

Characterization of Hyperbranched Polyol Polyesters Based on 2,2-Bis (methylol Propionic Acid) and Pentaerythritol

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ABSTRACT: Hyperbranched polyesters (HBPs) of fourth and fifth generation were synthesized by procedures involving one step (HBP4, HBP5), step by step (HBP4P, HBP5P), and combination of both of them (HBP1-4, HBP1-5) using 2,2-bis(methylol)propionic acid (DMPA), pentaerythritol (PE), and acid catalysis. The characterization of the polyesters was done by nuclear magnetic resonance (NMR), rheology on solution, Fourier transform infrared spectroscopy (FTIR), and acid and hydroxyl values. The degree of branching of polyesters (DB) and the average molecular mass and polymerization degree $_{\text{NMR}}$ were calculated by Frey and Fréchet methods and $(\text{DP})_{\text{NMR}}$, respectively, being higher for HBP4P sample. The molecu-

lar structure of polyesters depends mainly on of the synthesis method. The hydroxyl values were larger than 430 mg/g KOH for all HBPs, and the conversion was controlled between 90 and 93% to avoid excessive cyclization reactions. The steady shear viscosities at different temperatures and at 41.77 s^{-1} shear rate were measured for all HBPs solutions in dimethyl formamide (DMF) showing a shear thickening behavior. The flow activation energies (E_a) were calculated by Arrhenius equation. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 200–207, 2009

Key words: hyperbranched polyesters; NMR spectroscopy; rheology

INTRODUCTION

Hyperbranched polymers (Fig. 1) with dendritic architecture contain a large number of branching points and functional end groups.¹ Although the structure of these polymers is not as perfect as that of dendrimers, they have properties that resemble those of the dendrimers.² Therefore, they have gained interest for many researchers who had developed new routes for their synthesis by using different monomers.³ They are synthesized by one step or pseudo-one-step polymerization procedures.⁴ At the moment, the most intriguing and well known properties of hyperbranched polymers are their high solubility and reactivity because of the large number of end OH groups, low viscosity in solution and molten state as a result of their packed structure, the absence of entanglements, and good compatibility with other materials. These polymers have been used in several applications such as additives,⁵ coatings,⁶ blends,⁷ curing agents,⁸ etc. Additionally, some of

the hyperbranched polymers are already commercially available in the market.

Well defined monodisperse perfectly branched structures are characteristics of dendrimers, which consist of units, repeated branched dendritic, lineal and terminal units.⁹ Regardless of a convergent or divergent synthetic route, each generation is built up step-by-step with many synthetic protection and deprotection and purification steps, which make large-scale production difficult. On the other hand, hyperbranched polymers are simpler to produce on a large scale via one-pot synthesis. However, this simplified procedure yields less regular structures with very broad molar mass distributions.¹⁰ The molar mass and polydispersity index (PDI) of a hyperbranched polymer depend on the monomer functional group conversion (p) as well as its functionality. Hyperbranched polymers consist not only of dendritic and terminal repeat units but also of linear ones with one unreacted functional group. Linear units are regarded as defects in the branched structures.¹¹ The branching perfection of AB_2 systems is characterized by an average degree of branching (DB), which is defined by Fréchet et al.¹² as:

$$\text{DB} = \frac{D + T}{D + L + T} \quad (1)$$

Where D , L , T are the fraction of dendritic (two reacted hydroxyl groups and one reacted carboxyl

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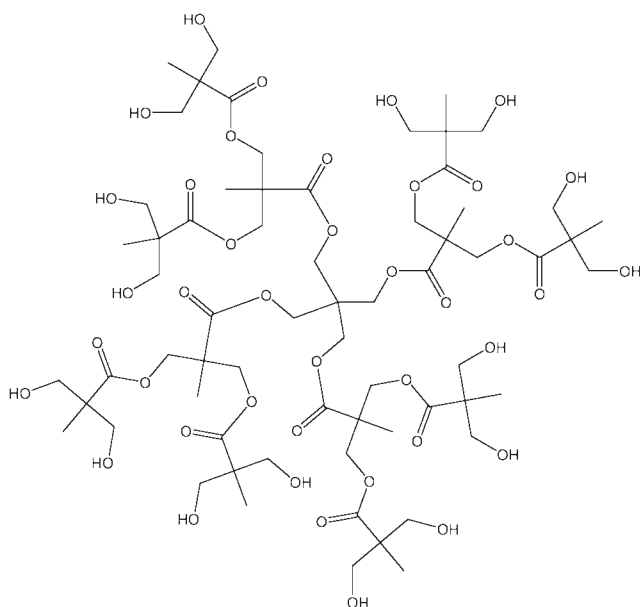


Figure 1 Typical structure of a hyperbranched polyester based on DMPA.

groups), linear (one reacted hydroxyl groups and one unreacted hydroxyl groups), and terminal repeat units (two unreacted hydroxyl groups and one reacted carboxyl groups). $DB = 1$ for a perfect dendrimer and it is <1 for hyperbranched polymers. Frey et al.¹³ proposed another definition of DB, which does not take into account the terminal units, given by:

$$DB = \frac{2D}{2D + L} \quad (2)$$

Theoretical and real systems reveal that the control on molecular mass average (MMA) and molar mass distribution (MMD) of HBPs can be achieved by using multifunctional core molecules as limiting stoichiometric reagent to the reaction system. Control on the molar mass and the polydispersity of the HB aliphatic polyesters has been demonstrated in step by step polycondensation reaction of AB_2 monomers using multifunctional core moieties, where stoichiometric amounts of DMPA monomer, corresponding to the theoretical dendritic composition of each specific generation, were added successively to the core molecules in bulk under acidic catalysis.^{4,11}

Most of the studies published in the literature have focused on the synthesis and relationship between molecular structure and properties of hyperbranched polymers, as well as on their applications.^{11–16} Because of the relationship between rheology and processing properties, characterization of the rheological flow behavior of dendritic polymers is important. Such studies can provide insights into the intermolecular interactions and the effects that molecular variables such as generation number, na-

ture of peripheral functional groups, and degree of branching have on bulk properties.^{13,17}

The aim of this work was to characterize hyperbranched polyesters with a theoretical core/monomer ratio of 1/60 (fourth generation) and 1/124 (fifth generation) obtained by three different methods and compare the obtained results. The structural composition is determined by ¹H-NMR and ¹³C-NMR, infrared spectroscopy (FTIR). Furthermore, this work involves the rheological study of concentrated solutions of HBPs at different temperatures and the interactions between OH groups from flow activation energies.

EXPERIMENTAL

Materials

2,2-Bis(hydroxymethyl)propanoic acid (DMPA), pentaerythritol (PE), *p*-toluenesulfonic acid (PTAS), pyridine, acetic anhydride, xylene, acetone and isopropyl alcohol, *N,N*-dimethyl formamide (DMF) were obtained from Aldrich and used as received.

Syntheses of HBPs

Polyesters HBP1-4 and HBP1-5

The HBPs were obtained by the bulk polycondensation of DMPA with PE using PTAS as a catalyst according to the procedure presented by Seiler¹⁶ The respective amounts of DMPA and PE by Malström¹¹ for obtaining the first generation were mixed, under nitrogen atmosphere, into a reactor equipped with a mechanical stirrer, a condenser, and a regulated heating device. The system was heated until the reaction was complete and then the stoichiometric amount of DMPA and adequate amount of PTAS were added to obtain the wanted number of generation (fourth to HBP1-4 and fifth to HBP1-5).

Polyesters HBP4P, HBP5P, HBP4, and HBP5

HBP4P and HBP5P were obtained step by step, maintaining the same synthesis conditions of HBP1-4 and HBP1-5 but adding stoichiometric amounts of DMPA and PTAS for obtaining the respective generation, until to get the final fourth or fifth generation. On the other hand, HBP4 and HBP5 were synthesized at the same conditions as the others HBP but in one step.

Hydroxyl value and conversion

The conversion of the reaction, P , with respect to the acid value was calculated using the eq. (3):

$$\frac{P}{C_0} = \frac{C_0^- C_t}{C_0} \quad (3)$$

TABLE I
Hydroxyl Value and Percent of Conversion of the HBP

Sample	Hydroxyl value (mg/g) KOH	Conversion (%)
HBP4P	435.79	92.77
HBP4	454.19	92.16
HBP1-4	450.34	90.40
HBP5P	448.03	92.16
HBP5	443.36	90.16
HBP1-5	442.86	92.23

Where C_0 and C_t are the acid value at zero and t reaction time, respectively. The hydroxyl value was calculated according to the ASTM D-4274 standard test method.

Infrared analyses

The infrared analyses were realized in a Perkin-Elmer spectrometer Spectrum One model, between 4000 and 450 cm^{-1} , eight scans and 4 cm^{-1} of resolution.

NMR analyses

The ^{13}C and ^1H -NMR analyses were carried out in a Bruker AC 300 MHz spectrometer. The ^{13}C -NMR spectra were obtained using deuterated dimethylsulfoxide ($\text{DMSO-}d_6$) and ^1H -NMR spectra, in $\text{DMSO-}d_6$ and in $(\text{D}_2\text{O})/\text{DMSO-}d_6$ (1 : 4) as solvent. Chemical shifts were referenced to $\text{DMSO-}d_6$ at 39.43 ppm for the ^{13}C and at 2.5 ppm for the ^1H spectra. Quantitative ^{13}C -NMR spectra were recorded using inverse gated decoupling mode with a suppressed NOE effect (a relaxation delay of 20 s, an acquisition time of 5 s and up to 2000 repetitions). The HBPs were analyzed without further purification.

Rheological characterization

HBPs solutions of 25-wt % were prepared in N,N -dimethyl formamide (DMF). Flow and oscillatory experiments were done with each solution at fourth different temperatures (10, 23, 35, and 50°C). Viscosity and shear stress were measured as a function of shear rate at a strain of 2% by using MRC 301 rotational Rheometer and cylindrical geometry.

Dynamic light scattering analysis

The same 25 wt % solutions of all HBPs were filtered for the dynamic light scattering in a Zetasizer Nano S series (Malvern Instruments). The dynamic light scattering analysis (DLS) experiments were performed at different temperatures (10, 23, 35, and 55°C) and at wavelength of 633 nm.

RESULTS AND DISCUSSION

Hydroxyl and conversion values

Table I shows the different hydroxyl values and conversions of HBPs. All samples present high hydroxyl values, being higher for HBP4. The reaction conversion was followed measuring the acid value to obtain conversions between 90 and 93%, avoiding in this way cyclization reactions.

Infrared results: Evidence of the conversion of acid groups

The disappearance in the HBPs spectra of the 1685 cm^{-1} signal, assigned to the DMPA acid group, indicates that the reaction has been complete in all cases. The absorptions at 1725 cm^{-1} and 1306–1046 cm^{-1} are because of the presence of new formed ester groups (Fig. 2). The signals due to OH groups appear at 3420 cm^{-1} .

Determination of molecular mass average and degree of polymerization NMR

^{13}C -NMR of HBPs

In the ^{13}C -NMR spectrum of HBP4P (Fig. 3), quaternary carbons in the region 45.3–50.3 ppm, corresponding to terminal (T), linear (L) and dendritic (D) units can be observed. The quaternary carbons, adjacent to acid groups (focal points) around 45.6 ppm, are not observed for the HBPs studied here, although, it has been demonstrated that carboxyl groups in these type of materials are present mainly as focal dendritic points (two reacted hydroxyl groups and unreacted OH on the carboxyl groups). The absence of these quaternary carbons indicates

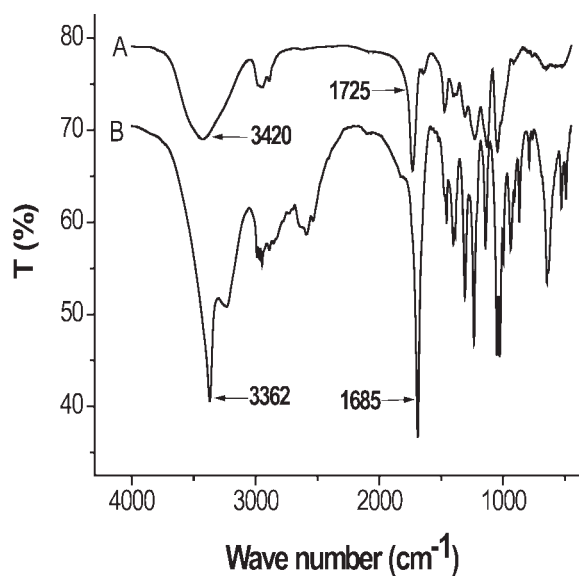


Figure 2 Infrared spectra; (a) HBP4 (b) DMPA.

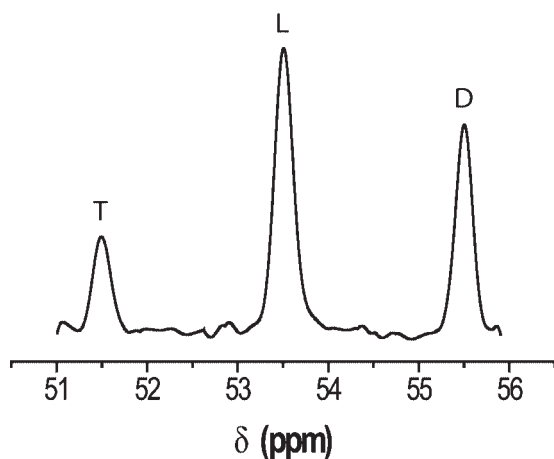


Figure 3 ^{13}C -NMR spectrum of HBP4P in $\text{DMSO-}d_6$ (3 wt %). The quaternary carbon region of the spectra has been magnified: T, terminal repeat units (50.33 ppm); L, linear repeat units (48.33); and D, dendritic repeat units (46.31).

that the homopolymerization reaction of the DMPA monomer, which leads to the formation of HBP structures without a core molecule (B_2) is not taking place appreciably. This happens because steric hindrance of the bulky HBP structure makes difficulties to the carboxyl groups accessibility.⁴

The DBPs were calculated according to eqs. (1) and (2). The HBP4P sample presents the highest DB value equal to 0.4745 (Table II). The maximum DB value for HBPs formed by a random polymerization of AB_2 monomers is 0.5 when the groups have the same reactivity. The DB value can be increased adding AB_x slowly to the core molecules B_f in solution¹⁸ or by activation of the second B group of the AB_2 monomers after the reaction of the first B group¹⁹ and by polymerization of the pre synthesized perfect dendrons.^{4,13}

The differences between the DB values obtained by both methods arise because Fréchet equation does not take in account the terminal units and the Frey one does it, therefore in Fréchet calculations there is overestimating of the DB value due to the presence of unreacted monomer.

The fractions of terminal, linear and dendritic units in the HBPs (Table III) were calculated from

TABLE II
Results Obtained From the ^{13}C NMR Spectra of HBPs: Intensities of the T, L, and D Signals and DBs Values Calculated According to Fréchet and Frey Equations

Sample	$I(\text{T})$	$I(\text{L})$	$I(\text{D})$	DB Fréchet	DB Frey
HBP4P	1.00	1.7500	0.5800	0.4745	0.3986
HBP4	1.00	2.4167	0.4167	0.3698	0.2564
HBP1-4	1.00	1.7275	0.5225	0.4685	0.3769
HBP5P	1.00	2.1267	0.2067	0.3620	0.1627
HBP5	1.00	2.2310	0.2675	0.3624	0.1934
HBP1-5	1.00	2.0267	0.2867	0.3883	0.2205

TABLE III
Fractions of Repeat Units in the HBPs

Sample	$X_T(\%)$	$X_L(\%)$	$X_D(\%)$
HBP4P	30.05	52.60	17.43
HBP4	26.10	63.00	10.90
HBP1-4	30.80	53.10	16.10
HBP5P	29.99	63.79	6.20
HBP5	28.58	63.77	7.65
HBP1-5	29.30	59.30	11.40

the intensities obtained from the ^{13}C -NMR spectrum. The terminal fraction is smaller for HBP obtained in one step and the dendritic fraction is smaller for HBP obtained by one fifth generation (HBP5P, HBP5, and HBP1-5). The fractions of dendritic units decrease when the generation increases producing more imperfect polymers.

^1H -NMR results of HBPs

The Figure 4(a) shows signals at 4.95 ppm (protons of the $-\text{OH}$ groups from the linear units), 4.64 ppm (protons of the $-\text{OH}$ groups from the terminal units), 4.108 ppm (methylene groups adjacent to reacted hydroxyl groups: $-\text{CH}_2\text{OR}$), and 3.39 ppm (methylene groups attached to unreacted hydroxyl groups: CH_2OH). The methyl protons belonging to the terminal (T), linear (L) and dendritic (D) units resonate at around 1.01, 1.07, and 1.16 ppm, respectively. Because the water protons appear in the same region of the methylene protons of CH_2OH causing interference in quantitative analysis, it was necessary to obtain the HBPs spectra using also 1 : 4 $\text{D}_2\text{O}/\text{DMSO-}d_6$ solvents mixture [Fig. 4(b)] as it is recommended by Vukovic.²⁰ The Figure 4(b) shows the separation of signals for water (4.0 ppm) and CH_2OH (3.5 ppm)

$$I(\text{CH}_2\text{OH})_{\text{DMSO}} = \frac{I(\text{CH}_3)_{\text{HBP,DMSO}} I(\text{CH}_2\text{OH})_{\text{mix}}}{I(\text{CH}_3)_{\text{HBP,mix}}} \quad (4)$$

Where $I(\text{CH}_3)_{\text{HBP,DMSO}}$, $I(\text{CH}_2\text{OH})_{\text{DMSO}}$, $I(\text{CH}_3)_{\text{mix}}$ and $I(\text{CH}_2\text{OH})_{\text{mix}}$ are the intensities of the $-\text{CH}_3$ group in $\text{DMSO-}d_6$ and the $\text{D}_2\text{O}/\text{DMSO-}d_6$ solvent mixture, respectively.

The intensities of the methylene protons $I(\text{CH}_2)_{\text{B}_4}$ in the PE are calculated according to eq. (5):

$$I(\text{CH}_2)_{\text{B}_4} = I(\text{CH}_2) - I(\text{CH}_2)_{\text{HBP+B}_2} \quad (5)$$

Where $I(\text{CH}_2)$ is the intensity of the methylene protons of the HBPs with both types of core (B_4 and B_2):

$$I(\text{CH}_2) = I(\text{CH}_2\text{OH}) + I(\text{CH}_2\text{OR}) \quad (6)$$

The intensity of the methylene protons of HBPs and B_2 core, $I(\text{CH}_2)_{\text{HBP+B}_2}$ is:

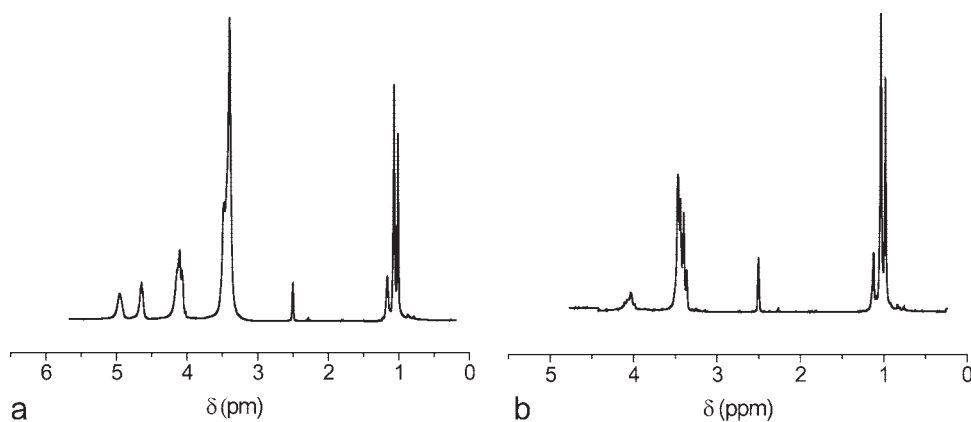


Figure 4 ^1H -NMR spectra of HBP4P; (a) $\text{DMSO-}d_6$, (b) 1 : 4 $\text{D}_2\text{O}/\text{DMSO-}d_6$.

$$I(\text{CH}_2)_{\text{HBP}+\text{B}_2} = \frac{4}{3} I(\text{CH}_3)_{\text{HBP}} \quad (7)$$

where $I(\text{CH}_3)_{\text{HBP}}$ is the sum of the intensities of the methyl groups of the HBP. The N_{B_4} fraction of core molecules and the $N_{\text{M}+\text{B}_2}$ fraction of monomer units plus the new core (B_2) molecules, and Table IV shows the values of the intensities of $(\text{CH}_3)_{\text{HB}}$, (CH_2OH) , (CH_2OR) and OH groups of HBPs, are calculated by eq. (8).

$$N_{\text{B}_4} = \frac{I(\text{CH}_2)_{\text{B}_4}}{8} \quad N_{\text{M}+\text{B}_2} = \frac{I(\text{CH}_3)_{\text{HBP}}}{3} \quad (8)$$

The average number of monomer plus B_2 core units per core molecule is:

$$\frac{N_{\text{M}+\text{B}_2}}{N_{\text{B}_4}} = n_L + n_D + n_T + n_{\text{B}_2} \quad (9)$$

Where n_L , n_D , n_T , n_{B_2} are the average numbers of terminal, linear, dendritic units and B_2 core molecules, respectively. These values can be calculated using the eqs. (9)–(12). n_{B_2} was zero in all the cases.

$$n_L = \frac{I(L)}{I(T)} n_T \quad (10)$$

$$n_D = \frac{I(D)}{I(T)} n_T \quad (11)$$

$$n_{\text{B}_2} = \frac{I(\text{COOH})}{I(T)} n_T \quad (12)$$

The average numbers of terminal, linear and dendritic units were higher for HBP4P. This polymer presents approximately an average value of thirty OH groups at the periphery and the HBP1-4 only eighteen (Table V). The average number of OH groups is very important because the modification with others polymers is more effective as the number of OH groups increases²¹. This result suggests that HBPs can be produced in fourth generation by combination of one step and step by step methods, which requires less reaction time. The polymer obtained by a fifth generation presents the smallest values of terminal units.

Because n_{B_2} is zero, the fractions of B_2 core molecules is zero. Then, the fraction of the monomer units is:

$$N_M = N_{\text{M}+\text{B}_2} \quad (13)$$

The degree of polymerization $(\text{DP})_{\text{NMR}}$ and number average molar mass (MMA) are calculated using eqs. (14) and (15), respectively.

$$(\text{DP})_{\text{NMR}} = \frac{N_M}{N_{\text{B}_4}} \quad (14)$$

TABLE IV
Intensities of the ^1H NMR Signals of Individual Groups for the HBPs

Sample	$I(\text{CH}_3)_{\text{HB}}$	$I(\text{CH}_2\text{OH})$	$I(\text{CH}_2\text{OR})$	$I(\text{OH})$
HBP4P	4.97	3.81	3.08	1.27
HBP4	4.76	3.64	3.29	1
HBP1-4	3.30	2.52	2.16	1
HBP5P	3.96	2.97	2.80	1
HBP5	4.40	3.22	3.29	1
HBP1-5	2.99	2.21	2.32	1

TABLE V
Average Number of Monomer Plus B_2 Core Molecules. Average Numbers of Terminal, Linear, and Dendritic Units

Sample	$N_{\text{M}+\text{B}_2}$	N_{B_4}	$N_{\text{M}+\text{B}_2}/N_{\text{B}_4}$	n_T	n_L	n_D
HBP4P	1.65	0.033	49.73	14.93	26.13	8.66
HBP4	1.58	0.073	21.77	5.67	13.72	2.37
HBP1-4	1.10	0.036	30.60	9.36	16.16	4.89
HBP5P	1.32	0.061	21.48	6.44	13.70	1.33
HBP5	1.46	0.081	18.18	5.19	11.59	1.38
HBP1-5	0.99	0.068	14.68	4.43	8.98	1.27

TABLE VI
Values of $(DP)_{NMR}$ and MMA

Sample	$(DP)_{NMR}$	MMA
HBP4P	49.73	5904.30
HBP4	21.77	2661.50
HBP1-4	25.77	3125.50
HBP5P	21.48	2627.80
HBP5	18.17	2244.60
HBP1-5	14.68	1839.20

$$MMA = (DP)_{NMR}[M_{DMPA} - M_{water}] + x_{B_4}M_{B_4} \quad (15)$$

Where M_{DMPA} , M_{water} , and M_{B_4} are the molar masses of DMPA, water and PE, respectively. x_{B_4} , fraction of the B_4 core molecules is 1.

As, it is expected according to the results of Table VI the value of DP and MMA for HBP4P, calculated by this method, were the highest ones. These values are smaller for the fifth generation HBPs. MMA is significantly lower than the theoretical molar mass (7096 and 14,520 g/mol for fourth and fifth generation, respectively). This can be due to the presence of side reactions that affects the MMA such as the intramolecular hydroxyl-ester interchange between groups of the same branch, which decreases the MMA.²² The $(DP)_{NMR}$ is higher for the fourth generation HBPs, obtained by different methods, than for those of the fifth generation.

The COOH (focal point) groups do not appear in ¹³CNMR spectra probably because most of them react with the less hindered OH groups of terminal units, by direct intramolecular esterification. This side reaction is not taken into account in the methodology employed in this quantitative study.

Rheological study: steady shear and flow activation energy

The viscosity of the HBPs decreases with increase of temperature but at all temperatures the HBP5P (Fig. 5), HBP1-5, HBP1-4, HBP4 present a considerable increase in their viscosity at high values of shear rate or "shear-thickening behavior". As the temperature increases, this increase in viscosity is more abrupt and occurs at lower shear rate values. A

TABLE VII
Flow Activation Energies of the HBPs

Sample	R^2	Slope(E_a/R)	E_a (KJ/mol)
HBP4P	0.994	1602.90	13.33
HBP4	0.996	2001.10	16.64
HBP1-4	0.981	1936.30	16.10
HBP5P	0.974	1851.50	15.39
HBP5	0.979	2148.40	17.86
HBP1-5	0.998	1924.20	15.99

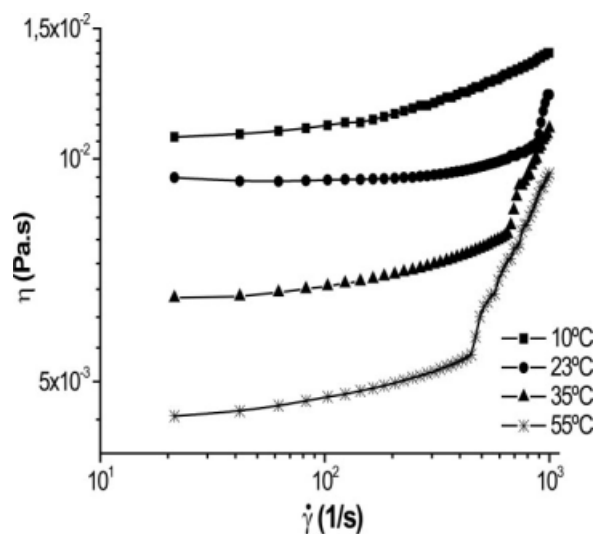


Figure 5 Steady shear viscosity at various temperatures for HBP5P.

thermolabile network formed due to the strong self-association of polar groups has been proposed to explain this viscosity enhancement phenomenon.²³

For HBP4P (Fig. 6) and HBP5 the abrupt increase of viscosity does not occur at 10 and 23°C, indicating less polar interaction than in the other ones.

In general, the HBPs exhibit a range of high linearity in the plots of shear stress versus shear rate due to the absence of physical entanglements (Fig. 7). The linearity disappears due to strong interactions between polar hydroxyl groups.

Because the steady shear viscosity of the HBPs increases linearly with temperature, it is possible to calculate their flow activation energies (E_a) by using the Arrhenius equation. The Figure 8 shows the

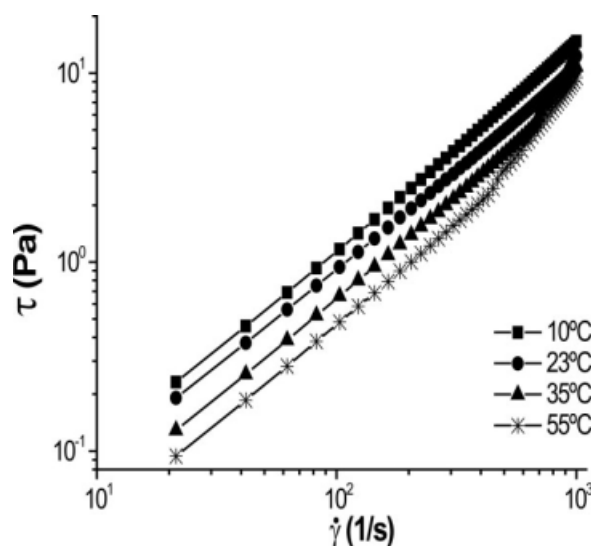


Figure 6 Steady shear viscosity at various temperatures for HBP4P.

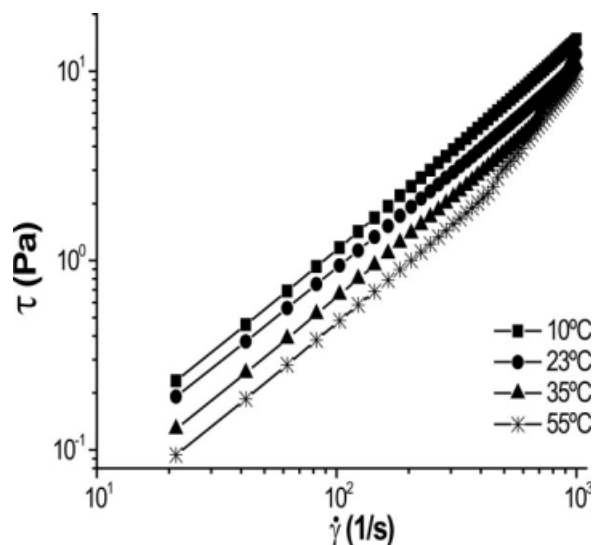


Figure 7 Shear stress versus shear rate for HBP1-4 at various temperature.

Arrhenius plots (\ln viscosity vs. $1/T$) for all of the 25 wt % HBPs solutions in DMF, obtained at 41.77 s^{-1} shear rate.

The correlation factors and flow activation energies of the HBPs indicate a good linear fit (Table VII). The high flow activation energy has been attributed to the presence of polar domains in the solutions, where strong intermolecular interactions between polar end-hydroxyl groups occur, increasing the flow resistance.²⁴

Excepting the HBPs obtained by combination of one step and step by step methods (HBP1-4 and HBP1-5), for which the E_a values are similar, all HBPs of fourth generation exhibit lower E_a values than the HBPs of fifth generation. Vukovic²⁰ shows that 30% wt solutions in *N*-methyl-2-pyrrolidinon of HBPs of fourth and fifth generation at temperature

between 10 and 50°C have a Newtonian behavior with EA values around 27.0 KJ/mol. The higher EA values in this case can be associated with solvent and concentration used for preparing the HBPs solutions.

DLS study: particle size and presence of agglomerates

The behavior of the HBPs in solution was studied by DLS to elucidate the effect of temperature, used in rheological analysis, on the particle size and therefore on the interaction of them. The intensity distribution versus particle size is very sensible for detecting the presence of aggregates because large particles scatter more the light than small ones. These distributions are shown in Figure 9(a–c) for HBP5P at three different temperatures. The average particle size increases as the temperature decreases (55°C: 0.87 nm, 35°C: 1.02 nm, 23°C: 2.31 nm) Furthermore, agglomerations are detected at all temperatures, indicating the presence of interactions of macromolecules.

However, the agglomerations represent a very small fraction because the distribution in number and volume shows practically only a population of particles (Fig. 10). Because the particle size depends not only on temperature but also on the shear effects, the information obtained by DLS in the absence of shear is not enough for explaining the interaction of the HBPs in presence of shear. But it is important to emphasize that at 23°C, it required more shear rate to observe interaction (Fig. 5), which is possibly because of a larger particle size and therefore smaller surface area, which generates lower interaction than at higher temperatures where smaller particle size were observed.

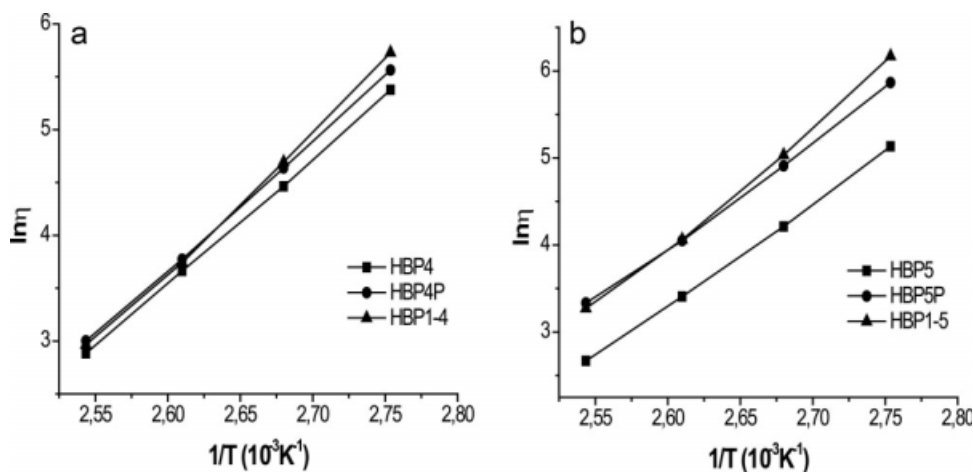


Figure 8 Arrhenius Plot of steady shear viscosity (η) for all HBP; (a) HBP4P, HBP1-4, and HBP4. (b) HBP5, HBP1-5, and HBP5P.

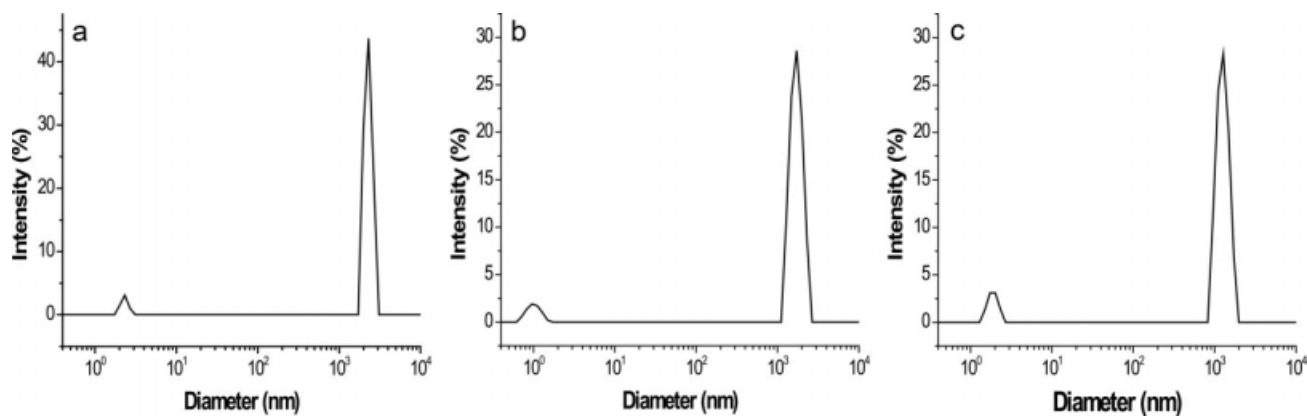


Figure 9 Intensity distribution of HBP5P: (a) 23°C (b) 35°C (c) 55°C.

CONCLUSIONS

In this study, an extensive characterization of hyperbranched polyol polyesters based on 2, 2-bis (methylol) propionic acid) and pentaerythritol and prepared by three different methods, is done.

The DB, $(DP)_{NMR}$, and MMA for the fourth generation HBPs obtained step by step are higher than those for the fifth generation and also higher than the values reported in the literature for the fourth generation HBPs.⁴ All MMA of the HBPs were lower than the theoretical values because of the occurrence of side reactions. The degree of imperfection of the HBPs increases as the generation increases, which are corroborated by the higher dendritic fraction for the fourth generation than for the fifth one. The presence of unreacted carboxyl groups was not detected by NMR or FTIR; and therefore, we can conclude that the homopolymerization did not take

place appreciably as one of the possible side reactions.

All of the HBPs exhibit a region of high linearity in the graphic shear stress versus shear rate because of the absence of the physical entanglement, followed by a shear thickening behavior due to interactions between molecules. The DLS study indicates that the HBPs have low agglomeration degree and are mainly constituted by particles with sizes between 0.8 and 2.3 nm.

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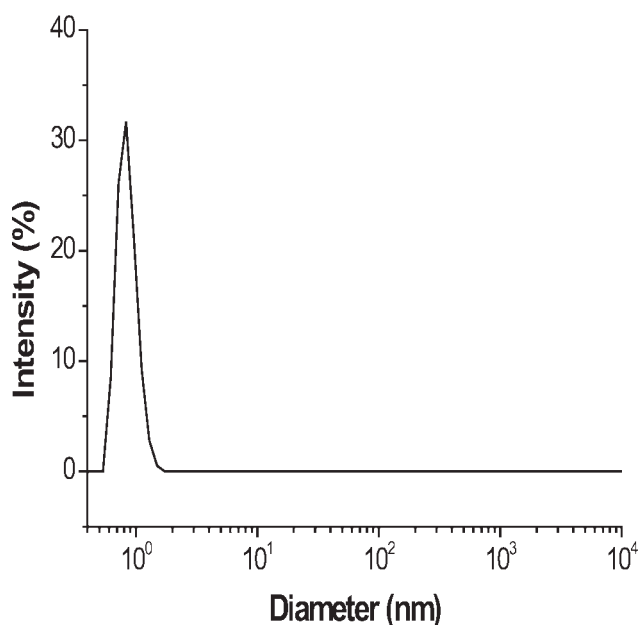


Figure 10 DLS number distribution of HBP5P at 35°C.