

Synthesis and Structural study of the Terpolymer derived from p-Hydroxybenzaldehyde, Adipic acid and Ethylene Glycol

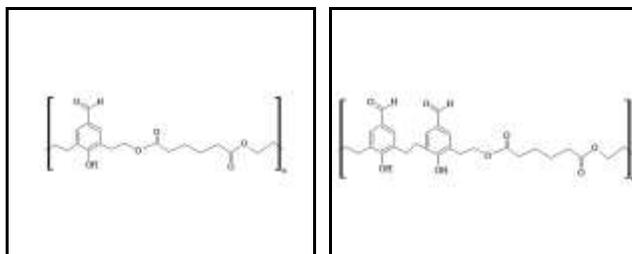
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Abstract - The terpolymer resins abbreviated as HBAE-I and HBAE-II were synthesized by polycondensation of p-hydroxybenzaldehyde, adipic acid and ethylene glycol using molar ratio 1:1:3 and 2:1:4 of monomers in presence of polyphosphoric acid as catalyst. The tentative structures of these resins are determined by Elemental analysis, ¹H NMR, FT-IR and UV-Visible spectra. The molecular weights of resins were determined by non-aqueous conductometric titration. The molecular weights of HBAE-I and HBAE-II were found to be 5568 and 7936 respectively. The tentative structures of resins were found to be



Index Terms – Polycondensation, Terpolymer, Molecular weight, Spectrum analysis.

I. INTRODUCTION

Terpolymers have a large number of practical applications in electronic controls, insulating materials, protective adhesives, aerospace industries etc, because of their high thermal stability, heat and chemical resistance and electrical insulation properties [1-3]. The present study deals with the synthesis and structural study of terpolymeric resin. The characterisation of terpolymers were carried out by elemental analysis, UV-VIS, FT-IR, ¹HNMR, non- aqueous conductometric titration for the determination of number of average molecular weight of terpolymer.

II. EXPERIMENTAL SECTION

Materials:

All chemicals were AR grade or chemically pure grade, p-hydroxybenzaldehyde, adipic acid, ethylene glycol and polyphosphoric acid were procured from s.d. fine chemicals, India.

Synthesis of resins derived from p-hydroxybenzaldehyde, adipic acid and ethylene glycol

The HBAE-I terpolymer resin was synthesized by polycondensation of p-hydroxybenzaldehyde, adipic acid with ethylene glycol in the presence of polyphosphoric acid as a catalyst with molar proportion 1:1:3 of reacting monomers at 120°C for 5.00 hrs. To a well-stirred and ice-cooled mixture of p-hydroxybenzaldehyde (1 M), adipic acid (1 M) and ethylene glycol (3 M), polyphosphoric acid (PPA, 20 gm) was added slowly with continuous stirring as a catalyst. The reaction mixture was left at room temperature for 30 min and heated in an oil bath at 120°C for 5.00 hrs. The reaction mixture was then cooled, poured on crushed ice and left over night. A reddish brown solid was separated out. It was collected by filtration and the product was washed several times with hot water to remove unreacted component. The dried product was crushed and squeezed with ether to remove unwanted copolymer and further the product was shacked with ether and air dried. The terpolymer

resin HBAE-I was air dried, powdered and kept in a vacuum desiccator for 4-5 hours. Yield was found to be 79%.

Similarly HBAE-II terpolymeric resin was prepared with varying molar proportion 2:1:4 of reacting monomers at 120°C for 5.00 hrs, in the presence of polyphosphoric acid as a catalyst and purified as per above method. Yield was found to be 81%.

III. RESULT AND DISCUSSION

Characterization of p-hydroxybenzaldehyde - adipic acid - ethylene glycol (HBAE) terpolymers

HBAE terpolymer resins were reddish brown in colour. The pure terpolymer resins were soluble in DMSO solvent and in NaOH solution.

Elemental analysis of HBAE terpolymer resins

The HBAE terpolymer resins were analyzed for percentage of carbon, hydrogen and nitrogen. The results were presented in following table 1. It can be seen that the values are in good agreement with calculated values. The results suggest that the molecular weight of repeat unit in HBAE terpolymer resins prepared by varying the composition of reactants p-hydroxybenzaldehyde, adipic acid and ethylene glycol.

Table 1 Elemental analysis of HBAE terpolymers

Resins	% C		% H		Mol. Formula repeat unit	Mol. Wt. repeat unit
	Calc	Found	Calc.	Found		
HBAE-I	59.3	58.8	7.2	7.1	(C ₁₉ H ₂₄ O ₆) _n	348
HBAE-II	67.74	67.70	6.45	6.37	(C ₂₈ H ₃₂ O ₈) _n	496

Molecular weight determination of HBAE terpolymer

Since all HBAE resins contain phenolic -OH group (weakly acidic group) the molecular weight of resin were determined by non-aqueous conductometric titration. The titration curves are obtained by plotting specific conductance versus m.eq. of KOH (0.1M) required per 100 g of resin as shown in figure 1. The ratio of m.eq. of KOH per 100 g of resin required for last break to that for first break gives degree of polymerization (\overline{Dp}). The molecular weight of resin was obtained by multiplying respective \overline{Dp} with molecular weight of repeat unit, obtained from elemental analysis. The table 2 shows that molecular weight increases with increase in composition of p-hydroxybenzaldehyde, ethylene glycol and vice versa [4].

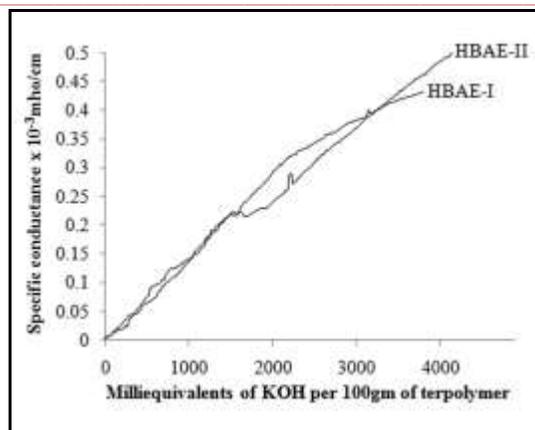


Figure 1 Non aqueous conductometric titration curve of HBAE resins

Table 2 Number average molecular weight of HBAE

Resins	M.eq. of KOH per 100 g of resin required for first Break	M.eq. of KOH per 100 g of resin required for last Break	\overline{Dp}	Molecular Weight of Repeat Unit	Molecular Weight (\overline{Mn})
HBAE-I	200	3160	15.8~16	348	5568
HBAE-II	260	4140	15.9~16	496	7936

UV-Visible spectra of HBAE terpolymers

UV-Visible spectrum of HBAE terpolymer in DMSO solvent recorded by UV-Visible double beam spectrophotometer, Shimadzu, model-1800 at department of Nano-technology, Shivaji Science College, Nagpur. The UV-Visible spectra of the HBAE terpolymer resins are shown in figure 2 and spectrum data is tabulated in table 3.

In HBAE-I, A peak at 257 nm was assigned to $n \rightarrow \pi^*$ transition for ether (-O-) group and peak at 264 nm was assigned to $\pi \rightarrow \pi^*$ transition for aromatic ring. $n \rightarrow \pi^*$ transitions at 293 nm was due to -CHO group [5].

In HBAE-II, A peak at 253 nm was assigned to $n \rightarrow \pi^*$ transition for ether (-O-) group and peak at 266 nm was assigned to $\pi \rightarrow \pi^*$ transition for aromatic ring. $n \rightarrow \pi^*$ transitions at 296 nm was due to -CHO group [6].

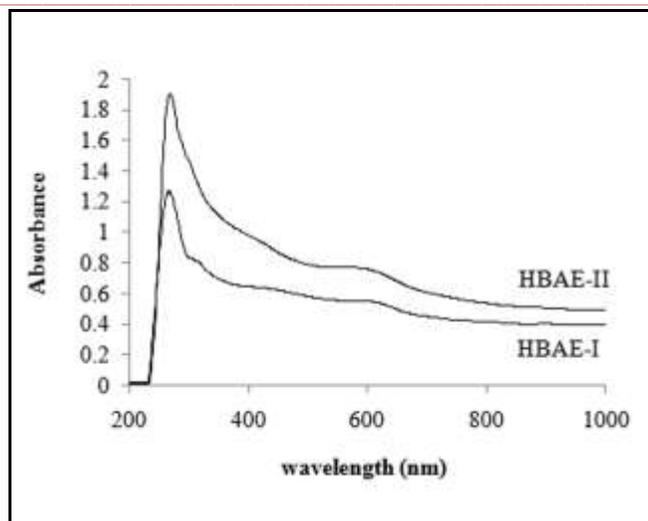


Figure 2 UV-Visible spectra of HBAE terpolymer

Table 3 UV-Visible spectral data of HBAE terpolymer

Transition	HBAE-I	HBAE-II	Group / moiety assigned
	wavelength (nm)	wavelength (nm)	
n → π*	257	253	Ether linkage (-O-)
π → π*	264	266	Aromatic ring
n → π*	293	296	-CHO group

IR spectra of HBAE terpolymers

FT-IR spectrum of HBAE terpolymer resins was recorded at department of pharmacy, R.T.M. Nagpur University, Nagpur using FT-IR spectrometer, Shimadzu, model no.8101A in the range of 4600-500 cm^{-1} . The IR-spectra of HBAE terpolymeric resins are shown in figure 3 and spectrum data is tabulated in table 4.

In HBAE-I, A broad absorption band appeared in the region 3434 cm^{-1} was assigned to the stretching vibrations of phenolic hydroxyl (-OH) group exhibiting intermolecular hydrogen bonding. The presences of peaks at 2922 cm^{-1} and 2847 cm^{-1} were due to the -C-H- stretch in the aldehyde (doublet due to Fermi resonance). 1671 cm^{-1} due to C=O stretch (ester). A peak at 1655 cm^{-1} assigned to C=O band (aldehyde). The presence of peak at 1603 cm^{-1} was due to aromatic-ring. A peak appeared at 1477 cm^{-1} due to ethylene bridge coupled with aromatic ring. Peak appeared at 1423 and 1358 cm^{-1} assigned to in plane bending vibration of phenolic -OH. Peak at 1355 cm^{-1}

was due to aldehyde C-H bend. The broad band displayed at 1228 cm^{-1} due to the C (=O)-O stretch (saturated ester) group. 1171 cm^{-1} was due to O-C-C band stretch. 1, 2, 3, 5- tetra substitution of aromatic ring was assigned to the peaks at 1096 and 967 cm^{-1} . The presence of peak at 830 cm^{-1} was due to the -CH₂- (wagging) [7-13].

In HBAE-II, A broad absorption band appeared in the region 3433 cm^{-1} was assigned to the stretching vibrations of phenolic hydroxyl (-OH) group exhibiting intermolecular hydrogen bonding. The presences of peaks at 2921 cm^{-1} and 2848 cm^{-1} were due to the -C-H- stretch in the aldehyde (doublet due to Fermi resonance). 1673 cm^{-1} due to C=O stretch (ester). A peak at 1654 cm^{-1} assigned to C=O band (aldehyde). The presence of peak at 1603 cm^{-1} was due to aromatic-ring. A peak appeared at 1480 cm^{-1} due to ethylene bridge coupled with aromatic ring. Peak appeared at 1420 and 1355 cm^{-1} assigned to in plane bending vibration of phenolic -OH. Peak at 1354 cm^{-1} was due to aldehyde C-H bend. The broad band displayed at 1229 cm^{-1} due to the C (=O)-O stretch (saturated ester) group. 1171 cm^{-1} was due to O-C-C band stretch. 1, 2, 3, 5- tetra substitution of aromatic ring was assigned to the peaks at 1098 and 965 cm^{-1} . The presence of peak at 828 cm^{-1} was due to the -CH₂- (wagging) [14].

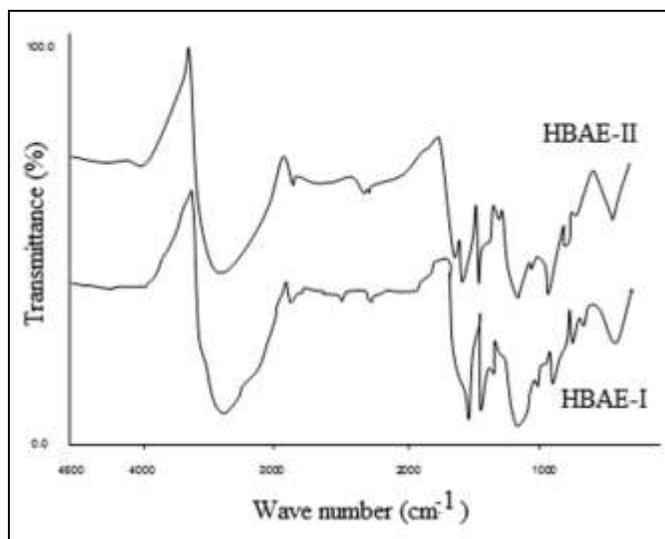


Figure 3 IR spectra of HBAE terpolymer resins

Table 4 IR spectral data of HBAE terpolymeric resins

Frequency (cm ⁻¹)		Assignment
HBAE-I	HBAE-II	
3434 (b)	3433 (b)	-OH bonded (phenolic)
2922 (w), 2847 (w)	2921 (w), 2848 (w)	C-H stretching in aldehyde (doublet due to Fermi resonance)
1671 (w)	1673 (w)	C=O stretch (ester)
1655 (w)	1654 (w)	C=O band (aldehyde)
1603 (s)	1603 (s)	Aromatic-ring
1477 (w)	1480 (w)	CH ₂ bending
1423 (w), 1358 (w)	1420 (w), 1355 (w)	-OH bending (phenol)
1355 (w)	1354 (w)	Aldehydic C-H bending
1228 (b)	1229 (b)	C(=O)-O stretch(saturated ester)
1171 (w)	1171 (w)	O-C-C band stretch
1096 (w), 967 (b)	1098 (w), 965 (b)	1,2,3,5 tetra substituted aromatic ring
830 (w)	828 (w)	-CH ₂ - (wagging)

(m) = medium, (b) = broad, (s) = sharp, (w) = weak

¹H NMR spectra of HBAE terpolymer

The ¹H NMR spectrum of HBAE-I and HBAE-II terpolymers are shown in figure 4 and 5 respectively. ¹H NMR spectrum data is presented in table 5.

In HBAE-I, The δ in the range 1.3 ppm was of-CH₂- in HBAE-I. The signal at 2.5 δ ppm was due to DMSO solvent. Signal at 3.4 δ ppm was attributed to CHOH moiety. The signal at 6.7 δ ppm was due to aromatic ring protons in HBAE I. The signal at 7.6 δ ppm was due to the aldehydic proton [15].

In HBAE-II, The δ in the range 1.4 ppm was ofCH₂- in HBAE-II. The signal at 2.4 δ ppm was due to DMSO solvent. Signal at 3.6 δ ppm was attributed to CHOH moiety. The signal at 6.6 δ ppm was due to aromatic ring protons in

HBAE-II. The signal at 7.8 δ ppm was due to the aldehydic proton [16].

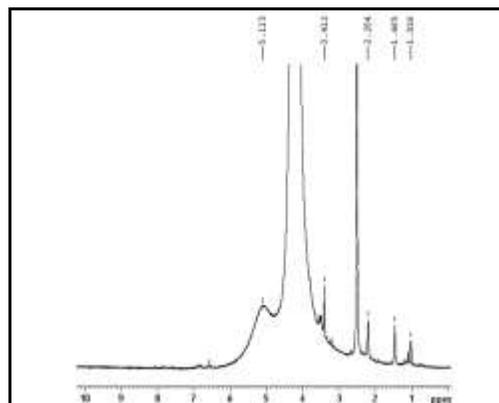


Figure 4 ¹H NMR spectra of HBAE-I terpolymer

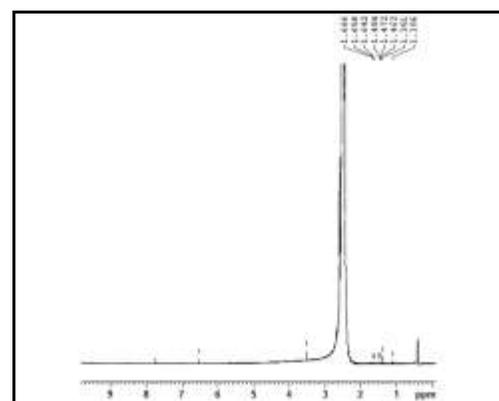


Figure 5 ¹H NMR spectra of HBAE-II terpolymer

Table 5 ¹H NMR spectral data of HBAE terpolymer resin

Chemical shift δ in ppm		Nature of proton assigned
HBAE-I	HBAE-II	
1.3	1.4	-CH ₂ -
2.5	2.4	DMSO solvent
3.4	3.6	CH-OH
6.7	6.6	Aromatic-H (asymmetrical substitution pattern)
7.6	7.8	-CHO

IV. CONCLUSION

In the data of Elemental Analysis, It can be seen that the values are in good agreement with calculated values. The results suggest that the molecular weight of repeat unit in HBAE terpolymer

resins prepared by varying the composition of reactants p-hydroxybenzaldehyde, adipic acid and ethylene glycol and Uv-Vis spectra, FTIR spectra, ^1H NMR spectra, non aqueous conductometric titrations supports to the below tentative structures of HBAE Terpolmeric resins.

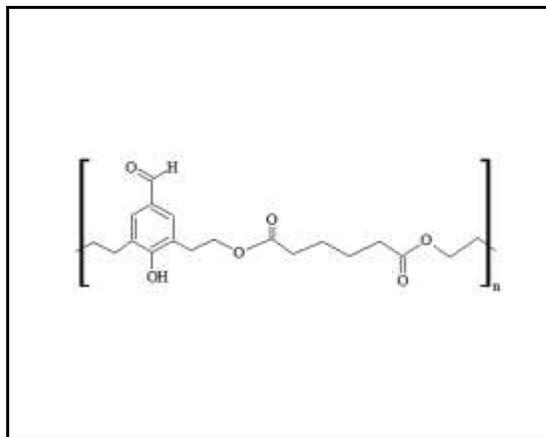


Figure 6 Tentative structure of HBAE-I terpolymer resin

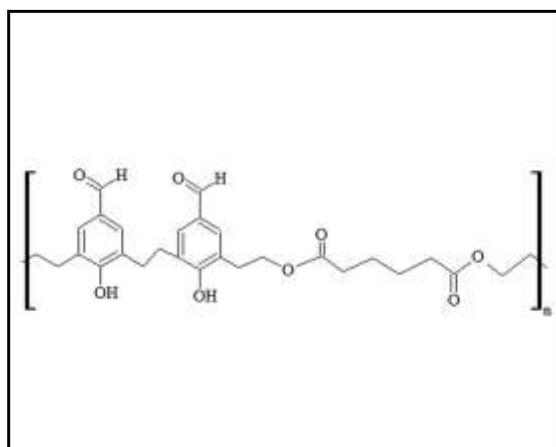


Figure 7 Tentative structure of HBAE-II terpolymer resin

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