SYNTHESIS AND CHARACTERIZATION OF COPOLYMER RESIN-II DERIVED FROM 2,2-DIHYDROXYBIPHENYL, FORMALDEHYDE AND PROPYLENE DIAMINE

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Abstract

Synthesis ofcopolymer resin (2,2'DBPDF) have been prepared by the condensation of 2,2-dihydroxybiphenyl (BP) and Propylenediamine(PD) with formaldehyde (F) in the presence of acid catalyst and using 2:1:3 molar ratio of reacting monomers. Copolymer resin compositions have been determined on the basis of their elemental analysis and the number average molecular weights of resin were determined by conductometric titration in non-aqueous medium. Viscometric measurements in dimethyl formamide (DMF) have been carried out with a view to ascertain the characteristic functions and constants. The UV-visible, FTIR and proton nuclear magnetic resonance (H^1 NMR) spectra were studied to elucidate the structure. The surface features and crystalline behavior of the ligand and its complexes were analyzed by scanning electron microscope (SEM).

Keywords: Synthesis, 2,2'-dihydroxyipheyl, propylenediamine, formaldehyde, polycondensation, resin, structure, degree of polymerization, characterization.

Introduction

Polymers very special classes of polymers are known for their versatile uses and are found to be amorphous, crystalline or resinous in nature. Phenolic resins have been the workhorse as matrix resins in composites for structural and thermal applications in aerospace because of their ease of processability, thermal stability, versatile characteristics and cost effectiveness. W. Tang and coworkers[1] studied the thermal decomposition kinetics of thermotyropiccopolyesters made from p-hydrocinnamic acid and p-hydrobenzoic acid. Copolymers occupy an intermediate position between organic and inorganic compounds and it is hoped that the study of copolymers will lead to the production of polymer, which are both thermally stable and useful as fabricating materials. P. E. P. Michael et al. studied synthesis, characterization and thermal degradation of 8-hydroxyquinoline–guanidine–formaldehyde copolymer[1].Rahangdale and coworkers studied thermal degradation of polymers derived from 2, 4-dihdroxy-acetophenone,dithioxamide and formaldehyde[2].

Copolymer resins are derived from 2,4-dihydroxypropiophenone, biuret, and formaldehyde in hydrochloric acid as catalyst and studied their thermal degradation[3]. Thermal degradation of*m*-nitroaniline, *m*-chloroaniline and *m*-aminophenol has been studied by Dash *etal.*[4]and 2-hydroxyacetophenone,oxamide and formaldehyde[5]. S. L. Oswal et al synthesized and studied thermal properties of copoly(maleimide-methylmethacrylate), terpoly(maleimide-methylmethacrylate-acrylicacid), and terpoly-(maleimide-methyl Methacrylatemethylacrylic acid). The thermal behaviour was studied by TG and DSC techniques[6]**.**Thermoanalysis and rheological behavior of copolymers of methyl methacrylate, N-phenylmaleimide and styrene studied by G. Jungang et al[7]. In order to synthesize polymers having numerous practical applications, there is a need to investigate the effect of heat on the polymers in order to establish their thermal stability. It must be pointed out that all the methods proposed have been developed by assuming that both activation energy and kinetic model do not change along the process. However, it has concluded from free- model kinetic methods of analysis that the activation energy is a function of the reacted fraction[8].

However, the literature studies have revealed that no copolymer has been synthesized using the monomer of 2.2'dihydroxybiphenyl, propelenediamine with formaldehyde. Therefore, in the present communication we report the synthesis, structural, characterization and thermal degradation studies of 2,2'DBPDFcopolymer.

Experimental

Preparation of 2,2'DBPDF copolymer resin

A mixture of 2,2'-dihydroxybiphenyl [0.2mol], melamine [0.1mol] and formaldehyde [0.3 mol] in the presence of 2M hydrochloric acid (200 ml) was heated in an oil bath at 124^0C ± 2^0C for 5 h with occasional shaking [9-10]. The separated resinous product (2,2'DBPDF) was washed with hot water to remove unreacted monomers. The resin was purified by dissolution in 8% NaOH and reprecipitated by dropwise addition of 1:1 (v/v) HCl / water with constant stirring. The precipitated resin product was filtered off, washed with hot water until it was free from chloride ions. The purified copolymer resin was finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yield of the copolymer resin was found to be 88%. The reaction taking place is as shown in Fig. 1.

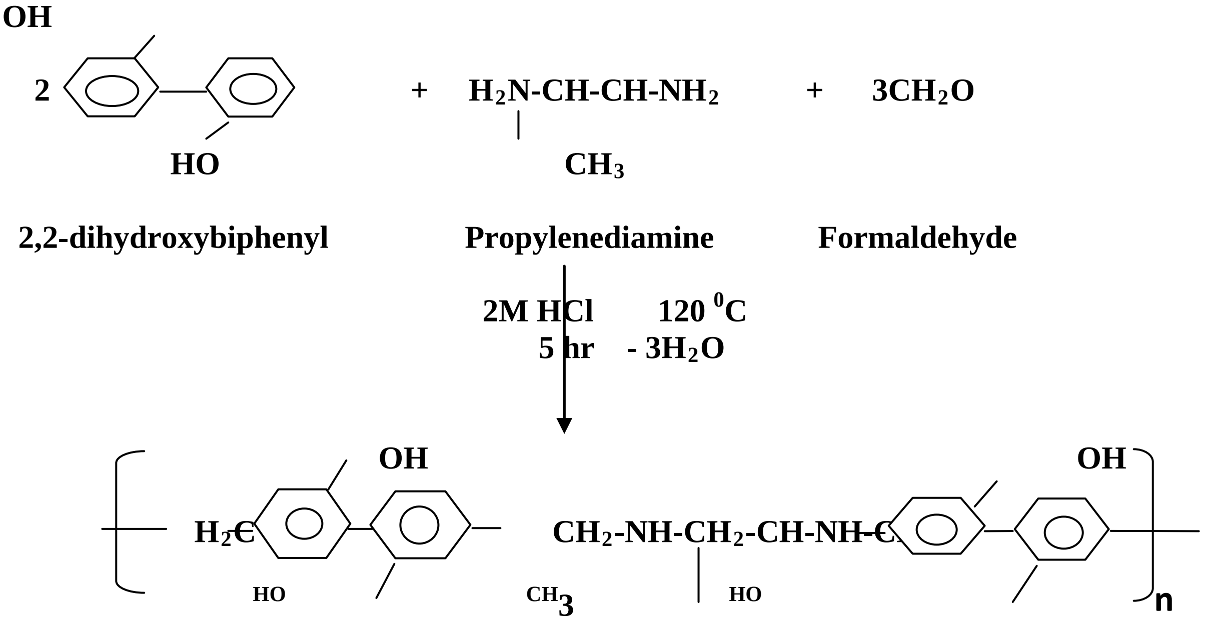

Fig.1. Synthesis of 2,2'DBPDF copolymer resin

RESULTS AND DISCUSSION

The copolymer resin (2,2'DBPDF) sample was brown in colour, insoluble in commonly used organic solvents but were soluble in DMF, THF, DMSO and aq. NaOH. The resin was analysed for carbon, hydrogen and nitrogen content. The resin synthesized do not show sharp melting point but undergo decomposition above 238^0C. This resin was then purified and analyzed for carbon, hydrogen and nitrogen content and found to be in agreement with calculated value.

The molecular weight $(\overline{Mn})$ 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. Inspection of such a plot revealed that there are many breaks in plot. From this plot the first break and the last break were noted. The calculation of $(\overline{Mn})$ by this method is based on the following considerations [13].

(1) The first break corresponds to neutralization of the more acidic phenolic hydroxy group of all the repeating units; and (2)

the break in the plot beyond which a continuous increase in conductance is observed represents the stage at which phenolic hydroxy group of all repeating units are neutralized. On the basis of . the average degree of polymerization $(\overline{Dp})$ is given by the following relation

$$\overline{Dp} = \frac{\text{Total meq.of base required for complete neutralization i.e. last break}}{\text{Meq.of base required for smallest interval i.e. first break}}$$

The number average molecular weight $(\overline{Mn})$ could be obtained by multiplying the $\overline{Dp}$ by the formula weight of the repeating unit [13]. The results are incorporated in Table 1.

Non-aqueous conductometric titration curve of 2,2’DBPDF copolymer

Viscometric measurements were carried out in DMF at 30°C. The resin showed normal behaviour. The intrinsic viscosity was determined by the Huggin [14] equation

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

And

Kraemers [21] equation :

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

The viscometric plots are shown in Fig. 2. In accordance with the above relations, the plots of η_{sp} / C and η_{rel} / C against C were found to be linear giving as slopes K_1 and K_2 respectively. The intercept on the axis of viscosity function gave the [η] value in both the plots. The calculated values of constants K_1 and K_2 in most of cases satisfy the relation. $K_1 + K_2 = 0.5$ favourably [14]. 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.

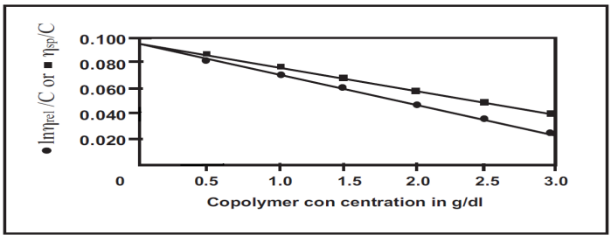

Fig.3. Viscometric plots of 2,2’DBPDFcopolymer

The electronic spectra of the 2,2’DBPDF copolymer resin is depicted in Fig.3. The spectra of the copolymer exhibit two absorption maxima in the region 250 to 280 nm and 330 to 340 nm. The intense band at 290 nm is due to (π – π*) allowed transition of 2.2’dihydroxybiphenyl moiety which readily attains coplanarity and the shoulders merging (loss of fine structure) band at 334 nm may be due to (n – π*) forbidden transition in saturated aliphatic carbonyl compounds [15]. The bathocromic shift from the basic values viz. 270 nm and 280 nm respectively may be due to combined effect of conjugation and phenolic hydroxy group (auxochrome) [15].

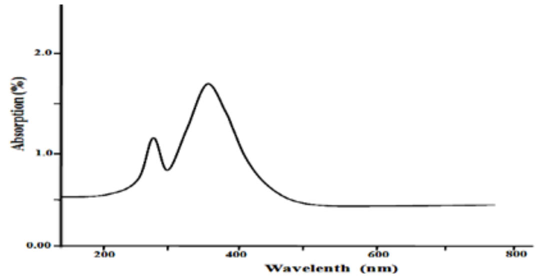

Fig.4. Electronic spectra of 2,2’DBPDF copolymer

The IR spectra of copolymer resin is presented in Fig. 4. The IR spectra revealed that the resin give rise to a broad band appearing in the region 3400-3800 cm^{-1} may be assigned to the stretching vibration of carboxylic acid groups exhibiting intermolecular hydrogen bondin[16]. The band at 2980 cm^{-1} assignable to –NH- stretching, bending and deformation out of plane vibrations of melamine moiety in copolymers respectively. The band at 1542 cm^{-1} may be ascribed to aromatic skeletal ring [16]. The presence of methylene bridges (-CH_2-) in the polymeric chain may be assigned due to presence of band at 1460-1470 cm^{-1}, 1385-1370 cm^{-1} and 798-763 cm^{-1} [-CH_2- rocking] [16].

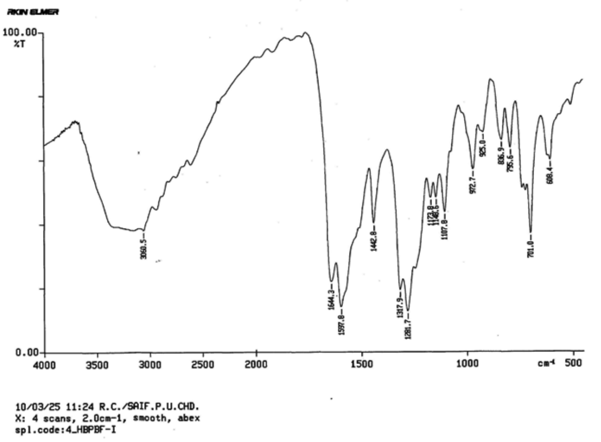

Fig. 5. Infrared spectra of 2,2’DBPDF copolymer

Proton NMR spectra of copolymer resin is presented in Fig.6. Proton NMR spectra of copolymer resin show the intense signal arising in the region 7.70 ppm which may occur on account of hydroxyl proton of -COOH group involved in the intermolecular hydrogen bonding[16]. The sharp intense peak at 6.70 ppm may be assigned to aromatic proton. A weak signal made its appearance at 3.80 ppm which may be due to amido protons of -NH bridge in the chain[17]. An intense signal appearing at 2.50 ppm may be due to methylene proton (-CH_2-). Copolymer show signal around 3.72 (□) ppm methylene bridges of Ar-CH_2-N linkage[17].

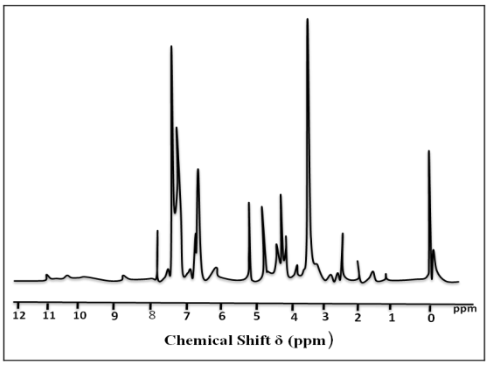

Fig.6. Proton NMR spectra of 2,2’DBPDF polymer

The SEM photographs obtained in different magnifications for the 2,2’DBPDF copolymer resin are shown in Fig. 7. It indicates that the PTMF copolymer has a net-like appearance and the surface features of the copolymer shows a fringed, scattered, and miscellaneous model of the crystalline–amorphous structure. Scanning electron microscopy of copolymer was carried out to understand the inner morphology and pore structure. The morphology of fracture surfaces of the copolymer is quite different from that of polymer–metal complexes. It is clear from SEM that the copolymer is porous in nature. The morphology of the copolymer shows a fringed model of the semicrystalline nature. The fringes represent the transition between the crystalline and the amorphous phases. 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. The presence of few holes and cracks are noted which may be due to air voids[7].

On the basis of the nature and reactive positions of the monomers, elemental analysis, electronic, IR, NMR spectra and molecular weight, the most probable structures have been proposed for copolymer resin as shown in Fig. 1.

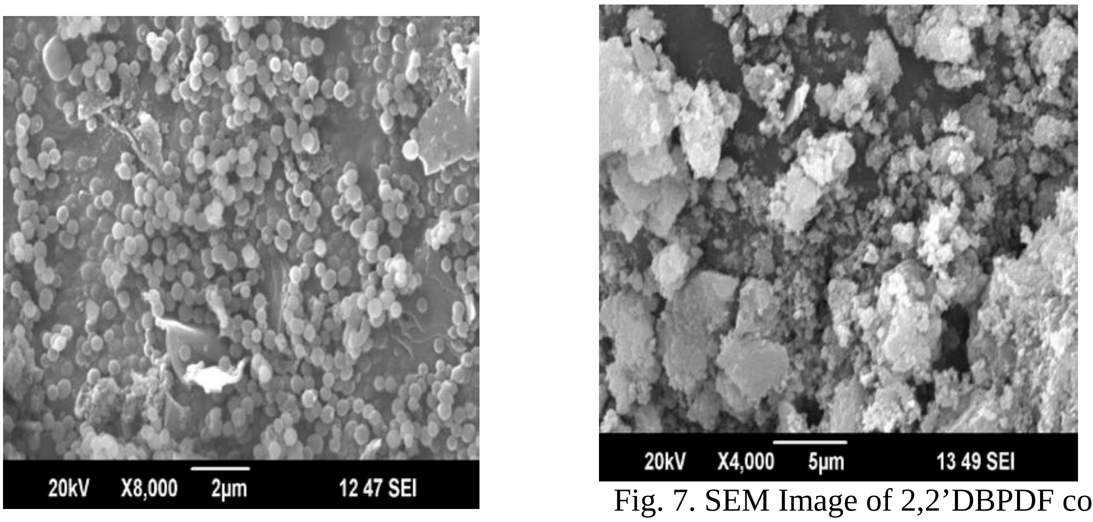

Fig. 7. SEM Image of 2,2'DBPDF copolymer resin

Table1

Molecular Weight Determination and Viscometric Data of copolymer

Copolymer	Expirical formula of repeating unit	Empirical formula weight	$\overline{Dp}$	$\overline{Mn}$	Intrinsic viscosity dl g^{-1}	Huggin's constant (K_1)	Kraemer constant (K_2)	K_1+K_2
2,2'DBPDF	$C_{13}H_{11}N_6O_4$	315	14.37	5104	0.144	-0.320	0.2448	0.56

CONCLUSIONS

Copolymer resin 2,2'DBPDF based on polycondensation reaction of 2,2'dihydroxybiphenyl and propylene diamne 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 structure suggested for copolymer resin. The copolymer resin can be used as ion-exchanger and can also be used for the preparation of polychelates with transition metal ions.

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