Sigma J Eng & Nat Sci 35 (2), 2017, 239-251

Sigma Journal of Engineering and Natural Sciences
Sigma Mühendislik ve Fen Bilimleri Dergisi

Research Article

HYDROXYL-FUNCTIONALIZED HYPERBRANCHED ALIPHATIC POLYESTERS BASED ON 1,1,1-TRIS(HYDROXYMETHYL)PROPANE (TMP) AS A CORE MOLECULE: SYNTHESIS AND CHARACTERIZATION

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Received: 14.12.2016 Revised: 24.02.2017 Accepted: 23.03.2017

ABSTRACT

The aim of this study is to synthesize and characterize the new hydroxyl-functionalized hyperbranched aliphatic polyesters with various generations for potential use in cancer therapy as targeted drug delivery system. For this purpose, a series of novel hydroxyl-functionalized hyperbranched aliphatic polyesters (HBPs) based on 2,2-bis(hydroxymethyl)butyric acid (Bis-HBA) as AB_2-type monomer and 1,1,1-tris(hydroxymethyl) propane (TMP) as B_3 core molecule were synthesized *via* acid catalyzed polyesterification reaction in three different generations and named as HBP-2G, HBP-4G and HBP-5G. The synthesis route was a simple pseudo-one-step reaction where AB_2-type monomer and B_3 core molecule are polycondensed in the presence of an acid catalyst. The chemical structures of the synthesized HBPs were confirmed by FTIR, ^{13}C NMR and ^{1}H NMR analysis. The degree of branching (DB) of the HBPs as calculated from ^{1}H NMR results were between 0.87 and 0.92. These results showed that all synthesized HBPs had a high degree of branching. TGA measurements exhibited that all of HBPs had similar and good thermal stability. Glass transition temperatures (Tg) of samples were identified using DSC analysis and were found to be between 66.2 °C and 69.1 °C. Low generation HBPs have considerably higher solubility in organic solvents than high generation HBPs. All synthesized HBPs displayed extremely low water solubility but extremely high solubility in dimethyl sulfoxide. It was concluded that new HBPs which were synthesized in this study have reasonable characteristics for hyperbranched polymers applications.

Keywords: Hyperbranched aliphatic polyesters, dentritic polymer, hydroxyl-functionalized hyperbranched polyesters.

1. INTRODUCTION

Highly branched three-dimensional polymers, also named dendritic polymers (more specifically dendrimers) were described 30 years ago. After that, they progressively became one of the most exciting areas of polymer science and engineering [1] due to their perfect chemical and physical properties as well as promising potential in applications in drug/gene carriers, coatings, additives, macromolecular building blocks, separation processes involving solvent extraction, absorption or extractive distillation, nanotechnology and supramolecular science [2-8].

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Dendritic polyme rs are divided into four subclasses, namely, (1) hyperbranched, (2) dendrigrafts, (3) dendrons, and (4) dendrimers [9]. Dendrimers are well-defined perfectly branched synthetic macromolecules with a three-dimensional architecture, free of defects [10], in contrast, hyperbranched polymers have a less perfect structure than the dendrimers [11, 12]. The hyperbranched polymers have a large number of functional groups which determine the unusual properties like the good solubility, the strong influence of the end group on the glass transition temperature and the low viscosities [13, 14].

Dendrimers are obtained using step by step synthesis with time-consuming and expensive purification procedures, it is very apparent that such multi-step processes are not desirable from an industrial point of view [15-19]. In contrast to dendrimers, hyperbranched polymers can easily be prepared by a simple one-pot synthesis in large quantities which reduce the cost [13, 16, 20, 21]. Thus they are preferred in industrial applications [22]. The branching factor or the degree of branching (DB) is extensively used as a parameter to indicate the chemical structure of the hyperbranched polymers [23,24]. DB represents the percentage of dendritic and terminal monomers among the total monomers in the hyperbranched polymer structure. It is generally determined by NMR spectroscopy on the basis of low molecular weight model compounds [23-26]. In hyperbranched polymers, three types of repeating units are found, which is differentiated as dendritic (D), linear (L), and terminals (T) while dendrimers contain dendritic and terminal units [23]. Linear segments are known as defects [8]. Two equations for the average DB have been suggested [8]. As recommended by Frey, DB for an ideal dendrimer is 1, while a linear polymer and hyperbranched polymer has a DB of 0 and tend to be close to 1, respectively [23, 26]. According to Frey, in an ideal case (in hyperbranched polymers based on AB_2 system when the core fully reacts), the amount of dendritic and terminal units have to be the same or very close to each other. Thus, DB are going to be at almost 0.5 [27].

In the hyperbranched polymers based on AB_2-type monomers, DB was determined by the following both the Frechet and Frey equations [13, 25, 26, 27, 28].

$$\mathrm{DB}_{\mathrm{Frechet}} = \frac{\mathrm{D} + \mathrm{T}}{\mathrm{D} + \mathrm{L} + \mathrm{T}} \tag{1}$$

$$\mathrm{DB}_{\mathrm{Frey}} = \frac{2\mathrm{D}}{2\mathrm{D} + \mathrm{L}} \tag{2}$$

where D, T and L are the segments of dendritic, terminal and linear units situated in the structure of the hyperbranched polymers determined by integration of NMR signals [27].

The aim of this study is to synthesize and characterize the new hydroxyl-functionalized hyperbranched aliphatic polyesters with various generations for potential use in cancer therapy as targeted drug delivery system. For this purpose, this paper focuses on the synthesis of a series of new hydroxyl-functionalized hyperbranched aliphatic polyester with various generations (HBP-2G, HBP-4G and HBP-5G) in the molten state from 2,2-bis(hydroxymethyl) butyric acid (Bis-HBA) as an AB_2-type monomer and 1,1,1-tris(hydroxymethyl)propane (TMP) as B_3 core molecule. This simple preparation process is an esterification performed under the bulk conditions in the presence of an acid catalyst and involves no extra purification steps, which is essential for large-scale rapid and cheap production.

2. EXPERIMENTAL

2.1. Materials

2,2-Bis(hydroxymethyl)butyric acid (Bis-HBA), *p*-toluenesulfonic acid (p-TSA) and 1,1,1-tris(hydroxymethyl)propane (TMP) were acquired from Aldrich (USA) and used as received. Acetone, hexane and dimethyl sulfoxide (DMSO) were acquired from Merck (Germany). All the other reagents and solvents were of analytical grade and were used without further purification.

2.2. Synthesis of HBPs (HB P-2G, HBP-4G and HBP-5G)

Bis-HBA and TMP (stoichiometric ratios between AB_2-type monomer and B_3 core molecule are presented in Table 1) and a catalytic amount of p-TSA (0.5 % of AB_2-type monomer weight) were firstly added into a three-necked cylindrical glass reactor equipped with a Dean-Stark apparatus, a nitrogen inlet and a mechanical stirrer system. The reactor was purged with nitrogen and fixed in a pre-heated oil bath at 140 °C. The reaction mixture was monitored at regular time intervals by determination of the acid value (AV) *via* a simple titration method [29] and was allowed to continue until the AV of the reaction mixture was below 30 (approx. 5 h). The AV was determined by titration of the samples dissolved in acetone with 0.1 N methanolic KOH solution. For purification, the crude polymer was dissolved in acetone, precipitated in cold hexane and dried at 25 °C in a vacuum chamber. After the reaction, white-coloured sticky solid products in high yields (>99%) were obtained. All HBPs were prepared according to this simple pseudo one-step reaction procedure. The second, fourth and fifth generations of the HBPs are named as HBP-G2, HBP-4G and HBP-5G, respectively.

Table 1. Symbols, the amount of the reagents and theoretical molar mass of the HBPs.

Sample name	Generation	Molar ratio TMP/Bis-HBA	Molar mass ($g.mol^{-1}$)
HBP-2G	second	1/9	1305
HBP-4G	fourth	1/45	5989
HBP-5G	fifth	1/93	12235

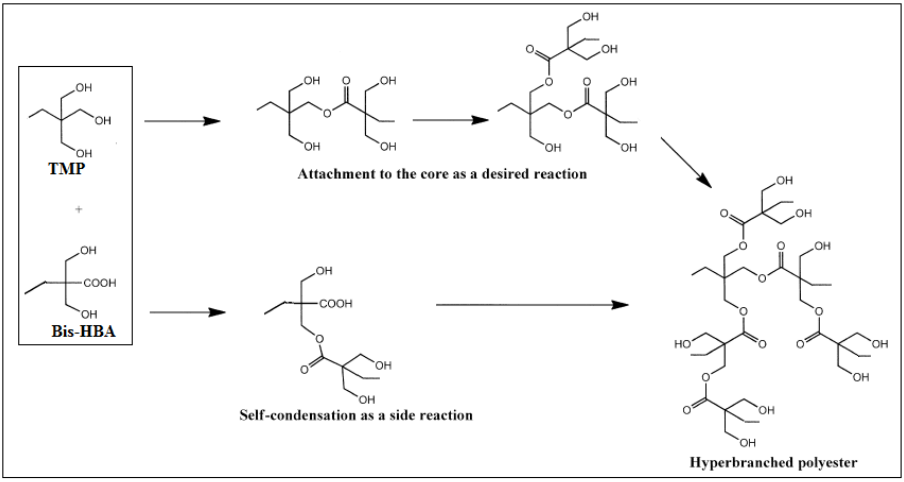
2.3. Equipments

FTIR spectra were obtained on a Digilab Excalibur-FTS 3000 MX model spectrometer (USA). The experiments were performed by preparing a pellet using 1 mg of the sample and 200 mg of KBr. A hydraulic press was used to prepare the pellets by applying a force of 10^5 N. The absorption spectra were collected in the wave number range of 4000-500 cm^{-1}. ^1H-NMR and ^{13}C-NMR spectra were recorded on a Varian UNITY INOVA spectrometer (USA) operating at 500 MHz using $CDC1_3$ and DMSO-d_6 as the solvent at 25°C, respectively. Tg of HBPs were obtained from the DSC analysis. The experiments were performed using a Linseis DSC PT10 model (Germany). Sample amounts of 8-10 mg were taken in sealed aluminum pans. The samples were heated at 10 °C/min between 25 °C and 150 °C in a nitrogen atmosphere. TGA of the HBPs were carried out using a Linseis STA PT 1750 Model Thermo-Analyser System (Germany) at a temperature range of 25-700 °C with a heating rate of 10 °C/min in a nitrogen atmosphere.

3. RESULTS AND DISCUSSION

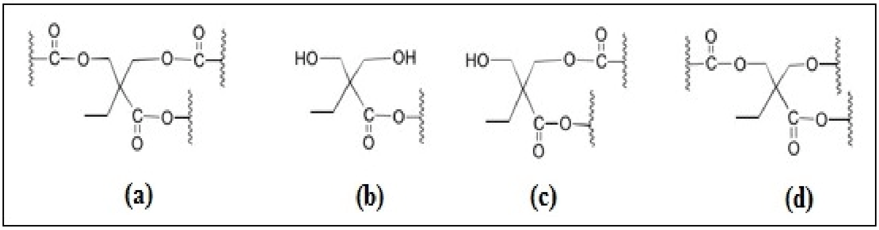
3.1. Synthesis and Characterization of HBPs

HBPs with different generations (HBP-2G, HBP-4G and HBP-5G) were synthesized according to the well known acid-catalyzed esterification procedure which is outlined in Scheme 1. In this study, the acid-catalyzed esterification process was carried out under bulk and also maintained high conversion by continuous water removal. In order to prevent crosslinking, a catalytic amount of p-TSA (0.5 % of AB_2-type monomer weight) was used, otherwise, either gelation would occur or the polymerization would proceed out of control [17]. In addition, low esterification temperature, 140 °C, was chosen to prevent unwanted side reactions such as trans-esterifications and etherificatios [30]. The resulting HBPs are white solids at room temperature.



Scheme 1. Schematic representation of HBPs.

Hyperbranched polymers contain three various kind of repeating units: D, L, and T, as shown in Scheme 2. The fully esterified Bis-HBA (scheme 2a) is assumed to be the dendritic building block in the inner layers. Terminal units at the outer layers (scheme 2b) and linearly incorporated repeating units (scheme 2c) have two and one hydroxyl group on the Bis-HBA left unreacted, respectively. In addition, the linear repeating units may be regarded as a defect as it does not contribute to branching.



Scheme 2. Possible structural repeating units in the HBP molecules.

FTIR spectra

The structure of HBPs was analyzed by FTIR, ^{1}H and ^{13}C NMR spectroscopy. FTIR spectra of HBPs can give some information about their chemical structure [9]. In this study, FTIR experiments were performed to confirm the formation of HBPs. In Figure 1, FTIR spectra of the HBPs with various generations (HBP-2G, HBP-4G and HBP-5G) and starting materials (Bis-HBA and TMP) are shown. The disappearance of the sharp absorption peaks at 1694 cm^{-1} and 1402 cm^{-1} corresponding to the –C=O of the –COOH groups and small absorption bands between 2685 cm^{-1} and 2539 cm^{-1} corresponding to the –OH stretching vibrations of the –COOH groups, which exist in the FTIR spectra of Bis-HBA, are clearly observed. In addition, the intensities of the absorption bands which were observed at 3100-3600 cm^{-1}, 1478 cm^{-1}, 1344 cm^{-1}, 1062 cm^{-1}, 1020 cm^{-1}, 872 cm^{-1} and 690 cm^{-1} in TMP spectra significantly reduced in the FTIR spectra of HBP-2G, HBP-4G and HBP-5G and these bands were observed as the small and broad shoulders or these bands shifted/disappeared. On the spectrum of HBP-2G, HBP-4G and HBP-5G, the new sharp absorption band appeared at 1735 cm^{-1}due to C=O stretching of ester groups [31]. All three hyperbranched polyester samples showed a characteristic hydroxyl peak around 3400 cm^{-1} [32]. FTIR analysis confirmed that the esterification reaction mainly occurred between -COOH groups of Bis-HBA and -OH groups of TMP during the synthesis of HBPs.

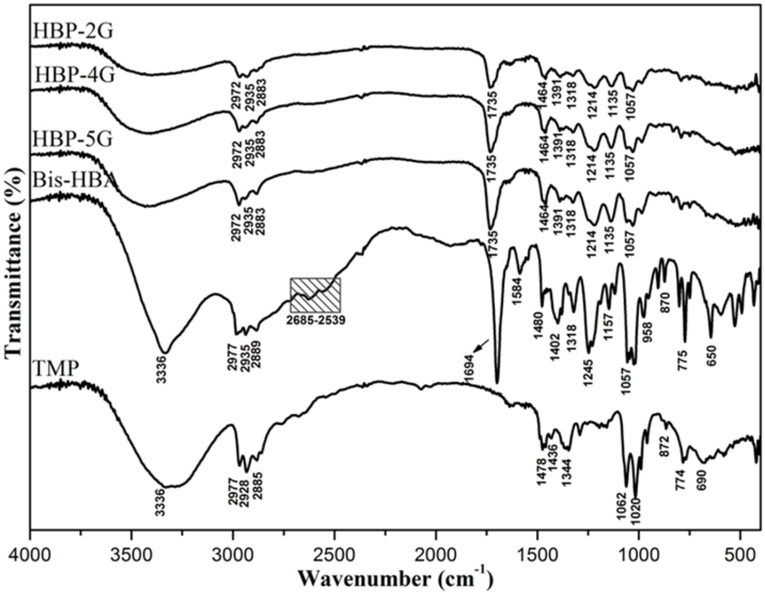


Figure 1. FTIR spectra of AB_2-type monomer (Bis-HBA), core molecule (TMP) and HBPs with different generations (HBP-2G, HBP-4G and HBP-5G)

^{1}H NMR and ^{13}C NMR analysis

^{1}H NMR spectroscopy is the key technique for a quantitative determination of structural units especially in hyperbranched polymers [13, 14, 33, 34]. The ^{1}H NMR spectra of HBP-4G and HBP-5G are given in Figure 2 and Figure 3 and the signal assignments are summarized in Table 2 and Table 3. In addition, the methyl proton regions of HBP-4G and HBP-4G spectra were magnified as shown in Figure 2a and Figure 3a.

In the ^{1}H NMR spectrum of HBP-4G (Figure 2a-2b), resonance assignments (ppm) are as follows: 1.19 (terminal -CH_3), 1.22 (linear -CH_3), 1.26 (dendritic -CH_3), 3.68 (-CH_2OH), 3.94 (-$COOCH_2$), 4.27 $(-OH)_T$, and 4.41 $(-OH)_L$. In the ^{1}H NMR spectrum of HBP-5G (Figure 3a-3b), resonance assignments (ppm) are also as follows: 1.19 (terminal -CH_3), 1.22 (linear -CH_3), 1.26 (dendritic -CH_3), 3.68 (-CH_2OH), 3.95 (-$COOCH_2$), 4.28 $(-OH)_T$, and 4.42 $(-OH)_L$.

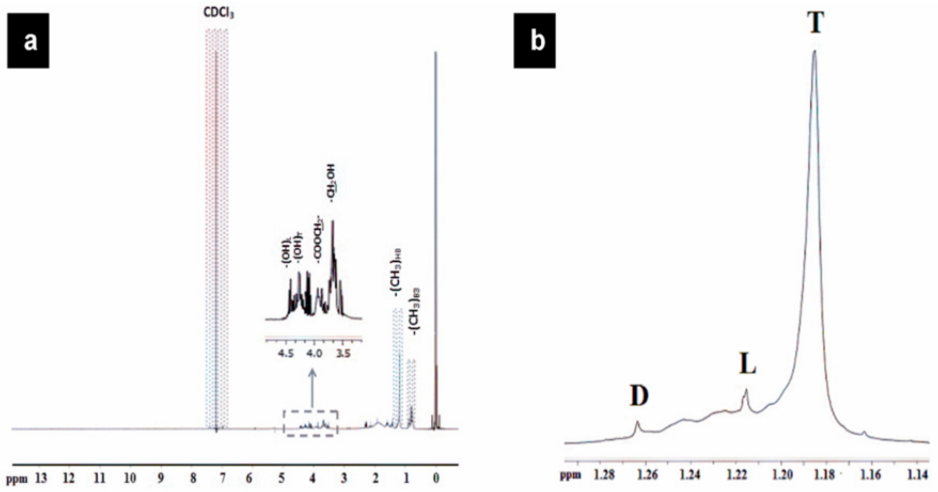


Figure 2. ^{1}H-NMR spectra of HBP-4G in $CDCl_3$ (a) and magnification of the ^{1}H-NMR spectra of HBP-4G in $CDCl_3$ (b).

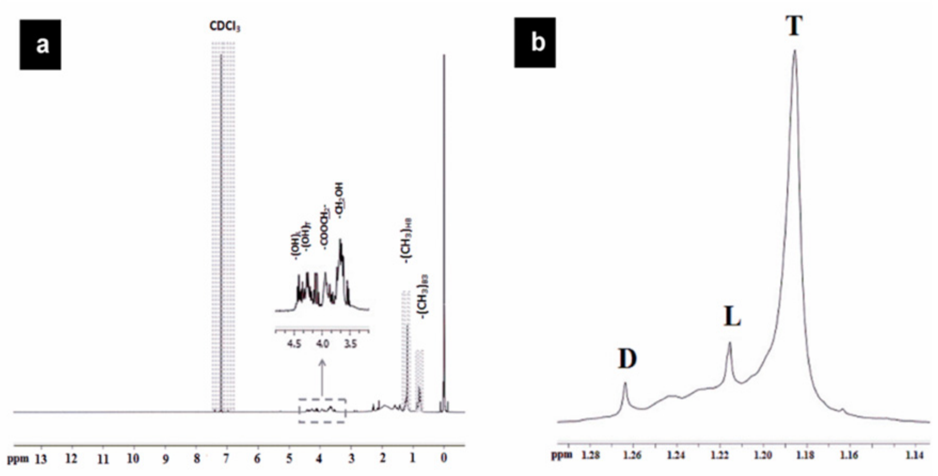


Figure 3. ^{1}H-NMR spectra of HBP-5G in $CDCl_3$ (a) and magnification of the ^{1}H-NMR spectra of HBP-5G in $CDCl_3$

NMR spectroscopy represents an important tool for a detailed characterization of hyperbranched polymers since the spectral analysis permits to extract information on the extent of branching [24]. In this study, the branching perfection of synthesized HBPs were performed by the calculations of DB according to both the Frechet and Frey equations (Eq. 1 and Eq. 2) [12, 24, 25, 26, 27] and all results are given in Table 3. The calculations of DB were performed according to both the Frechet and Frey equations, values obtained according to the Frey equation were lower than the ones obtained by the method of Frechet et al. [26]. In Table 3, the DB values of HBP-4G and HBP-5G are 0.92 and 0.87, respectively, according to the equation suggested by Frechet et al. [28], 0.40 for both according to the equation introduced by Frey et al. [24, 25, 27]. These results demonstrate that a highly branched structure was obtained. The degree of branching seems to be almost independent of the stoichiometric ratio between the core molecule and the repeating unit. The composition of the HBPs was also confirmed by ^{13}C NMR spectroscopy from the quaternary carbon signals representing the segments of the structural units [13, 35, 36]. In the ^{13}C NMR spectra of HBP-4G (Figure 4a), the methyl ($-CH_3$) and methylene ($-CH_2$) groups of Bis-HBA resonate at around 8.86 ppm and 22.96 ppm, respectively. The other peak assignments (ppm) are as follows: 51-55 (quaternary carbons) and 173-176 (carbonyl groups) [35, 36]. Figure 4b shows the magnified quaternary carbon region of the ^{13}C NMR spectra of the HBP-4G in DMSO-d_6. The signals of the quaternary carbon which belong to the D, L and T units were observed at 51.8 ppm, 52.7 ppm and 54.3 ppm, respectively.

Determination of the number degree of polymerization, $(P_n)_{NMR}$ and the number average molar mass $(Mn)_{NMR}$ of the HBPs may appear complex because of the highly-branched structure. In this work, the samples were examined by ^1H NMR spectra and $(P_n)_{NMR}$ was calculated according to Equation (3) [13]:

$$(P_n)_{NMR} = \frac{N_M}{N_{B2}+N_{B4}} \quad (3)$$

This approach based on the amounts of molecules in the reaction system is, due to the self-condensation of the monomer units, equal to the total HBPs containing the core moiety (N_{B4}) and HBPs without the core moiety (N_{B2}) [13]. N_{B2} equals 0 because the peak of –COOH groups was not detected in the ^{13}C and ^1H NMR spectrum [33]. As a result, a recent B2 core between monomer units didn't occur during the reaction.

As shown in Table 4, $(P_n)_{NMR}$ values of HBP-4G and HBP-5G were 21.93 and 40.31, respectively. This means HBP-4G has approximately 22 monomer units and HBP-5G has approximately 40 monomer units in their highly-branched structure. The calculated $(P_n)_{NMR}$ values are normally considerably lower than the monomer/core ratios used, (Table 1). This can be explained by the formation of low molecular weight cyclic side-products which are removed during the precipitation of the HBPs [24, 37].

In the following we focused on the determination of the number average molar mass of the HBPs, $(Mn)_{NMR}$, (Table 4). $(Mn)_{NMR}$ was calculated according to Equation (4) [13]:

$$(Mn)_{NMR} = (P_n)_{NMR}\,[M_{bis-HBA} - M_{water}] + x_4\, M_{B4} + x_2 M_{B2} \quad (4)$$

Where $M_{bis\text{-}HBA}$, M_{water} and M_{B4} are the molar masses of bis-HBA (148.16 g mol^{-1}), water (18 g mol^{-1}) and TMP (134.17 g mol^{-1}), respectively [13]. Calculations were performed with hypothesis that alternative side-reactions (cyclization or intermolecular etherification) didn't happen during the reaction. In Table 4, the molecular weights of HBP-4G and HBP-5G are 2989 and 5381 g mol^{-1}, respectively. As predicted, the results show that molecular weights of HBPs samples increased with the increasing of monomer/core ratio. In addition, the comparison of theoretical and experimental results of molecular weights (Tables 1 and 3) displays some differences, which may be connected to the presence of side-reactions as discussed above.

Table 2. Assignment of the ^1H NMR signals (compare Figure 2 and 4)

Sample	δ_H, ppm						
	CH_3 (D)	**CH_3 (L)**	**CH_3 (T)**	**$C\underline{H}_2OH$**	**$COOC\underline{H}_2$**	**OH (L)**	**OH (T)**
HBP-4G	1,26	1,22	1,19	3,68	3,94	4,41	4,27
HBP-5G	1,26	1,22	1,19	3,68	3,95	4,42	4,28

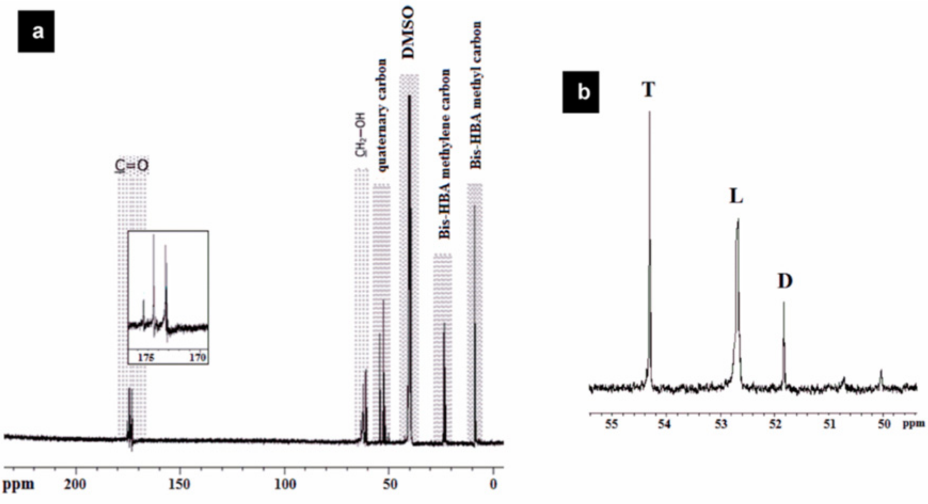


Figure 4. ^{13}C-NMR spectra of HBP-4G in DMSO-d_6 (a) and magnification of the quaternary carbon region of ^{13}C NMR spectra of HBP-4G (b).

Table 3. Results obtained from the ^{1}H NMR spectra of HBP samples.

Sample	Content (%)			Integrated intensities of the signals			DB$_{Frechet}$[a]	DB$_{Frey}$[b]	$(P_n)_{NMR}$[c]	$(M_n)_{NMR}$[d] (g mol^{-1})
	D	L	T	I(D)	I(L)	I(T)				
HBP-4G	5.65	11.90	82.45	1	3.04	32.76	0.92	0.40	21.93	2989
HBP-5G	7.86	15.67	76.47	1	3.11	19.43	0.87	0.39	40.31	5381

[a] Calculated from (Equation1) and [b] Calculated from (Equation2)
[c] Calculated from (Equation3) and [d] Calculated from (Equation4).

3.2. Thermal properties of HBPs

The thermal properties of the HBPs were investigated by TGA and DSC techniques. The thermogravimetry curves of the HBPs in a nitrogen atmosphere are plotted in Figure 5a. Values of the characteristic temperatures, including the temperature of percentage weight loss of HBPs are presented in Table 4. As seen in Figure 5a, all HBPs exhibited one decomposition step in nitrogen. The main featuring of degradation of HBPs was similar to each other. Thermal stability in terms of a higher onset temperature of degradation was better in the high generation HBP (HBP-5G) than that of low generation HBP (HBP-2G). The onset degradation temperatures of HBP-2G, HBP-4G and HBP-5G were 257 °C, 259 °C and 268 °C, respectively (Figure 5b). In brief, HBP-5G is quite stable to decomposition under nitrogen atmosphere up to the onset temperature of ~268 °C and there is approximately 11°C increment in the onset temperature of the thermal degradation compared with the HBP-2G. It is well known that a thermal stability of polyester is highly affected by the concentration of the end functional group which determines molecular weight, and thereby higher molecular weight polyesters is likely to display a better thermal stability performance [38]. Therefore, the high generation HBPs are capable of having the better thermal stability depending on the increase in molecular weights.

Table 4. Weight losses (%) at various temperatures and the final degradation temperature determined from the TGA data of HBPs.

Weight Loss (%)	**HBP-2G**	**HBP-4G**	**HBP-5G**
	Limit of Temperature (°C) for Weight Loss (%)		
5	258	251	273
10	274	273	284
20	291	292	300
30	302	304	311
50	320	322	333
80	358	368	376
90	385	406	401
95	528	451	536

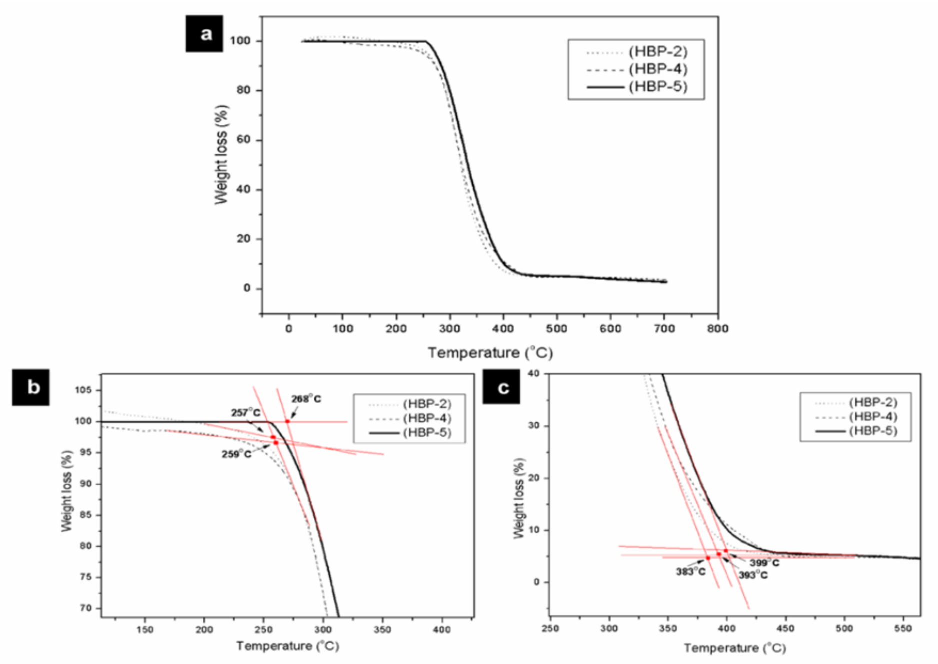


Figure 5. TGA measurement of all the HBPs as a function of temperature from 25 °C to 700 °C, with a heating rate of 10°C in a nitrogen atmosphere (a), determination of the onset (b) and offset (c) temperature for the all HBPs.

Additionally, the temperature values required for reaching definite weight losses acquired from the TGA measurements are listed in Table 4. The thermal degradation temperature of HBP-2G, HBP-4G and HBP-5G at 80% weight loss have been shown at 358 °C, 368 °C and 376 °C, respectively. Consequently, HBP-5G is more stable than HBP-2G and HBP-4G. The Tg values of the HBPs were obtained from the DSC measurements. The DSC curves of the HBPs in a nitrogen atmosphere are plotted in Figure 6. HBP-2G, HBP-4G and HBP-5G have almost same T_g at around 66.2 °C, 69.3 °C and 69.1 °C, respectively. The Tg values of HBP-2G, HBP-4G and HBP-

5G were almost independent of the theoretical molar mass. Malmström and Hult reported [39] that increasing the number of the end groups of the HBPs reduces the Tg value, while it is raised by the increasing number of branching points of the HBPs. In addition, Kim and Webster [40] put forward that the Tg value of the HBPs moved toward higher temperatures with rising polarity of the end functional groups due to the translational mobilities instead of segmental chain mobility. In the light of this information, the above-mentioned parameters come close to a maximum Tg value after approximately the fourth or the fifth generation as mentioned in the literature [39].

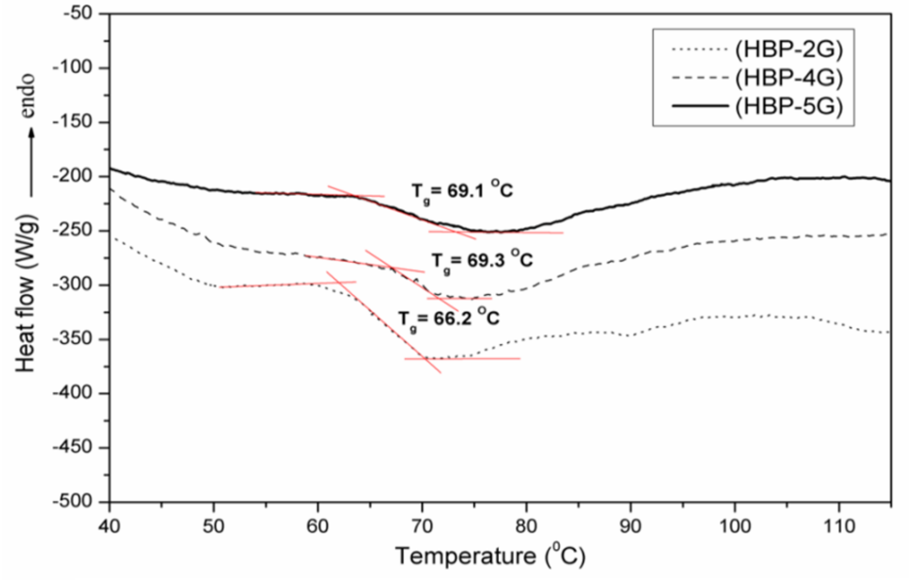


Figure 6. DSC thermograms and Tg values of HBPs samples (heating rate 10 °C/min).

Consequently, the type and the temperature of the reaction and the molar ratio of the core molecule/monomer, which were used for the synthesis of the hyperbranched polymers affect significantly the characteristics of the product polymer such as degree of branching, molecular mass and Tg value. Soccio et al. [17] stated that when the synthesis of hyperbranched polymer using 2,2-bis(hydroxymethyl)butyric acid monomer and (1,1,1-tris-(hydroxylmethyl)propane core molecule were carried out according to the multi-step reaction at 160-190 °C, the values of DB, calculated Mn and Tg of the final polymer were found to be 0.32-0.53, 500-2000 and 25-45 °C, respectively. In this study, since a simple pseudo-one-step reaction was applied at 140 °C for the synthesis of the hyperbranched polymers using same monomer and core molecule with the different molar ratios, the values of DB, calculated Mn and Tg of the final polymer were found to be 0.87-0.92, 1300-12250 and 66-69 °C, respectively.

3.3. Solubility Properties of HBPs

The solubility of HBP-2G, HBP-4G and HBP-5G is summarized in Table 5. All HBPs were found to be completely soluble only in the polar organic solvent DMSO, but were partially soluble in most of the organic solvents such as ethanol, methanol, dichloromethane (DCM), ethyl acetate (EA), dimethylformamide (DMF) and tetrahydrofuran (THF). In addition, these samples were insoluble in typical solvents such as water, toluene and hexane. Although the HBP-4G and HBP-5G were partially soluble in the nonpolar solvent acetone, the HBP-2G was totally soluble. Hawker and Chu reported that the solubility of the hyperbranched polymers was found to be dependent on both the nature of the chain ends and the highly-branched structure of these materials [41]. It is clear that the solubility of the HBPs in acetone decreases with an increase of the molar mass. On the other hand, solubility of the HBPs can be improved by the modification of the end groups [42].

Tablo 5. The solubility properties of HBP-G2, HBP-4G and HBP-5G.

Sample	Water	Acetone	Ethanol	Methanol	DCM	EA	Toluene	Hexane	DMSO	DMF	THF
HBP-G2	-	+	±	±	±	±	-	-	+	±	±
HBP-G4	-	±	±	±	±	±	-	-	+	±	±
HBP-G5	-	±	±	±	±	±	-	-	+	±	±

+: soluble, -:insoluble; ±: partially soluble

4. CONCLUSIONS

The results of this work demonstrated that hydroxyl-functionalized HBPs based on TMP and Bis-HBA monomers could be prepared by an acid catalyzed bulk polyesterification reaction in different generations (HBP-2G, HBP-4G and HBP-5G). According to the synthesis method, these new type HBPs with various generations were produced by simple pseudo-one-step reaction. Their DB values were found to be in the range 0.87–0.92, indicating that the polymers are highly branched. In addition, the molecular weights of HBP-4G and HBP-5G (calculated by ^{1}H NMR spectra) are from 2989 up to 5381 g mol^{-1}, respectively. The thermal properties of the HBP-2G, HBP-4G and HBP-5G showed essentially no decomposition up to 257 °C, 259 °C and 268 °C, respectively, confirming their good thermal stability. HBP-2G, HBP-4G and HBP-5G exhibited glass-transition temperature (T_g) at around 66.2 °C, 69.3 °C and 69.1 °C, respectively. The results obtained in this study were in good correlation with the earlier studies performed with similar hyperbranched polymers. It was concluded that new HBPs which were synthesized in this study have reasonable characteristics for hyperbranched polymers applications due to their structural properties.

Acknowledgements

This work was supported by Scientific Research Project Coordination Unit of Istanbul University. Project number: 15349

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