

S. Karpagam^{1*}, S. Guhanathan²¹Organic Chemistry Division, School of Advanced Sciences, VIT University, Vellore, Tamil Nadu, India²Chemistry Division, Muthurangam Government Arts College, Vellore, Tamil Nadu, India

Synthesis and Properties of Nitrogen Heterocycle-Functionalized Core-Shell Hyperbranched Polyester

Core-shell hyperbranched polyesters (HBPE) of third generation prepared from 2,2'-bis (hydroxymethyl) propionic acid (Bis-MPA) as an AB_x monomer and N-heterocyclic (indole, piperidine and piperazine) phosphoryl dichloride as a core molecule by melt condensation process. These polymers were characterized by FT-IR, ¹H NMR, ¹³C NMR, ³¹P NMR, elemental analysis, and MALDI spectroscopy. The thermal behavior of the polymers has been investigated by thermo gravimetric analysis (TGA) and differential scanning calorimetry (DSC). There is no weight loss observed until 250°C under nitrogen atmosphere. DSC showed that the glass transition temperatures was about -14 and -30°C for the prepared core-shell HBPE. The dielectric properties such as dielectric constant and loss factor for these polyesters were also studied with respect to change of frequency (50 Hz to 5 MHz).

1 Introduction

Dendritic macromolecules are attractive scaffolds due to their well defined and unique macromolecular structure. These applications extended in various fields such as catalysis, medicinal chemistry, magnetic resonance imaging, combinatorial chemistry, light harvesting, emission and amplification function (Arehut and Vogtle, 1998; Astrue and Chardae, 2001; Fisher and Vogtle, 1999; Grayson and Frechet, 2001;). Like dendrimers, hyperbranched polymers are built from AB_x type monomers. Because of the similarity in branching, hyperbranched polymers and dendrimers have many common features such as improved solubility compared to linear polymers (Czech et al., 2005; Hult et al., 1999; Jikei et al., 2002; Voit, 2000). Since, the pioneering works are well defined by Vogtle (Buhleier et al., 1978), Tomalia (Tomalia et al., 1985a, 1986b) and Newkome (Newkome et al., 1985) in dendrimers, hyperbranched polymers have been increasing at an amazing rate.

* Mail address: Subramanian Karpagam, Organic Chemistry Division, School of Advanced Sciences, VIT University, Vellore -14, Tamil Nadu, India
E-mail: skarpagam80@yahoo.com

The properties of hyperbranched polymers are strongly determined by the nature of the terminal groups (Beyerlein et al., 2001; Tomuta et al., 2012; Turner et al., 1993a, 1993b). For example, solubility mainly depends on end group structure which may be regulated by the partial or total chemical modification of the terminal groups (Thomasson et al., 2006). Due to the irregularities of hyperbranched polymers in their molecular architecture, these functional groups can be located not only in the peripheries which are also located inside the globular branched structure (Scherrenberg et al., 1998). These functional groups are easily modified with small reagents to form a functionalized hyperbranched polymer (Brenner et al., 1996; Wooley et al., 1994).

Existing phosphorous compound in the polymer structure plays an important role in the high performance of thermally stable materials. This contributes to inhibit ignition and promote char formation. Therefore, phosphorous containing polymers were synthesized and characterized to improve the thermal properties (Connel et al., 1995; Hashimoto et al., 1977; Kimura and Kajiwara, 1995). Synthesis of polymer which contains phosphorous and nitrogen in the main chain attracts the attention of many researcher due to their peculiar characteristics viz., non-flammability, thermal stability, high melting points and appreciable biological activities. Among the nitrogen containing heterocyclic compounds, six member heterocyclic compounds are used in various applications as herbicides, pharmaceuticals and adhesives. Five membered heterocyclic compounds are used in electrical and pharmaceuticals applications (Yasuhiko and Takayuki, 2004). Sibdas et al. has synthesized heterocyclic polymer with s-triazine moiety and studied the flame retardant property (Sibdas and Niranjana, 2007).

From the literature, the hyperbranched polymer merely synthesized by AB_x monomer without a core molecule of B_y functionality. 2,2'-Bis (hydroxyl methyl) propionic acid (bis-MPA) is used as AB_x monomer for core-shell hyperbranched polyester preparation (Zagar and Zigon, 2011). The core molecule provides a tool for controlling the molar mass and polydispersity of the final polymer. So, we have used bis-MPA as AB₂ monomer and N-heterocyclic phosphoryl dichloride (IN-PD, PD-PD and PZ-PD) as B₂-functional core molecule.

Dielectric properties provide information about the segmental mobility within a polymer. Only one literature study was

found on the dielectric relaxation behavior of hyperbranched polyester (Malmstrom et al., 1994). So, we wish to report dielectric properties such as dielectric constant and dielectric loss of the prepared hyperbranched polymer.

In this paper, we designed a new core-shell hyperbranched polyester (HBPE) (as shown in Scheme 1), which has N-heterocyclic compound as core moiety and Bis-MPA as monomer group. The resulting polymer was investigated by thermal and dielectric measurements.

2 Experimental

2.1 Materials

Indole, piperidine, piperazine, p-toluene sulphonic acid (p-TSA) and bis-MPA were purchased from Sigma-Aldrich, Mumbai, India. Phosphorus oxychloride, tetrahydrofuran (THF), dimethyl formamide (DMF) dimethyl sulfoxide (DMSO) and acetone was purchased from sd-fine chemicals, Chennai. All the solvents and monomers were purified as per standard procedures before use.

2.2 Methods

Fourier transform infrared (FTIR) spectra were recorded between 400 and 4000 cm^{-1} on Thermo Nicolet 330 using KBr pellets. All NMR spectra were acquired using a Bruker AVANCE III 500 MHz spectrometer. Elemental analysis has

been carried out by using Vario EL III Carlo Erba 1108 instrument.

The MALDI-TOF mass spectra were taken in the positive mode on a MALDI-TOF Voyager-De pro, SAIF office at IIT, Chennai. The matrix was alpha cyano 4-hydroxy cinnamic acid with a concentration of 10 mg ml^{-1} and solvent was THF.

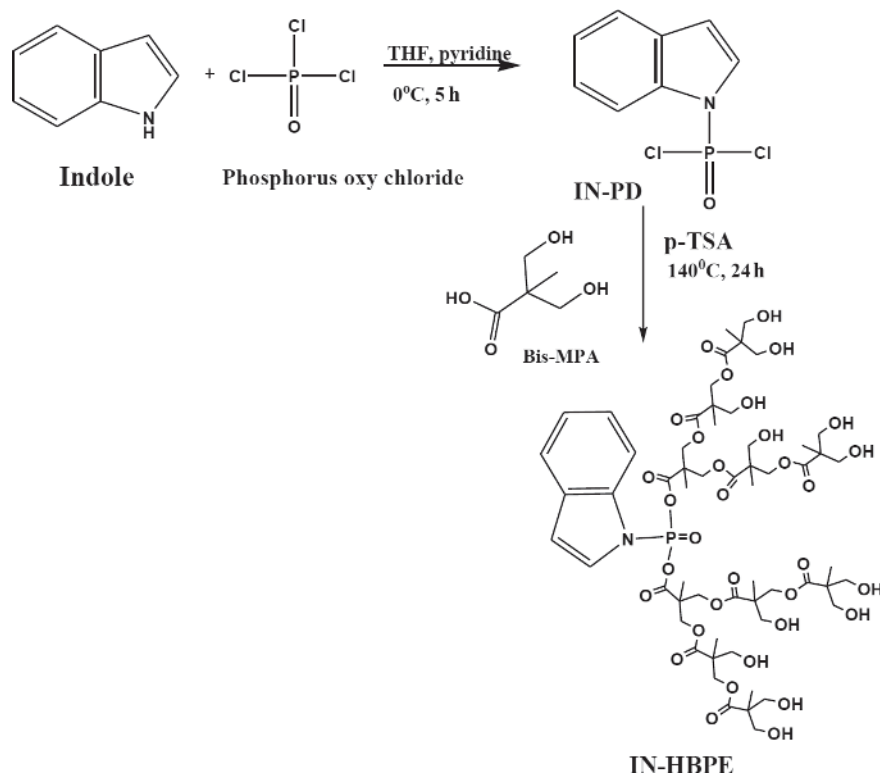
Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses were carried out in Netzsch STA 409 thermal analyzer at a heating rate 10 $^{\circ}\text{C}/\text{min}$ in nitrogen atmosphere. Flame retardance can be tested from the char residue on pyrolysis. Van Krevelen has established a linear relationship between limiting oxygen index (LOI) and char residue for halogen free polymers. The LOI was calculated by using van Krevelen's equation. (van Krevelen, 1975)

$$\text{LOI} = 17.5 + 0.4(\sigma),$$

where σ is the percentage of char yield. The crystalline melting point and glass transition temperature of the polymers was determined by Netzsch DSC 204 differential scanning calorimeter (DSC).

2.3 Measurements of Dielectric Properties

Dried and powdered hyperbranched polyester (IN-HBPE, PD-HBPE and PZ-HBPE) was pressed at 500 MPa into a pellet with 0.83 mm thickness (d) and 13 mm in diameter used for the study of dielectric properties such as dielectric constant and loss factor. The instrument HIOKI-3532.50 LCR Hi tester model was used and tested at fixed temperature (300 K). The pellet was coated with an electronic grade silver paste that acts



Scheme 1. Reaction

as an electrode. The dielectric constant is calculated from the recorded values of the capacitance (C_p) obtained directly from the instrument at a frequency of 50 Hz to 5 MHz using the equation,

$$\text{Dielectric constant} = C_p d / A \epsilon_0,$$

where ϵ_0 = permittivity of vacuum = 8.85×10^{-12} Farad/m and A = cross-sectional area of the sample = πr^2 , r is the radius of the sample pellet

2.4 Synthesis of N-Heterocyclic Phosphoryl Dichloride

IN-PD, PD-PD and PZ-PD were prepared as per our earlier report (Karpagam et al., 2008). 1 mmol of purified Indole (0.117 g) and 2 mmol of phosphorous oxychloride (0.153 g) were dissolved in dry THF which was added slowly with constant stirring for 15 min at 0 °C under nitrogen atmosphere in the presence of pyridine as catalyst in three necked round bottomed flask. The progress of the reaction was monitored by TLC. After completion of the reaction pyridine hydrochloride was filtered and evaporated the solvent to get 1H-indole-1-phosphoryl dichloride (IN-PD), (Scheme 1). FT-IR (KBr): 1239 (P=O); 1008 (N-P); 484 (P-Cl) cm^{-1} ; ^1H NMR (CHCl_3): 7.2 to 7.7 ppm (aromatic protons).

Similar procedure was adopted for the synthesis of 1H-piperidine -1-phosphoryl dichloride (PD-PD). FT-IR (KBr): 1212 (P=O); 1027 (N-P); 489 (P-Cl) cm^{-1} . ^1H NMR (CHCl_3): 2.1, 3.2 ppm (aliphatic protons) and 1H-piperazine-1-phosphoryl dichloride (PZ-PD). FT-IR (KBr): 1280 (P=O); 1012 (N-P); 410 (P-Cl) cm^{-1} . ^1H NMR (CHCl_3): 2.2, 2.6 ppm (aliphatic protons).

Note: For Piperazine, 4 mmol of phosphorous oxychloride was taken, because it reacts with both the acidic protons.

2.5 Synthesis of Phosphorous Containing Third Generation (G_3) of N-Heterocyclic Hyperbranched Polyester (HBPE)

The monomer (Bis-MPA), the core (N-heterocyclic phosphoryl dichloride) and the catalyst (p-TSA) of different stoichiometric ratios has been calculated as per our earlier finding for the formation of different generation viz., first (G_1) and second (G_2) and third (G_3) (Viswanath and Guhanathan, 2007). The third generation has been selected for further studies. This may be due to the abundance of OH group for convenient end capping (Goswami and Singh, 2004). The reaction sequence, product code and product description for N-Heterocyclic HBPE product was given in Table 1 and Table 2.

Bis-MPA (28.16 g, 0.21 mol), IN-PD (1.26 g, 0.01 mol) and p-TSA (0.020 g, 0.18 mmol) were mixed in a three-necked round bottom flask (RB) which is equipped with a nitrogen inlet and a drying tube. This was placed in an oil bath at 140 °C with constant stirring for 10 h under nitrogen atmosphere to remove the water molecules formed from the reaction mixture. Evolution of HCl was detected at once by test paper. The reaction mixture was further heated to 140 °C and maintained for 24 h with continuous stirring. Then, methanol was added into the resultant as a solvent, and the freshly distilled triethylamine

was added dropwise into to neutralize the residual HCl until no white smoke was observed. The formed triethylamine hydrochloride salt was removed by filtration and then the solvent was distilled out. The obtained brown solid product was washed thrice with water. The obtained phosphorus containing indole hyperbranched polyester (IN-HBPE) was dried under vacuum at 90 °C. FT-IR (KBr): 1225 cm^{-1} (P=O), 1124 cm^{-1} (N-P), 1727 cm^{-1} (C=O of ester), 3410 cm^{-1} (O-H) cm^{-1} 1035 cm^{-1} (P-O-C). ^1H NMR (DMSO): 7.1, 7.4, 7.9 ppm (aromatic protons), 3.6, 3.7, 3.8, 4.1 ppm (methylene protons), 1.05, 1.2, 1.69 ppm (methyl protons). 2.2 ppm(OH protons). ^{13}C NMR (DMSO- d_6) δ (ppm): 46.5 to 50.5 (quaternary carbon); 39.1 to 41.5 and 65.04, 66.35 (Methylene carbon); 157 to 161.6 (phenyl); 18.1 (methyl carbon); 173, 174, 175 (ester carbonyl). ^{31}P NMR: 28.31 ppm Anal. Calcd for $\text{C}_{58}\text{H}_{88}\text{O}_{33}\text{NP}$: C, 51.29%; H, 6.53%; N, 1.03% Found; C, 51.45%; H, 6.23%; N, 1.59%.

Similar procedure was adopted for the synthesis of phosphorus containing piperidine hyperbranched polyester (PD-HBPE). FT-IR (KBr): 1231 cm^{-1} (P=O), 1156 cm^{-1} (N-P), 1713 cm^{-1} (C=O of ester), 3400 cm^{-1} (O-H) cm^{-1} 1041 cm^{-1} (P-O-C). ^1H NMR (DMSO): 1.5, 2.7 ppm (piperidine protons), 3.6, 3.8, 4.2 ppm (methylene protons), 1.14, 1.67, 1.74 ppm (methyl protons). 2.1 ppm (OH) protons ^{13}C NMR (DMSO- d_6): 174, 177, 178 ppm (C=O, ester), 44.2 to 50.3 ppm (quaternary carbon), 64.2 to 65.7 ppm (methylene), 16.1 to 16.8 ppm (Methyl carbon). 49.5 to 50.3 (Piperidine carbon). ^{31}P NMR: 21.52 ppm Anal. Calcd for $\text{C}_{50}\text{H}_{84}\text{O}_{30}\text{NP}$: C, 49.62%; H, 7.00%; N, 1.16%, Found; C, 49.76%; H, 6.58%; N, 1.14%.

Similar procedure was also followed for phosphorus containing Piperazine hyperbranched polyester (PZ-HBPE). FT-IR (KBr): 1233 cm^{-1} (P=O), 1127 cm^{-1} (N-P), 1730 cm^{-1} (C=O of ester), 3430 cm^{-1} (O-H), 1046 cm^{-1} (P-O-C). ^1H NMR (DMSO): 2.81 ppm (piperazine protons), 3.7, 3.8, 4.4 ppm (methylene protons), 1.2, 1.4, 1.5 ppm (methyl protons). 2.4 ppm(OH) protons ^{13}C NMR (DMSO- d_6): 172, 173, 175 ppm (C=O, ester), 46 to 49.5 ppm (quaternary carbon), 38.8 to 40.5 and 64.1 to 65.7 ppm (methylene), 16.2 to 16.9 ppm (Methyl carbon). 49.5 to 50.3 ppm (piperazine carbon). ^{31}P NMR: 30.88 and -59.52 ppm Anal. Calcd for $\text{C}_{79}\text{H}_{132}\text{O}_{51}\text{N}_2\text{P}_2$: C, 47.73%; H, 6.69%; N, 1.41%, Found; C, 46.51%; H, 6.33%; N, 1.11%.

3 Results and Discussion

3.1 Synthesis of Hyperbranched Polyesters

The acid-catalyzed esterification procedure (Scheme 1) has been used for the synthesis of HBPE and water was removed continuously by passing nitrogen during reaction. To increase the probability of the reaction between unreacted acid groups with hyperbranched skeleton (not with another free monomer), the concentration of free bis-MPA was kept as low as possible.

Therefore, bis-MPA added in successive portions corresponding to the stoichiometric amount for third generation. The use of low esterification temperature (140 °C) suppress the unwanted etherification and trans-esterification. Due to low solubility of bis-MPA in most of the organic solvents the synthesis was carried out by heating the reactants without sol-

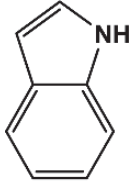
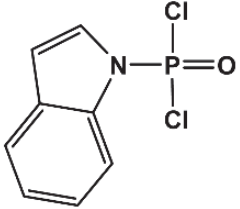
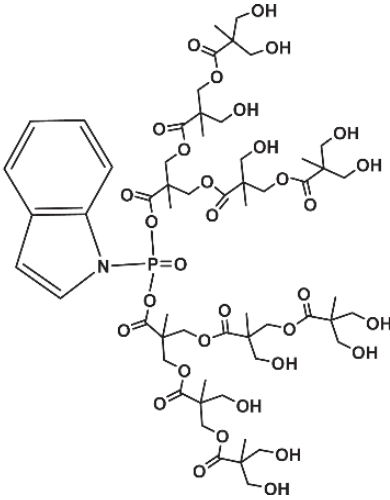
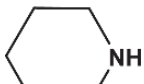
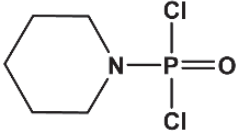
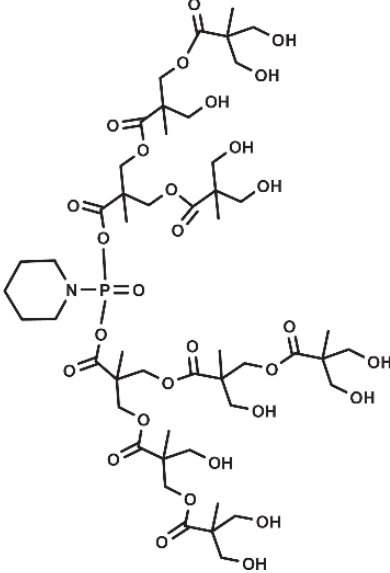
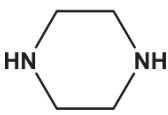
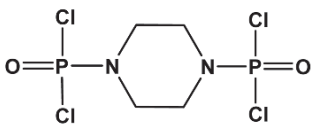
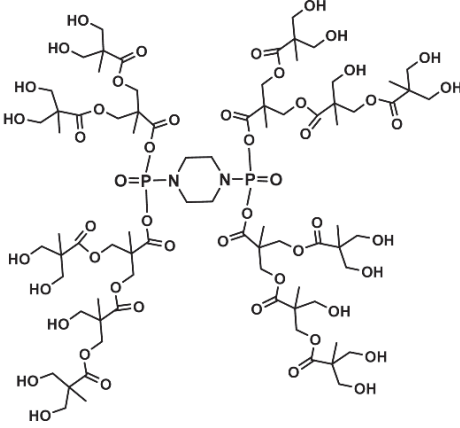
N-Heterocyclic compounds	N-Heterocyclic phosphoryl dichloride (stage I)	Phosphorus containing N-heterocyclic hyperbranched polyester (stage II)	Product notations
 <p>Indole</p>			IN-HBPE
 <p>piperidine</p>			PD-HBPE
 <p>piperazine</p>			PZ-HBPE

Table 1. Reaction sequence and product notations

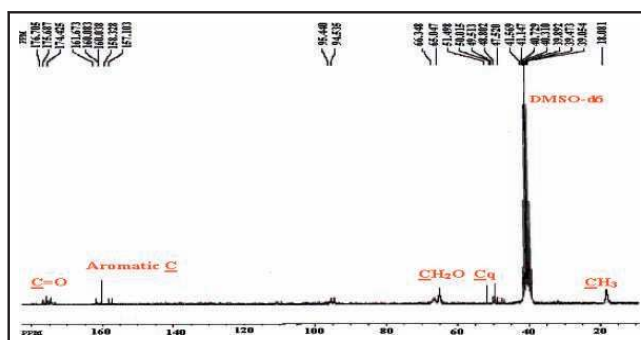
	IN-HBPE	PD-HBPE	PZ-HBPE
Yield (%)	90	88	80
Solvent	THF, DMSO	THF, DMSO	THF, DMSO
Color	Dark brown	Brown	White

Table 2. Product descriptions

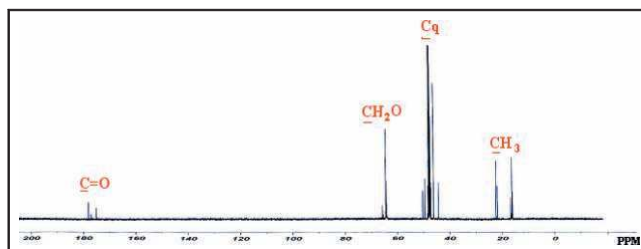
vent which result melt condensation technique. P-TSA used as a catalyst to increase the rate of the reaction. In its absence, bis-MPA is deposited in the colder areas of the reaction which results erratic branching. When the reaction starts, bis-MPA dissolves in the polymer and melts which results thick dispersion of the solid and it becomes a clear liquid. The viscosity of the reaction mixture increases with the progress of the reaction (Goswami and Singh, 2004).

3.2 Characterization of Hyperbranched Polyesters

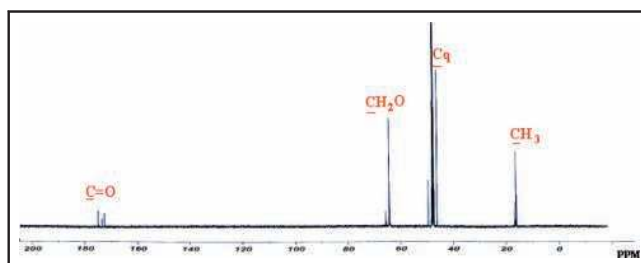
The synthetic procedure and product description for various polyester outlined in Table 1 and Table 2. Phosphorous containing indole and imidazole synthesized by reacting N-heterocycle (indole or piperidine or piperazine) with POCl_3 at a molar ratio of 1 : 2 using pyridine as a catalyst. The mechanism of the product formation described in our previous report (Karpagam et al., 2008). Third generation of aromatic N-heterocyclic HBPE may be prepared by using IN-PD, PD-PD and PZ-PD with Bis-MPA at a molar ratio of 1 : 21 using p-TSA as a catalyst. The chemical structure of HBPE was characterized by FT-IR, ^1H NMR, ^{13}C NMR and elemental analysis. FT-IR results the three N-Heterocyclic HBPE shows the strong absorption of hydroxyl group appeared nearly at 3400 cm^{-1} . Ester group of $\text{C}=\text{O}$ formed at around 1735 cm^{-1} and disappeared the acid $\text{C}=\text{O}$ in Bis-MPA confirms formation HBPE. From the spectra, $\text{P}=\text{O}$ and $\text{P}-\text{O}-\text{C}$ peak also found in 1224 and 1134 cm^{-1} . From the ^1H NMR spectra, the signal at 7.1 – 7.9 ppm indicates the presence of aromatic protons. Methylene protons were appeared at 3.6 to 4.1 ppm and methyl protons appears in 1.2 to 1.7 ppm for IN-HBPE. Aliphatic signals appeared in PD and PZ-HBPE. OH protons observed in 2.2 ppm for IN-HBPE, 2.1 ppm for PD-HBPE and 2.4 ppm for PZ-HBPE which shows the formation of N-heterocyclic HBPE with OH termination. The detailed assignment of all N-heterocyclic HBPE for ^{13}C NMR given in Fig. 1, the signals at around 47.5 to 51.5 ppm indicates the existence of quaternary carbon



A)



B)



C)

Fig. 1. ^{13}C -NMR spectrum of (A) IN-HBPE, (B) PD-HBPE, (C) PZ-HBPE

and methylene carbon appears in around 65.1 to 66.3 ppm region for three HBPE. Three carbonyl carbons formed nearly at 174 , 175 and 176 ppm which used to identify the degree of branching for HBPE. On checking the phosphorus content in hyperbranched polyester by using ^{31}P NMR spectroscopy, IN-HBPE and PD-HBPE shows one sharp signal at 28.31 and 21.52 ppm. Because of two different direction of phosphorus in PZ-HBPE, two signals appeared at 28.32 and -59.52 . The elemental analysis data of the HBPE was given in Table 3 which support the structures of the polyesters shown Table 1.

Product code	Calculated %			Found %		
	C	H	N	C	H	N
IN-HBPE	51.29	6.53	1.03	51.45	6.23	1.59
PD-HBPE	49.52	7.00	1.16	49.76	6.58	1.14
PZ-HBPE	47.73	6.69	1.41	46.51	6.33	1.11

Table 3. Elemental analysis of N-Heterocyclic HBPE

From the results, the theoretical values are in good agreement with the experimental data.

3.3 Degree of Branching

The structural perfection of the hyperbranched polyesters is characterized by the determination of their degree of branching (DB), which determined either by Frechet's equation (Hawker et al., 1991)

$$DB \text{ (Frechet)} = (D + T)/(D + T + L),$$

$$\text{or Frey equation } DB \text{ (Frey)} = 2D/2D + L,$$

where D, T, L is the number of dendritic, terminal and linear units of the HBPE.

The integration of the peaks for the respective units dendritic (D), linear (L) and terminal (T) in the polymer can be distinguished by CH₃ protons signals in ¹H NMR and ¹³C NMR using either the carbonyl peaks (C=O) [172 to 178 ppm] or quaternary carbons (Cq) [47 to 51 ppm]. These three particular areas of the NMR spectra are presented in Fig. 1 and summarized in Table 4. The main difference lies because DB (Frechet) takes into account the linear propagation as a branching direction and thus overestimates DB for small molecules, whereas both definitions merge for higher molar masses. For C=O signals in HBPE, the average values of DB_{Frechet} is ~ 0.75 (DB_{Frey} is ~ 0.73). DB values of all polyester exhibits near to hyperbranched structure (< 1.0) rather than linear (=0) and dendrimer (=1) (Sibdas and Niranjana, 2007).

3.4 Molecular Weight and Molecular Weight Distribution

MALDI-TOF profile of the polymerization products IN-HBPE, PD-HBPE and PZ-HBPE are shown in Fig. 2 and the data are summarized in Table 5. From these data, the polydispersity, Mn, M_w and M_z were calculated using universal calibration. The number average molecular weight (M_n), the weight average molecular weight (M_w), average molar mass (M_z) and polydispersity index (PD) can be determined by using the mass of the ith hyperbranched polymer ions (M_i) and the

corresponding signal intensity of q molecular ion with degree of polymerization i (N_i). M_w and M_n are calculated using

$$M_n = \sum N_i M_i / \sum N_i,$$

$$M_w = \sum N_i M_i^2 / \sum N_i M_i,$$

$$M_z = \sum N_i M_i^3 / \sum N_i M_i^2,$$

$$PD = M_w / M_n.$$

The results of theoretical study (Radke et al., 1998) and computer simulation (Hanselmann et al., 1998) is to model the kinetics of the core-dilution/slow monomer addition process. Slow addition of AB_x monomers to B_f core molecules strategy is used to prepare hyperbranched polymer can provide the resulting product in controlled molecular weight, lower polydispersity and enhanced degree of branching. As shown in Table 5, the Mn is 477 to 610 and Mw is 724 to 1099 for N-heterocyclic HBPE. The corresponding polydispersity of IN-HBPE, PD-HBPE and PZ-HBPE are 1.51, 1.85 and 1.80 respectively. In an ideal case, the effect of core molecular functionality (f) on the molecular weight distribution can be described by the expression

$$PD = 1 + 1/f.$$

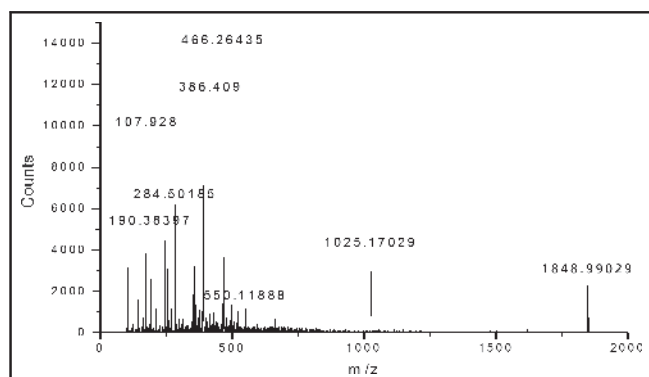
The molecular weight distributions are shifted to higher molecular weight while increasing the ratio of monomer to core. This indicates that a slow addition procedure permits to control the molecular weight of the resulting hyperbranched polymers. In the present study, the functionality of core molecule is 2 and the ideal polydispersity according to equation is 1.5. This can be proved from the polymer IN-HBPE (Table 4) which is a smaller molecular weight and narrower molecular weight distribution with the polydispersity (1.51).

3.5 Electrical Properties

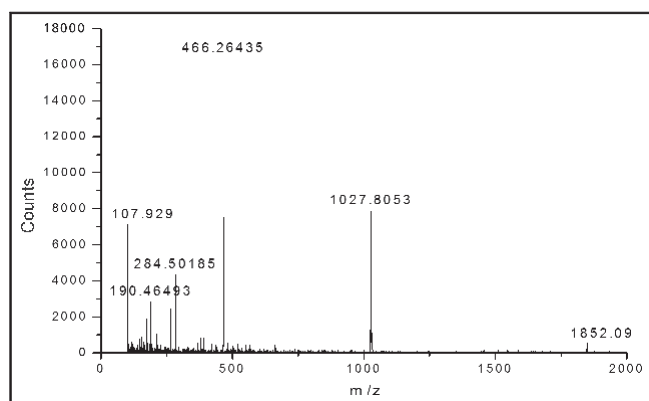
Dielectric constant of a material is the ratio of its permittivity to the permittivity of vacuum. Figure 3 gives the variation of the dielectric constant ε' with frequency at fixed temperature

Product	Signals	D		L		T		DB Frechet	DB Frey
		PPM	Unit	PPM	Unit	PPM	Unit		
IN-HBPE	C=O(¹³ C)	173.4	0.42	174	0.38	175	0.225	0.63	0.69
	Cq(¹³ C)	46.5	0.16	48.5	0.825	50.5	0.2	0.31	0.28
	CH ₃ (¹ H)	1.690	1.18	1.209	0.68	1.053	2.71	0.85	0.77
PD-HBPE	C=O(¹³ C)	174	1.28	177	0.465	178	1.98	0.87	0.84
	Cq(¹³ C)	44.2	1.485	48.4	2.14	50.3	1.18	0.55	0.58
	CH ₃ (¹ H)	1.752	1.2	1.675	0.7	1.140	2.88	0.85	0.77
PZ-HBPE	C=O(¹³ C)	172	1.22	173	0.87	175	1.43	0.75	0.73
	Cq(¹³ C)	46.0	1.12	47.9	0.675	49.5	0.54	0.75	0.76
	CH ₃ (¹ H)	1.51	1.31	1.45	0.68	1.26	2.5	0.84	0.79

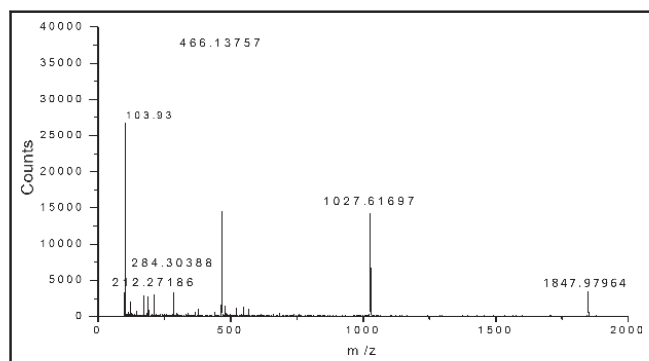
Table 4. ¹³C NMR and ¹H NMR analysis of N-Heterocyclic HBPE



A)



B)



C)

Fig. 2. MALDI-TOF full spectrum of (A), IN-HBPE (B), PD-HBPE (C), PZ-HBPE

Product code	Mn	Mw	Mz	PD
IN-HBPE	477.18	724.92	1106.12	1.51
PD-HBPE	512.88	949.20	1582.34	1.85
PZ-HBPE	610.37	1099.92	1681.78	1.80

Table 5. Average molecular weights and polydispersity index (PD) of N-Heterocyclic HBPE

(300 K) for all three polyesters. At 300 K, marked differences found in dielectric constant between IN-HBPE, PD-HBPE and PZ-HBPE. The decrease of dielectric constant with increasing frequency is the expected behavior in most dielectric materials. An important observation is that dielectric constant increases considerably from aromatic core (IN-HBPE) to aliphatic core containing hyperbranched (PD-HBPE and PZ-HBPE) polyester. The initial high value of dielectric constant at relatively lower frequencies may be due to the contributions from space charge polarization in the bulk material, structural defects and electrode effects (Hippel et al., 1953). Variation of dielectric constant with frequency shows that the possibility of the presence of an interfacial polarization (Goswani and Varma, 1975; Smyth, 1955). From a structural point of view, the dielectric relaxation involves the orientation polarization which depends upon the molecular arrangement of dielectric to be material. So, at higher frequencies, the rotational motion of the polar molecules of dielectric is not rapid for the attainment of equilibrium with the field, hence dielectric constant seems to decrease with increasing frequency (Smyth, 1955).

Figure 4 shows the variation of dielectric loss factor ϵ'' with frequency at fixed temperature for all the three hyperbranched

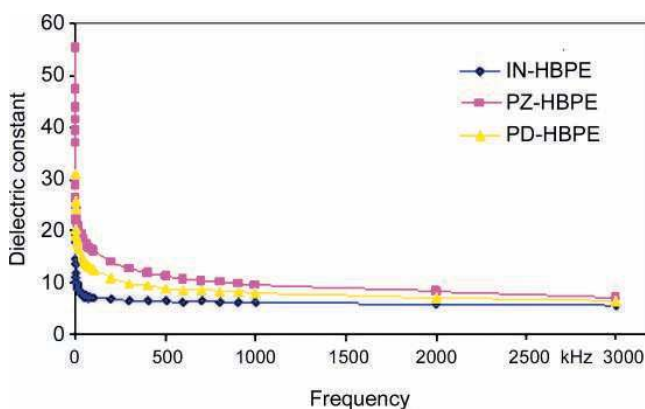


Fig. 3. Variation of dielectric constant with frequency of hyperbranched polyester

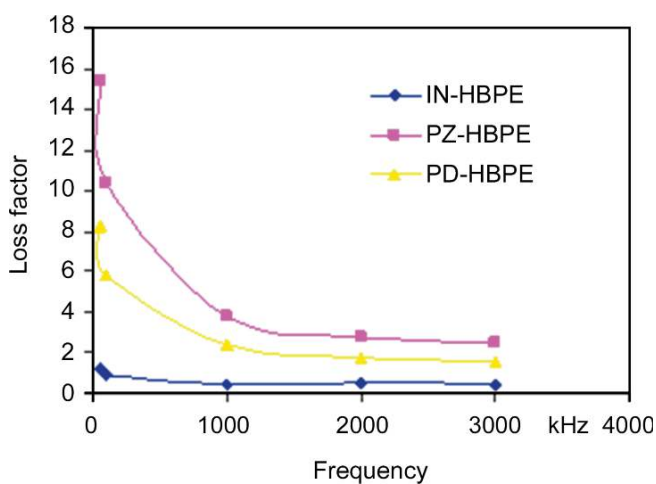


Fig. 4. Variation of loss factor with frequency of hyperbranched polyester

polyester (IN-HBPE, PD-HBPE and PZ-HBPE). The value of dielectric loss decrease with the increase of frequency at fixed temperature was observed in all three polyesters. The higher loss peak at low frequency was observed in PZ-HBPE and PD-HBPE and is due to the free charge motion within the materials. But, the loss peaks was observed at about 50 kHz in PZ-HBPE, 100 kHz in PD-HBPE and not observed in IN-HBPE. At high frequencies, the dielectric loss factor is low, because the orientation polarization due to chain motion of polymer cannot keep phase with the rapidly oscillating electric field (Akram et al., 2005).

3.6 Thermal Properties

The thermal properties of three kinds of N-Heterocyclic HBPE were investigated with thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). As shown in Fig. 5, the initial 3 to 4% weight loss is due to loss of moisture and/or trapped solvent present in both cases. In this study the same amount of weight loss was observed for all polyester with no structural change. Thermal stability reached up to the temperature of 245 °C for PZ-HBPE, 268 °C for PD-HBPE and 280 °C for IN-HBPE which was observed with no decomposition in the TG traces (Fig. 5). High thermal stability may be due to the presence of N-heterocyclic and phosphorus moiety present in the polymer structure. The weight losses 5, 20, 50 and 80 mass % (T_5 , T_{20} , T_{50} and T_{80} , respectively) as well as char residue at 600 °C were determined which is represented in Table 6. From this table, it has been seen that the hyperbranched polyester of indole core moiety (IN-HBPE) is slightly higher in initial decomposition temperature and char residue than piperidine and piperazine core moiety of hyperbranched polyester (PD-HBPE and PZ-HBPE). This is due to the structural defects in the polymer (IN-HBPE) and contains aromatic core of O=P-O structure whereas there is no aromatic in PD-HBPE and PZ-HBPE (aliphatic core with O=P-O).

It has already been reported that nitrogen based heterocyclic polymer (Hu et al., 2004) and phosphorus based aliphatic HP (Deng et al., 2004) has good flame retardant behaviors for their excellent charring effect. This is due to the presence of phosphorus-nitrogen based flame retardant in polymer structure (Liang et al., 2013). They also have advantage like low toxicity, corrosion free, low smoke, good compatibility, good flame retardance etc. In this case, the LOI value was used as an indicator to evaluate flame retardancy of a polymer. The LOI value of the polymers at 700 °C is 21 to 23.4, which is higher than HBPE (LOI value was 19). It was confirmed that

the heterocyclic modified HBPE showed good flame retardant than virgin HBPE.

For the DSC measurements, the samples were heated at a rate of 10 °C/min from 50 to 300 °C under N_2 atmosphere then cooled to 50 °C. Figure 6 shows the thermographs of the N-heterocyclic HBPE. From the DSC thermogram, the glass transition temperature formed for IN-HBPE at -30 °C, for PZ-HBPE at -14 °C and for PD-HBPE at -23 °C. This is due to the free movement of low molecular weight HBPE chains. All the thermographs confirm the formation of homogeneous amorphous polymer without any crystallization.

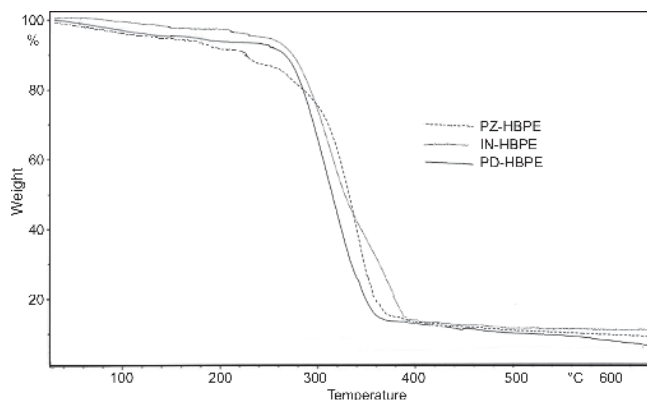


Fig. 5. TG of N-Heterocyclic HBPE

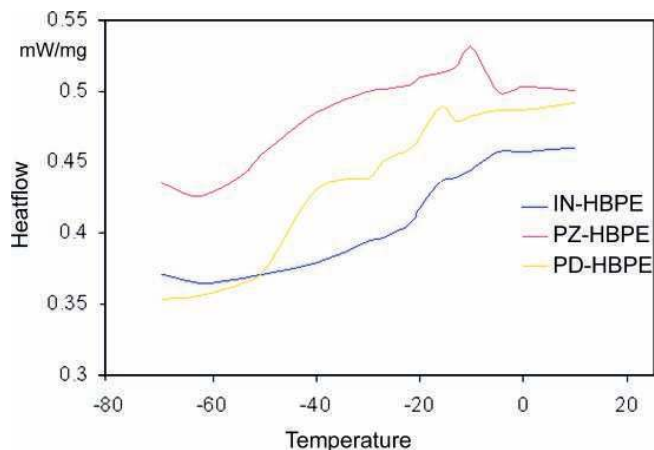


Fig. 6. DSC thermographs of N-Heterocyclic HBPE

Code	T_5 °C	T_{20} °C	T_{50} °C	T_{80} °C	Char residue at 600 °C %	LOI
IN-HBPE	280	311	350	396	14.5	23.3
PD-HBPE	255	311	344	366	9.9	21.4
PZ-HBPE	255	320	359	375	10	21.5

Table 6. Thermal analysis of HBPE determined at a heating rate of 10 °C/min under nitrogen atmosphere

4 Conclusions

The following points summarize the conclusions of the present investigation:

1. The new nitrogen and phosphorus bonded third generation of IN-HBPE, PD-HBPE and PZ-HBPE was synthesized by melt condensation method.
2. Formation of these polyesters were characterized by using FT-IR, ^1H NMR ^{13}C NMR and elemental analysis.
3. Degree of branching confirms the formation of hyperbranched structure of polyesters.
4. The MALDI-TOF spectra were used for determination of average molecular weight and the nature of the end groups. The elemental analysis supported the observation from mass analysis.
5. Frequency dependence of dielectric constant and dielectric loss of hyperbranched polyesters has been studied in the frequency range of 50 Hz to 5 MHz.
6. The thermogravimetric data indicated that the IN-HBPE is more thermally stable than PD-HBPE and PZ-HBPE.

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