



## Characterization of hydroxylated hyperbranched polyesters of fourth and fifth generation

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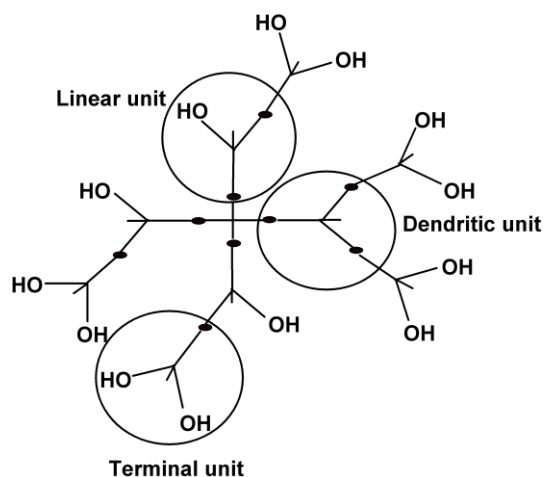
**Abstract:** Hydroxylated hyperbranched polyester (HBPs) of fourth and fifth generation were obtained by three methods; one step (HBP4, HBP5), step by step (HBP4P, HBP5P) and combinations of one step and step by step (HBP1-4, HBP1-5). The HBPs were synthesized in bulk from 2,2-bis(hydroxymethyl)propionic acid (DMPA) and pentaerythritol (PE) using acid catalysis (p-toluenesulfonic acid) and characterized by infrared analysis, <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance, gel permeation chromatography, vapor pressure osmometry, electro spray ionization-mass spectrometry, dynamic light scattering, refractive index, thermogravimetric and differential scanning calorimetric analysis. The refractive index of HBPs were low, the infrared and nuclear magnetic resonance analysis showed evidence of the occurrence of reaction between from 2,2-bis(hydroxymethyl) propionic acid (DMPA) and pentaerythritol (PE). The molar mass values of the HBPs determined by gel permeation chromatography were different to vapor pressure osmometry measurements due to small hydrodynamic volume of the HBPs. The mass spectrometry analysis showed different acyclic and cyclic units in the HBPs. The distributions of HBPs studied by dynamic light scattering were monomodal in number and volume and bimodal in intensity. The thermal stability of the fifth generation HBPs was higher than that the fourth generation. All HBPs presented amorphous behavior.

### Introduction

Dendritic polymer have received increasing attention in recent years due to their unique chemical and physical properties such as solubility, viscosity, thermal and rheological properties, compared to linear polymers [1,2]. The term dendritic refers to dendrimers and hyperbranched polymers (HPs). The dendrimers are fully branched, perfectly regular three-dimensional structures with globular shape and HPs are imperfectly branched or irregular structures [3, 4]. The HPs contain linear units in their structure; this is the origin of imperfections. These polymers are built of AB<sub>x</sub> (x is 2 or more) functional monomers attached to a B<sub>y</sub>-functional core (y ≥ 1), A are molecules with a reactive group of a certain type and B are reactive group of a different species. The core typically consists of a polyfunctional molecule, where the functionality governs the number of branches that extend from it. The intermediate layer is built from monomers with mixed reactivities, which are chain extenders [5]. Each repeating unit layer is referred to as a generation. In a polymer based on an AB<sub>2</sub> monomer, the molar mass and the number of end-groups are doubled with each successive generation [6, 7]. One of the most widely investigated families of HPs are hydroxylated aliphatic hyperbranched polymers synthesized from DMPA and various core molecules e.g. tris-(methylol)propane or ethoxylated pentaerythritol as B<sub>y</sub>

monomer [8-10]. Fig. 1 shows a schematic representation of the HBPs. In this type of synthesis, the control over molar mass averages and molar mass distribution of HPs is achieved by the core and the most effective polymerization procedure involves slow addition of  $AB_x$  to core molecules. This has been demonstrated in the synthesis of HPs from DMPA and various core molecules [4, 8].

Most studies reported in the literature focus on the characterization of hydroxylated hyperbranched polyesters mainly the commercially available Boltorn H20, H30, H40 and H50 which are supplied by Perstorp Specialty Chemical AB [10-12]. These polymers are modified for obtaining materials with specific applications [13-15]. Hyperbranched polymers obtained by one step have also been reported in the literature [16-17]. The aim of this work is to characterize and compare the structural, solution and thermal properties of the fourth and fifth generation of HBPs.

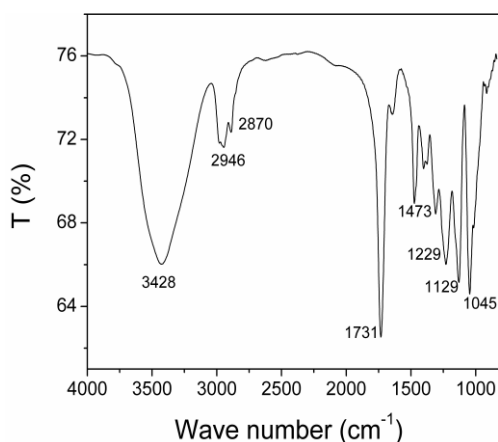


**Fig. 1.** Schematic representation of HBPs structure.

## Results and discussion

### *Infrared analyses*

In the infrared spectrum of polyester HBP1-4 (Fig. 2) there appear two bands at 2946 and 2870  $\text{cm}^{-1}$  due to C–H stretching aliphatic, at 1731  $\text{cm}^{-1}$  the band of carbonyl group of ester.

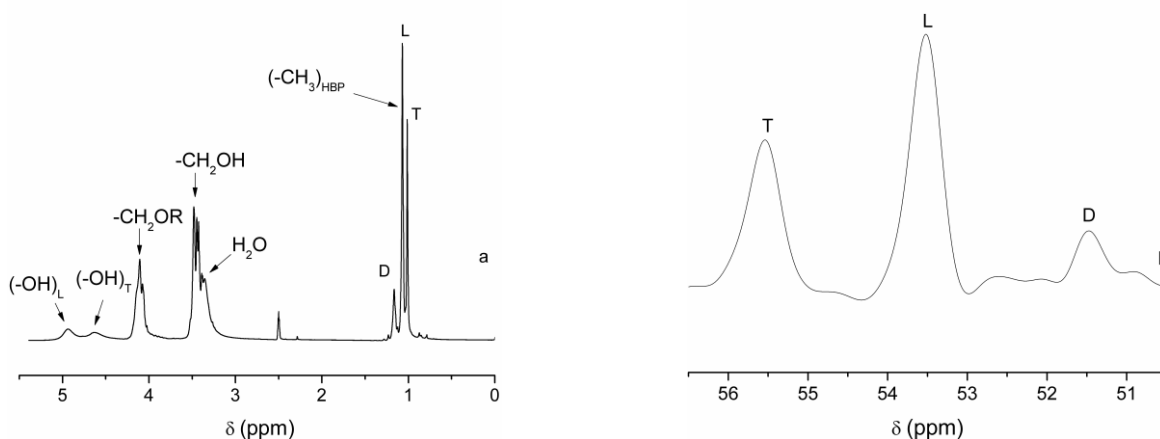


**Fig. 2.** Infrared spectrum of the HBP1-4 sample.

These are an evidence of the formation of polyester. At  $1473\text{ cm}^{-1}$  appears a band due to the angular deformation of  $\text{CH}_2$  group. At  $1229$ ,  $1129$  and  $1045\text{ cm}^{-1}$  appears the C-O stretching vibrations of ester group.

### *$^1\text{H}$ and $^{13}\text{C}$ Nuclear magnetic resonance (NMR)*

Average degree of branching determined by RMN of these HBPs was reported in previous studies [18]. In the  $^1\text{H}$  NMR spectra of HBP1-4 (Fig. 3a) appear different signals:  $\text{CH}_3$  group of terminal (1.01 ppm), linear (1.07 ppm) and dendritic (1.17 ppm) repeating units;  $\text{H}_2\text{O}$  protons at 3.36 ppm, methylene protons attached to OH group at 3.45 ppm, methylene protons in vicinity of reacted hydroxyl groups ( $-\text{CH}_2\text{OR}$ ) appear at 4.11 ppm and OH groups of linear and terminal repeating units appear at 4.90 ppm and 4.63 ppm respectively. In the  $^{13}\text{C}$  NMR spectrum (Fig. 3b) of the HBP1-4, appears signal due to quaternary carbons. The terminal units are observed (T) at 55.52 ppm, linear units (L) at 53.49 ppm and dendritic units (D) at 51.46 ppm. The quaternary carbons, adjacent to acid groups are not observed for the sample HBP1-4.



**Fig. 3.** NMR spectra of HBP1- 4 sample a)  $^1\text{H}$  NMR and b) quaternary carbon magnified region of the spectra  $^{13}\text{C}$  RMN.

### *Gel permeation chromatography (GPC)*

The results of molar mass are shown in the Tab. 1. The results are lower than theoretic values for fourth (7096 g/mol) and fifth (14520 g/mol) generation HBPs. There is not a big difference between values of average number molar mass ( $M_n$ ) and average weight molar mass ( $M_w$ ). The HBPs polydispersity index (PI) is lower for fourth generation HBPs than fifth generation HBPs. This result is an indication that the PE/PDMA molar relation is very important in the molar mass control because the diminution of this relation increases PI. Zagar and coworkers [10] demonstrated that the elution of this polymer type is governed by size exclusion and adsorption and these processes are irreversible for species of low molar mass. Therefore the behavior exhibited for the HBPs, was possibly due to these phenomena. The PI of HBPs obtained at one step (HBP4 and HBP5) was higher than HBPs obtained by other methods. The PI of HBPs obtained by combinations of methods step by step and one step (HBP1-4 and HBP1-5) presented a PI intermediate between two methods; this result is very good since HBPs can be obtained with good PI. Step by

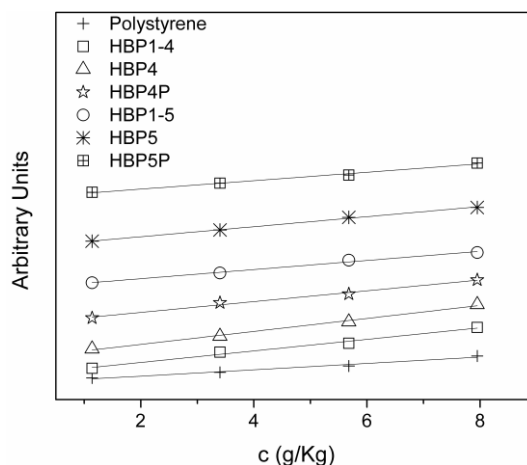
step synthesis method of the HBPs (HBP4P and HBP5P) although present lower PI, their synthesis times are longer.

**Tab. 1.**  $M_n$ ,  $M_w$  and PI values of the HBPs.

HBPs	$M_n$ (g/mol)	$M_w$ (g/mol)	PI
HBP1-4	1951	2925	1.49
HBP4	1918	3072	1.60
HBP4P	2019	2795	1.38
HBP1-5	2053	3386	1.64
HBP5	2055	3588	1.74
HBP5P	2093	3180	1.52

### Vapor pressure osmometry (VPO)

The average number molar mass ( $M_n$ ) of HBPs was determined by VPO (Fig. 4), dividing the product of the slope of curve of polystyrene standard and average number molar mass of polystyrene by slope of respective HBPs curve as reported by Sunder and coworkers [19]. In case of aggregation due to hydrogen bonding, the slope of the concentration-dependent plots would be expected to decrease with increasing concentration. This behavior was not observed evidencing the absence of aggregation in this concentration range.



**Fig. 4.** Plot of the HBPs obtained from results of VPO.

Tab. 2 shows values of slope and  $M_n$  of HBPs. All  $M_n$  values were lower than theoretic molar mass value, for fourth (7096 g/mol) and fifth (14520 g/mol) generation; this is due to unreacted OH group (linear units) that reduces the  $M_n$ . As expected the polymers of fifth generations presented higher  $M_n$  than of fourth generation. The polymer obtained by combination of two methods (HBP1-4 and HBP1-5) presented higher values of  $M_n$  that the polymer obtained in one step (HBP4 and HBP5). The polymer obtained by step to step (HBP4P and HBP5P) had the highest value of  $M_n$  because less linear units are present since by this method is easier to control the structural regularity of the HBPs.

The values of  $M_n$  obtained by VPO were higher than GPC. This is attributable to GPC is dependent of hydrodynamic volume and VPO is independent. Furthermore, for the quantifications of  $M_n$  by GPC, linear polystyrene standards were employed. The  $M_n$

values of the HBPs determined by GPC and VPO are higher than those obtained by NMR in previous studies [18]; which is due to the fact that NMR does not account side reactions, such as, intramolecular and intermolecular etherification [20]. There is not a great difference in  $M_n$  value of HBPs obtained by different methods of synthesis.

**Tab. 2.** Values of  $M_n$  of the HBPs.

HBPs	Slope	$M_n$ (g/mol)
HBP1-4	1.6422	5030
HBP4	1.8451	4477
HBP4P	1.5365	5375
HBP1-5	1.2946	6381
HBP5	1.4267	5790
HBP5P	1.1977	6898
Polystyrene	0.7866	

### *Electrospray ionization-mass spectrometry (ESI-MS)*

Mass spectrometry shows the presence of the cyclizations in the HBPs which cannot be detected by NMR analysis. The molar mass of the acyclic ( $M_1$ ) and cyclic ( $M_2$ ) macromolecules were determined using the following equations [4, 20]:

$$M_1 = X (M_{\text{DMPA}} - M_{\text{water}}) + M_{\text{water}} \quad (1)$$

$$M_2 = X (M_{\text{DMPA}} - M_{\text{water}}) \quad (2)$$

where  $X$ ,  $M_{\text{DMPA}}$  and  $M_{\text{water}}$  are the DMPA unit number in the macromolecule, DMPA molar mass and water molar mass respectively.

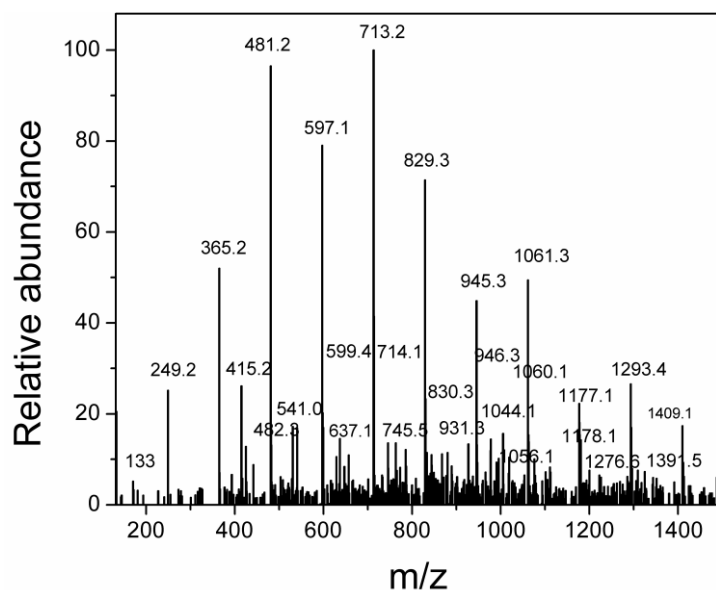
Cyclic macromolecules molar mass with PE in the core that suffer intramolecular etherification and acyclic macromolecules produced by intermolecular etherification between two PE units are given by:

$$M_3 = M_{\text{PE}} + X (M_{\text{DMPA}} - M_{\text{water}}) \quad (3)$$

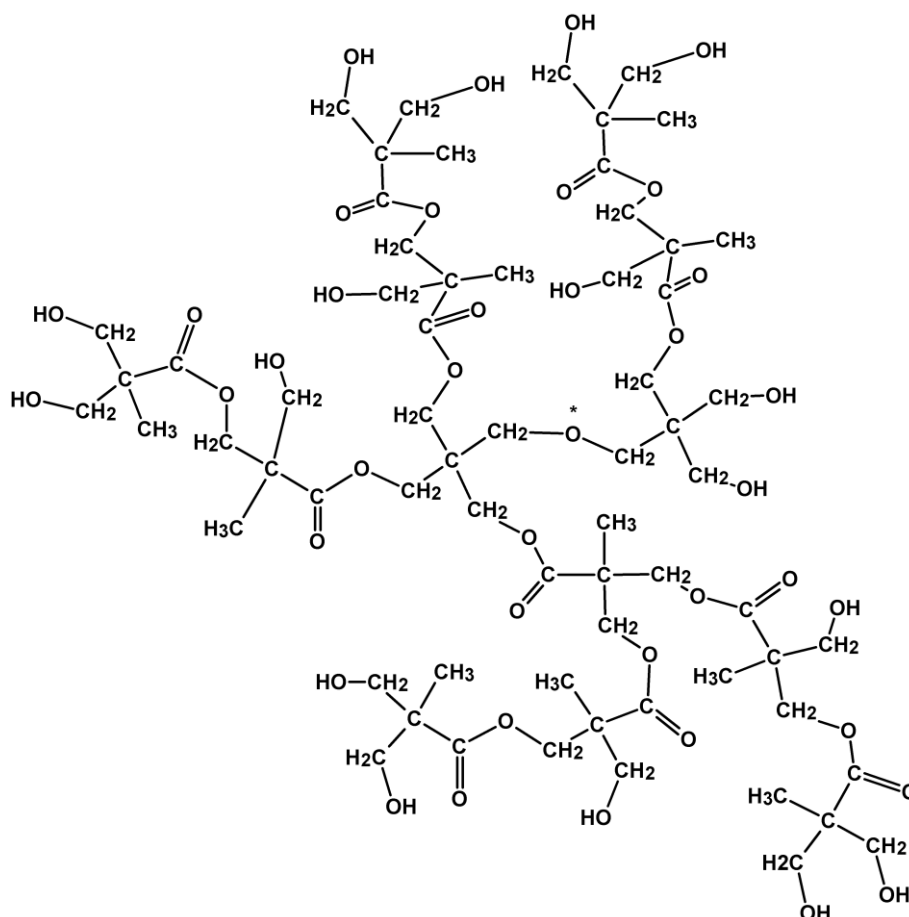
$$M_4 = 2M_{\text{PE}} + X (M_{\text{DMPA}} - M_{\text{water}}) - M_{\text{water}} \quad (4)$$

where,  $M_{\text{PE}}$  is PE molar mass. In the mass spectrum of the sample HBP1-4 (Fig. 5) an intense peak appears at  $m/z=116$  at the same distance between two peaks corresponding to the molecular ions of acyclic species of DMPA repetitive units ( $M_{\text{DMPA}} - M_{\text{water}}$ ), these signals at  $m/z= 249.2, 365.2, 481.2, 597.1$  have high intensity, at  $m/z= 1064.1$  appear peaks due to cyclic macromolecules ( $x=8$ ) with PE in the core that caused intramolecular etherification, at  $m/z=1044.1$  appears a peak due to cyclic macromolecules ( $x=9$ ) and at  $m/z= 1066.1$  ( $x=7$ ) appears a peak of macromolecules acyclic produced by intermolecular etherification between two PE units (Fig. 6). According to the results, during the synthesis of the HBPs cyclic structures were formed due to side reactions and furthermore etherification occurs between PE units, the acyclic units were higher than cyclic units.

The reactions of intramolecular etherification occurs between OH groups of the same molecule (Fig. 7a) and intramolecular hydroxy-ester interchange take place between groups of different branches of the same macromolecule (Fig. 7b). Both side reactions produce cyclic units. In the case of hydroxy-ester interchange reductions on  $M_n$  occur due to fragmentation of the macromolecule (Fig. 7b).

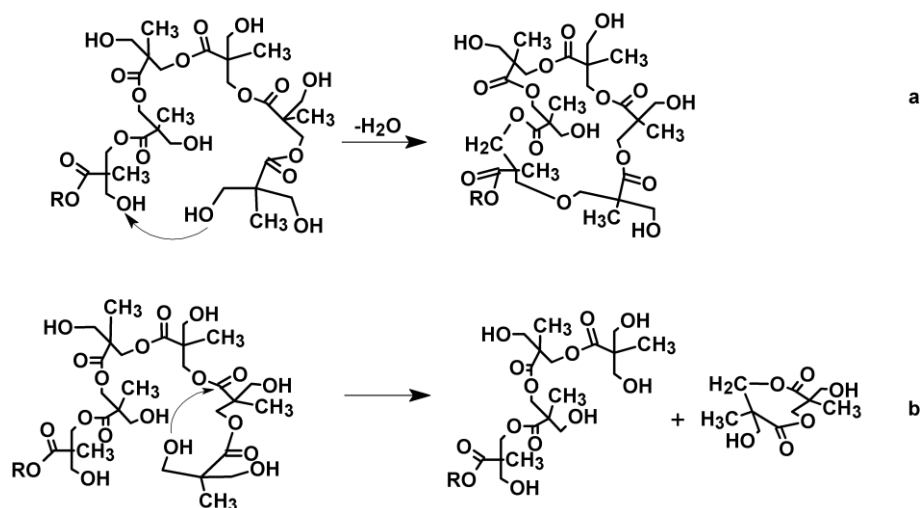


**Fig. 5.** Mass spectra of the HBP1-4 sample.



**Fig. 6.** Intermolecular etherification between two PE units (\*).

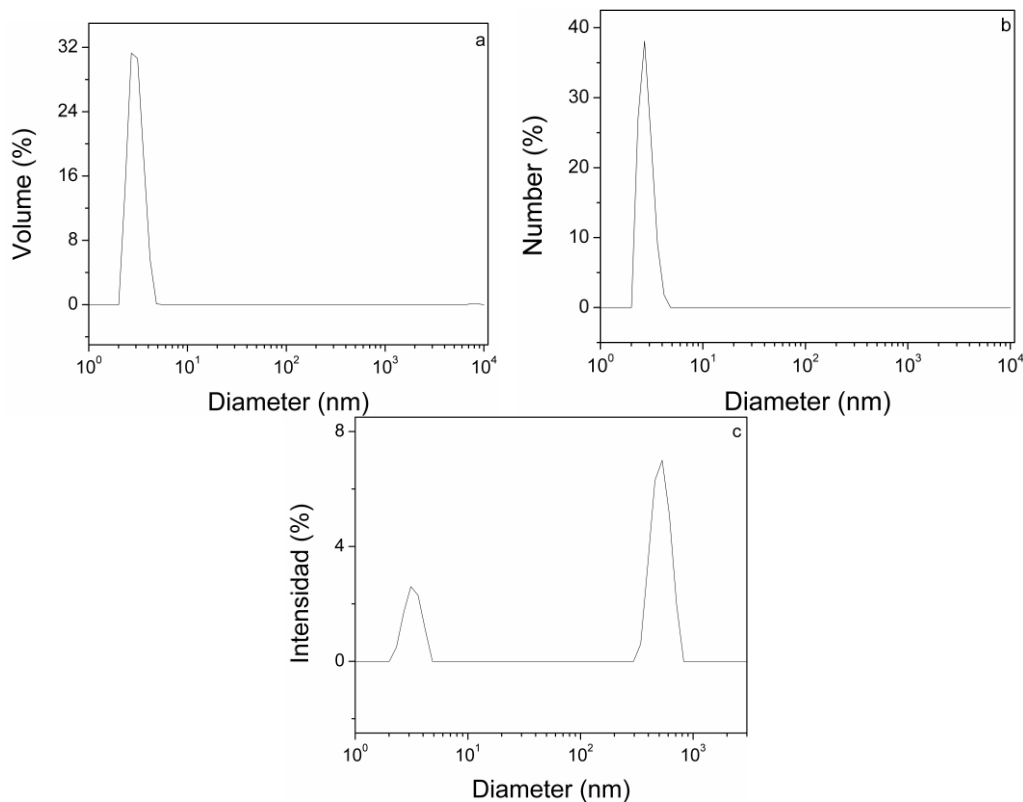
Possibly the small differences observed on Mn value of HBPs obtained of the same generation was due to side reactions that occurred in different proportion during the synthesis of this materials and presence of linear units.



**Fig. 7.** a) Intramolecular etherification and b) Intramolecular hydroxy-ester interchange.

### *Dynamic light scattering analysis (DLS)*

Fig. 8 shows the DLS analysis of HBP4P sample. The number and volume distributions (Fig. 8a and 8b) showed only one peak but the intensity distribution (Fig. 8c) showed two peaks, this behavior is an indication of the presence of aggregates in the HBP4P sample, this is due to the interactions between terminal OH groups, these aggregations have been observed even in DMF which is considered an excellent solvent for these materials [21]. The agglomerations are not observed in number and volume distributions due to their low amount in HBP4P sample.



**Fig. 8.** Hydrodynamic dimensions of HBP4P a) Volume, b) Number y c) Intensity.



Tab. 3 presents all hydrodynamic dimensions of the HBPs. The hydrodynamic diameter obtained for one step HBPs (HBP4 and HBP5) is smaller than HBPs obtained by combination of one step and step by step method (HBP1-4 and HBP1-5), but there is not a great difference, which suggests that the synthesis method has not a big influence in the hydrodynamic dimensions of HBPs.

The results of VPO and GPC indicates that HBPs hydrodynamic dimensions should be different because the molar mass is lower to fourth generation HBPs than fifth generation HBPs; this behavior is due to interactions between OH group, because this interaction leads to the formation of aggregates. Furthermore, there is no correlation between HBPs hydrodynamic dimensions and degree of branching reported in previous publication for these materials [18], this is due to the presence of aggregates, which was observed in all HBPs.

**Tab. 3.** Volume, number and intensity hydrodynamic diameter of the HBPs.

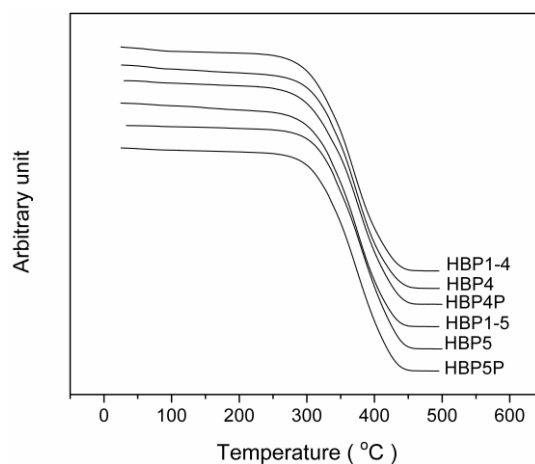
HBPs	Volume (nm)	Number (nm)	Intensity (nm)
HBP1-4	3.03	2.81	3.28 (521)
HBP4	2.37	2.13	2.72 (398)
HBP4P	4.06	3.71	4.54 (229)
HBP1-5	2.29	2.14	2.51 (165)
HBP5	2.23	2.01	2.47 (502)
HBP5P	1.81	1.40	2.69 (278)

### Refractive index

The HBPs refractive index values were: HBP5P, 1.4288; HBP5, 1.4276; HBP1-5 1.4285; HBP4P, 1.4282; HBP4, 1.4280 and HBP1-4, 1.4281. Since the refractive index of DMF is 1.427, we can conclude that the HBPs refractive index values does not change significantly, which is important for applications of this material in coating industry where color resins have to be low [22].

### Thermogravimetric analysis (TGA)

Fig. 9 shows the thermogram of HBPs. Tab. 4 presents decomposition temperature of the HBPs.



**Fig. 9.** TGA of the HBPs samples.



The thermal stability was greater to HBPs of the fifth than fourth generation; the difference in decomposition temperature ( $T_d$ ) between the HBPs of fourth generation obtained by different method is higher than the fifth generation, this is an expected results since it had been reported that the temperature of decomposition of the HBPs depend on terminal OH groups and molar mass [23].

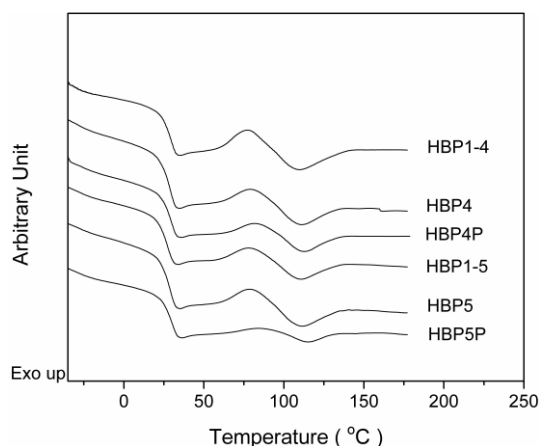
**Tab. 4.** Descomposition temperature of the HBPs.

Fourth G.	$T_d$ ( $^{\circ}\text{C}$ )	Fifth G.	$T_d$ ( $^{\circ}\text{C}$ )
HBP1-4	225.24	HBP1-5	239.46
HBP4	236.61	HBP5	242.87
HBP4P	219.55	HBP5P	244.57

Dusek et. al. [24] has shown that during synthesis of these materials occur, cyclizations reactions, this process increases the thermal stability of the HBPs. The formation of cyclic macromolecules influence more the thermal stability than the increase in mass molar and terminal OH groups [23, 24]. The synthesis method, have an influence in thermal stability only for the hydroxylated hyperbranched polyesters of fourth generation.

#### *Differential scanning calorimetric (DSC)*

All HBPs present a glass transition temperature ( $T_g$ ); between  $37.5^{\circ}\text{C}$  and  $130^{\circ}\text{C}$  is observed an endothermic peak (Fig. 10) corresponding to the fusion of ordered domains of hydrogen bonds due to the interaction of terminal OH groups [9,10]. Tab. 5 shows the glass transition, crystallization and melting temperatures ( $T_m$ ). The values of  $T_g$  of HBPs determined by DSC were between  $27.07^{\circ}\text{C}$  and  $30.45^{\circ}\text{C}$ , fifth generation HBPs had higher value of  $T_g$  than fourth generation obtained by step and combination of one step and step by step method, there are no marked  $T_g$  differences between HBPs obtained by different methods.



**Fig. 10.** DSC of the HBPs.

In HBP4P sample the segmental mobility is restricted, as it can be inferred from the higher value for crystallization temperature ( $T_c = 79.86^{\circ}\text{C}$ ). On the other hand, the melting temperature ( $T_m$ ) for HBP5P was the highest indicating that the size of the crystals is larger as compared to the other HBPs samples. The melting enthalpy

( $\Delta H_m$ ) increases with the amount of crystals; therefore the HBP5P sample presented the lower crystallinity. The difference in thermal behavior of these HBPs is due to the interaction between terminal OH groups.

**Tab. 5.** Thermal transitions and enthalpy of HBPs.

HBPs	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)	$\Delta H_f$ (°C)
HBP1-4	28.02	78.35	108.47	10.85
HBP4	28.40	76.78	109.68	5.94
HBP4P	29.62	79.86	108.57	6.09
HBP1-5	27.07	75.60	108.94	7.11
HBP5	29.02	75.12	107.92	7.75
HBP5P	30.45	78.68	113.51	2.59

## Conclusions

The HBPs presented similar refractive index values and the difference between refractive index values between solvent and HBPs solutions is low. With infrared and NMR analysis were observed the characteristic signal of the HBPs structure.

The methodology of combining two methods (one step and step by step) is a good alternative synthesis method for these materials because it allows synthesizing polymer with higher molar mass and lower polydispersity than one step method. Furthermore, the polydispersity increases with generation for all synthesis methods.  $M_n$  values of the HBPs determined by VPO were higher than GPC since VPO unlike GPC is independent of molecular structure, the order on  $M_n$  values for the methods employed in the synthesis of HBPs was: step by step > combination of methods > one step for all HBPs the same generation. All HBPs hydrodynamic dimension was nanometric and all presented aggregates. The TGA results showed that  $T_d$  of HBPs was high for HBPs of fifth generation and DSC analysis indicated that HBPs are mainly amorphous but present some crystallinity grade due to interaction between OH groups. Furthermore, in the synthesis of HBPs, side reactions may take place such as hydroxy-ester interchange and intramolecular and intermolecular etherification [21], affecting the  $M_n$ . Furthermore there is no relation between  $M_n$  and the thermal behavior observed for samples synthesized by different methods, which is attributed to side reaction, although it is well known that those side reactions occur, it is difficult to know which one is predominant.

## Experimental

### Materials

2,2-Bis(hydroxymethyl)propionic acid (DMPA), pentaerythritol (PE), p-toluenesulfonic acid (PTAS), methanol, acetone, N,N-dimethylformamide (DMF) and tetrahydrofuran (THF) were obtained from Sigma Aldrich.

### Synthesis of hydroxylated hyperbranched polyesters (HBPs)

The PE/DMPA theoretical ratio of 1/60 (fourth generation) and 1/124 (fifth generation) were employed in the synthesis of these materials. They were obtained by three different methods: one step (HBP4, HBP5), step by step (HBP4P, HBP5P) and

combination of both of them (HBP1-4, HBP1-5) using acid catalysis (PTAS). Details of the synthesis of HBPs are reported in the literature [18].

### *Characterization of HBPs*

#### **-Infrared analyses**

This was performed in a Perkin Elmer spectrometer Spectrum One model. The number of scans were 8 scans and the resolution was 4  $\text{cm}^{-1}$ .

#### **- $^{13}\text{C}$ and $^1\text{H}$ Nuclear magnetic resonance (NMR)**

The  $^{13}\text{C}$  and  $^1\text{H}$  NMR analyses were carried out in a **Bruker** AC 300 MHz spectrometer. The  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra were obtained using deuterated dimethylsulfoxide ( $\text{DMSO-d}_6$ ).

#### **-Gel permeation chromatography (GPC)**

Samples were dissolved in tetrahydrofuran and the analyses were performed in Waters 600 equipment using a column styragel with dimension of 4.6 x 300 mm, the runs were done at 30  $^\circ\text{C}$ , millennium 2000 software was used for data acquisition and linear polystyrene standards for the quantifications.

#### **-Vapor pressure osmometry (VPO)**

The analysis of vapor pressure osmometry was carried out using a Knauer vapor pressure osmometer in tetrahydrofuran at 45  $^\circ\text{C}$  in a concentration range of 1.14-7.95 g/Kg. Polystyrene standard (average number molar mass=10.500 g/mol) was used for calibration.

#### **-Electrospray ionization-mass spectrometry (ESI-MS)**

Electrospray ionization-mass spectrometry (ESI-MS) measurements were performed on an Agilent 1200 mass spectrometer (Finnigan, MAT) with an electrospray ionization (ESI) interface. A mixture of 0.1 vol.% ammonia in methanol/water (8:2, v/v) was used as the mobile phase with a flow rate of 0.8 ml/ min. The injection volume was 20  $\mu\text{l}$ . The ESI-MS conditions were as follows: drying gas temperature - 350  $^\circ\text{C}$ , ion time - 5.00 ms, drying gas flow pressure ( $\text{N}_2$ ) - 12 l/min, nebulizer pressure - 6 psi, source voltage - 4.50 kV, capillary voltage - 30.00 V. Negative scan was obtained at m/z values from 100.0 to 1500.0.

#### **-Dynamic light scattering analysis (DLS)**

Measure of dynamic light scattering were carried out on a Zetasizer Nano S series (Malvern Instruments). The DLS experiments of the 1.0 % (w/v) HBPs solution filtered previously were carried out at a temperature of 25  $^\circ\text{C}$  and at a wavelength of 633 nm.

#### **-Refractive index**

The refractive index of solutions of HBPs with concentrations of 0.5 mg/ml in DMF were obtained in a refractometer at 589 nm wave length.

### -Thermogravimetric analysis (TGA)

The thermal degradation of the HBPs was determined in nitrogen atmosphere at heating rate of 10 °C/min using TA Instruments model 2920 equipment.

### -Differential scanning calorimetry (DSC)

The glass transition temperatures ( $T_g$ ) were determined in a TA Instruments model 2920 equipment, using a heating/cooling rate of 20 °C/min, in nitrogen atmosphere.

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### References

- [1] Prevec, G.; Yagar, E.; Yigon, M. *Kem. Ind.* **2006**, *55*, 365.
- [2] Voit, B.I. *C.R. Chimie.* **2003**, *6*, 821.
- [3] Song, W.; Song, Q.; Wu, Ch. *e-Polymers.* **2006**, *53*, 1.
- [4] Zagar, E.; Majda, Z.; Podzimek, S. *Polymer.* **2006**, *47*,166.
- [5] Mckee, M. G.; Unal, S.; Wilkes, G. L.; Long, T. E. *Prog. Polym. Sci.* **2005**, *30*, 507.
- [6] Tomalia, D. *Prog. Polym. Sci.* **2005**, *30*, 294.
- [7] Malmstrom, E.; Hult, A.; Gedde, W. *Polymer.* **1997**, *38*, 4873.
- [8] Malmstrom, E.; Johansson, M.; Hult, A. *Macromolecules* **1996**, *28*, 1698.
- [9] Thomasson, D.; Boisson, F.; Girard-Reydet, E.; Mechin, F. *React. & Funct. Polym.* **2006**, *66*,1462.
- [10] Zagar, E.; Zigon, M. *J. of Chromat. A* **2004**, *1034*, 77.
- [11] Zagar, E.; Huskic, M.; Grdadolnik, J.; Zigon, M.; Zupancic-Valant, A. *Macromolecules* **2005**, *38*, 3933.
- [12] Zagar, E.; Zigon, M. *Macromolecules* **2002**, *35*, 9913.
- [13] Asif, A.; Shi, W.; Shen, X.; Nie, K. *Polymer* **2005**, *46*, 11066.
- [14] Núñez, C. M.; Chiou, B.; Andrady, A. L.; Khan, S. A. *Macromolecules* **2000**, *33*,1720.
- [15] Xu, N.; Shi, W.; Gong, M.; Feng, J. *J. Mater. Sci.* **2006**, *41*:3707.
- [16] Soccio, M.; Finelli, L.; Lotti, N.; Marchese, P.; Siracusa, V.; Munari, A. *e-Polymers* **2007**, *49*, 1.
- [17] Dzunuzovic, E.; Tasic, S.; Bozic, B.; Jeremic, K.; Dunjic, B. *React. & Funct. Polym.* **2006**, *66*, 1097.
- [18] Murillo, E. A.; Vallejo, P. P.; Sierra, L.; López, B. L. *J. Appl. Polym. Sci.* **2009**, *112*, 200.
- [19] Sunder. A.; Hanselmann, R.; Frey, H.; Mulhaupt, R. *Macromolecules* **1999**, *32*, 4240.
- [20] Chikh, L.; Tessier, M.; Fradet, A. *Polymer* **2007**, *48*, 1884.
- [21] Xu, M.; Yan, X.; Cheng, R.; Yu, X. *Polym. Int.* **2001**, *50*, 1338.
- [22] Ikhuria, E. U.; Aigbodion, A. I.; Okieimen, F. E. *Prog. Org. Coat.* **2005**, *52*: 238.
- [23] Vukovic, J.; Steinmeier, D.; Lechner, M. D.; Jovanovic, S.; Bozic, B. *Polymer. Degrad. and Stability* **2006**, *91*, 1903.
- [24] Dusek, K.; Somvarsky, J.; Smrcková, M.; Simonsick, W. J.; Wilczek, L. *Polymer Bull.* **1999**, *42*, 489.