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SYNTHESIS AND STRUCTURAL STUDY OF THE TERPOLYMER DERIVED FROM P-HYDROXYBENZALDEHYDE, TEREPHTHALIC ACID AND ETHYLENE GLYCOL

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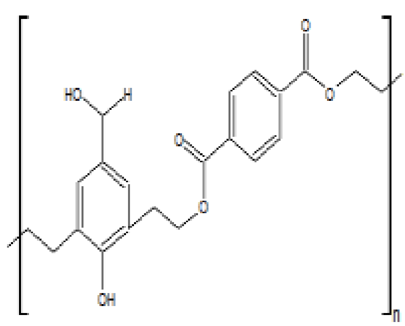
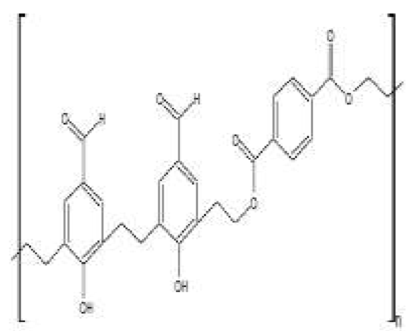
Abstract

The terpolymer resins abbreviated as HPEG-I and HPEG-II were synthesized by polycondensation of p-hydroxybenzaldehyde, terephthalic 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 were determined by Elemental analysis, ^{1}H NMR, FT-IR and UV-Visible spectra. The molecular weights of resins were determined by non-aqueous conductometric titration. The molecular weights of HPEG-I and HPEG-II were found to be 4416 and 6708 respectively. The tentative structures of resins were found to be



HPEG-I terpolymer resin



HPEG-II terpolymer resin

Keywords: Polycondensation, Resin, Molecular weight, Terpolymer

Introduction

Terpolymer resins have a large number of practical application in electronic controls, insulating materials, protective adhesives, aerospace industries etc, because of their high thermal stability, heat & chemical resistance and electrical insulation properties [1-3]. Terpolymers of salicylic acid, thiourea with trioxane and p-hydroxy benzoic acid, thiourea with trioxane have been reported in literature [4-7].

Recently Shah et. al. reported the chelating ability of the phenolic resins synthesized by a microwave irradiation technique involving salicylic acid and formaldehyde with resorcinol[8]. Synthesis of o-nitrophenol, thiourea and paraformaldehyde tercopolymer was reported and its chelation ion exchange properties were investigated by a static batch equilibrium method [9].

The present study deals with the synthesis, and structural study of terpolymeric resin by various spectral studies. The characterisation of terpolymeric resins was carried out by elemental analysis, UV-VIS, FT-IR, ^{1}HNMR, non- aqueous conductmetric titration for the determination of number of average molecular weight of terpolymer.

EXPERIMENTAL SECTION

Materials:

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

Synthesis of resins derived from p-hydroxybenzaldehyde, terepthalic acid and ethylene glycol (HPEG)

The HPEG-I terpolymer resin was synthesized by polycondensation of p-hydroxybenzaldehyde, terepthalic acid with ethylene glycol in the presence of polyphosphoric acid as a catalyst with molar proportion 1:1:3 of reacting monomers at 120^{o}C for 5.30 hrs. To a well-stirred and ice-cooled mixture of p-hydroxybenzaldehyde (0.1 M), terepthalic acid (0.1 M) and ethylene glycol (0.3

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 5.30 hrs. The reaction mixture was then cooled, poured on crushed ice and left over night. A light 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 HPEG-I was air dried, powdered and kept in a vacuum desiccator for 4-5 hours. Yield was found to be 82%.

Similarly HPEG-II terpolymeric resin was prepared with varying molar proportion as 2:1:4 of reacting monomers at 120°C for 5.30 hrs, in the presence of polyphosphoric acid as a catalyst and purified as per above method. Yield was found to be 85%.

Reaction schemes of HPEG-I and HPEG-II are shown in figure 1 and 2 respectively. Table 1 show that the synthesis details of HPEG terpolymer resins and table 2.6 shows the solubility of HPEG terpolymer resins in different solvents.

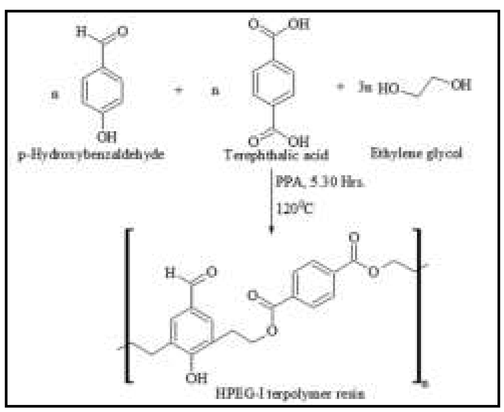


Figure 1 Reaction scheme of HPEG-I terpolymer resin

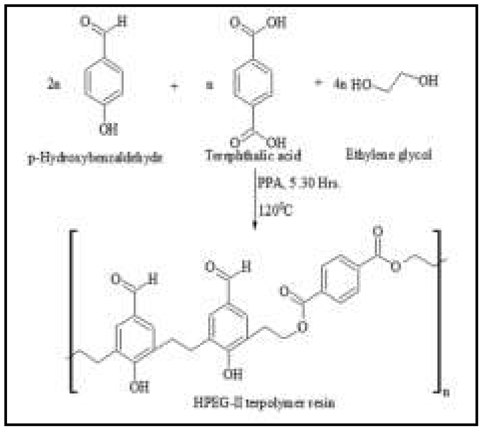


Figure 2 Reaction scheme of HPEG-II terpolymer resin

Table 1 Synthesis details of HPEG terpolymer resins

Terpolymer resins	HPEG-I	HPEG-II
p-Hydroxybenzaldehyde	1M	2M
Adipic acid	1M	1M
Ethylene glycol	3M	4M
Catalyst (Polyphosphoric acid)	20 gm	20 gm
Reflux Temperature ± 2°C	120	120
Time (Hours)	5.30	5.30
Yield	82%	85%
Colour of synthesized resin	Light reddish brown	Light reddish brown

RESULTS AND DISCUSSION

Characterization of p-Hydroxybenzaldehyde-Terepthalic acid-Ethylene glycol (HPEG) resins

HPEG terpolymer light resins were reddish brown in color. The pure terpolymer resins were soluble in DMSO solvent and in NaOH solution.

1. Elemental analysis of HPEG terpolymer resins

The HPEG terpolymer resins were analyzed for percentage of carbon, hydrogen and nitrogen. The results were presented in following table 2.

Table 2 Elemental analysis of HPEG terpolymer resins

Resins	% C		% H		Mol. Formula repeat unit	Mol. Wt. repeat unit
	Calc.	Found	Calc.	Found		
HPEG-I	68.48	68.40	5.43	5.39	$(C_{21}H_{20}O_6)_n$	368
HPEG-II	69.77	69.71	5.43	5.37	$(C_{30}H_{28}O_8)_n$	516

2. Molecular weight determination of HPEG terpolymer resins

Since all HPEG resins contain phenolic –OH group (weakly acidic group) the molecular weight of resins was 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 3. 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 [10-12]. The table 3 shows that molecular weight increases with increase in composition of p-hydroxybenzaldehyde, ethylene glycol and vice versa.

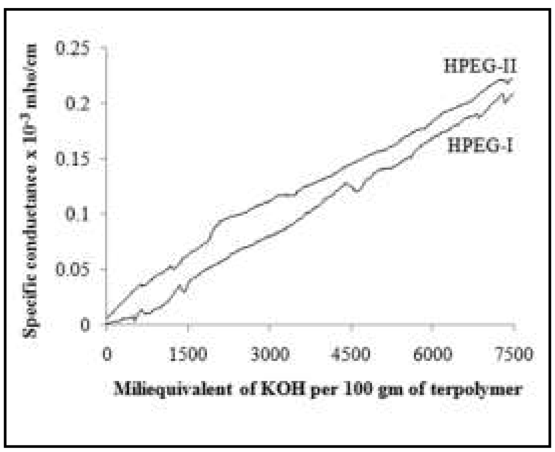


Figure 3 Non aqueous conductometric titration curve of HPEG resins

Table 3 Number average molecular weight of HPEG terpolymer resins

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 first Break	$\overline{Dp}$	Molecular Weight of Repeat Unit	Molecular Weight ($\overline{Mn}$)
HPEG-I	600	7240	12	368	4416
HPEG-II	580	7260	12.5~13	516	6708

. UV-Visible spectra of HPEG terpolymer resins

The UV-Visible spectra of HPEG terpolymer resins are shown in figure 4 and spectrum data is tabulated in table 4.

In HPEG-I, A peak at 242.0 nm was assigned to ñ □ transition for ether (–O–) group and peak at 279.5 nm was assigned to □ □ transition for aromatic ring. ñ □ transitions at 341.5 nm was due to -CHO group [13-14].

In HPEG-II, A peak at 234.5 nm was assigned to ñ □ transition for ether (–O–) group and peak at 279.5 nm was assigned to □ □ transition for aromatic ring. ñ □ transitions at 343.5 nm was due to -CHO group [15-16].

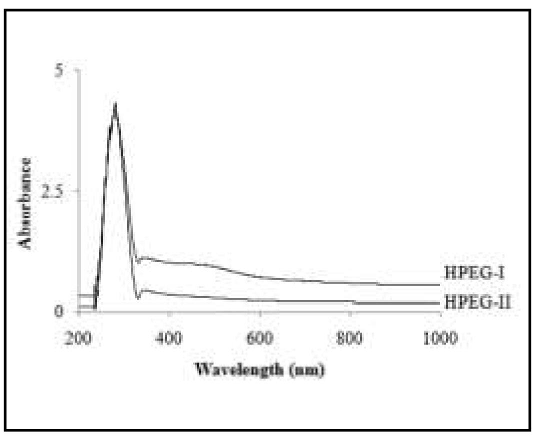


Figure 4 UV-Visible spectra of HPEG terpolymer resins

Table 4 UV-Visible spectral data of HPEG terpolymer resins

Transition	HPEG-I resin wavelength (nm)	HPEG-II resin wavelength (nm)	Group / moiety assigned
ñ □	242.0	234.5	Ether linkage (–O–)
□̃ □	279.5	279.5	Aromatic ring
ñ □	341.5	343.5	-CHO group

4. IR spectra of HPEG terpolymer resins

IR spectra of HPEG terpolymer resins are shown in figure 5 and spectrum data is tabulated in table 5.

In HPEG-I, A broad absorption band appeared in the region 3440 cm^{-1} was assigned to the stretching vibrations of phenolic (-OH) group exhibiting intermolecular hydrogen bonding. The presences of the peaks at 2930 cm^{-1} and 2820 cm^{-1} were due to the –C-H- stretch in the aldehyde (doublet due to Fermi resonance). 1680 cm^{-1} was due to C=O stretch (ester). A peak at 1650 cm^{-1} assigned to the C=O band (an aldehyde). The presence of peak at 1601 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 1424 cm^{-1} was assigned to in plane bending vibration of phenolic –OH. Peak at 1350 cm^{-1} was due to aldehyde C-H bend. The broad band displayed at 1230 cm^{-1} was due to the C-O stretch in ester group. 1170 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 1113 and 947 cm^{-1}. The presence of peak at 833 cm^{-1} was due to the $-CH_2-$ (wagging) [17-22].

In HPEG-II, A broad absorption band appeared in the region 3443 cm^{-1} was assigned to the stretching vibrations of phenolic (-OH) group exhibiting intermolecular hydrogen bonding. The presences of the peaks at 2931 cm^{-1} and 2818 cm^{-1} were due to the –C-H- stretch in the aldehyde (doublet due to Fermi resonance). 1679 cm^{-1} was due to C=O stretch (ester). A peak at 1652 cm^{-1} assigned to the C=O band (an aldehyde). The presence of peak at 1602 cm^{-1} was due to aromatic-ring. A peak appeared at 1478 cm^{-1} due to ethylene bridge coupled with aromatic ring. Peak appeared at 1425 cm^{-1} was assigned to in plane bending vibration of phenolic –OH. Peak at 1351 cm^{-1} was due to aldehyde C-H bend. The broad band displayed at 1232 cm^{-1} was due to the C-O stretch in ester group. 1169 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 1115 and 945 cm^{-1}. The presence of peak at 832 cm^{-1} was due to the $-CH_2-$ (wagging) [23-27].

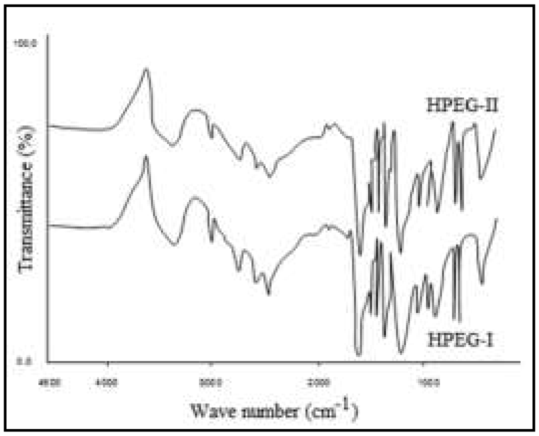


Figure 5 IR spectra of HPEG terpolymer resins

Table 5 IR spectral data of HPEG terpolymer resins

Frequency (cm^{-1})		
HPEG-I	**HPEG-II**	**Assignment**
3440 (b)	3443 (b)	-OH bonded (phenolic)
2930 (w), 2820 (w)	2931 (w), 2818 (w)	C-H stretches in aldehyde (doublet due to Fermi resonance)
1680 (w)	1679 (w)	C=O stretch (ester)
1650 (w)	1652 (w)	C=O band (an aldehyde)
1601 (s)	1602 (s)	Aromatic-ring
1480 (w)	1478 (w)	CH_2 bending
1424 (w)	1425 (w)	-OH bending (phenol)
1350 (w)	1351 (w)	Aldehydic C-H bonds
1230 (b)	1232 (b)	C-O stretch in ester group
1170 (w)	1169 (w)	The O-C-C band stretch
1113 (w), 947 (b)	1115 (w), 945 (b)	1,2,3,5 tetra substituted aromatic ring
833 (w)	832 (w)	$-CH_2-$wagging

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

5. [1]H NMR spectra of HPEG terpolymer resins

The [1]H NMR spectra of HPEG-I and HPEG-II terpolymer resins are shown in figure 6 and 7 respectively. [1]H NMR spectra data is tabulated in table 6.

In HPEG-I, The δ in the range 1.3 ppm was of -C**H**$_2$- in HPEG-I. The signal at 2.5 δ ppm was due to DMSO solvent. Signal at 3.9 δ ppm was attributed to C**H**-OH moiety. The signal at 6.8 δ ppm was due to aromatic ring protons in HPEG-I. The signal at 8.0 δ ppm was due to the aldehydic proton [28-30].

In HPEG-II, the δ in the range 1.1 ppm was of -C**H**$_2$- in HPEG-II. The signal at 2.5 δ ppm was due to DMSO solvent. Signal at 3.7 δ ppm was attributed to C**H**-OH moiety. The signal at 6.5 δ ppm was due to aromatic ring protons in HPEG-II. The signal at 8.0 δ ppm was due to the aldehydic proton [31- 38].

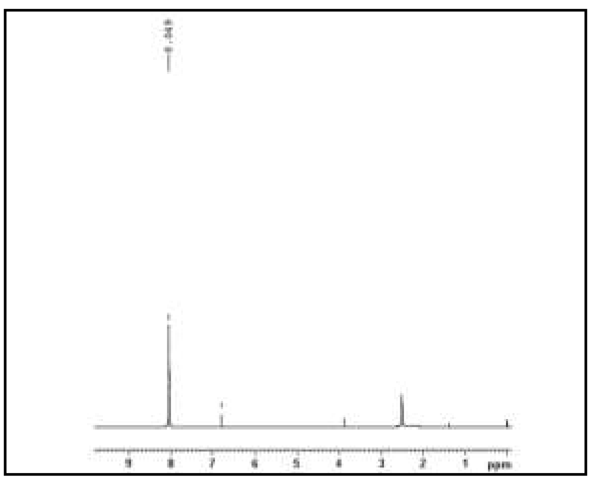


Figure 6 [1]H NMR spectra of HPEG-I terpolymer resin

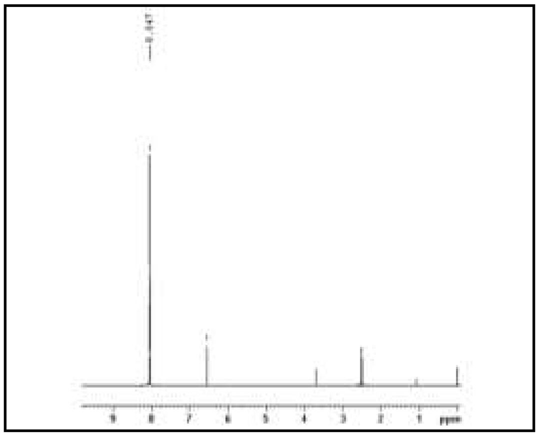


Figure 7 ^{1}H NMR spectra of HPEG-II terpolymer resin

Table 6 ^{1}H NMR Spectral data of HPEG terpolymer resins

Chemical shift δ in ppm		**Nature of proton assigned**
HPEG-I	**HPEG-II**	
1.3	1.1	-C**H**$_2$-
2.5	2.5	DMSO solvent
3.9	3.7	C**H**-OH
6.8	6.5	Aromatic-**H** (asymmetrical substitution pattern)
8.0	8.0	-C**H**O

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 HPEG terpolymer resins prepared by varying the composition of reactants p-hydroxybenzaldehyde, terepthalic acid and ethylene glycol and Uv-Vis spectra, FTIR spectra,^{1}H NMR spectra, non aqueous conductometric titrations supports to the above tentative structures of HPEG Terpolmeric resins.

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