

Rheological Behavior in the Molten State and Solution of Hyperbranched Polyester of Fourth and Fifth Generation

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ABSTRACT: The rheological behavior in the molten state and solution of hyperbranched polyol polyesters (HBPs) obtained by one step (HBP4, HBP5), step by step (HBP4P, HBP5P), and combination of both (HBP1-4, HBP1-5) was studied. Under conditions of dynamic oscillatory shear, all HBPs presented a shear-thinning behavior and under steady shear they showed a Newtonian behavior. Also, the steady shear viscosities decreased with increasing temperature. The behavior of HBPs was mainly viscous, except for the HBP4P that showed higher storage modulus and reduction of complex viscosity when increasing the angular frequency. The HBPs presented higher complex viscosity than steady shear and they did not fol-

low the Cox-Merz rule. The HBPs in solution presented a plateau region at shear rate lower than 40 s^{-1} but a shear-thickening behavior at shear rate higher than 40 s^{-1} . The viscosities of HBPs in solution (in the plateau region) and molten state increase in the following order: HBP5P > HBP1-5 > HBP4P > HBP1-4 > HBP4 > HBP5. These results are not in agreement with the values of the number average molar mass obtained by vapor pressure osmometry due to different interaction between HBPs molecules. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 929–935, 2011

Key words: polyesters; hyperbranched; rheology; solution properties

INTRODUCTION

Hyperbranched polymers (HBPs) are members of a polymer family called dendritic polymers, which are a novel class of macromolecules with highly branched structures and unique important characteristics. The dendritic polymers are monodisperse (perfect structures), and they are highly branched with a high peripheral functionality. They are synthesized from molecules possessing at least two different functional groups such as AB_x .¹ The HBPs are polydisperse and have linear units that introduce irregularities in the structures² as illustrated in the Figure 1. HBPs have attracted great attention recently due to their intriguing molecular structures and potential applications on the synthesis of materials, such as coating,³ resins,^{4,5} sensors,⁶ catalysts, photochemical molecular devices,⁷ and membranes.^{8–10} They can be readily synthesized on a larger scale at a more reasonable cost than dendritic polymers.¹¹ HBPs have better properties, such as high solubility in solvents and low viscosity in molten state compared with lin-

ear polymers due to the lack of entanglements and to their packed structure.¹² Rheological flow behaviour is one of the most important macroscopic properties for the HBPs. It depends on the molecular features, such as size, shape, density, flexibility, and the specific nature of the intermolecular interactions.¹³

The rheology is an important technique for the determination of the molecular-level structural properties of polymeric materials, and it provides engineering parameters for different applications such as materials processing.^{14,15} Due to the close relationship between rheology and processing properties, characterization of the rheological flow behavior of the HBPs is of fundamental importance. Indeed, HBPs rheological study can provide insight of the effects that molecular variables, such as generation number, nature of peripheral functional groups and degree of branching have on bulk properties.¹⁶ HBPs have a significantly lower intrinsic viscosity, Mark-Houwink exponent, hydrodynamic volume, and radius of gyration, in comparison to their linear analogues of the same molar mass. Also, the second virial coefficient for a branched polymer is always lower than that for the homologous linear polymer.¹⁷ It has been found that dendrimers solutions with concentrations as high as 75 wt % exhibit typical Newtonian behavior and that dendrimers in molten state do not show abrupt slope change in zero-shear viscosity when plotted as a function of molecular weight on a

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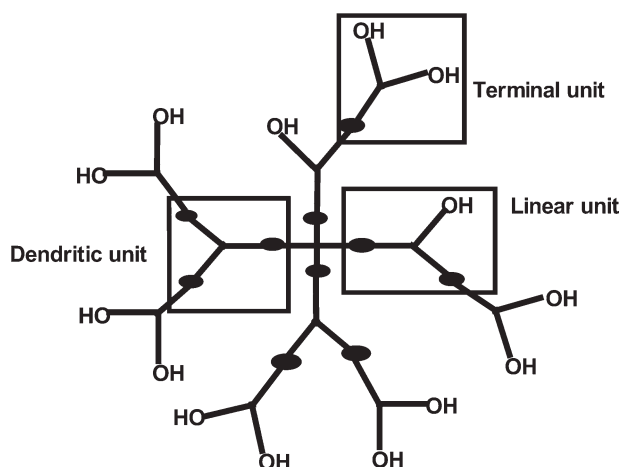


Figure 1 Typical structure of hyperbranched polyol polyester.

logarithmic scale.^{13,18} These results indicate that no physical entanglements are present in these systems.

Although many dendritic materials have been successfully synthesized and characterized,^{19–21} the melt rheology of HBPs has been less studied. One of the few melt rheology study is reported by Hsieh et al.²² for aliphatic HBPs of second, third, fourth, and fifth generation obtained in one step named Boltorn H20, H30, H40, and H50. The results showed that HBPs of lower generation (H20 and H30) have the higher number of end OH groups and therefore higher interactions between them. Also, they exhibited shorter linear viscoelastic (LVE) regions compared with Boltorn polymers of higher generations (H40 and H50). Furthermore, Boltorn H20 and H30 showed shear-thinning behavior in both oscillatory and steady shear whereas H40 and H50 are Newtonian in both deformation conditions. The Cox-Merz rule does not apply for all the Boltorn polymers.²²

The aim of this study is to undertake rheological characterization in the molten state and solution of a series of HBPs with a theoretical core/monomer ratio of 1/60 (fourth generation) and 1/124 (fifth generation). The Cox-Merz rule and the relationship between molecular weight and viscosity were investigated.

EXPERIMENTAL

Materials

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

HBPs synthesis

All HBPs of fourth generation; HBP1-4, HBP4, HBP4P and fifth generation; HBP1-5, HBP5 and HBP5P were synthesized by the bulk polycondensation of DMPA with PE using PTAS as a catalyst according to the procedure given by Malström et al.²³ and Murillo et al.²⁴ Some properties of these materials, such as hydroxyl value, degree of branching, and conversion percent are reported in a previous paper.²⁴

Rheological characterization

MRC 301 rotational rheometer was used to determine rheological properties under oscillatory and steady shear conditions; 25-mm parallel-plate fixtures were used with a constant gap of 1.0 mm for all measurements. The oscillatory experiments were performed in the linear viscoelastic region and the measurements were performed at a frequency of 1 Hz and strain of 2% in the temperature range

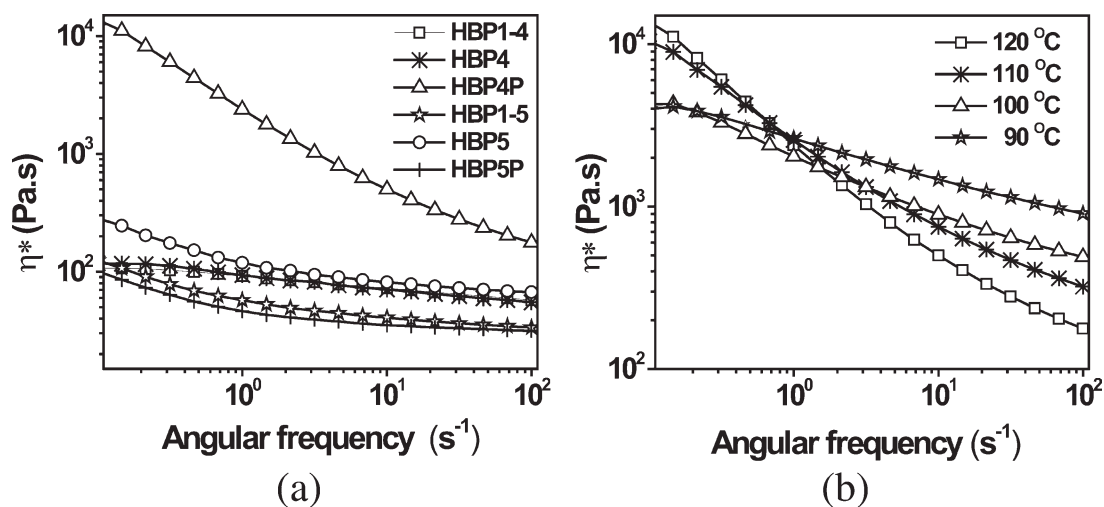


Figure 2 Complex viscosity vs. angular frequency; (a) all HBPs at 120°C and (b) HBP4P at 90, 100, 110, and 120°C.

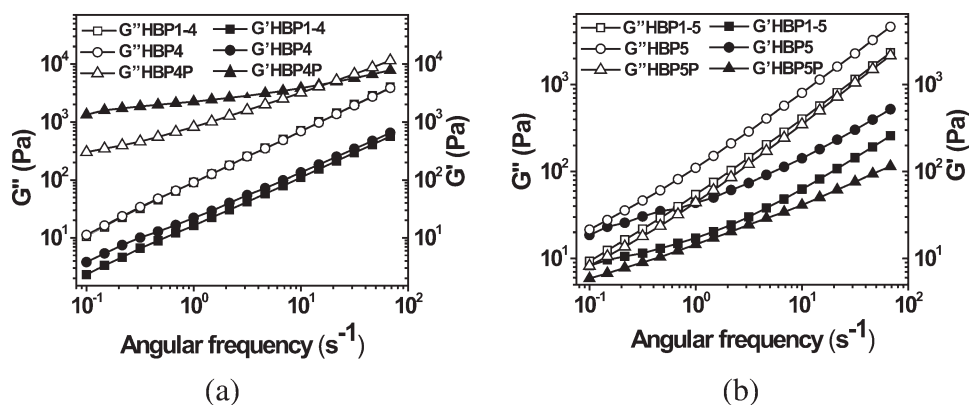


Figure 3 Storage and loss modulus vs. angular frequency of the HBPs at 120°C; (a) Fourth generation and (b) Fifth generation.

between 90 and 120°C. In all experiments the temperature was controlled with a peltier plate and a precision of 0.1°C.

Flow experiments were done to HBPs concentrated solutions (25 wt %) in DMF at 23°C at a strain of 2%.

Vapor pressure osmometry

Vapor pressure osmometry (VPO) was carried out in Knauer vapor pressure osmometer using DMF in a concentration range of 10.55–42.19 g/kg at 100°C. Benzil was used for calibration. The experiments were repeated five times and the data reported was the average of the five measurements.

RESULTS AND DISCUSSION

Dynamic oscillatory shear

The study of complex viscosity (η^*) of HBPs versus angular frequency at 120°C showed that all HBPs presented a decreases of η^* with increasing angular frequency [Fig. 2(a)]. This is due to the interaction between OH groups which are in the periphery of the macromolecules and under the experimental conditions; the interactions disappeared because they are broken easily. The η^* for HBP4P showed higher reduction due to the higher number of OH groups in the periphery, and therefore higher interactions [Fig. 2(a)] and also η^* decreased with increasing the temperature [Fig. 2(b)].

The study of elastic and loss modulus (G' and G'') versus angular frequency for all fourth generation [Fig. 3(a)] and fifth generation [(Fig. 3(b))] HBPs at 120°C showed that HBP4P was the only sample that presented transition from elastic to viscous. The elastic behavior predominated from 0.1 and 21.5 s^{-1} ($G' > G''$) [Fig. 3(a)]. Then, after 21.5 s^{-1} angular frequency, predominated the viscous behavior ($G' < G''$).

For the other HBPs, G'' is higher than G' indicating a viscous behavior for the frequency range studied.

Figure 4 showed the behavior of G' and G'' versus angular frequency at 90, 100, and 110°C of the HBP4P sample. At low angular frequency (between 0.1–1 s^{-1}), G' increased with increasing temperature. This sample presented the transition from elastic to viscous at 110°C and at angular frequency of 3.16 s^{-1} . It is observed that the elastic to viscous transition at 120°C appeared at higher angular frequency [Fig. 3(a)]. Therefore, it can be concluded that with increasing temperature, elastic behavior also increases. The presence of intersection between G' and G'' was observed at 110 and 120°C for the HBP4P sample. This behavior can be due to the presence of strong interactions between OH groups present, but are not due to the presence of entanglements.^{18,22} These interactions led to the formation of some kind of supramolecular microstructure or transient quasinet network capable of elastic deformation when it is exposed to external stress.¹⁴ This behavior was not observed at 90 and 100°C.

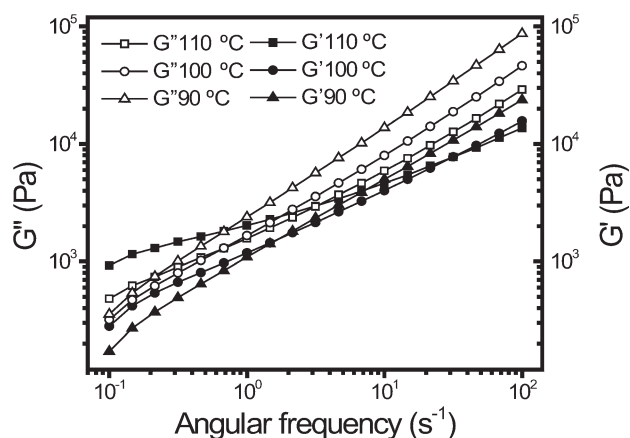


Figure 4 Storage and loss modulus vs. angular frequency of the HBP4P at different temperatures.

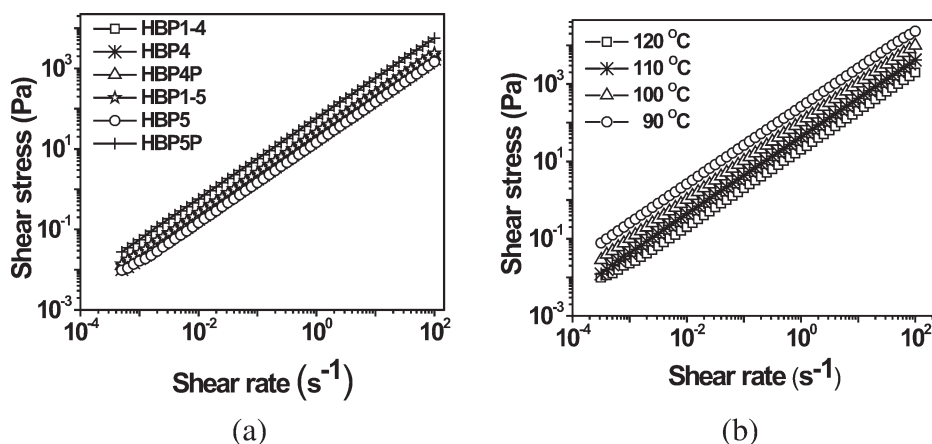


Figure 5 Shear stress vs. shear rate relationships; (a) all HBPs at 120°C and (b) HBP4P at different temperatures.

Steady shear viscosity in molten state

Figure 5(a,b) showed the shear stresses versus log shear rates for HBPs at 120°C and for HBP4P at 90, 100, 110, and 120°C, respectively. A linear behavior is observed indicating that the structures of HBPs did not present physical entanglements. The viscosity decreased with increasing temperature due to higher mobility of the macromolecules.

A plot of steady shear viscosity versus shear rate is shown for all HBPs at 120°C [Fig. 6(a)] and for HBP4P at 90, 100, 110, and 120°C [Fig. 6(b)]. It can be observed that all HBPs showed constant viscosity in the total range of shear rates utilized and since HBPs viscosities are independent of shear rate, all HBPs including HBP4P exhibited typical Newtonian behavior at all temperatures studied. The viscosity values were affected by the molecular weight and the interaction of OH groups,^{25,26} increasing in the following order: HBP5P > HBP1-5 > HBP4P > HBP1-4 > HBP4 > HBP5. The HBPs in molten state under low steady shear conditions do not present entanglements, as the steady shear viscosity analysis

showed that the HBP4P sample exhibited a Newtonian behavior.

Verification of Cox-Merz rule of HBPs

Figure 7(a,b) showed a comparison of η^* and η of HBPs at 120°C for the fourth and fifth generation, respectively. It can be observed that for all HBPs η^* is higher than η , indicating that both systems do not follow the Cox-Merz rule^{18,21} that establishes that $\eta^*(\omega) = \eta(\dot{\gamma})$. This results differs with the reports for dendrimers,²⁷ hyperbranched polymer,^{14,18,22} and isotropic linear polymers²⁸ that establish that they obey this rule. A possible explanation of this behavior is that the HBPs presented higher interactions due to high number of OH groups at the periphery. Furthermore, the rupture of interactions is more effective at low oscillatory conditions.

The difference in behavior between dynamic rheological properties (shear-thinning) and steady shear viscosity (Newtonian) is due mainly to interactions of intermolecular H-bonding of OH groups. The

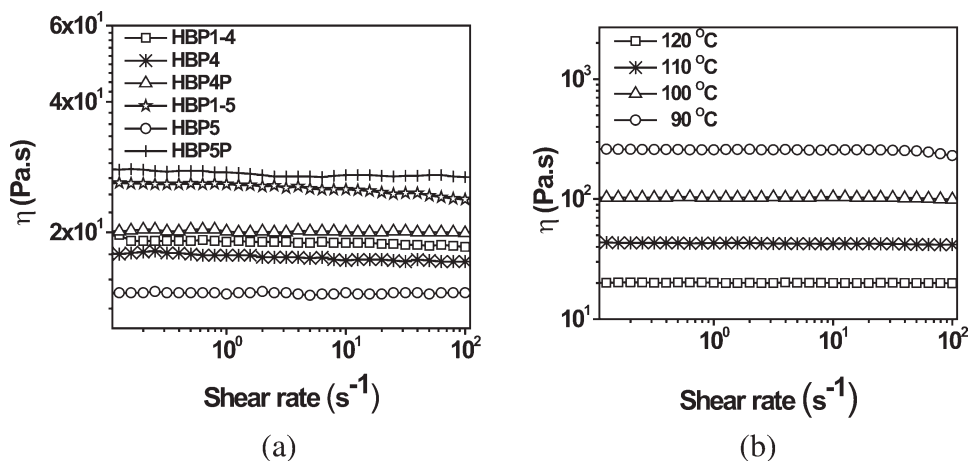


Figure 6 Viscosity vs. shear rate relationships; (a) all HBPs at 120°C and (b) HBP4P at different temperatures.

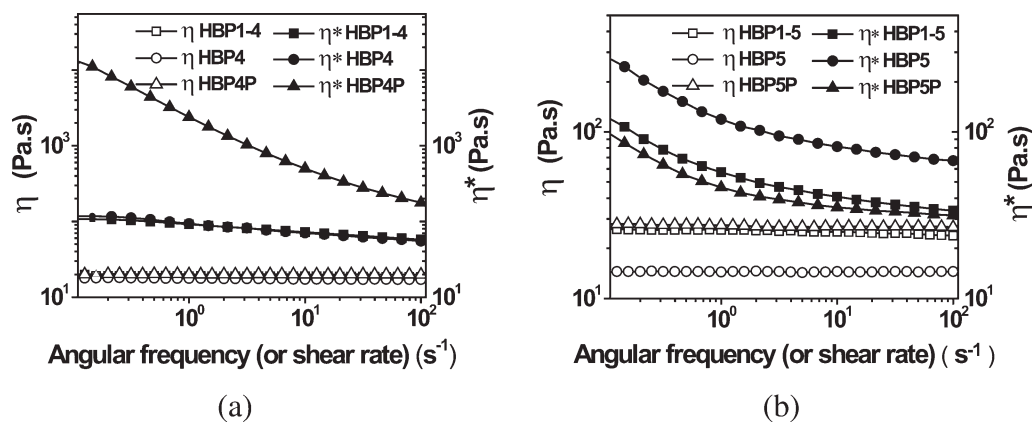


Figure 7 Comparison of η^* and η of HBPs at 120°C; (a) Fourth generation and (b) Fifth generation.

values of η^* (higher than those of η) for all HBPs in the molten state are likely due to the formation of microstructures, which are formed by the interaction of OH groups of several macromolecules that respond differently upon the application of steady and oscillatory shear. Oscillatory shear behavior is an indication of interactions in the HBPs. However, at low shear rate used in this study, the structure of the materials is not altered. Steady shear enables rearrangement of the molecular packing of HBPs in the direction of the shear.²²

Steady shear viscosity in solution

The characteristics of HBPs in solution were studied using DMF as a solvent. The behavior of the viscosity (Fig. 8) is different at 10 [Fig. 8(a)] and 23°C [Fig. 8(b)]; this can be explained by the fact that the interactions of the HBPs with the solvent are temperature dependent. This behavior was not observed for the HBPs in the molten state. All polymers exhibited shear thickening behavior, as the viscosity increases with the shear rate at 23°C and there is a strong increase in viscosity near 1000 s^{-1} . This phenomena can be explained by the formation of a thermolabile network formed due to the strong self-asso-

ciation of polar groups.^{29,30} This process is favored by the temperature because it was not observed at 10°C.

Vapor pressure osmometry

The number average molar mass (M_n) of the HBPs was determined from this equation³¹:

$$\frac{\Delta V}{C} = \frac{K_c}{M_n} + A \rho C K_c \quad (1)$$

where ΔV is the potential change, measured by the change in resistance of the thermistor, C is the concentration of the solution in g/kg, A is the second virial coefficient of vapor pressure osmosis, ρ is the density of the solvent and K_c is a theoretical calibration constant. The K_c value was 157.71 kg/mol determined from the benzil calibration curve. The M_n of the HBPs were calculated from eq. (1), after determination of the intercept and A slope of the $\Delta V/C$ versus C plot. Figure 9(a,b) showed the VPO plots for benzil and HBPs, respectively.

Table I showed the values of M_n , A , and correlation factor for all HBPs. The value of A indicated that the interaction order of the HBPs with the solvent was the following $\text{HBP1-5} > \text{HBP5} > \text{HBP5P} >$

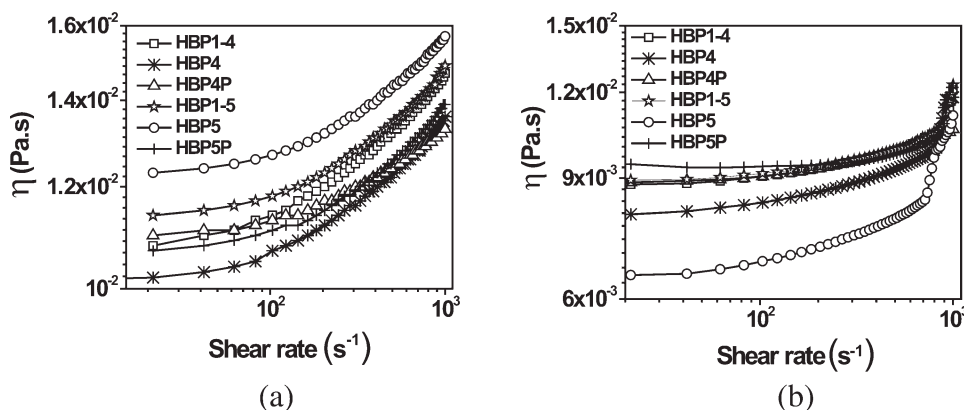


Figure 8 Steady shear viscosity of HBPs in solution; (a) at 10°C and (b) 23°C.

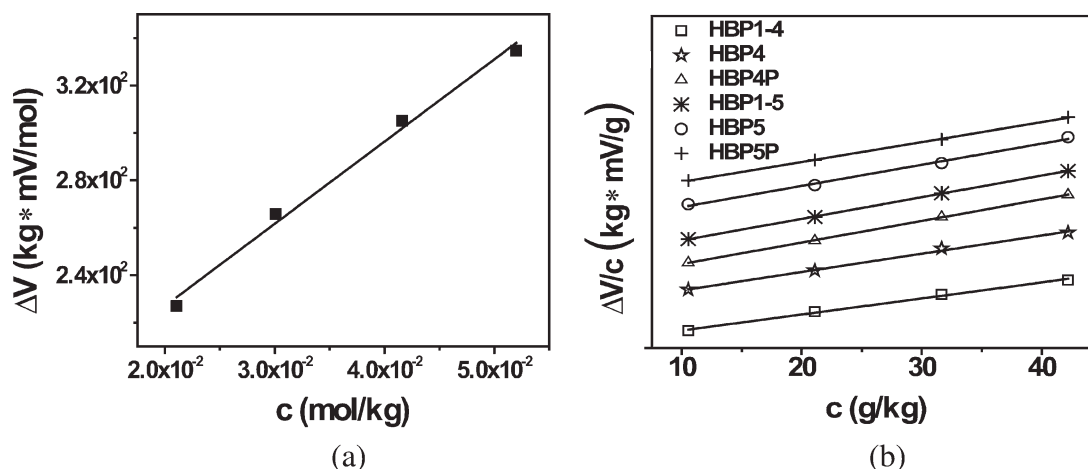


Figure 9 VPO measurements; (a) Benzil and (b) HBPs.

HBP4 > HBP1-4 > HBP4P. This order is in agreement with the OH group number in the periphery of HBPs, which was reported in a previous paper.²⁴

The number average molar mass obtained by VPO is independent of the molecular structure of the polymer, contrary to the ones obtained by gel permeation chromatography, which depends on hydrodynamic volume. As expected the fifth generation polymers exhibit higher M_n than those of fourth generation, but all values were lower than the theoretic molar mass value of 7096 g/mol for fourth and 14520 g/mol for fifth generation. This is an indication that these polymers still have unreacted OH groups since during the synthesis of these materials, several side reactions, such as intramolecular etherification and intramolecular hydroxyl-ester occur, which reduce the molecular weight and also produces a polymer with high number of linear units as it was reported Chikh et al.³² Other important aspects is that the polymer obtained by combination of two methods (HBP1-4 and HBP1-5) presented higher M_n values than those of the polymers obtained in one step since the polymer obtained in one step presented high number of linear units (high imperfection) and this reduced the M_n .^{6,26}

TABLE I
Values of Slope, M_n Virial Coefficient and Correlation Factor of the HBPs

HBPs	Intercept $\times 10^2$ (kg/g)	Slope \times 10^3	M_n (g/mol)	$A \times$ 10^6 (cm ³ kg/g ²)	Correlation factor
HBP1-4	3.10	1.01	5087	6.76	0.994
HBP4	3.49	1.16	4518	7.75	0.996
HBP4P	2.80	0.85	5632	5.71	0.994
HBP1-5	2.44	1.37	6463	9.16	0.998
HBP5	2.60	1.34	6065	8.96	0.992
HBP5P	2.25	1.26	7009	8.43	0.997

These results allow concluding that the methodology of combination of two methods (one step and step by step) is an alternative good synthesis method because it allows obtaining HBPs with higher molecular weight than the one step method. Results of M_n are not in agreement with the viscosity data indicating the presence of different interaction between HBPs molecules. The correlation factor was excellent in all cases.

The result of M_n obtained in this study is different to obtained by nuclear magnetic resonance(NMR)²⁴ due to these calculations by NMR have not account intermolecular etherification and intramolecular hydroxy-ester interchange reactions, which reduce M_n .³²

CONCLUSIONS

Under oscillatory conditions in the molten state, all HBPs showed shear-thinning behavior. The polymer HBP4P showed the higher reduction in complex viscosity with increasing the angular frequency, indicating that HBP4P exhibited greater intermolecular interaction (H-bonding) than other HBPs. Also, for HBP4P, the reduction in complex viscosity is higher with increasing temperature. Furthermore, this sample was the only one that presented a transition from elastic to viscous and also, greater storage and loss moduli. According to the viscosity values obtained at steady shear, all HBPs exhibited Newtonian behaviour. However, shear thinning behavior at dynamic oscillatory shear is due to the fact that these polymers in molten state have certain microstructures that respond differently upon the application of steady and oscillatory shear. Oscillatory shear although gave an indication of interactions of HBPs, the structure of materials is not altered at low conditions of shear rate used in this study. Steady shear is able to rearrange molecular packing of HBPs in the same direction of the shear. Therefore none of the HBPs obeyed the Cox-Merz rule. The behavior of

HBP in solution presented a shear-thickening behavior at a shear rate greater than 40 s^{-1} . This was due to the formation of thermolabile network produced by strong self-association of polar groups. The behavior of the HBPs under steady shear in solution and molten state in the plateau region presented the same order of increasing viscosity; HBP5P > HBP1-5 > HBP4P > HBP1-4 > HBP4 > HBP5. VPO analysis does not show the presence of aggregations since the slope always increased with increasing the concentration in the range of concentration used under this study. VPO analysis showed that HBPs of the fifth generation presented higher M_n and second virial coefficient (A) than HBPs of the fourth generation and the sample HBP4P exhibited lower interaction with the solvent. All correlation factors were excellent.

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