

Resin-IV: Synthesis and Characterization of Terpolymers Derived from 2-Hydroxyacetophenone, Melamine, and Formaldehyde

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ABSTRACT: Terpolymer resins (2-HAMF) were prepared by the condensation of 2-hydroxyacetophenone and melamine with formaldehyde in the presence of acid catalyst and using varied molar ratios of reacting monomers. Compositions of terpolymers have been determined by elemental analysis. The number average molecular weights (M_n) have been determined by conductometric titration in nonaqueous medium. Viscometric measurements

in dimethyl sulfoxide have been carried out with a view to ascertain the characteristic functions and constants. Electronic spectra, infrared and nuclear magnetic resonance spectra were studied to elucidate the structure. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3315–3320, 2008

Key words: synthesis; resins; polycondensation

INTRODUCTION

Ion-exchange may be defined as reversible exchange of ions between the substrate and surrounding medium. Ion exchange technique can remove traces of ionic impurities from water/process liquor and give out the product of ultra pure quality in a simple efficient and techno-economically viable manner. Ion-exchangers are widely used in analytical chemistry, hydrometallurgy, antibiotic purification, and separation of radioisotopes and in large scale water treatment and pollution control.^{1,2} A large number of synthetic resins derived from hydroxy and amino aromatic compounds have attracted the attention of many research workers because of their versatile uses as ion-exchangers, photographic binders, thermal stabilizers, etc. We have reported the synthesis and characterization of the resins derived from a large number of hydroxy phenols, diamides, and formaldehyde.^{3–7} Various hydroxybenzoic acid-formaldehyde copolymers have been reported to have found use as ion-exchangers.^{8,9} Terpolymers can also be synthesized by the condensation of a mixture of phenols or hydroxybenzoic acid, various amines, and formaldehyde.^{10,11} A literature survey reveals that ion-exchange copolymer resins have been syn-

thesized from salicylic acid, thiourea, and trioxane and also from *p*-hydroxybenzoic acid, urea and formaldehyde.^{12,13} This article describes the synthetic and structural characterization of new terpolymer derived from 2-hydroxyacetophenone, melamine, and formaldehyde.

EXPERIMENTAL

Materials

The chemicals 2-hydroxyacetophenone, melamine and formaldehyde (37%) used are of analytical grade and chemically pure which is purchased from Merck, India. Solvents like *N,N*-dimethyl formamide and dimethyl sulfoxide were used after distillation.

Preparation of 2-HAMF terpolymer resin [2-HAMF-I]

The 2-HAMF terpolymer resins were prepared by condensing 2-hydroxyacetophenone (1.3615 g, 0.1 mol) and melamine (6.3 g, 0.1 mol) with formaldehyde (11.25 mL, 0.3 mol) in the mole ratios of 1 : 1 : 3 in the presence of 2M HCl. The mixture was heated at 130°C ± 2°C in an oil bath for 5 h.^{1–5} The solid product obtained was immediately removed from the flask as soon as the reaction period was over. It was washed with cold water, dried and powdered. The powder was repeatedly washed with hot water to remove unreacted monomers. The air dried terpolymer resin was extracted with ether to remove excess of 2-hydroxyacetophenone-formaldehyde.

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TABLE I
Synthesis and Physical Data of Terpolymer

Terpolymer	Reactants			Reflux temp. ± 2 K	% yield	Color	Elemental analysis (%)					
	2-Hydroxy acetophenone (mol)	Melamine (mol)	Formaldehyde (mol)				C		H		N	
							Calc.	Found	Calc.	Found	Calc.	Found
2-HAMF-1	0.1	0.1	0.3	403	84.4	Cream	50.98	50.84	5.88	5.70	27.72	27.00
2-HAMF-2	0.2	0.1	0.3	403	84.5	Cream	58.53	58.00	5.09	5.00	18.62	18.82
2-HAMF-3	0.3	0.1	0.5	403	82.6	Cream	62.64	62.30	5.38	5.60	13.77	13.40
2-HAMF-4	0.4	0.1	0.7	403	85.4	Cream	61.15	61.85	5.09	5.20	17.44	17.92

hyde copolymer, which might be present along with 2-HAMF terpolymer resin. It was further purified by dissolving in 8% NaOH and filtered. It was precipitated by dropwise addition of 1 : 1 (v/v) conc. HCl/water with constant stirring and filtered. The process was repeated twice. The resulting polymer sample was washed with boiling water and dried in vacuum at room temperature. The purified terpolymer resins were finally ground well to pass through a 300 mesh size sieve and kept in vacuum over silica gel. The yields of these terpolymer resins were found to be 80%.

Similarly the other resins samples of 2-hydroxyacetophenone, melamine, and formaldehyde viz. 2-HAMF-II, 2-HAMF-III, and 2-HAMF-IV in the ratio 2 : 1 : 3, 3 : 1:5, and 4 : 2 : 7 were synthesized using different molar ratios, respectively. Details of synthesis of terpolymers along with color and yield are incorporated in Table I.

Characterization of terpolymers

The terpolymers resins were subject to microanalysis for carbon, hydrogen, and nitrogen on Perkin-Elmer C, H, N, S analyzer. The number average molecular weights (M_n) were determined by conductometric titration in DMF using KOH as titrant. From the plots of specific conductance against milliequivalents of titrant base added, the first break and the last break were noted. The degree of polymerization (DP) of the terpolymer resin samples were obtained from the ratio of total milliequivalents of base used for neutralization of all COOH groups to the milliequivalents of base used for neutralization of first COOH

group (first break). The value of DP was multiplied by the average molecular weight of the repeating unit to get the number average molecular weight.^{1-5,14}

The viscosities were determined using Tuan-Fuoss viscometer at six different concentration ranging from 3.0 to 0.5 wt % of resin in DMF at 30°C. The intrinsic viscosity $[\eta]$ was calculated by the Huggins eq. (1) and Kraemer¹⁵ eq. (2).

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

$$\ln \eta_r/C = [\eta] - K_2[\eta]^2 \cdot C \quad (2)$$

Electronic absorption spectra of the terpolymers resins in DMF were also recorded on Varian DMS 80 UV-VIS Double Beam Spectrophotometer. Infrared spectra of 2-HAMF terpolymer resins were recorded in Nujol Mull on Specord IR-75 spectrophotometer in KBr pellets in the range 4000–400 cm^{-1} . Proton NMR spectra of 2-HAMF terpolymers were recorded on Varian VXR-300 S 300 MHz proton NMR spectrophotometer using DMSO- d_6 as a solvent at Sophisticated Analytical Instrumentation Facility, Punjab University, Chandigarh.

RESULTS AND DISCUSSION

All the 2-HAMF terpolymer resins are yellow in color. The purified resins are soluble in *N,N*-dimethyl formamide (DMF), aqueous sodium and potassium hydroxide, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF). The melting points of these resins were found to be in the range 360–400°C.

TABLE II
Molecular Weight Determination and Viscometric Data of Terpolymer

Terpolymer	Empirical formula of repeating unit	Empirical formula weight	DP	M_n	Intrinsic viscosity $[\eta]$ dL g^{-1}	Huggin's constant (K_1)	Kraemer constant (K_2)	$K_1 + K_2$
2-HAMF-I	$\text{C}_{13}\text{H}_{18}\text{O}_3 \cdot 2\text{H}_2\text{O}$	306	12.8	3916	0.1191	0.218	0.278	0.496
2-HAMF-II	$\text{C}_{22}\text{H}_{22}\text{N}_6\text{O}_4$	434	9.83	4267	0.1234	0.238	0.262	0.500
2-HAMF-III	$\text{C}_{32}\text{H}_{32}\text{N}_6\text{O}_6$	596	8.16	4867	0.1322	0.252	0.264	0.516
2-HAMF-IV	$\text{C}_{44}\text{H}_{43}\text{N}_{12}\text{O}_8$	867	8.16	7080	0.1389	0.250	0.280	0.530

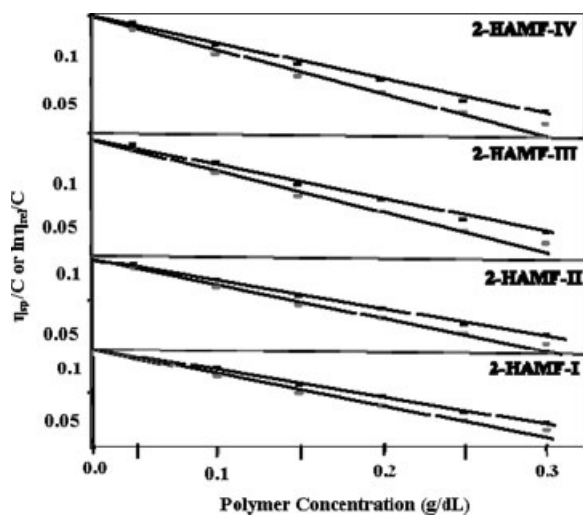


Figure 1 Viscometric plots of terpolymers.

These resins were analyzed for carbon, hydrogen, and nitrogen content (see Table I).

The number average molecular weights are collected in Table II. The molecular weight (M_n) of the terpolymer resin was determined by nonaqueous conductometric 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 terpolymers 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 (M_n) by this method is based on the following considerations.^{14,16}

(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 (DP) is given by the following relation.

$$DP = \frac{\text{Total meq. of base required for complete neutralization}}{\text{meq. of base required for smallest interval}}$$

The number average molecular weight (M_n) could be obtained by multiplying the DP by the formula weight of the repeating unit.¹⁷ The results are incorporated in Table II.

Viscometric measurements were carried out in DMSO at 33°C. All the resins showed normal behav-

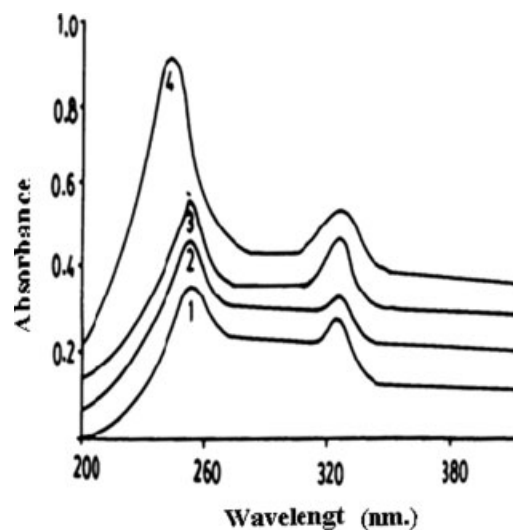


Figure 2 Electronic spectra of terpolymers.

ior. The reduced viscosity of a 3% solution of terpolymer resins 2-HAMF (1 : 1 : 2) has been found to be 0.11 dL/g. It decreased to about 0.062 dL/g when concentration of solution was reduced to 0.5 wt %. From the plots of η_{sp}/C versus concentration (C) and $\ln\eta_r/C$ versus concentration (C) were found to be 0.119 dL/g for the terpolymer resins 2-HAMF-I, 2-HAMF-II, 2-HAMF-III, and 2-HAMF-IV.^{1-5,18,19} The intrinsic viscosity was determined by the Huggin²⁰ equation

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

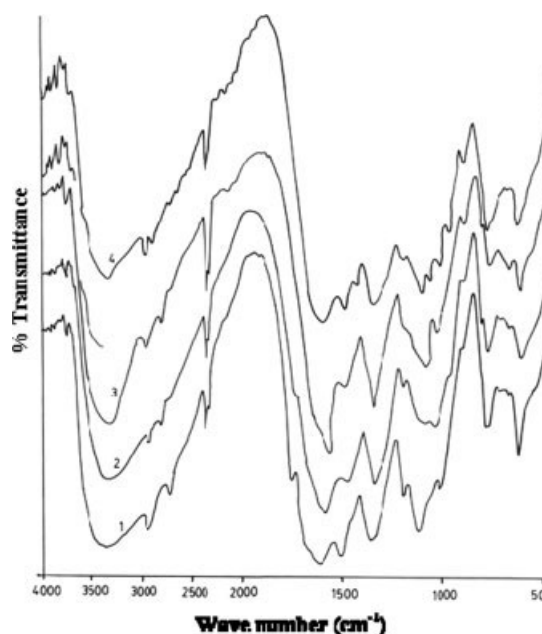


Figure 3 Infrared spectra of terpolymers.

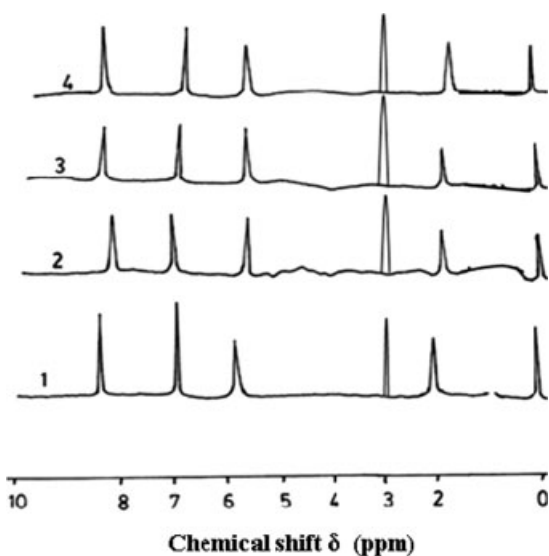


Figure 4 NMR spectra of terpolymers.

Kraemers²¹ equation

$$\ln \eta_r/C = [\eta] - K_2[\eta]^2 \cdot C \quad (2)$$

The viscometric plots are shown in Figure 1. In accordance with the above relations, the plots of η_{sp}/C and η_r/C against C were found to be linear giving as slopes K_1 and K_2 , respectively. Intercept on the

axis of viscosity function gave the $[\eta]$ value in both the plots. The calculated values of constants K_1 and K_2 (Table II) in most of cases satisfy the relation $K_1 + K_2 = 0.5$ favorably.²² The values of $[\eta]$ obtained from eqs. (1) and (2) were in close agreement with each other. It has been observed that the intrinsic viscosity increases with the increase in molecular weight of terpolymer.

The UV-visible spectra (Fig. 2) of all the 2-HAMF terpolymer samples in pure DMSO were recorded in the region of 190–700 nm at a scanning rate of 100. nm min⁻¹ and at a chart speed of 5 cm min⁻¹. All of the four 2-HAMF terpolymer samples displayed two characteristic broad bands at 320–330 nm and 250–260 nm. Both of these bands seem to be merged with each other because of their very broad nature. These observed positions for the absorption bands indicate the presence of a carbonyl (>C=O, ketonic) group containing carbon–oxygen double bond in 1,3,5-triazine ring and is assigned $\Pi \rightarrow \Pi^*$ transitions.²³

The bathochromic shift (shift towards longer wavelength) from basic values viz. 250 and 322 nm, respectively, may be due to the combined effect of conjugation and phenolic hydroxy group (auxochrome). It is observed from the UV-visible spectra of 2-HAMF-I < 2-HAMF-II < 2-HAMF-III and 2-HAMF-IV may be due to introduction of more chro-

TABLE III
IR Spectral Data of 2-HAMF Terpolymers

Observed band frequency (cm ⁻¹)				Assignment	Expected band frequency
2-HAMF-I	2-HAMF-II	2-HAMF-III	2-HAMF-IV		
3342	3354	3360	3408 (b, St)	-OH phenolic intramolecular hydrogen bonding	3750–3300
2915	2916	2915	2925 (Sh, w)	>NH stretching	2800–3500
2859	2859	2861	2863 (Sh, w)	-CH ₃ assymmetric vib.	2860–2845
1510	1595	1505	1597 (sh, w)	Aromatic ring	1500–1475
1435	1435	1438	1438 (b, m)	>CH ₂ rocking	1440–1432
1595	1351	1350	1350 (Sh, m)	>CH ₂ (methylene bridge)	1350–1360
1110	1120	1121	1114 (Sh, m)	1, 2, 3, 5 substitution in benzene skeleton	820,1040,1120
1030	1099	1030	1035 (Sh, m)		
1010	1040	1010	1040 (Sh, m)		
784	783	785	776 (b, m)		

TABLE IV
Nuclear Magnetic Resonance Spectral Data of 2-HAMF Terpolymers

Nature of proton assigned	Chemical shift (δ) ppm of terpolymer				Expected value
	2-HAMF-I	2-HAMF-II	2-HAMF-III	2-HAMF-IV	
Proton of phenolic -OH (involved in hydrogen bonding)	8.31	7.80	8.31	8.703	8.0–12
Aromatic proton (Ar-H) (unsymmetric pattern)	6.95	6.94	6.98	6.98	6.2–8.5
Proton of -NH- bridges	5.75	5.754	5.75	5.75	5.1–6.0
Methylene proton Ar-CH ₂ -N moiety	2.73	2.753	2.72	2.73	2.0–3.0
Methyl proton of Ar-COCH ₃ group	2.50	2.27	2.27	2.27	2.55–3.60

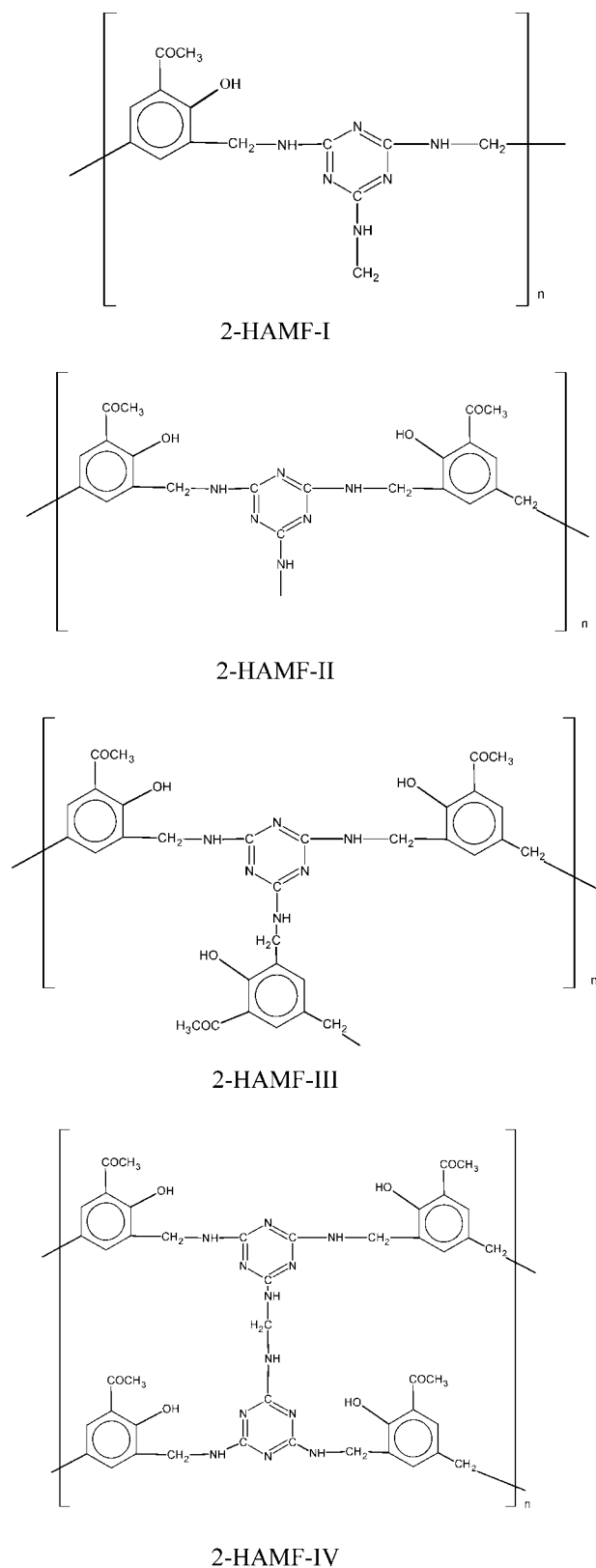


Figure 5 Suggested structures of terpolymers.

mophore ($>C=O$) groups and auxochrome (phenolic $-OH$) groups in the repeat unit structure of terpolymers.²⁴

The IR spectra of all four terpolymer resin are presented in Figure 3 and IR spectral data are incorporated in Table III. The IR spectra reveal that all these resins give rise to nearly similar pattern of spectra. A broad band appears in the region $3342\text{--}3408\text{ cm}^{-1}$ may be assigned to the stretching vibrations of phenolic hydroxy group exhibiting intermolecular hydrogen bonding with carbonyl group of different polymeric chain i.e., OH phenolic intermolecular polymeric association.^{25–28} The band at $2915\text{--}2925\text{ cm}^{-1}$ may be due to $-NH$ stretching vibrations.^{25–28} A band at $2859\text{--}2863\text{ cm}^{-1}$ is due to $-CH_3$ vibration. The band at $1505\text{--}1597$, which is due to aromatic ring. The presence of methylene bridges ($-CH_2-$) in the polymeric chain may be assigned due to presence of band at $1345\text{--}1351\text{ cm}^{-1}$ and band at $1435\text{--}1438\text{ cm}^{-1}$ and band at $1435\text{--}1438\text{ cm}^{-1}$ is due to $-CH_2-$ rocking.^{25–28} Bond obtained at $1110\text{--}1121\text{ cm}^{-1}$, $1030\text{--}1099\text{ cm}^{-1}$, $1010\text{--}1040\text{ cm}^{-1}$, suggest the aromatic ring is 1,2,3,5 substituted.^{25–29}

Proton NMR spectra of all four terpolymer resins are presented in Figure 4 and NMR spectral data are incorporated in Table IV. Proton NMR spectra of all terpolymer resin show a multiplet signal (unsymmetrical pattern) in a region $7.80\text{--}8.70$ (δ) ppm, which is due to proton of phenolic $-OH$ group involved in hydrogen bonding.^{28,29,30}

A broad signal in the region $6.94\text{--}6.98$ (δ) ppm, which is due to aromatic proton.^{29,30} A signal at 5.75 (δ) ppm shows proton of $-NH$ bridges. A signal at $2.53\text{--}2.73$ (δ) ppm may be assigned to protons of $Ar-CH_2-N$ moiety of methylene proton.^{30–33} A signal in the region $2.27\text{--}2.50$ (δ) ppm may be due to proton of $Ar-COCH_3$ group. On the basis of the nature and reactive position of the monomer, elemental analysis, electronic, IR, NMR spectra, and molecular weight, the most probable structures have been proposed for terpolymer resins as shown in Figure 5.

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