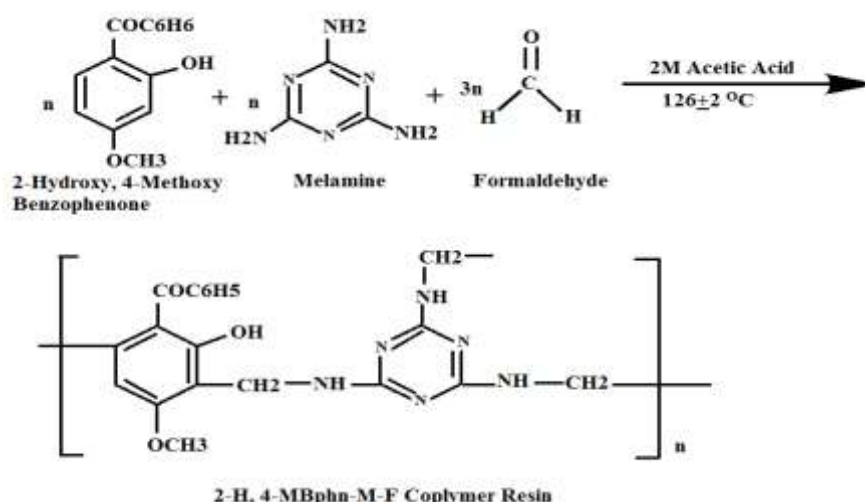

Fig. 1: Reaction of the 2-H, 4-MBphn-M-F Copolymer

Characterization of Copolymer Resin

The carbon, hydrogen, nitrogen and oxygen elemental analysis was carried out on a Perkin Elmer 2400 Elemental Analyzer instrument. The UV–Visible studies were out carried using Scimadzu UV-1800 Spectrophotometer in the range 200-800 nm. The Infrared spectrum was recorded in the region of 500–4000 cm-1 on Shimadzu Affinity-1 FTIR Spectrophotometer, ^{1}H-NMR studied using Bruker Avance-II FT-NMR Spectrometer in DMSO-d[6] solvent. All the analytical and spectral studies for the newly synthesized copolymer were carried out at SAIF Punjab, Chandigarh. The viscosities were determined using Tuan-Fuoss viscometer at six different (concentration ranging from 3.0 wt % to 0.5 wt % of resin in DMF at 330C. The intrinsic viscosity was calculated by the Huggins equation (1) and Kramer equation (2)

$$\eta_{sp}/C = [\eta] + K_1 [\eta]^2 C \quad ....(1)$$

$$\ln \eta_{rel}/C = [\eta] - K_2 [\eta]^2 C \quad ....(2)$$

Result and Discussion

　　　　This resin colour was yellow and insoluble in organic solvent but soluble in DMF, DMSO, THF and aq. NaOH. The resin was analyzed for carbon, hydrogen, nitrogen and oxygen content. Then resin was purified and found value of content agreement with calculated value as

Calculated for $C_{20}H_{19}N_6O_3$: C :(63.69)%, H: 4.86%, N: 21.49%

Found for $C_{20}H_{19}N_6O_3$: C**:** 63.40%, H: 4.60%, N: 21.20%

The molecular weight (Mn) of the copolymer resin was determined by non-aqueous coductometric titration in DMF against KOH in 50% (v/v) DMF/ alcohol mixture using 100 mg of resin sample. A plot of specific conductance against the milliequivalents of potassium hydroxide required for neutralization of 100 g of copolymers was made. After inspection of this a plot revealed that there are many breaks. From this plot the first break and the last break were noted (Fig.-2). The calculation of (Mn) by this method is based on the following considerations.

(1) The first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units; and

(2) after last the break in the plot a continuous increased in conductance which represents the stage at which phenolic hydroxy group of all repeating units are neutralized. On the basis of the average degree of polymerization (Dp) is given by the following relation-

Total meq. of base required for complete neutralization i.e. last break

$$\overline{Dp} = \frac{Total\ meq.\ of\ base\ required\ for\ complete\ neutralization}{Meq.\ of\ base\ required\ for\ smallest\ interval}$$

$$\overline{Mn} = \overline{Dp} \times Repeat\ unit\ weight$$

The number average molecular weight (Mn) could be obtained by multiplying the Dp by the formula weight of the repeating unit[5]. Rahangadale et al [6] have prepared the copolymer from salicyladoxime, melamine and formaldehyde under different conditions. They carried out conductometric titration of these copolymers in formic acid against perchloric acid as a titrant to estimate the molecular weight of the resin.
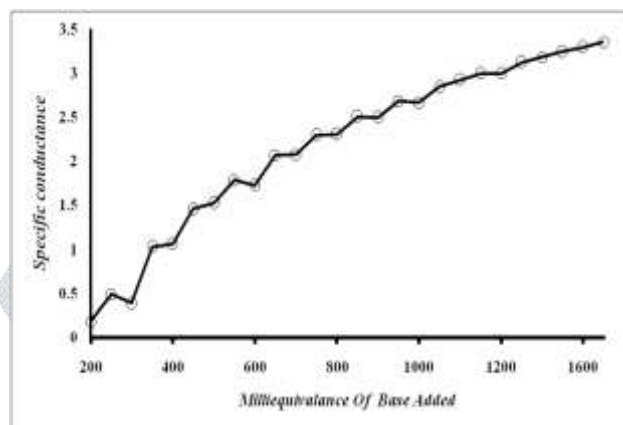

Fig.2. Conductometric Titration curve for 2-H, 4-MBphn-M-F Copolymer.

The viscometric measurements of 2-H, 4-M, Bph-M-F copolymer resins were carried out in dimethyl sulphoxide at 313 K using Taun-Fuoss viscometer. The intrinsic viscosity was determined by the Huggin[7] equation and Kraemers[8] equation :

$$\eta_{red} = \eta_{sp}/C = [\eta] + K_1[\eta]^2C \qquad (1)$$

$$ln\ \eta_{rel}/C = [\eta] - K_2[\eta]^2C \qquad (2)$$

The reduced viscosity η_{red} of the copolymer resin samples were calculated by the formula η_{sp}/C. Reduced viscosity versus concentration was plotted for each set of data. The intrinsic viscosity [η] was determined by the corresponding linear plots (Fig. 3). According to the above relations, the plots of $\eta_{sp/C}$ and $ln\ \eta_{rel/C}$ against C were linear with slopes of K_1 and K_2, respectively. Intercepts on the viscosity function axis gave [η] value in both plots. The calculated values of the constants K1 and K2 in most cases satisfy the relation K1 + K2= 0.55 favourably
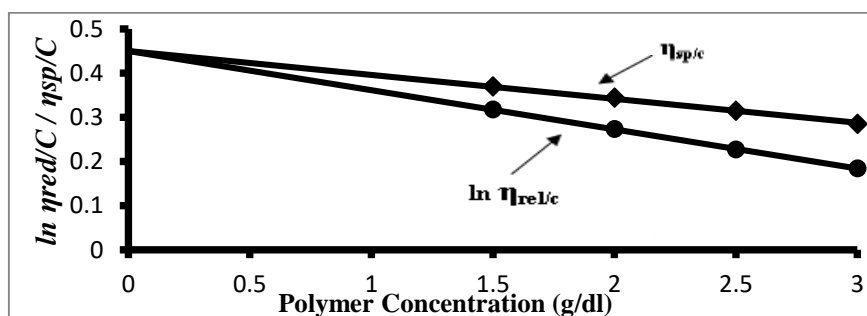

Fig.3: Viscometric plots of 2-H, 4-MBphn-M-F Copolymer

The values of [η] obtained from equation (1) and equation (2) were in close agreement with each other. It has been observed that the intrinsic viscosity increases with the increase in molecular weight of copolymer.
The electronic spectra of the 2-H, 4-M, Bph-M-F copolymer in pure DMSO was recorded and displayed two characteristic broad bands at 230 and 380 nm, presented in Fig.4. The observed positions of the absorption bands with different intensities indicate the more intense band 230 nm is due to ($\pi \rightarrow \pi^*$) allowed transition which readily attains coplanarity and shoulder merging (loss of fine structure) and also due to chromophore groups like >C=C, >C=N, >C=O groups are in conjugation with an aromatic nucleus

and the less intense band at 380 nm may be due to (n→ π^*) forbidden transition in >C=N and –OH groups. The presence of aromatic nuclei and n→ π^* transition indicates the presence of –NH and –OH group. The bathochromic shift from the basic value viz. 230 nm and 380 nm may be due to combined effect of conjugation (due to chromophore) and phenolic hydroxyl groups as well as –NH groups (auxochrome). The hyperchromic effect is due to the presence of –OH and –NH groups, which act as auxochrome. [9].
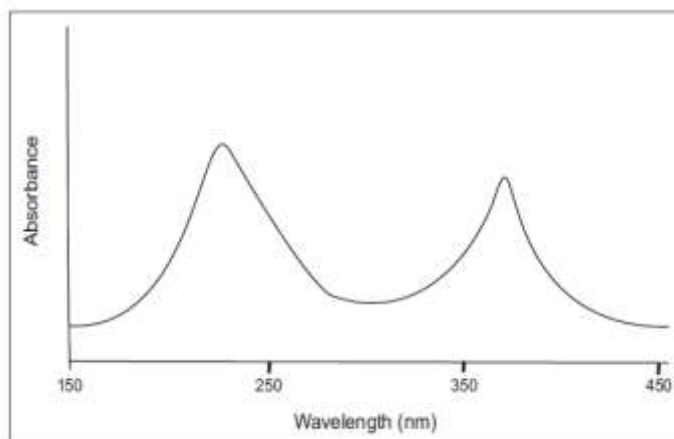

Fig.4. UV-Visible Spectra of 2-H, 4-M, Bph-M-F Copolymer Resins

The FTIR spectra of four 2-H, 4-M, Bph-M-F copolymer is presented in Fig.5. The copolymer spectrum showed a broad absorption band appeared in the region 3388 cm^{-1} may be assigned to the stretching vibrations of phenolic hydroxyl (-OH) groups exhibiting intramolecular hydrogen bonding [10]. The presence of sharp and strong band at 3061 cm^{-1} indicates the presence of –NH bridge. This band seems to be merged with very broad band of phenolic hydroxyl group. A band appeared at 2943 cm^{-1} is assigned to aromatic ring (-CH) stretching modes The1,2,4,5,6 substitution of aromatic ring is confirmed from the sharp, medium/weak bands appearing at 1024, 1113, 1205, 1303 and 1263 cm^{-1}, respectively. A weak band appeared at 2845 cm^{-1} is attributed to –CH$_2$ group present in the copolymer. The band appeared in the region of 1381 cm^{-1} to 1348 cm^{-1} is attributed to –CH$_2$-bending (twisting and wagging) mode of vibrations. Stretching mode and a strong band at 1581 cm^{-1} is attributed to C=N stretching of quinoline ring.
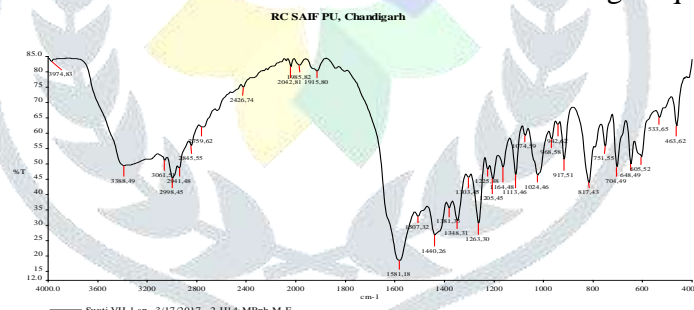

Fig. 5: FTIR Spectra of 2-H, 4-M, Bph-M-F Copolymer Resins

In the spectrum of copolymer, the resonance signal appeared in the range at 9.04 (δ) ppm may be due to phenolic hydroxyl protons. The much downfield chemical shift for phenolic –OH indicates clearly the intramolecular hydrogen bonding of -OH group[11]. The signals in the region 7.44 (δ) ppm are attributed to protons of –NH bridge present in the ligand structure and the signals appeared in the range of 4.67 ppm are assigned to methylene protons of Ar-CH2-N moiety. The weak multiplate signals (unsymmetrical pattern) in the region of 8.97 (δ) ppm may be attributed to aromatic proton (Ar-H)[12]. The signals appeared in the region of 8.23 ppm is assigned to aromatic protons and the signal appeared in the region of 3.86 ppm is attributed to methylene bridges. The signal appeared for –NH bridge is 6.56 in the spectrum
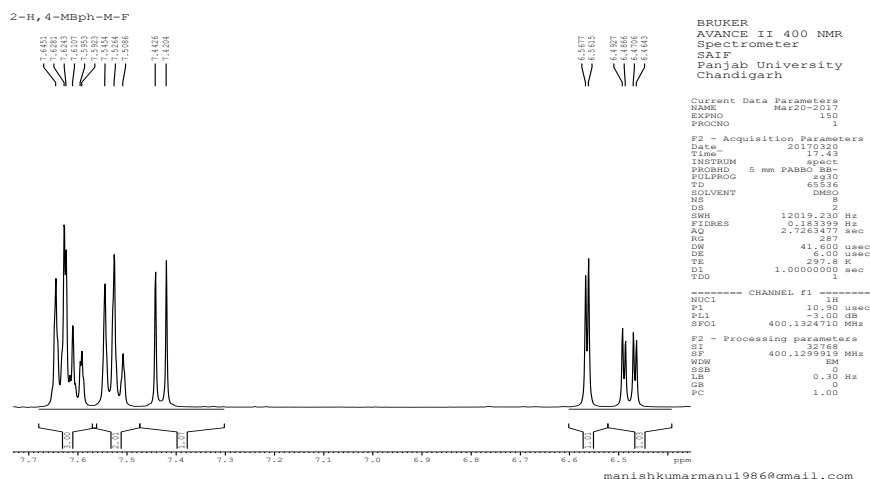
Fig. 6: ^{1}H−NMR Spectra of 2-H, 4-M, Bph-M-F Copolymer

     Surface analysis of polymer has carried out for understanding the surface features of the materials. By scanning electron micrographs the morphology obtained in different magnifications for this resin was investigated are shown in Fig.7. This information is useful for studying surface topography and defect in the structure. This copolymer show fringed and spherulites model. The spherules are complex polycrystalline which the aggregate of crystallites embedded with amorphous regions. Spherulites the amorphous region shows secondary structural feature such as corrugations and having deep pits. The spherulite structure of the 2-H, 4-M, Bph-M-F copolymer indicates the presence of crystalline structure of the polymer. The corrugation in the surface area of resin with deep pits shows the amorphous nature of the resin. Fringes model of terpolymer shows the crystalline amorphous structure. The photograph shows the fringed and spherulite structure having deep pits represent the transition between crystalline and amorphous. The presence of close-packed surface having deep pits and the reactivity of active sites buried in the copolymer matrix exhibits a more amorphous character of copolymer. The presence of few holes and cracks are noted which may be due to air voids [13].

 The polymer under study is copolymer and hence, it is very difficult to assign their exact structures. The most probable structures of copolymer resin have been proposed on the basis of the nature and reactive, position of the monomer, elemental analysis, electronic, FT-IR, ^{1}H NMR, spectra, SEM and molecular weight.
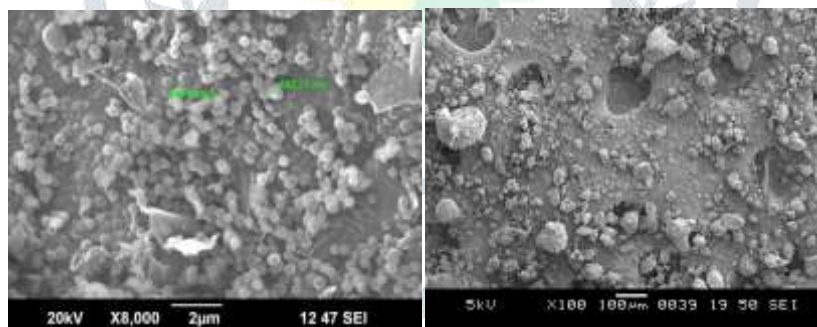

Fig.7.Scanning Electron Microscopy Images of 2-H, 4-M, Bph-M-F Copolymer Resin.

Table-1: molecular weight determination and viscometric data of copolymer

Copolymer	Emprical Formula of Repeating Unit	Emprical Formula Mass	($\overline{Dp}$)	($\overline{Mn}$)	Intrinsic viscosity [η] dl g-1	Huggin's constant K_1	Kraemer constant K2	K1+ K2
2-H, 4-M, Bph-M-F	$C_{20}H_{19}N_6O_3$	391	7	2737	0.45	0.247	-0.198	0.049

Conclusion

Copolymer (2-H, 4-M, Bph-M-F) was synthesized by using monomers 2-Hydroxy, 4-Methoxy, Benzophenone and melamine was condensed with formaldehyde in the presence of acid catalyst have been prepared. On the basis of elemental analysis, UV-Visible spectra, FTIR, NMR spectra and conductometric titration in non-aqueous medium, the proposed structure of the copolymer resin is as shown in the Fig. 1.

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