

Synthesis And Functionalisation Of Aromatic Hyperbranched Polyester From 2" Nitrilotriethanol And Benzene 1,3dicarboxylic Acid

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Abstract: Aromatic hyperbranched polyesters (HBPE) are an important class of hyper branched polymers having wide range of industrial applications. HBPE were synthesized from 2,2, 2" Nitrilotriethanol as a core molecule and benzene 1,3dicarboxylic acid as a chain extender by polycondensation method using P-toluene sulphonic acid as an acid catalyst. All synthetic procedures were made under a dry nitrogen atmosphere. The chosen molar ratio of 2,2, 2" Nitrilotriethanol to benzene 1,3dicarboxylic acid were 1:3, 1:6, 1:21 for G₁, G₂ and G₃ generations respectively. The resulting HBPE were further reacted with acrylic acid to modify the end groups. The resulting polyester molecules were characterised by ¹H' NMR, FT-IR spectroscopy and GPC.

Keywords: HBPE, Synthesis, Characterization, HBP, polycondensation, acrylic acid.

INTRODUCTION

Hyperbranched polymers are a new class of Polymeric material belonging to the group of macromolecules with highly branched structures and a large number of end groups. The structure of these Polymers has a great impact on their physical and chemical properties such as low viscosity, high solubility, multifunctionality, good compatibility and reactivity.

The properties of hyperbranched polymers differs from traditional linear polymers in that they have relatively low molecular volume for a given molecular weight and have a high concentration of end groups. In addition the end groups concentration remains relatively constant as molecular weight increases^[1-6]. They are characterized by several unique features such as high number of reactive sites, relatively low viscosity and high solubility multifunctionality investigated hyper-branched architectures are very attractive for functional biointerfaces of biomaterials with cells or tissues in biomedical

applications, coating, rheological modification, membrane and supermolecular science^[7-13]. HBPEs are an important class of hyperbranched polymers and are characterized by good thermal, mechanical and chemical properties. The successful attempts in synthesizing HBPE from easily available and inexpensive raw materials have prompted many research groups to investigate HBPEs in details^[14-16]. Fan et al^[17] have been synthesized of HBPE by melt and solution polymerization with different monomer ratios, using terephthaloyl chloride (TCI) and 1,1,1-tris(4-trimethylsiloxyphenyl)ethane (THPE) monomers. Compared with the products prepared in the melt, the HBPEs prepared from solution polymerization had higher yields. Turner et al.^[18] were synthesized of HBPE by the melt polymerization of 3,5-diacetoxybenzoic acid. Acid hydrolysis of the acetate groups yielded phenolic terminated HBPE with a very similar branched structure to that product prepared from the melt polymerization of 3,5-bis(trimethylsiloxy)benoyl chloride. These HBPEs could dissolve in a number of common

organic solvents and had very low intrinsic viscosities even at high molecular weights. Linda chikh ^[20] had investigated a series of HBPE of pseudo generation obtained by reacting 2,2-bis(hydroxy methyl) propanoic acid and tetra(hydroxy methyl)methane. Esterification reaction were carried out in the bulk in nitrogen atmosphere at 140°C in the presence of P-TSA as catalyst. The hydroxyester interchange reaction, inter and intramolecular etherification reaction were analysed by ¹³CNMR and MALDI-TOF. Intermolecular etherification reaction led to mass increase and resulted in polymer gelation upon prolonged heating

EXPERIMENTAL

Materials

Benzene 1,3dicarboxylic acid, DMSO, Acrylic acid were procured from SD fine chemicals. 2,2, 2'' Nitrilotriethanol, was procured from Aldrich chemicals. P-toluene sulphonic acid were purchased from Rankam chemicals. The reagents were of research grade and were distilled before use.

Characterization

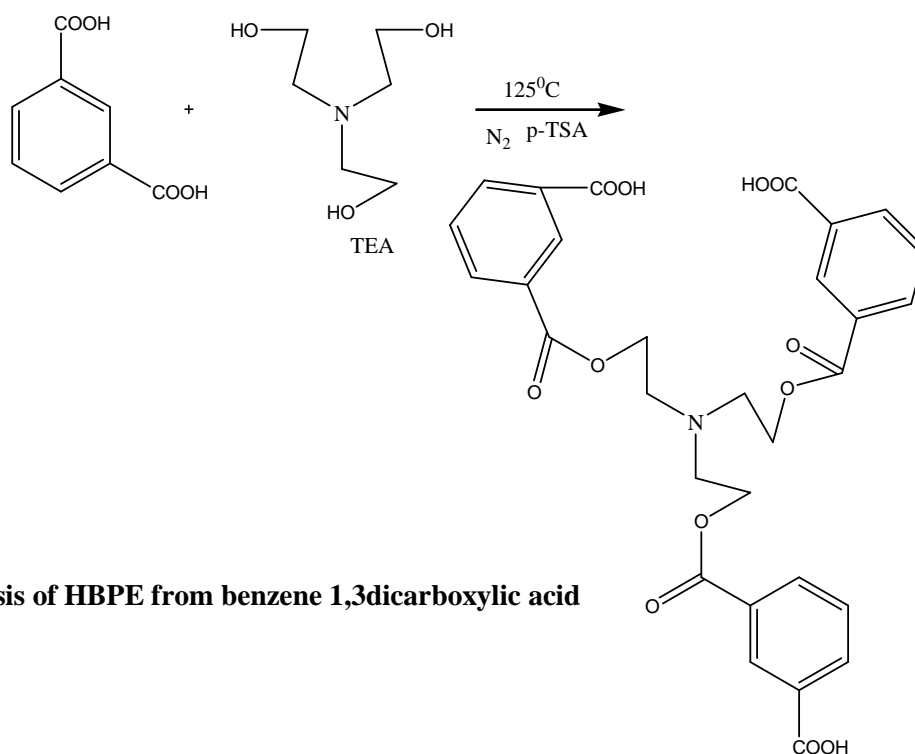
GPC was carried out using a water 515 instrument with tetrahydrofuran as a eluent, the flow rate was 1mL/min and polystyrene as standard. Fourier transform infrared (FTIR) spectra was measured at 400-4000cm⁻¹ (shimadza Instrument). ¹H NMR spectra were recorded on a Bruker (400MHz) NMR spectrometer at room temperature using DMSO as the solvent.

End group analysis

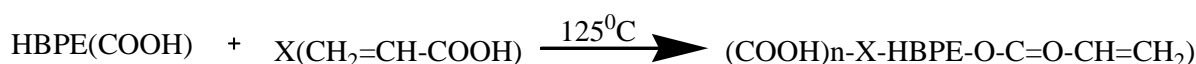
The end group analysis was carried out using approximately of 0.21g sample in 20ml of a 1:1 mixture of acetone: ethanol. After this process the sample were titrated with 0.1mol/L KOH solution as phenolphthalein indicator and the acid value is calculated.

Synthesis

AHBPE has been synthesized by polycondensation at 90°C of 2,2, 2'' nitrilotriethanol and benzene 1,3dicarboxylic acid and P-TSA act as catalyst. The monomers were reacted in different ratio in a 500 ml of four necked flask equipped with N₂ inlet, a magnetic stirrer and a drying tube. The finally stage of AHBPE are reacted with acrylic acid to functionalize the end group ^[19]. The schematic representation of the reactions is given in Scheme 1 and 2.



Scheme-1 Synthesis of HBPE from benzene 1,3dicarboxylic acid



Scheme-2 Synthesis of Acrylic modified HBPE

RESULT AND DISCUSSION

AHBPE of generation (G_1 to G_5) has been produced by reacting 2,2, 2'' Nitrilotriethanol and benzene 1,3dicarboxylic acid. The reaction were refluxed out in three different generations G_1 , G_2 and G_5 in the molar ratio of 1:3, 1:6 and 1:21. Fig-1 shows the FTIR spectra of benzene 1,3dicarboxylic acid monomer. The absorptions band of 1691 cm^{-1} is corresponding to the presence of the carboxylic acid groups and the sharp peak at 2881 cm^{-1} is due to the methine group and the absorptions band of 1165 cm^{-1} is corresponding to the presence of the carbonyl acid groups and the peak occurred at

1581 cm^{-1} due to the presence of C=C group. The ^1H NMR spectrum of benzene 1,3dicarboxylic acid is shown in Fig-2 : $\delta(\text{ppm})$ 7.6-8.4 benzene(-CH-), 13.3 (-COOH). The FTIR spectrum of 2,2, 2'' Nitrilotriethanol core molecule is presented in Fig-3. The absorption band of 3342 cm^{-1} due to the presence of the hydroxy group and the peak at 2881 cm^{-1} is due to CH_2 stretching and the peak occurred at 1724 cm^{-1} due to the presence of carbonyl group. Fig.4 depict the ^1H NMR spectrum of the 2,2, 2'' Nitrilotriethanol core molecule - : $\delta(\text{ppm})$ 2.55, 3.42 methylene (- CH_2).

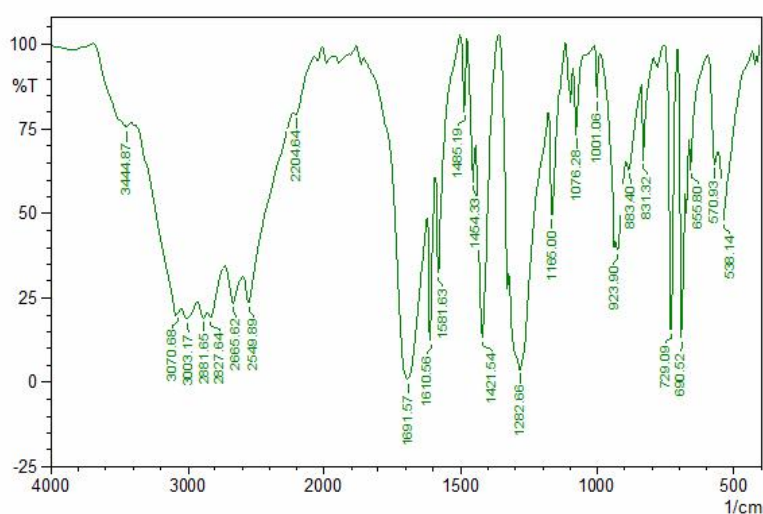


Fig.1. FTIR spectrum of benzene 1,3dicarboxylic acid

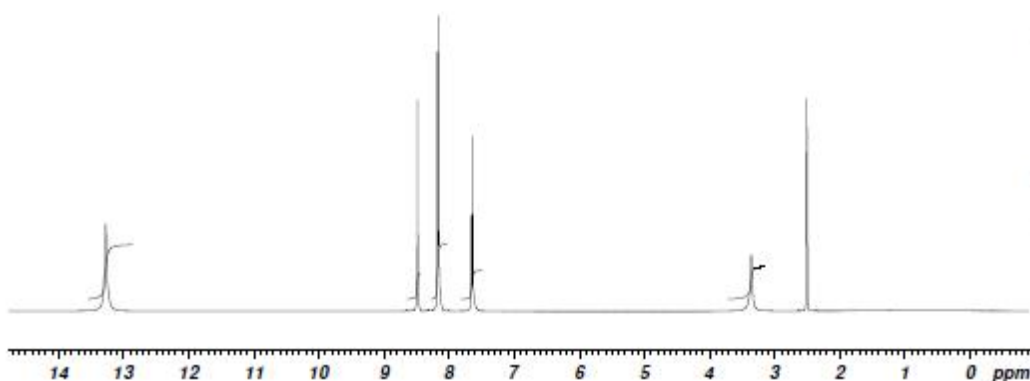


Fig.2. ^1H NMR of benzene 1,3dicarboxylic acid

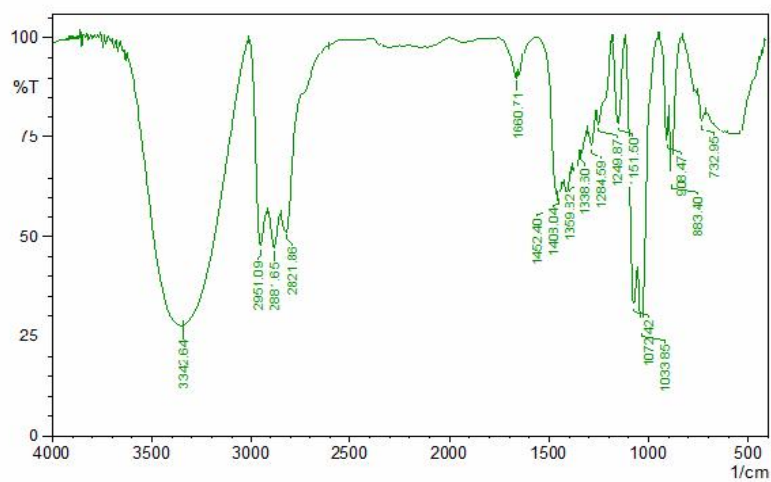


Fig.3. FTIR spectrum of 2,2, 2'' nitrilotriethanol

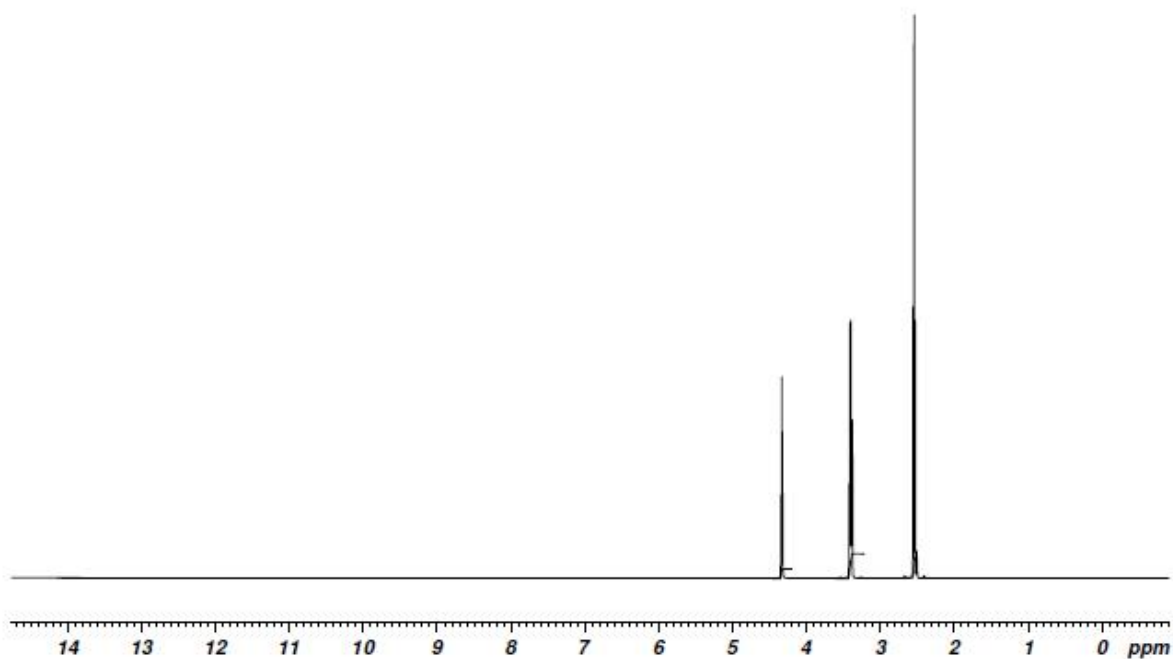


Fig.4. ¹H NMR spectrum of 2,2, 2'' nitrilotriethanol

First Generation of AHBPE

3.542g (4.9839g,30ml) of benzene 1,3dicarboxylic acid and 1.419ml of 2,2, 2'' Nitrilotriethanol were added to a 250 ml three necked flask equipped with a magnetic stirrer 0.04g of P-TSA was added as an acid catalyst. The reaction mixture was stirred for 1 hour at 90°C. The resulting polyester were obtained as a yellow colour gel. The FTIR spectrum of G₁ stage is given in Fig.5. It showed ester C=O stretching bands at 1701cm⁻¹ and the peak at 3151 corresponding to carboxylic acid groups. The broad peak around 3381cm⁻¹ corresponds to the hydroxy groups and the stretching of C-O-R is seen at 1183cm⁻¹.

Second Generation of AHBPE

In the G₂ stage, the core molecule 2,2, 2'' Nitrilotriethanol (1.491ml,10mmol) and benzene 1,3dicarboxylic acid (9.967g,60mmol) chain extender added in the ratio of 1:6 in the presence of P-TSA (0.067g) as a catalyst. The reaction was refluxed out at 90°C for 6 hours. The FTIR spectrum of G₂ stage of HBPE is given in Fig.6. It showed ester C=O stretching bands at 1699 cm⁻¹ and the peak at 3151 is carboxylic acid groups. The broad peak around 3356cm⁻¹ corresponds to the hydroxy groups and the stretching of C-O-R is seen at 1163cm⁻¹.

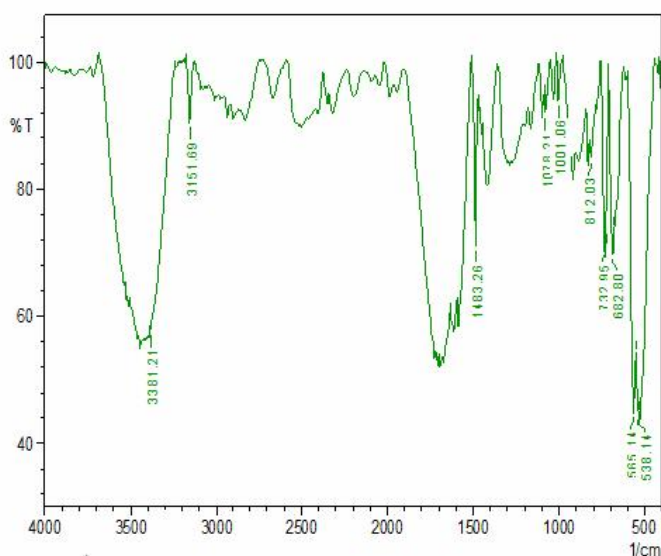


Fig.5- FTIR Spectrum-G₁ stage of HBPE

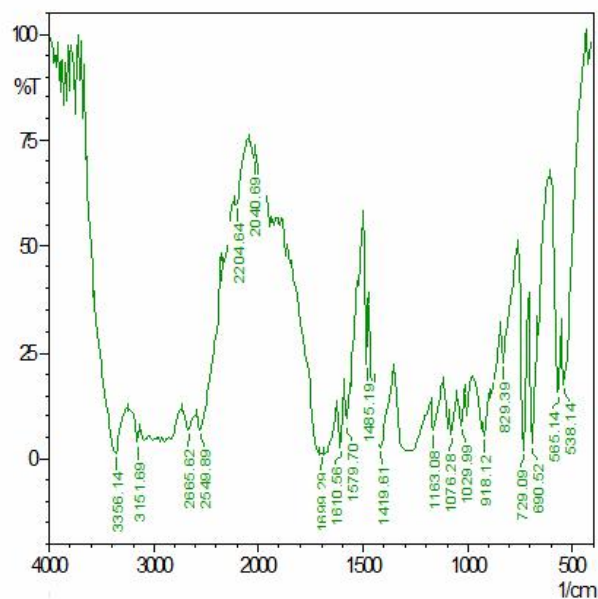


Fig.6.- FTIR Spectrum-G₂ stage of HBPE

Fifth Generation of AHBPE

In the G₅ stage, the core molecule 2,2, 2'' Nitrilotriethanol (1.491ml,10mmol) and chain extender benzene 1,3dicarboxylic acid (34.88g, 60mmol) were reacted with in the ratio of 1:21 in the presence of P-TSA (0.177g) as a catalyst. The reaction was refluxed out at 90°C for 10 hours. The FTIR spectrum of G₅ stage of HBPE is given in Fig.7. It showed ester C=O stretching bands at 1683 cm⁻¹ and the peak at 3149 is carboxylic acid groups. The broad peak around 3356cm⁻¹ corresponds to the hydroxy groups and the stretching of C-O-R is seen at 1165cm⁻¹. The ¹HNMR spectrum of G₅ stage of HBPE are shown in Fig-8. : *d(ppm)* 2.36-2.6(O-CH₂-CH₂-N),3.4-

3.56 (O-CH₂-CH₂-N). The weight average molecular weight and number average molecular weight of HBPE are 311 and 362. The ratio of Mn to Mw gives the polydispersity HBPE which is found to be 1.161. As no appropriate Hyperbranched polymer ester standards are available for calibration, the results obtained are relative to linear polyethylene standards and are therefore not absolute values. The Carboxyl equivalent of the HBPE were found to be increasing from G₁, G₂ to G₅ stages gradually. The values were found to be 0.624, 0.979 and 1.743 grams per 100g. This indicates the increasing functionality from G₁ to G₅ stages.

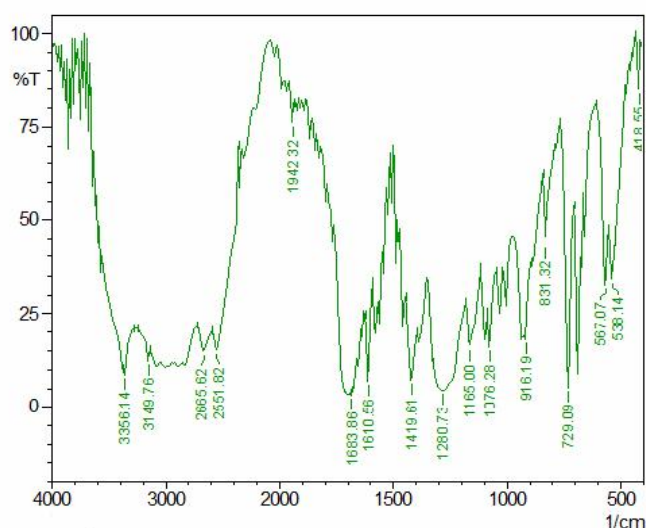


Fig.7.- FTIR Spectrum-G₅ stage of HBPE

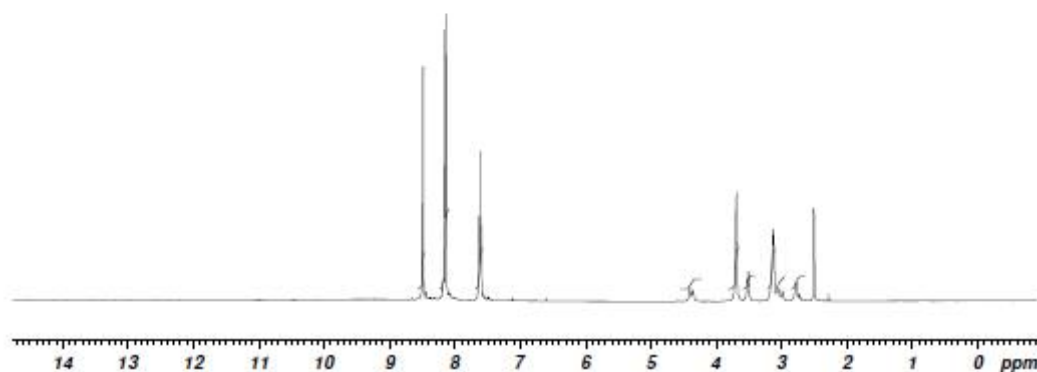


Fig.8.- ¹HNMR spectrum of G₅ stage of HBPE

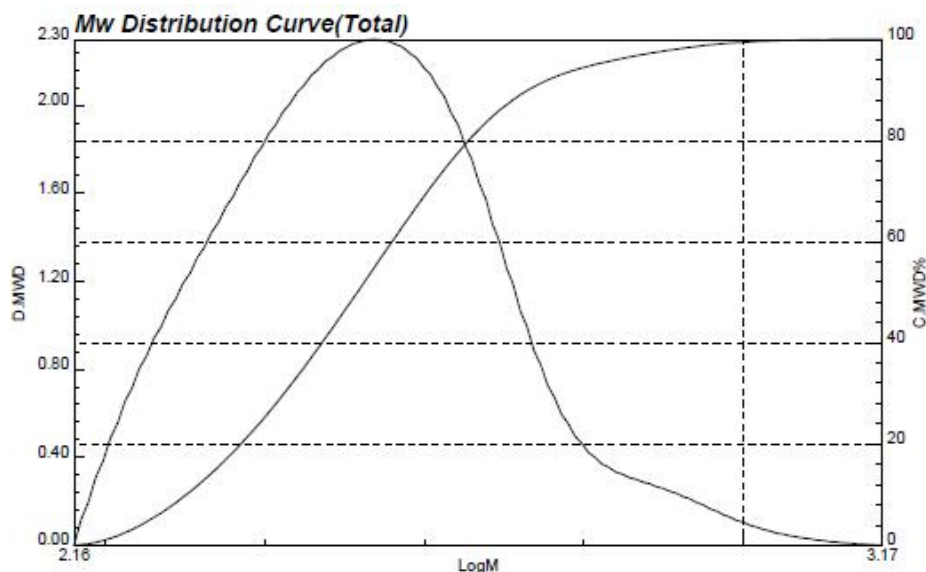


Fig.9.- GPC spectrum of HBPE

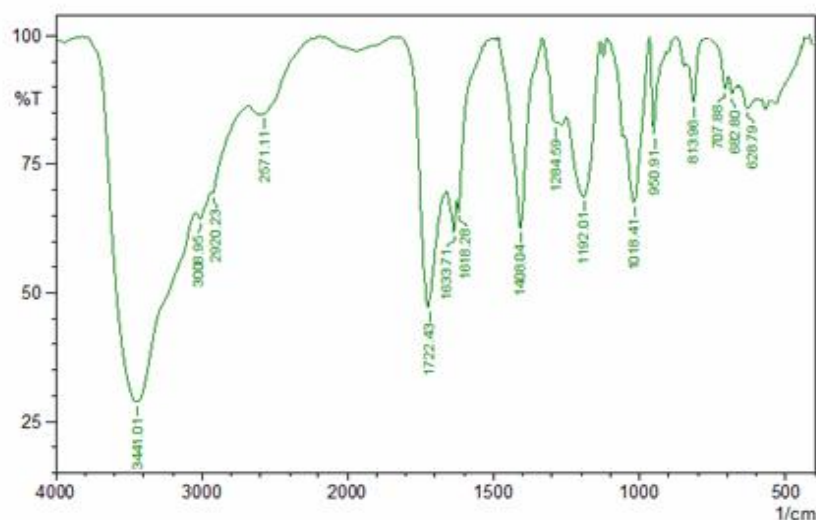


Fig.10.- FTIR Spectrum for end group modified HBPE

Synthesis of Acrylic modified HBPE

The Final product of G₅ HBPE was further functionalised using acrylic acid. The HBPE (1g.0.001ml) was dissolved in DMSO (10ml). This was further reacted with acrylic acid (2ml) in a three necked round flask equipped with a magnetic stirrer and a nitrogen gas inlet using P-TSA (0.0172g) as catalyst. The reaction was refluxed for 5 hours at 120°C. FTIR spectrum of the product is given in Fig. 10. FTIR spectra show a peak at 1633 cm^{-1} in FTIR spectrum corresponding to C=C bond of HBPE. The absorption of ester group appeared at 1722 cm^{-1} and C-O-R stretching occurred 1192 cm^{-1} . The intensity of the peak around 3200–3600 cm^{-1} in G₅ HBPE corresponding to hydroxyl groups decreased after functionalisation.

CONCLUSION

Aromatic hyperbranched polyesters were synthesized in this work by melt polycondensation via an acid-catalyzed esterification procedure using benzene 1,3dicarboxylic acid and 2,2, 2'' Nitrilotriethanol. Samples of different generation were obtained by changing different molar ratio. The resulting polyesters were reacted with acrylic acid to change the end groups.

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