

Synthesis and Functionalisation of Water Soluble Aliphatic Hyperbranched Polyester and its Acrylic Based Coating

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Abstract

Aliphatic hyperbranched polyesters (AHBPE) 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 butane dioic 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 characteristics of HBPE were determined using Fourier transform infrared (FTIR), Nuclear magnetic spectroscopy (¹H NMR), ¹³CNMR and GPC. The FTIR spectrum indicates the completion of reaction indicating the possibility of using the prepared HBPE as an additive in water based acrylic coatings. The molecular weight, water solubility and Hydroxyl equivalent were found to be increased

Keywords: HBPE, Synthesis, Characterization, HBP, polycondensation, acrylic coating

1.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. HBP's are highly branched macromolecule with three dimensional dendritic architecture. The fact that HBP's can be prepared by one pot reaction more rapidly and economically even on larger scales is increasing its popularity. These high network structures when used as template, metal cations will be localized before reduction leading to stabilized metal nanoparticle. The high functionality combined with the low solution viscosity of HBPEs led to early attention on the application of this material in coatings (21–24,29). The features of HBPEs are very favorable in coating applications: the large number of end groups offer versatile crosslinking possibilities, the approximately globular structure of HBPEs enables very low viscosity even at high molecular weights, and they also act as carrier molecules for dyes and biocides. The properties of linear polymers can be tailored by partial replacement of the linear structures with highly branched structures like HBPs to attain the desired products (25–28). Several HBPEs with acrylate or methacrylate end groups have been described in recent years. The unique properties of HBPEs make them extremely interesting for UV and EB curing applications, if they contain acrylate or at least methacrylate end groups. 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 (TCl) 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 ^{13}C NMR and MALDI-TOF. Intermolecular etherification reaction led to mass increase and resulted in polymer gelation upon prolonged heating

The aim of the present work was to prepare a novel HBPE using the 2, 2', 2'' nitrilotriethanol as a core molecule and butanedioic acid as a chain extender. HBPE was coupled with acrylic acid to modify the end groups. The resulting products were analyzed by FT-IR, ^1H NMR, ^{13}C NMR and GPC,

2. EXPERIMENTAL

Materials

Butane dioicacid 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.

2.1. Structural characterization

FT-IR

FTIR spectra were obtained on a JASCO 400 infrared spectrometer in transmission mode between 400 and 4000 cm^{-1} . Samples were pressed into potassium bromide (KBr) pellets.

NMR

^1H NMR and ^{13}C NMR spectra of HBPE were recorded in d_6 DMSO on a Bruker (400MHz) at room temperature.

VISCOSITY MEASUREMENT

The reduced viscosity of HBPE was obtained using an Ostwald viscometer. HBPE of different concentrations were prepared by the dilution of the samples. The capillary viscometer was filled with 20 mL of sample and was equilibrated in a water bath at $30 \pm 0.1^\circ\text{C}$ for 10 min. The sample was allowed to flow through the capillary and the flow times were noted down to calculate reduced viscosity. Three measurements were made for each sample.

ADHESION TEST

Adhesion test was used to observe the scratch resistant HBPE, values of the films according to the Elcometer Cross Hatch Cutter can be used in accordance with the following International Standards; ASTM D3359.

SHINKAGE

The shrinkage was calculated from the densities of the weight before and after curing.

$$\text{Shrinkage} = 100 \times d_p - d_l / d_p \quad \text{----- (2)}$$

Where

d_p is the weight of TLC glass plate

d_l is the weight of the polymer

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.

Hydroxy value

A general procedure was established for the chemical determination of OH functions for modified and unmodified HBPE synthesized polymer sample of 0.5 g each were taken in 250mL conical flask. This was dissolved in 5mL of acetic anhydride reagent (60mL of acetic anhydride+ 7.2g p-TSA +180 ml ethyl acetate) and heated at 70-72°C for 1 hour. At the end of the reagent period pyridine-water reagent (3 ml of pyridine+ 1 mL of water) was added in to each flask and kept for heating for 10 minutes to complete titrated with 0.5 N methanolic KOH solution using thymol blue as indicator. The hydroxyl value was obtained with respect to the titration to a black solution and calculated using the equation given below.

$$\text{Hydroxy value} = \frac{(\text{mL KOH blank}) - \text{mL KOH sample} \times N \text{ KOH} \times 56.1}{\text{gram of sample}} \quad (1)$$

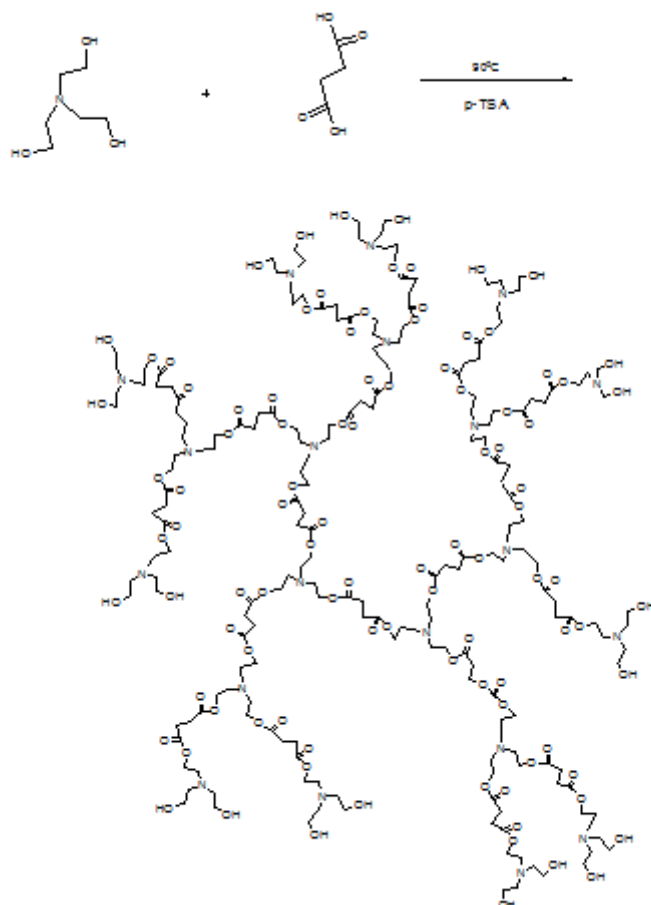
Drying

Acrylic modified HBPE weighed and coated on the entire surface of the TLC glass plate and kept for under UV radiation for drying.

3. SYNTHESIS OF HBPE

Alternative route based on easily available A_2+B_3 monomers is preferred for synthesizing HBPEs. In order to increase the probability that unreacted acid groups reacted with hydroxyl functionality of HBP skeleton and not with another free monomer, the ratio of butane dioic acid was kept as low as possible. The reaction was maintained at relatively low temperature, 120°C, with an optimised time reaction to minimize unwanted side reactions and to avoid gelation. It is well known that direct polycondensation of A_2 and B_3 monomers generally results in gelation. Thus, the crucial problem of this approach was to avoid gelation, and obtain soluble three dimensional macromolecules. The monomer ratio was maintained as 1:1 in the present case. HBPE was synthesized by melt polycondensation at 120°C of 2,2',2''-

nitrilotriethanol and butane dioic acid. The monomers were reacted in 1:1 ratio for 7 hours in a 500 mL four necked flask equipped with N₂ inlet, a magnetic stirrer and a drying tube. The reactant mixture was slowly heated and then maintained at 120°C for 7 hours to complete the reaction. The schematic representation of the reactions is given in Scheme . 1



Scheme .1: Synthesis of HBPE from butanedioic acid and 2,2',2''- nitrilotriethanol

4. RESULT AND DISCUSSION

4.1. FTIR ANALYSIS OF HBPE

The FTIR spectra of HBPE and modified HBPE are given in Figure .1. The FTIR spectrum of butanedioic acid (A) shows an absorptions band at 3065 cm⁻¹ due to the presence of carboxylic acid groups and a sharp band at 2675 cm⁻¹ due to the CH₂ stretching group. The FTIR spectra of HBPE shows ester C=O stretching bands at 1735 cm⁻¹. A broad band around 3421 cm⁻¹ corresponds to the hydroxy groups and the stretching of C-O-R is seen at 1163 cm.⁻¹ The band at 2920 cm⁻¹ is due to CH₂

stretching and the peak at 1040 cm^{-1} is due to C-N stretching.

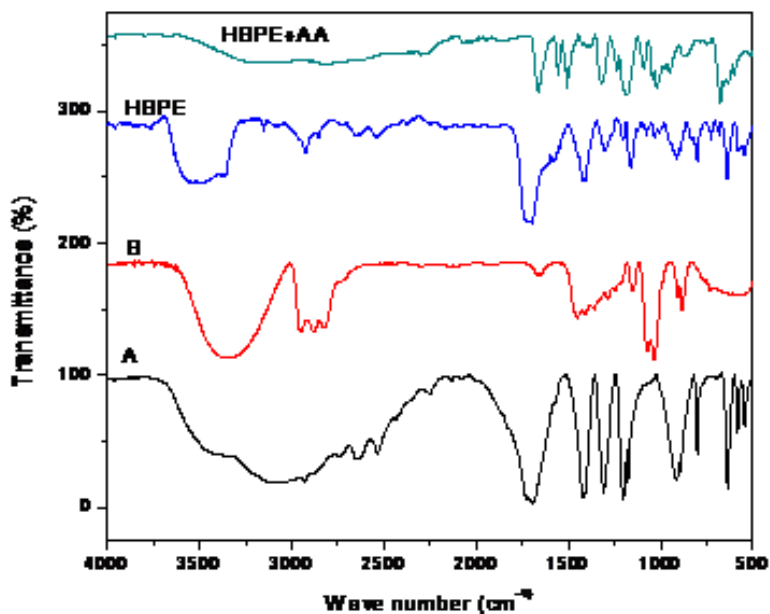


Figure 1: FTIR spectra of HBPE and acrylic modified HBPE

4.2. NMR ANALYSIS OF HBPE

The ^1H NMR spectrums of HBPE are shown in Figure.2. The signals appearing around 6.4 can be attributed to the hydroxyl proton and the peak in the range of 3.4 to 3.9 ppm is assigned to the methylene protons attached to the ester units. The ^{13}C NMR spectra of HBPE are given in Figure.3. The signal at 172-176 ppm could be attributed to the carbonyl carbon of ester and the peaks at 53–57 ppm are due to themethylene carbon of ester and alcohol unit. This confirms the formation of HBPE with ester linkage. Unlike the well investigated classical hyperbranched polymers prepared from AB_2 -type monomers, it is still difficult to define and understand well the structure of A_2+B_3 type HBP system precisely. Several concepts, such as the definition of repeat units and DB, were borrowed from the traditional HBPs prepared from AB_2 -type monomers. The percentage of T, L and D units present in HBPEs, were calculated from the integral area ratios of methylene and quaternary carbon zone of ^{13}C -NMR spectra. The DB was determined by using Equation (1) (Frey et al [30]). The DB value was found to be 0.66

$$\text{DB}_{\text{Frey}} = \frac{2D}{2D+L} \quad \text{----- (1)}$$

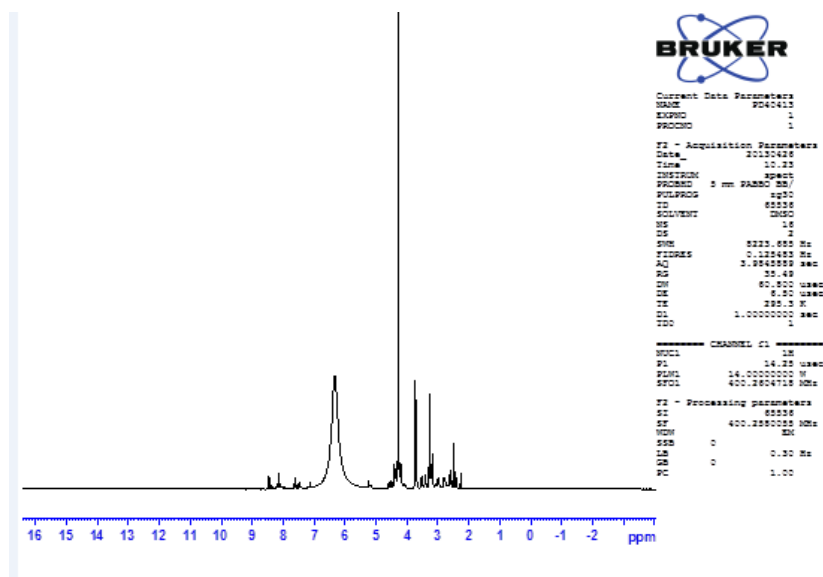


Figure 2: ¹H NMR spectrum of HBPE prepared from butanedioic acid and 2,2',2''-nitrilotriethanol

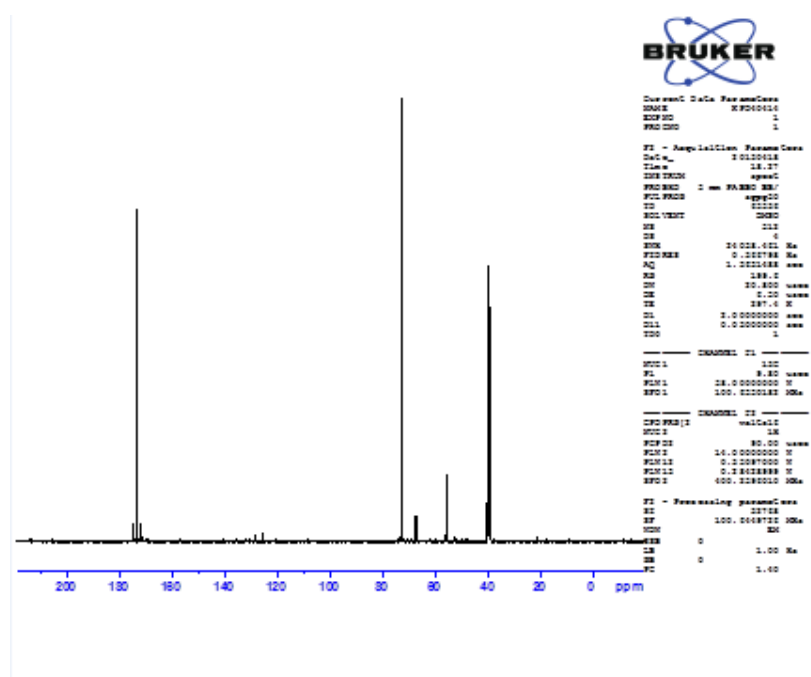
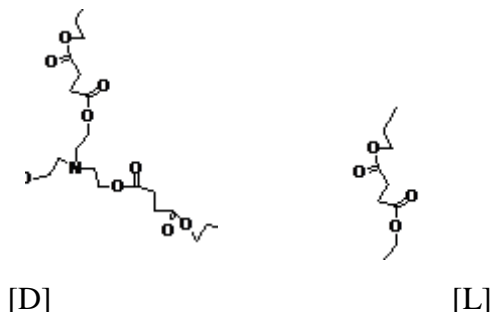


Figure .3: ¹³C NMR spectrum of HBPE prepared from butanedioic acid and 2,2',2''-nitrilotriethanol

Where D, and L refer to the number of dendritic, and linear units in the structure of the polymer, respectively.



4.3 OTHER PROPERTIES OF HBPE

The number-average molecular weight (M_n), weight-average molecular weight (M_w) and polydispersity index of HBPE are 942 g/mol, 973g/mol and 1.03 respectively (Figure 4.). As no appropriate HBP standards are available for calibration, the results obtained are relative to linear polyethylene standards and are therefore not absolute values. The intrinsic viscosity of HBPE was found to be 1.4 dL/g. The qualitative solubility behaviour of the polymers were studied in different solvents. The HBPE exhibited good solubility in polar aprotic solvents including DMF, NMP and DMSO. Results of the elemental analysis for the HBPE were shown in Table .1. The theoretical and observed values have been comparable with each other.

Table .1: Elemental analysis of HBPE

Polymer	Theoretical value (%)				Experimental value (%)			
	C	H	N	O	C	H	N	O
HBPE	51.72	7.48	6.19	34.62	51.80	6.25	6.40	35.55

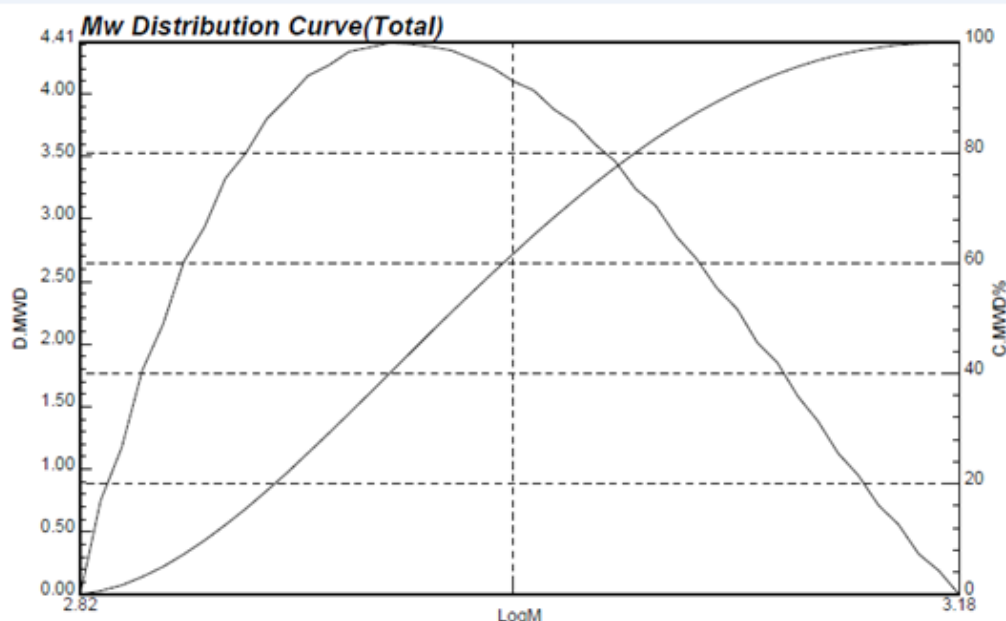


Figure 4 : GPC profile of HBPE from butanedioic acid and 2,2',2''-nitrilotriethanol

4.4 MODIFICATION OF HBPE

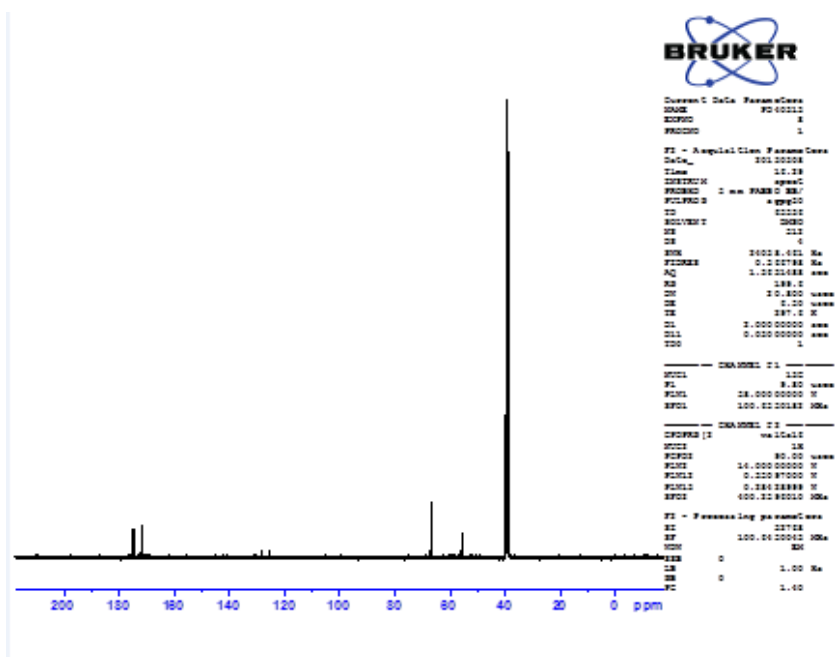
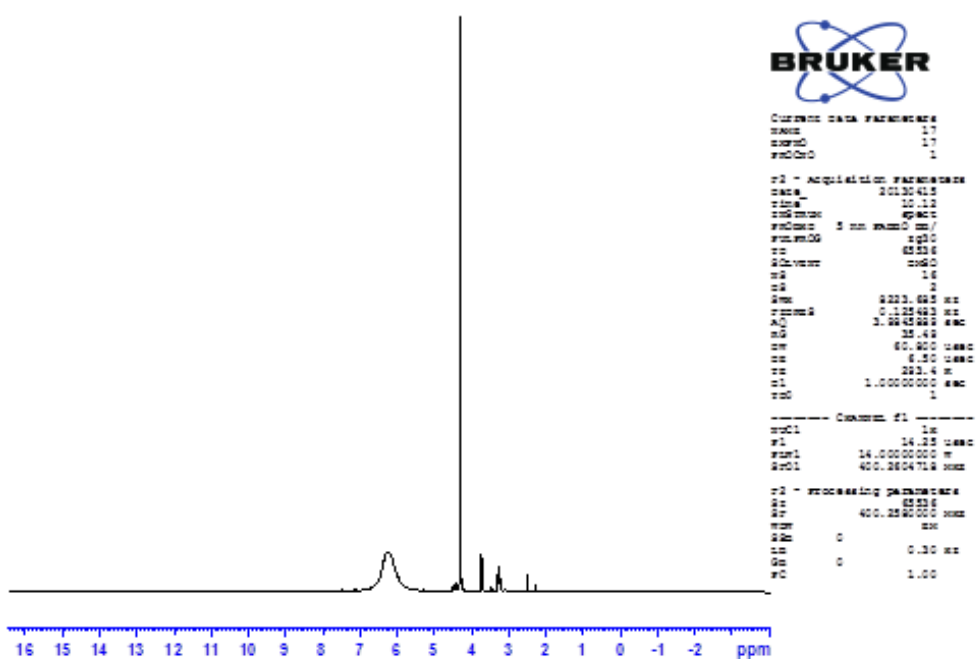
The 1:1 ratio of HBPE was coupled with acrylic acid. 2g of HBPE was dissolved in 10 mL water. This was reacted with acrylic acid (2 mL) in a three necked round flask equipped with a magnetic stirrer and a nitrogen gas inlet using p-TSA (0.017g) as catalyst and then maintained at 80°C for 5 hours. The schematic representation of the reaction is given in Scheme 2.



Scheme 2: Synthesis of acrylic modified HBPE

4.5. CHARACTERIZATION OF ACRYLIC MODIFIED HBPE

The FTIR spectra of acrylic modified HBPE is given in Figure.1. A band at 1661 cm^{-1} is attributed to C=C bond indicating the presence of acrylic group into HBPE and the band at 1701 cm^{-1} indicates the presence of ester group. The ^1H NMR spectrum of HBPE is given in Figure.5. The peak in between 3.4 to 3.9 ppm are assigned to the methylene protons attached to the ester units.. The ^{13}C NMR spectrum of HBPE are given in Figure. 6. The peaks at 172-176 ppm could be attributed to the carbonyl carbon of ester. The hydroxy peak has almost disappeared, indicating the reaction has proceeded via esterification .

Figure 5: ^1H NMR spectrum of acrylic modified HBPEFigure 6: ^{13}C NMR spectrum of acrylic modified HBPE

4.6 SHRINKAGE, ADHESION AND DRYING PROPERTIES OF MODIFIED HBPE

The shrinkage percentage of acrylic modified HBPE is 0.37%. Adhesion is an essential characteristic of most coatings. The adhesion of the HBPE on substrates was found to be very strong and the adhesion ratings were found to be 4B. No flaking occurred after making cuts and applying the adhesive tape. The films were found to cure under UV in 12 minutes.

5. CONCLUSION

Aromatic hyperbranched polyesters were synthesized in this work by melt polycondensation via an acid-catalyzed esterification procedure using butane dioic acid and 2,2, 2'' Nitrioltriethanol. Samples of different generation were obtained by changing different molar ratio. The resulting polyesters were reacted with acrylic acid to change the end groups. The acrylic modified HBPE showed good curing, shrinkage and adhesion properties.

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