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Synthesis and Characterization of Endcapped Hyperbranched Polyesters

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The synthesis of third generation of hyperbranched polyester (HBPE) based on AB_2 type monomer, 2,2-*bis*(hydroxymethyl) propionic acid (*bis*-MPA) and phloroglucinol as a core molecule *via* melt condensation procedure with *p*-TSA as a catalyst. Efforts have been taken for the endcapping of hyperbranched polyester by using phosphorus containing indole and imidazole (IN-PD and IM-PD) to form N-heterocyclic based polyesters (IN-HBPE and IM-HBPE). The synthesized compounds were subjected to characterization *viz*., FT-IR, ^{1}H and ^{13}C NMR and elemental analysis. The spectral studies were supports the formation of compounds. ^{13}C NMR gives the information about degree of branching of these polymers.

Key Words: Hyperbranched polyester, Heteroaromatics, Spectral studies.

INTRODUCTION

Dentritic macromolecules are attractive scaffolds due to their well defined and unique macromolecular structure. These applications extended in various fields like catalysis, medicinal chemistry, magnetic resonance imaging, combinatorial chemistry, light harvesting, emission and amplification function[1-4]. 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 that of linear polymer[5-8]. Since, the pioneering work are well defined by Vogtle[9], Tomalia[10,11] and Newkome[12] in dendrimers and hyperbranched polymers has been increasing at an amazing rate.

The properties of hyperbranched polymers are indeed strongly determined by the nature of their terminal groups[13-16]. For example, solubility, which is mainly depends on end group structure, may be regulated by the partial or total chemical modification of the "terminal" groups[17]. Due to the irregularities of hyperbranched polymers in their molecular architecture, these functional groups can be located not only in the periphery, as in perfect dendrimers, but also inside the globular branched structure; even the terminal functional groups of dendritic macromolecules

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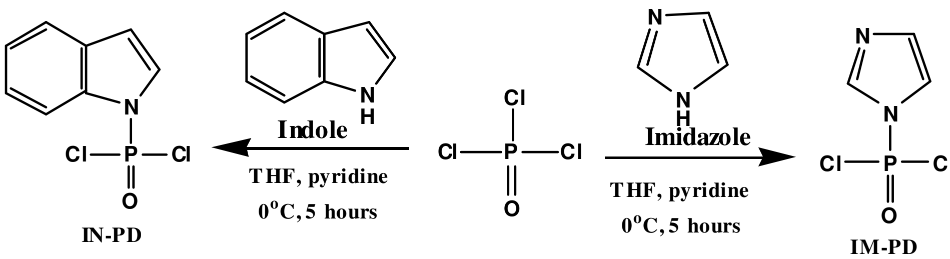
can fold back to the inside[18]. Nevertheless, several authors could show that nearly all functional groups were accessible for small reagents[19,20], which easily allows a quite total modification of functionalized hyperbranched polymers.

The synthesis of polymer which contains phosphorous and heteroaromatics in the terminal chain attracts the attentions of many researchers due to their peculiar characteristics *viz*., non-flammability, thermal stability, high melting points, appreciable biological activities[21-23]. Among the nitrogen containing heterocyclic compounds, six membered heterocyclic compounds are used in various applications as herbicides, pharmaceuticals and adhesives. Five membered heterocyclic compounds are used in electrical and pharmaceuticals applications[24]. Functional group modification of hyperbranched polyester or introducing functional groups into the third generation of hyperbranched polyester has been believed to have basic significance with expanding its applications. Present investigation was devoted for partial endcapping of phosphorous containing N-heterocyclic compounds like indole, imidazole onto hyperbranched polyester matrix offers vast openings in many fields of applications.

EXPERIMENTAL

Indole, imidazole, 2,2-*bis*(hydroxymethyl) propionic acid (*bis*-MPA) were purchased from Sigma-Aldrich. Phosphorus oxychloride, phloroglucinol, tetrahydrofuran (THF), dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), acetone were purchased from S.D. Fine Chemicals, Chennai. Thermonicolet-330 and JEOL model GSX400 instruments were used to record FT-IR and NMR studies, respectively. Elementat Vario EL III Carlo Erba 1108 instrument was used for elemental analysis.

Synthesis of 1*H*-indole-1-phosphonyl dichloride and 1*H*-imidazole-1-phosphonyl dichloride: IN-PD and IM-PD was prepared as per our earlier report[25]. 1 mmol of purified indole (0.117 g) and 2 mmol of phosphorous oxychloride (0.153 g) were dissolved in dry THF added slowly with constant stirring for 15 min at 0 ºC under nitrogen atmosphere in the presence of pyridine as catalyst in three necked round bottomed flask. The progress of the reaction was monitored by means of TLC. After completion of the reaction pyridine hydrochloride was filtered and evaporated the solvent to get 1*H*-indole-1-phosphonyl dichloride (IN-PD), (**Scheme-I**). FT-IR (KBr, ν_{max}, cm^{-1}): 1239 (P=O); 1008 (N-P); 484 (P-Cl); ^{1}H NMR (CHCl$_3$): 7.2-7.7 ppm (aromatic protons).



Scheme-I

Similar procedure was adopted for the synthesis of 1*H*-imidazole -1-phosphonyl dichloride (IM-PD) (**Scheme-I**). FT-IR (KBr, ν_{max}, cm^{-1}): 1250 (P=O); 1017 (N-P); 501 (P-Cl). ^{1}H NMR ($CHCl_3$): 7.3, 7.4 and 7.8 ppm (aromatic protons).

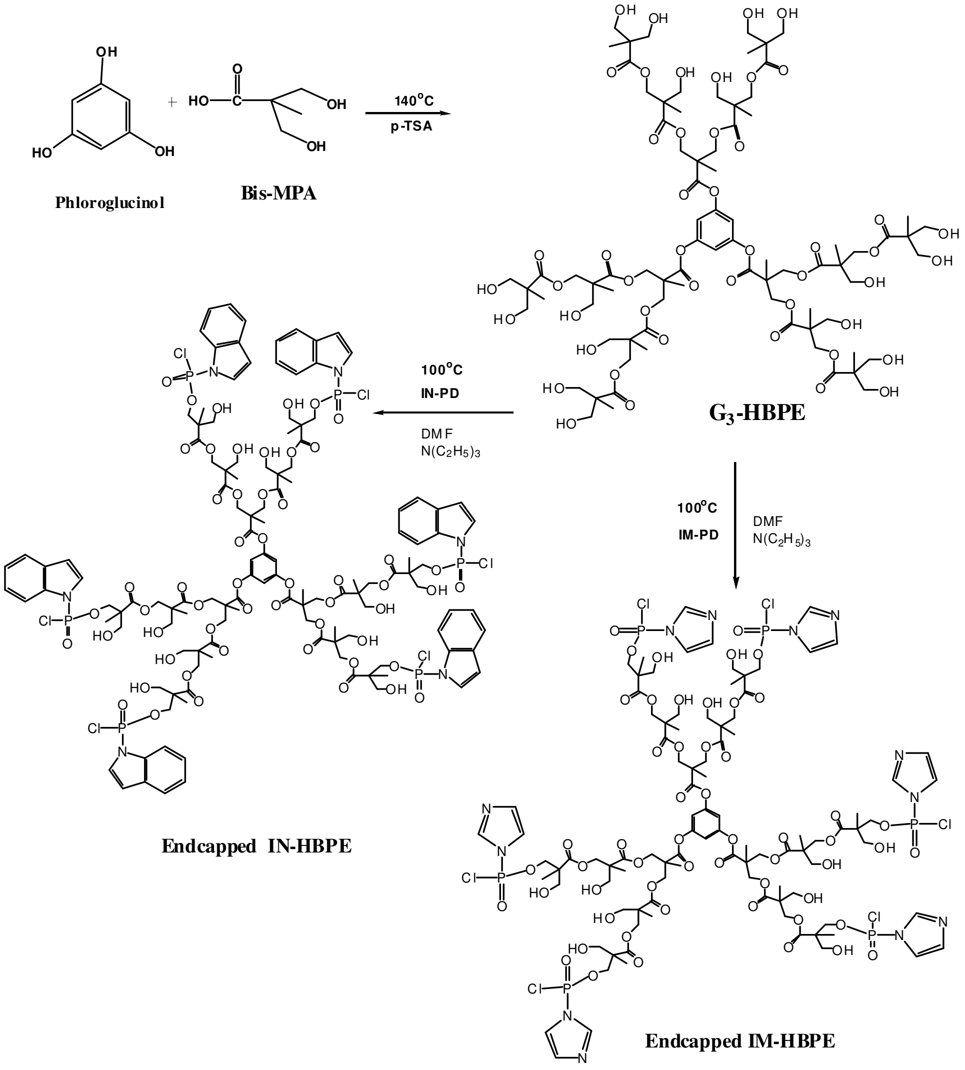
Synthesis of third generation (G_3) of hyperbranched polyester (HBPE): The monomer 2,2-*bis*(hydroxymethyl) propionic acid (*bis*-MPA), the core (phloroglucinol) and the catalyst (*p*-TSA) of different stoicometric ratios has been calculated as per our earlier finding for the formation of different generation *viz*., first (G_1) and second (G_2) and third (G_3)[26]. The third generation has been selected for further studies. This may be due the abundance of OH group for convenient end capping. The product description for HBPE and endcapped product was given in Table-1.

TABLE-1
PRODUCT DESCRIPTION

	HBPE	IN-PD	IN-HBPE	IM-PD	IM-HBPE
Yield (%)	85	88	85	88	80
Solvent	Acetone DMSO	DMF DMSO	Acetone DMSO	DMF DMSO	DMSO
Colour	Red	Crimson red	Crimson red	Dark red	Light pink

Bis-MPA (28.16 g, 0.21 mol), phloroglucinol (1.26 g, 0.01 mol) and *p*-TSA (0.020 g, 0.18 mmol) were mixed in a three-necked round bottom flask equipped with a nitrogen inlet and a drying tube. The RB flask was placed in an oil bath at 140 ºC with constant stirring for 10 h under nitrogen atmosphere in order to remove the water molecules formed from the reaction mixture. The reaction was monitored by TLC and the formation of the red waxy product was purified by using column chromatography (Silica gel with petroleum ether/ethyl acetate as the gradient eluent). FT-IR (KBr, ν_{max}, cm^{-1}): 1735 (C=O of ester); 3433 (OH); 2979 (aromatic C-H); ^{13}C NMR (DMSO-d_6) δ (ppm): 47.52-51.49 (quaternary carbon); 39.1-41.5 and 65.04, 66.35 (methylene carbon); 157-161.6 (phenyl); 18.1 (methyl carbon); 174.42, 175.68, 176.71 (ester carbonyl). Anal. calcd for $C_{81}H_{126}O_{48}$: C, 52.09 %; H, 6.8 %; Found; C, 51.26 %; H, 6.12 %.

Synthesis of 1*H*-indole-1-phosphonyl dichloride end-capped HBPE (IN-HBPE): 1*H*-Indole-1-phosphonyl dichloride (4.6 g, 10 mmol) and HBPE (0.474 g, 1 mmol) were dissolved in dry DMF (50 mL) and stirred for 26 h at 100 ºC in the presence of triethylamine (TEA) as acceptor of HCl. As the reaction proceeds, triethylamine hydrochloride precipitates from the reaction medium and its quantity corresponds to consume IN-PD. A precipitate of triethylamine hydrochloride was filtered off and the solvent DMF was completely removed by vacuum distillation. Crimson red waxy IN-HBPE was obtained and dried in vacuum oven at 60 ºC. The final product was purified by column chromatography (Silica gel with petroleum ether/ethanol as the gradient eluent). The scheme of the reaction displayed in **Scheme-II**. FT-IR (KBr, ν_{max}, cm^{-1}): 1260 (P=O), 1021 (N-P), 1734 (ester carbonyl), 3404 (O-H), 2966 (aromatic, C-H), 1163 (P-O-C), 494 (P-Cl); ^{1}H NMR (DMSO-d_6): 7.108, 7.128, 7.473, 7.493, 7.938, 8.925 ppm (aromatic protons), 3.424, 3.645, 3.794



Scheme-II

3.845, 4.096 ppm (methylene protons), 1.690, 1.209, 1.053 ppm (methyl protons). ^{13}C NMR (DMSO-d_6): 173, 174, 175 ppm (C=O, ester), 46.5-50.5 ppm (quaternary carbon), 39.1-40.3 and 64.09-64.24 ppm (methylene), 17.1, 17.2, 17.4 ppm (methyl carbon). Anal. calcd. for $C_{122}H_{156}N_6O_{54}P_6Cl_6$: C, 50.75; H, 5.15; N, 2.75 found; C, 50.45; H, 5.23; N, 2.59.

Similar procedure was adopted for the synthesis of 1*H*-imidazole-1-phosphonyl dichloride end-capped HBPE (IM-HBPE) shown in **Scheme-II**. The light pink waxy polymer was obtained and purified by using column chromatography (silica gel with petroleum ether/ethanol as the gradient eluent). FT-IR (KBr, ν_{max}, cm^{-1}): 1210 (P=O), 1008 (N-P), 1732 (C=O of ester), 3417 (O-H), 2961 (aromatic, C-H), 1162

(P-O-C), 503 (P-Cl); ^{1}H NMR (DMSO): 7.108, 7.128, 7.478, 7.498, 7.926, 8.955 ppm (aromatic protons), 3.626, 3.774, 3.812, 4.084 ppm (methylene protons), 1.752, 1.675, 1.140 ppm (methyl protons). ^{13}C NMR (DMSO-d_6): 135, 137, 138 ppm (C=O, ester), 45.5-50 ppm (quaternary carbon), 38.8-40.5 and 63.82-64.7 ppm (methylene), 17.09 ppm (methyl carbon). Anal. calcd. for $C_{99}H_{138}N_{12}O_{54}P_5Cl_6$: C, 43.10; H, 5.04; N, 6.09. Found; C, 42.76; H, 5.58; N, 6.75.

RESULTS AND DISCUSSION

Synthesis of third generation HBPE: The synthetic procedure for various polymers outlined in **Scheme** (**I-II**). Phosphorous containing indole and imidazole was first synthesized by condensation of indole or imidazole with $POCl_3$ at a molar ratio of 1:2 using pyridine as a catalyst. The mechanism of the formation of the product was described in present earlier findings[25]. Then third generation of aromatic HBPE can be prepared by using phloroglucinol and *bis*-MPA at a molar ratio of 1:2 using *p*-TSA as a catalyst. The chemical structure of HBPE was characterized by FT-IR, ^{13}C NMR and elemental analysis. From FT-IR, the strong absorption of ester C=O formed at 1735 cm^{-1} and disappears the acid C=O in *bis*-MPA confirms the formation HBPE. The FT-IR spectrum also shows a strong absorption peak at around 3433 cm^{-1} corresponding to the O-H stretching. Fig. 1 expressed the ^{13}C NMR, the signals at 47.5-51.4 ppm indicates the existence of quaternary carbon. Because

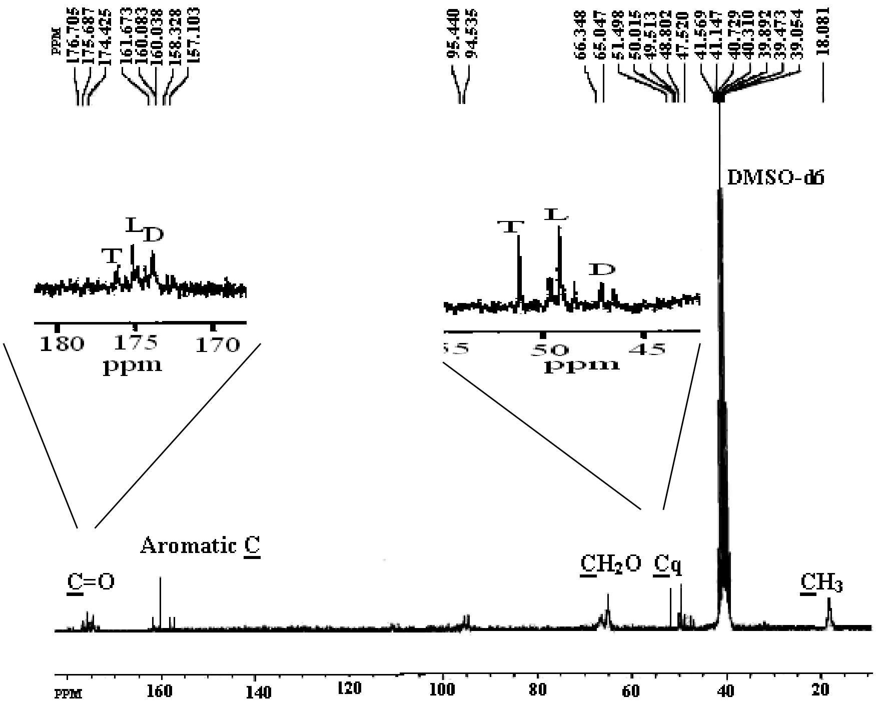


Fig. 1. ^{13}C NMR of HBPE

of methylene carbon attached with dendritic carbons and free OH, it appears in 39.1- 41.5 and 65.1-66.3 ppm region. Three carbonyl carbons formed at 174, 175 and 176 ppm used to identify the degree of branching for HBPE. The elemental analysis data found C, 51.26 %; H, 6.12 %; are in good agreement with that C, 52.09 %; H, 6.8 %; calculated for $C_{81}H_{126}O_{48}$. From this we have calculated the approximate theoretical molecular weight found from elemental analysis is 1867 g.

Synthesis of IN-HBPE and IM-HBPE: End capping of HBPE was achieved by reacting of IN-PD and IM-PD with HBPE was shown in **Scheme-II**. The formation of the end-capped products was confirmed by ^{1}H and ^{13}C NMR spectroscopy. FT-IR spectrum reveals the strong absorption around 1260 cm^{-1} corresponds to the vibration with P=O group, P-O-C bond formed at 1163 cm^{-1} and C=O appears at 1734 cm^{-1}. Formation of P-O-C and existence of P-Cl bonds and OH bonds in IN-HBPE an IM-HBPE indicates partial endcapping was achieved. From the ^{1}H NMR spectrum, the signals at 7.108-8.925 ppm indicate the presence of aromatic protons. Methylene protons were appeared at 3.424-4.096 ppm. Methyl protons appear in 1.053-1.690 ppm for IN-HBPE and 1.140-1.752 for IM-HBPE. OH protons observed in 2.279 ppm for IN-HBPE and 2.273 for IM-HBPE shows partial endcapping was achieved with HBPE. The detailed assignment for ^{13}C NMR given in Figs. 2 and 3. From this study, tertiary carbon peak appears in the range of 45.5-50.0 ppm. Methyl carbon signal was observed in 17.1-17.2 ppm and methylene carbon showed in two regions

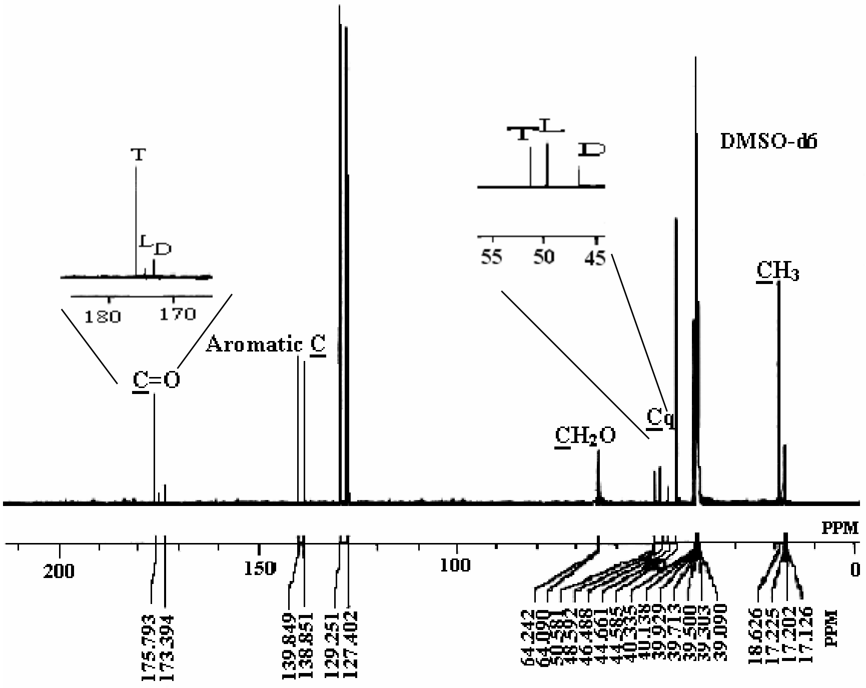


Fig. 2. ^{13}C NMR of IN-HBPE

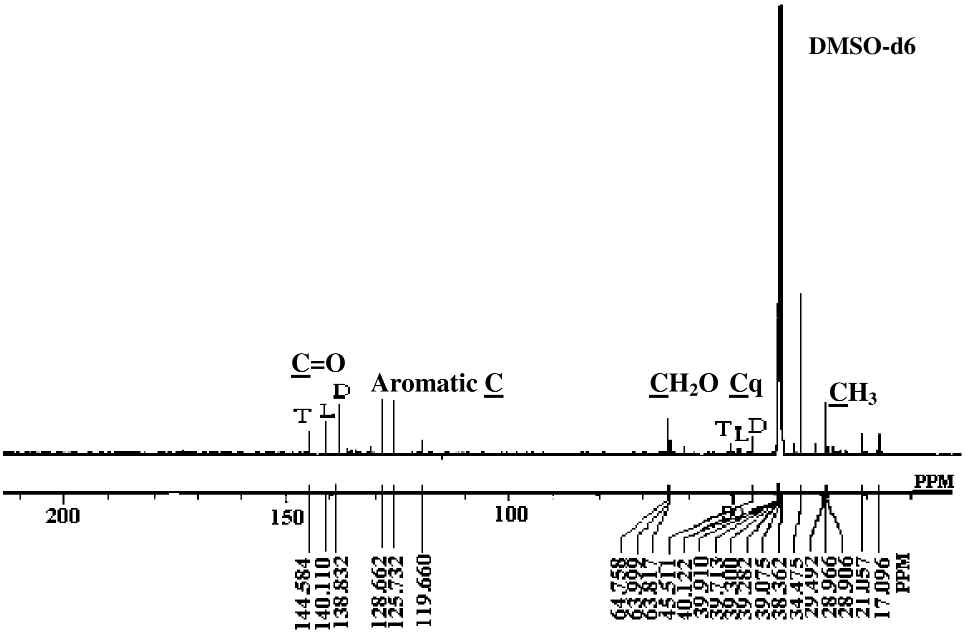


Fig. 3. ^{13}C NMR of IM-HBPE

as 39.1- 40.3 and 63.8-64.7 ppm. This range of signals also proves IN-PD and IM-PD functionalize partially with OH containing HBPE. Formation of three carbonyl carbons at 173 and 175 ppm confirms the tilting three different direction of branching of HBPE with IN-PD compounds. Due to the presence of electronegativity in imidazole moiety (contains two nitrogen present in the ring) for IM-HBPE, the ester carbonyl (C=O) peak was shifted to down field and therefore, three carbonyl carbons formed at 138, 140 and 144 ppm, respectively, confirms branching of HBPE in IM-PD compounds. Similar to our conclusions, Kou *et al.*[27] reported for this system. Percentage of carbon, hydrogen and nitrogen present in the endcapped polymers are shown in experimental section. From the results of the elemental analysis, it is evident that the results of the chemical analysis are in good agreement with the calculated values of the respective polymers, *i.e.*, on the basis of the emperical formula ($C_{122}H_{156}N_6O_{54}P_6Cl_6$), ($C_{99}H_{138}N_{12}O_{54}P_5Cl_6$) for the polymer IN-HBPE and IM-HBPE. On analyzing the reason for partial endcapping, OH groups in HBPE are not equal-reactive and more precisely that terminal type hydroxyls are more reactive towards IN-PD and IM-PD than linear type hydroxyls. This has been found in the literature in terms of a screening effect that would be most important for inner linear hydroxyls[28,29].

Degree of branching: The structural perfection of the hyperbranched polymers is usually characterized by the determination of their degree of branching (DB), which was determined either by Fretchet's equation[30]

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

or

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

where D, T and L refer to the number of dentritic, terminal and linear units in the structure of the polymer, respectively. The integration of the peaks for the respective units dentritic (D), linear (L) and terminal (T) in the polymer can be distinguished by CH_3 protons signals in ^{1}H and ^{13}C NMR using either the carbonyl peaks (C=O) [171-175 ppm] or that of the quaternary carbons (Cq), [45-51 ppm]. These three particular areas of the NMR spectra are presented in Figs. 1-3 and summarized in Table-2. The main difference lies in the fact that DB (Frechet) takes into account the linear propagation as a branching direction and thus overestimates degree of branching (DB) for small molecules, whereas both definitions merge for higher molar masses. For C=O signals, the average values of DBFrechet-0.55 (DBFrey-0.54) for HBPE was observed in present investigation. After endcapping of HBPE with IN-PD and IM-PD, the DB was increased (Table-2) and hence, degree of branching for all polymer exhibits near to hyperbranched structure rather than linear and dendrimer (according to the literature[31], degree of branching closes to zero for linear, less than 1 for hyperbranched and 1 for dendrimer).

TABLE-2
^{13}C AND ^{1}H NMR ANALYSIS OF HBPE AND ENDCAPPED HBPE

Product	Signals	D		L		T		DB	DB
		ppm	Unit	ppm	Unit	ppm	Unit	Frechet	Frey
HBPE	C=O (^{13}C)	174.4	0.165	175.6	0.280	176.7	0.18	0.55	0.541
	Cq (^{13}C)	47.5	0.195	49.5	0.4	51.4 0	0.525	0.64	0.49
IN-HBPE	C=O (^{13}C)	173.4	0.33	174	0.14	175 1	1.845	0.93	0.825
	Cq (^{13}C)	46.5	1.2	48.5	1.995	50.5 1	1.47	0.57	0.54
	CH_3 (^{1}H)	1.690	1.18	1.209	0.68	1.053	2.71	0.85	0.77
IM-HBPE	C=O (^{13}C)	138.8	0.42	140.1	0.255	144.5	0.28	0.80	0.76
	Cq (^{13}C)	45.5	0.13	48.8	0.135	50 0	0.18	0.69	0.65
	CH_3 (^{1}H)	1.752	1.2	1.675	0.7	0.140	2.88	0.85	0.72

Conclusion

The following points summarize the conclusions of the present investigation: Third generation of HBPE was synthesized by melt condensation method. Endcapped IN-HBPE, IM-HBPE was synthesized by using IN-PD and IM-PD with HBPE. Formation of the compounds were confirmed by using, FT-IR, ^{1}H and ^{13}C NMR studies and elemental analysis, respectively. Degree of branching confirms the formation of hyperbranched polyesters.

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