

Melt Rheology of Aliphatic Hyperbranched Polyesters

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ABSTRACT: Rheological behavior in melt of aliphatic hyperbranched polyesters (AHBP), synthesized using pseudo-one-step and one-step procedure, was investigated in this work. Three commercially available AHBP were also examined. Because of the presence of relatively strong hydrogen bonds between numerous end hydroxyl groups, AHBP of lower generation number, as well as the sample of tenth pseudo generation, show non-Newtonian behavior in the entire investigated frequency and temperature region. However, for other examined AHBP, the slope of the frequency dependence of complex viscosity ($\eta^* = f(\omega)$) becomes smaller with the temperature

increase. Therefore, samples of fourth, fifth, and sixth pseudo generations show Newtonian behavior at temperatures higher than 70°C. Value of glass transition temperature, melt flow activation energy, fractional free volume, and thermal expansion coefficient were determined for the investigated AHBP. The influence of the type of end groups on rheological properties of AHBP was also examined. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2925–2934, 2009

Key words: hyperbranched; polyesters; rheology; activation energy

INTRODUCTION

The scientific importance of dendritic polymers, that is, dendrimers and hyperbranched polymers, has been already proved by numerous publications, where different synthetic pathways and various characterization methods were applied to obtain and investigate these three-dimensional polymers.^{1–13} Hyperbranched polymers (HB) are usually considered as irregular analogues of dendrimers and can be used in applications where the perfect structure of dendrimers is less important. The imperfection of their structure originates from the fact that beside fully reacted (dendritic) units, HB polymers also contain linear units. Because of that the inner layers of these polymers are usually called pseudo generations. Rheological properties of dendritic polymers depend on the structure, dimensions, type of inter- and intramolecular interactions, and in some cases are quite different from those observed for the analogue linear polymers. Therefore, knowledge about rheological behavior of dendritic polymers can be used to determinate their application fields. Melts and concentrated solutions of dendrimers usually show Newtonian behavior.^{14–16} On the other side,

different results have been obtained for melts of HB polymers,^{17–24} even for the same type of polymers (Newtonian flow or shear thinning behavior).^{25–27} The examples of latter are commercial aliphatic HB polyesters (Boltorn[®]), which are at the same time the most investigated HB polyesters presented in the literature. Different authors have shown that their rheological behavior depends on thermal prehistory.^{25–27} This specific property is attributed to the formation of hydrogen bonds between hydroxyl groups, which can be removed by preheating of the samples at around 160°C. After this thermal treatment, different generations of Boltorn[®] HB samples exhibited Newtonian behavior in melt, at temperature ~ 100°C.

In this work, rheological properties of two series of hydroxy-functional aliphatic HB polyesters (AHBP), synthesized using pseudo-one-step (samples of the series I) and one-step (samples of the series II) procedure were examined. The influence of the procedure for the synthesis, number of pseudo generation, degree of branching, frequency, and temperature on the rheological properties of these polymers in melt was investigated. Obtained results were compared with determined rheological properties of commercial Boltorn[®] AHBP samples. In which manner, the rheological behavior of AHBP samples depends on the type of end groups was also investigated in this work, by rheological

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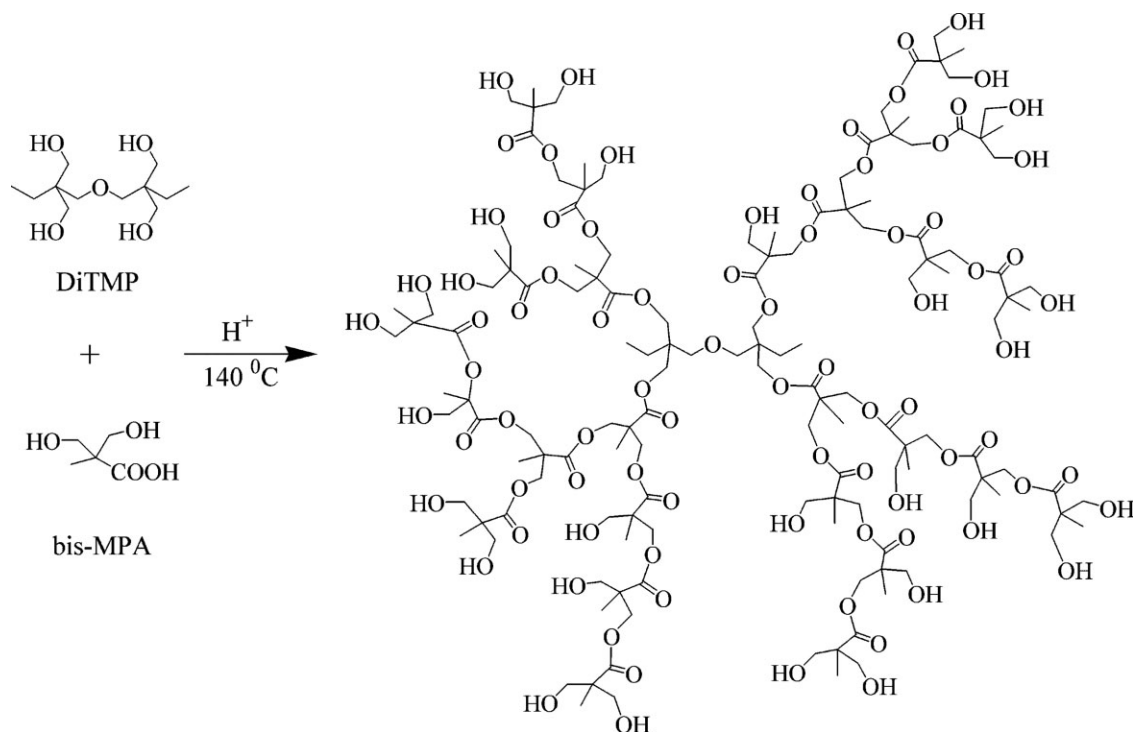


Figure 1 Schematic representation of the synthesis of AHBP samples.

characterization of third pseudo generation AHBP, whose end —OH groups were modified with stearic acid.

EXPERIMENTAL

Materials

Two series of hydroxy-functional aliphatic hyperbranched polyesters were synthesized via an acid-catalyzed polyesterification reaction starting from 2,2-bis(hydroxymethyl)propionic acid, bisMPA, (Aldrich), as an AB₂ monomer, and ditrimethylolpropane, DiTMP, (Fluka Chemika), as the tetrafunctional core molecule (Fig. 1).²⁸ Samples of the series I of the second (AHBP-2I), third (AHBP-3I), fourth (AHBP-4I), fifth (AHBP-5I), sixth (AHBP-6I), eighth (AHBP-8I), and tenth (AHBP-10I) pseudo generation were synthesized using pseudo-one-step procedure. On the other side, samples of the series II of fourth (AHBP-4II), sixth (AHBP-6II), and eighth (AHBP-8II) pseudo generation were synthesized using one-step procedure. Methanesulphonic acid, purchased from Aldrich, was used as a catalyst. Three commercially available aliphatic HB polyesters (Boltorn[®]) of the second (BH-2), third (BH-3), and fourth (BH-4) pseudo generation, supplied by Perstorp (Specialty Chemicals AB, Sweden), were also investigated in this work. Commercial AHBP were synthesized via pseudo-one-step procedure from the bisMPA as monomer and a tetrafunctional ethoxylated pentaerythritol core. All other chemicals were obtained

from Aldrich and used as received, without further purification.

Modification of Ahbp-3I with stearic acid

End —OH groups of AHBP sample of third generation (AHBP-3I) were modified with stearic acid by melting 48.62 g of AHBP-3I, mixed with small portion of xylol (3 mass % of reaction mass), in a four-necked flask equipped with an N₂ inlet, a drying tube, Dean-Stark unit (filled with xylol), and a stirrer. The flask was heated with an electrical heater. In a molten AHBP-3I, 126.62 g (0.45 mol) of stearic acid was added and this mixture was then heated up to the 230°C. After 7.5 h, the mixture was cooled down until temperature of 130°C was reached. The N₂ stream was then turned off and the flask was connected to a vacuum line. After that, mixture was heated 45 min at 200°C. The modified sample AHBP-3ISA was obtained as pink waxy solid. According to the hydroxyl number titration of AHBP-3ISA and comparison of the obtained result with hydroxyl number of AHBP-3I, it was calculated that 80% of end —OH groups were in AHBP-3ISA successfully modified with stearic acid.

Characterization

The hydroxyl number of investigated AHBP samples was determined according to the procedure described elsewhere.²⁹

^{13}C NMR spectra of self-synthesized samples were recorded on Bruker (250 MHz) NMR spectrometer at room temperature, using deuterated dimethylsulfoxide ($\text{DMSO-}d_6$) as solvent. The degree of branching, DB, was calculated from the values obtained by integration of the peaks from the ^{13}C NMR spectra, corresponding to the dendritic, linear, and terminal units and using equations developed by Fréchet³⁰ and Frey.³¹

Vapor pressure osmometry (VPO) of synthesized and commercial samples was carried out using a Knauer vapor pressure osmometer. Measurements were done in *N,N*-dimethylformamide as a solvent at 90°C. For the calibration, benzil was used.

Determination of the molar mass distribution of AHBP was performed with GPC technique using a Spectra-Physics chromatograph equipped with Rheodyne universal injector and Spectra-Physics differential refractometer as detector. The separation was achieved across a set of two gel columns (MZGPC columns) with porosities of 1000 Å. Tetrahydrofuran was used as eluent at a nominal flow rate of 1 cm³/min. The quantity of injected polymer was 100 µL ($c \sim 20$ g/L) and the measurements were carried out at 25°C. The molar mass characteristics of the polymers were calculated by a polystyrene calibration curve, constructed with narrow molar mass distribution polystyrene standards (Polymer Standards Service), using the Chrom Gate 3.1.4. software (Knauer).

The viscosity measurements of AHBP diluted solutions in *N*-methyl-2-pyrrolidinon were performed in an Ubbelohde capillary viscometer (Schott, capillary sizes 0_a and l) using an automatic timer (Schott AVS 300), at $25 \pm 0.1^\circ\text{C}$. The limiting viscosity number, $[\eta]$, of the samples was determined graphically by extrapolation of the η_{sp}/c values (determined at five different concentrations) to infinite dilution, using Huggins equation.³²

A Carri-Med CSL-100 stress controlled cone and plate rheometer (TA Instruments), fitted with a 2 cm diameter cone (2° cone angle), was used to measure the rheological properties of AHBP samples. Oscillatory experiments of the AHBP in the molten state were performed in the linear viscoelastic region using a frequency and temperature ramp. The frequency ramp was done at thirteen different temperatures (30–80°C) for the investigated nonmodified AHBP and at 10 different temperatures (15–60°C) for the sample AHBP-3ISA, in the frequency region between 0.1 and 40 Hz and at the strain of 2%. The temperature ramp was performed at a frequency of 1 Hz and strain of 2% in the temperature region between 20 and 80°C (i.e., between 15 and 60°C for the sample AHBP-3ISA). The dependence of storage modulus, G' , loss modulus, G'' , complex viscosity, η^* , and $\tan \delta$ versus frequency and temperature were measured. In all experiments, the temperature

control was achieved with a Peltier plate (0–80°C) to a precision of 0.1°C.

Dynamic mechanical analysis (DMA) of AHBP was performed on Mettler Toledo DMA861^e instrument. Experiments were made in shear mode, using temperature sweep from 0 up to 110°C, with heating rate of 3°C/min, at three frequencies: 1, 10, and 100 Hz (multifrequency mode). The dependence between storage modulus and temperature was determined. Dynamical measurements were performed in predetermined linear viscoelastic region. Samples of AHBP were prepared for DMA using compression molding. The dry powder of AHBP was placed between two aluminum sheets in adequate mold and heated up to $\sim 70^\circ\text{C}$, under minimal pressure. After 5 min, samples were cooled down to room temperature. In this manner, small plates with thickness of ~ 1.4 mm and diameter of ~ 13.5 mm were obtained.

RESULTS AND DISCUSSION

Schematic representation of the synthesis of AHBP samples is presented in Figure 1, whereas some important properties of investigated AHBP samples are listed in Table I. During the synthesis of investigated polyesters, side reactions such as self-condensation of bisMPA, intramolecular esterification and etherification (cyclization) occurred. Because of these unwanted reactions, the formation of AHBP samples having high, that is, theoretically expected molar mass was disabled. Experimentally determined values of molar masses listed in Table I confirm this. Another consequence of these unwanted reactions is the slight increase of molar mass up to the sixth pseudo generation of AHBP from series I. The same trend can also be observed for limiting viscosity number values (Table I). A detailed description and discussion of the side reactions, which occurred during the synthesis of these AHBP using pseudo-one-step and one-step procedure, are presented elsewhere.²⁸ Values of DB are higher for the samples of the series I than for the samples synthesized by one-step procedure (series II). It should be mentioned that DB calculated according to Frey, DB_{Frey} , is considered to be more accurate for HB polymers of low molar mass.³¹ Values of the mass fraction of end $-\text{OH}$ groups (linear and terminal), w_{OH} , and percentage of terminal $-\text{OH}$ groups per molecule, $(-\text{OH})_T$, of investigated AHBP samples (Table I) were calculated using the values of theoretical and experimentally determined hydroxyl numbers, and the results obtained from ^{13}C NMR spectra.²⁸ Both parameters show that low generation AHBP have a higher number of hydroxyl groups per molecule than samples of the higher pseudo generation.

TABLE I
Values of the Theoretical Number of Pseudo Generation, n_{theor} , Theoretical Molar Mass, M_{theor} , Number Average Molar Mass Determined by VPO, $(M_n)_{\text{VPO}}$, Polydispersity Index Determined by GPC, $(M_w/M_n)_{\text{GPC}}$, Degree of Branching According to Fréchet, $\text{DB}_{\text{Fréchet}}$, and Frey, DB_{Frey} , Mass Fraction of end —OH Groups, w_{OH} , Percentage of Terminal —OH Groups per Molecule, $(-\text{OH})_T$, and Limiting Viscosity Number, $[\eta]$, of Investigated AHBP Samples

Sample	n_{theor}	M_{theor} (g/mol)	$(M_n)_{\text{VPO}}^{\text{a}}$ (g/mol)	$(M_w/M_n)_{\text{GPC}}^{\text{a}}$	$\text{DB}_{\text{Fréchet}}^{\text{a}}$	$\text{DB}_{\text{Frey}}^{\text{a}}$	w_{OH}^{a} (mass %)	$(-\text{OH})_T$ (%)	$[\eta]^{\text{a}}$ (cm^3/g)
AHBP-2I	2	1642	—	1.4	0.47 ^a	0.28 ^a	16.4	58.7	6.2
AHBP-3I	3	3498	2027	1.6	0.45 ^a	0.32 ^a	15.4	53.8	7.1
AHBP-4I	4	7210	2819	1.9	0.44 ^a	0.34 ^a	14.9	51.1	8.0
AHBP-5I	5	14,634	3044	2.2	0.45 ^a	0.37 ^a	14.8	51.1	8.7
AHBP-6I	6	29,482	3575	2.3	0.43 ^a	0.35 ^a	14.5	49.5	8.9
AHBP-8I	8	118,570	3571	2.2	0.43 ^a	0.35 ^a	14.4	48.9	8.3
AHBP-10I	10	474,922	3552	1.8	0.42 ^a	0.34 ^a	14.3	48.4	8.3
AHBP-4II	4	7210	5415	2.1	0.42 ^a	0.30 ^a	14.8	50.1	8.0
AHBP-6II	6	29,482	—	2.5	0.43 ^a	0.29 ^a	14.2	52.1	9.2
AHBP-8II	8	118,570	3284	2.3	0.37 ^a	0.22 ^a	14.1	46.6	9.3
BH-2	2	1747	1343	1.4	0.43 ^b	0.30 ^b	15.2	—	6.0
BH-3	3	3604	3081	1.9	0.42 ^b	0.31 ^b	14.4	—	7.4
BH-4	4	7316	2716	2.8	0.40 ^b	0.34 ^b	14.3	—	8.6

^a Results for $(M_n)_{\text{VPO}}$, $(M_w/M_n)_{\text{GPC}}$, $\text{DB}_{\text{Fréchet}}$, DB_{Frey} , w_{OH} , and $[\eta]$ are presented in Ref. [33,34].

^b Data of Luciani et al.²⁷

For all AHBP investigated in this work, the dependence of storage modulus, G' , loss modulus, G'' , complex viscosity, η^* , and $\tan \delta$ versus frequency, at different temperatures (30–80°C), in the frequency region between 0.1 and 40 Hz and at the strain of 2% were measured. As an illustration, frequency dependences of η^* , G' , and G'' are presented in Figures 2–4 for some AHBP samples. In the examined temperature and frequency region, it was observed that samples AHBP-2I, BH-2, and BH-3 show non-Newtonian behavior with very high slope of the frequency dependence of η^* . As an example, the frequency dependence of the η^* for the sample AHBP-2I at different temperatures is presented in Figure 2(a). There is very low possibility that non-Newtonian behavior is a consequence of interpenetration between molecules in the melts of investigated AHBP, because they have low molar masses, compact structure of individual macromolecules,³⁴ and short branch length (the molar mass of chain portions between branch points) in comparison to the entanglement molar mass. The source of non-Newtonian behavior of AHBP samples is intermolecular polar interactions involving strong hydrogen bonding of large number of hydroxyl groups.^{26,27} It was expected that AHBP-2I, BH-2, and BH-3 will show high degree of polar interactions, due to the presence of higher portion of —OH groups per molecule, lower values of DB_{Frey} (Table I) and probably longer linear sequences between branch points, facilitating the formation of hydrogen bonds also between —OH groups which are in larger molecules blocked by steric hindrance. Because of the cleavage

of hydrogen bonds, η^* of these samples decreases through several decades with increase in the temperature and frequency. For samples AHBP-3I, AHBP-6II, AHBP-8I, and AHBP-8II, the slope of the dependence $\eta^* = f(\omega)$ (Fig. 2(b)) is much smaller than for AHBP-2I, BH-2, and BH-3. It also decreases with the temperature increase, and at temperatures higher than 65°C, the complex viscosity is constant at lower frequencies. On the other side, samples AHBP-4I, AHBP-5I, AHBP-6I, AHBP-4II, and BH-4 show Newtonian behavior at temperatures higher than 70°C, beside the fact that these samples were not thermally pretreated. As an example, the frequency dependence of the η^* for the sample AHBP-5I is presented in Figure 2(c). Non-Newtonian behavior was also observed for the sample AHBP-10I [Fig. 2(d)], but with higher slope of the dependence $\eta^* = f(\omega)$ than for AHBP-2I, BH-2, and BH-3. The reason for such behavior is probably the presence of large number of small molecules in the structure of AHBP-10I, due to the higher extent of side reactions, which occurred during the synthesis of this sample in comparison to the other HB polyesters.

The frequency dependence of the storage and loss modulus of the samples AHBP-2I and BH-3 at 45°C [Fig. 3(a)] show that for these two samples, the curve of the storage modulus is in the entire frequency region located above the curve of the loss modulus. This implies that these samples have mainly elastic behavior at 45°C. The same behavior was also obtained for AHBP-10I. However, all other investigated samples [Fig. 3(b)] show viscous behavior ($G'' > G'$) at 45°C up to the certain frequency, after

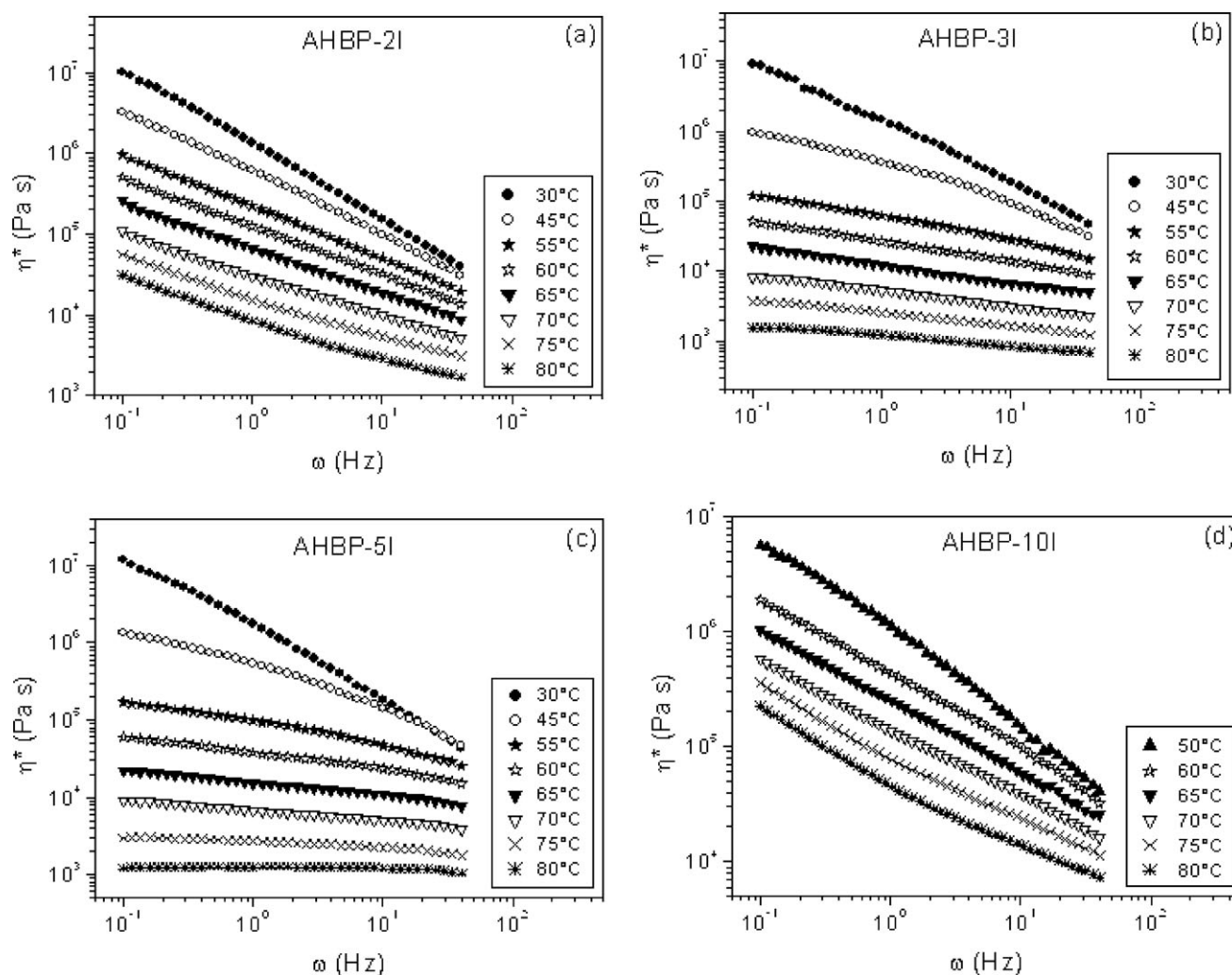


Figure 2 Frequency dependence of the complex viscosity determined at different temperatures for the samples (a) AHBP-2I, (b) AHBP-3I, (c) AHBP-5I, and (d) AHBP-10I.

which the transition from more viscous to more elastic behavior occurs ($G'' < G'$). The intersection where this transition occurs ($G'' = G'$) appears for AHBP-4II at around 1.0 Hz, while for the other two fourth generation samples at around 1.3 Hz. The crossover in G' and G'' appears for samples AHBP-3I and AHBP-8I at 0.3 Hz and 0.4 Hz, respectively, and for other investigated AHBP at 0.5 Hz.

The trend of the G' and G'' frequency dependence for AHBP-10I do not change considerably at 80°C [Fig. 4(a)]. Up to the ~ 10 Hz, G'' is lower than G' , whereas at higher frequencies, the transition from the elastic to viscous behavior still does not occur completely, because G'' is equal to G' up to the 40 Hz. On the other side, for the sample AHBP-2I at ~ 0.4 Hz, G'' becomes higher than G' . For the other samples at 80°C, G'' is higher than G' through the entire frequency region [Fig. 4(b)] and both G' and G'' rise without crossover indicating that the AHBP chains are nonentangled. Similar behavior was observed for other HB polymers.^{19,35,36}

When the rheological measurements of the investigated AHBP were performed at higher temperatures ($T > 75^\circ\text{C}$), it was observed that in the low frequency region most samples show classical terminal scaling of the loss modulus ($G'' \sim \omega$). The exceptions from this are samples AHBP-2I, BH-2, BH-3, and AHBP-10I, for which the exponent in the dependence $G'' = f(\omega)$ is lower than one. For the samples AHBP-3I and AHBP-8I, it was observed that $G'' \sim \omega^{0.84}$. On the other side, in the entire examined frequency and temperature region, investigated AHBP show deviation from the terminal scaling of the G' , that is, in the dependence $G' \sim \omega^b$, the exponent b is always lower than 2. Nonterminal G' scaling is also observed for other dendritic polymers and it is thought to be a consequence of the high branch density.^{24,37,38}

Temperature dependences of η^* , G' , G'' , and $\tan \delta$ for AHBP samples at a frequency of 1 Hz and strain of 2%, in the temperature region between 20 and 80°C, were also investigated in this work. As an

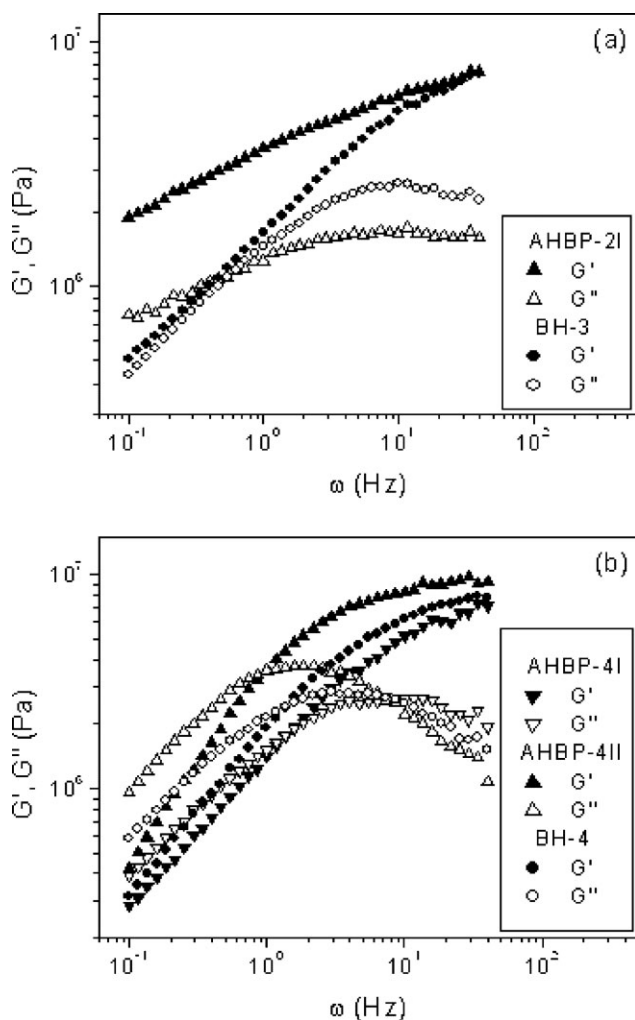


Figure 3 Frequency dependence of the storage and loss modulus of the selected AHBP, determined at 45°C (a) samples AHBP-2I and BH-3, (b) samples AHBP-4I, AHBP-4II, and BH-4.

illustration, temperature dependence of G' and G'' for the samples of sixth pseudo generation is presented in Figure 5. From these results, it can be observed that G' of AHBP constantly decrease, even above glass transition temperature (Table II). No rubbery plateau was detected in the investigated temperature region, unlike the case of entangled polymers. Similar behavior was observed for AHBP of other pseudo generations. For the sample AHBP-6II, the maximum of the G'' curve appears at higher temperature than for AHBP-6I, indicating somewhat higher values of the glass transition temperature, T_g . From the temperature dependence of η^* (Figure not shown), it was also observed that AHBP samples synthesized using one-step procedure have slightly higher values of complex viscosity than adequate samples synthesized by pseudo-one-step procedure, as a consequence of greater amount of linear units.

Values of the T_g (Table II) for the investigated AHBP were determined from the maximum of the

G'' temperature dependences, obtained by heating from 20 up to 80°C, $(G''_{\max})^{\text{heat}}$, and by cooling from 80 down to 20°C, $(G''_{\max})^{\text{cool}}$. Determined values of the T_g for the investigated AHBP are in the temperature range between 20 and 45°C. Values of the glass transition temperature, obtained from $(G''_{\max})^{\text{heat}}$ and $(G''_{\max})^{\text{cool}}$ are very similar between each other (Table II, Fig. 6), indicating significant accuracy of the determined T_g values. Values of the T_g were also determined from the maximum of the $\tan \delta$ temperature dependences, obtained by heating, and they are $\sim 10^\circ\text{C}$ higher than values determined from $(G''_{\max})^{\text{cool}}$.

Glass transition temperatures of certain self-synthesized and commercial AHBP were also determined using dynamic mechanical analysis (DMA). These experiments were performed using three different frequencies. T_g values were obtained from the inflection point of the temperature dependence of

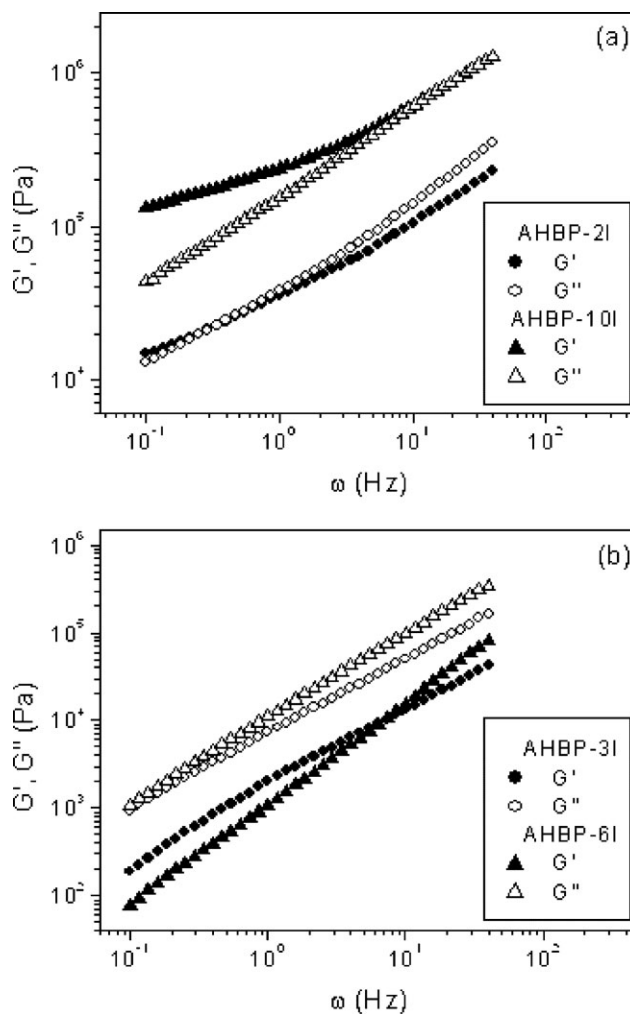


Figure 4 Frequency dependence of the storage and loss modulus of the selected AHBP, determined at 80°C (a) samples AHBP-2I and AHBP-10I, (b) samples AHBP-3I and AHBP-6I.

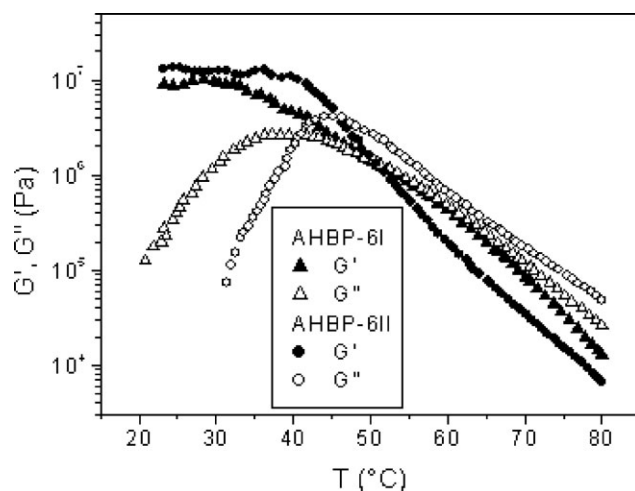


Figure 5 Temperature dependence (1 Hz) of the storage and loss modulus of the samples of sixth pseudo generation, obtained by heating from 20 up to 80°C.

storage modulus. As an example, in Figure 7 are presented DMA curves for the sample AHBP-4I, whereas determined values of T_g are listed in Table III. Results obtained with this technique show that storage modulus of all samples is lower than 10^3 MPa, indicating poor mechanical properties of these AHBP. T_g values obtained with DMA measurements at 1 Hz are $\sim 15^\circ\text{C}$ higher than values listed in Table II.

Using the time-temperature superposition principle, master curves of the determined rheological parameters were constructed for investigated AHBP. As an example, in Figure 8 are presented master curves of G'' for the fourth pseudo generation samples. Only shifts along the frequency scale were per-

TABLE II
Values of the Glass Transition Temperature, T_g , Determined from the Maximum of the Loss Modulus Temperature Dependences (1 Hz), Obtained by Heating of the AHBP Samples from 20 up to 80°C, ($G''_{\text{max}}^{\text{heat}}$) and by cooling of the AHBP samples from 80 down to 20°C, ($G''_{\text{max}}^{\text{cool}}$)

Sample	T_g (°C)	
	$(G''_{\text{max}})^{\text{heat}}$	$(G''_{\text{max}})^{\text{cool}}$
AHBP-2I	33	37
AHBP-3I	38	38
AHBP-4I	36	35
AHBP-5I	37	35
AHBP-6I	41	37
AHBP-8I	40	40
AHBP-10I	35	39
AHBP-4II	42	44
AHBP-6II	44	45
AHBP-8II	44	44
BH-2	21	27
BH-3	31	33
BH-4	31	29

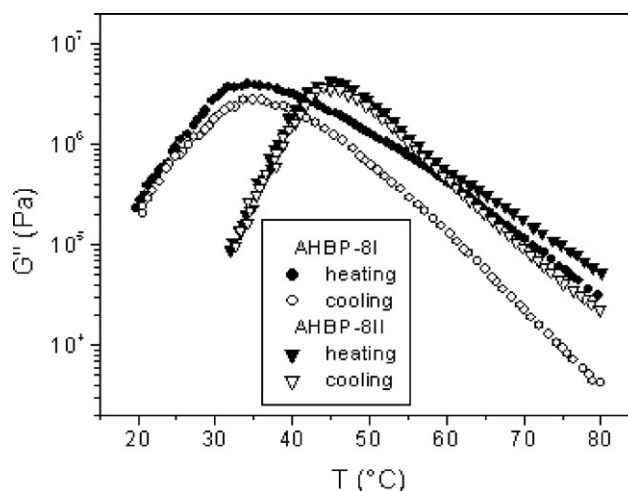


Figure 6 Temperature dependence (1 Hz) of the loss modulus for the samples of eighth pseudo generation, obtained by heating of AHBP from 20 up to 80°C and by cooling from 80 down to 20°C.

formed. Horizontal shift factors, a_T , were determined at temperatures higher than T_g (Table II), by shifting the frequency dependences of the G' and G'' along the horizontal axes to obtain superposition on the corresponding reference curve (reference temperature: $T_0 = 60^\circ\text{C}$). In this manner, frequency dependences of the G' and G'' were enhanced on the several decades of frequencies. The shift factors used to create a master curve were for all samples about the same (except for AHBP-2I and AHBP-10I), indicating similar structure of these polyesters. As an illustration, in Table IV are listed a_T values determined at 80°C. From the obtained values of the shift factors and linear form of Williams-Landel-Ferry (WLF) relation (Eq. (1)), constants C_1 and C_2 were determined and listed in Table IV.

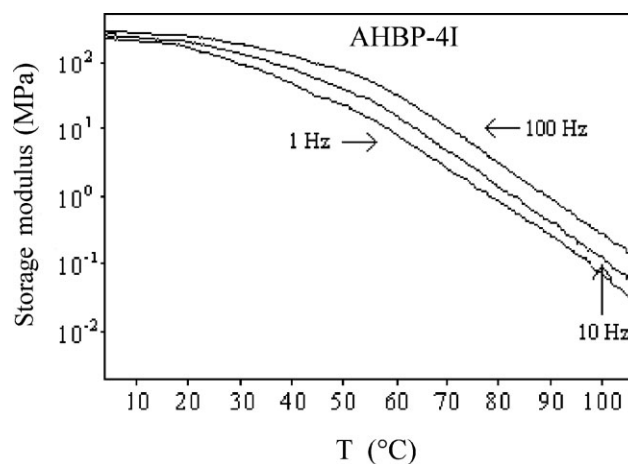


Figure 7 Temperature dependence of the storage modulus for the sample AHBP-4I, determined using dynamic mechanical analysis, at three different frequencies.

TABLE III
Values of the Glass Transition Temperature of Several AHBP, Determined at Three Different Frequencies, Using Dynamic Mechanical Analysis

Sample	T_g (°C)		
	1 Hz	10 Hz	100 Hz
AHBP-3I	53	59	63
AHBP-4I	49	49	55
AHBP-5I	52	56	57
AHBP-6I	54	51	56
AHBP-4II	40	43	49
AHBP-6II	41	44	50
AHBP-8II	46	49	53
BH-4	41	41	42

$$\log a_T = \frac{-C_1(T - T_0)}{C_2 + (T - T_0)} \quad (1)$$

In Table IV are also the listed values of the melt flow activation energy, E_a , calculated at 80°C according to the eq. (2):

$$E_a = \frac{2.303RC_1C_2T^2}{(C_2 + T - T_0)^2} \quad (2)$$

The WLF equation can also be presented in terms of the free volume theory, if it is assumed that the fractional free volume, f , increases linearly with temperature and that the chain mobility at any temperature depends on the free volume³⁹:

$$f = f_g + \alpha_f(T - T_g) \quad (3)$$

where f_g and α_f are the fractional free volume at T_g and the thermal expansion coefficient, respectively. These parameters can be calculated in the following way:

$$f_g = \frac{B}{2.303C_1^g} \quad (4)$$

$$\alpha_f = \frac{B}{2.303C_1^gC_2^g} \quad (5)$$

B is the empirical constant usually arbitrarily set to unity, whereas C_1^g and C_2^g are the constants from WLF equation, obtained when T_g is set as reference temperature.³⁹ These constants can be calculated from C_1 and C_2 in the following manner:

$$C_1^g = \frac{C_1C_2}{C_2 + T_g - T_0} \quad (6)$$

$$C_2^g = C_2 + T_g - T_0 \quad (7)$$

calculated values of the constants C_1^g and C_2^g , f_g , and α_f are also listed in Table IV. For the determination

of the constants $(G''_{\max})^{\text{heat}}$ and $(G''_{\max})^{\text{heat}}$, values of the glass transition temperature obtained from C_1^g were used (Table II).

The obtained values of the melt flow activation energy at 80°C indicate higher degree of the intermolecular hydrogen bonding for the samples AHBP-2I and AHBP-10I, which is in agreement with results presented in Figure 2. The decrease of the activation energy up to the sixth pseudo generation indicates reduction of the intermolecular hydrogen bonding with increase of the generation number, after which value of E_a for AHBP-8I and AHBP-10I increases. For the samples AHBP-4II, AHBP-8II, and BH-4, the melt flow activation energies have somewhat lower values than values obtained for the corresponding AHBP of the series I. The change of the fractional free volume at T_g for different samples is in accordance with the change of the melt flow activation energy. The increase of the f_g for the samples of the series I up to the sixth pseudo generation occurs as a consequence of the greater mobility of the branches. Calculated values of the f_g are for most investigated AHBP smaller than values usually reported for the linear polymers (0.025), but at the same time relatively close to the values obtained for other dendritic polymers,²⁷ even beside the fact that, due to the temperature restrictions of the instrument, relatively low reference temperature was used in this work.

The rheological behavior of the self-synthesized AHBP strongly depends not only on the number but also on the type of the end groups. Therefore, the melt rheology of the third pseudo generation sample, whose —OH groups were modified with stearic acid (AHBP-3ISA; $M_{\text{theor}} = 29,482$ g/mol), was also investigated. The strong influence of this type of modification on the rheological properties can be

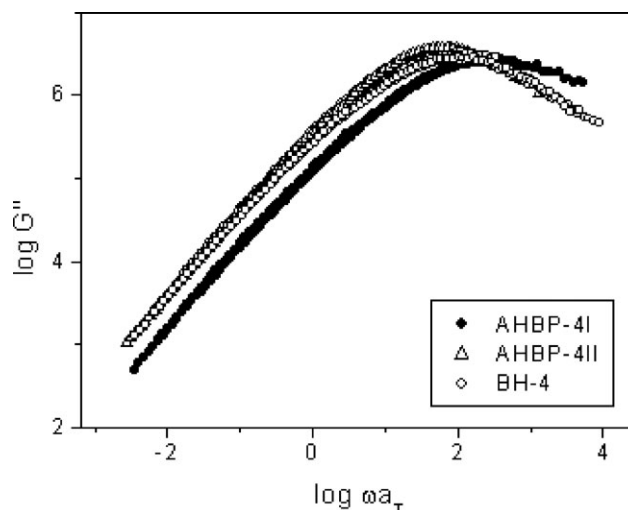


Figure 8 Master curves of the loss modulus for the fourth pseudo generation samples ($T_0 = 60^\circ\text{C}$).

TABLE IV
Values of the Shift Factors Determined at 80°C, a_T , Values of the WLF Parameters (C_1 , C_2 , C_1^g , and C_2^g , Melt Flow Activation Energy Calculated at 80°C, E_a , Fractional Free Volume, f_g , and Thermal Expansion Coefficient, α_f , of Investigated AHBP

Sample	a_T	C_1	C_2 (K)	E_a (kJ mol ⁻¹)	C_1^g	C_2^g (K)	f_g	α_f (10 ⁻⁴ K ⁻¹)
AHBP-2I	0.003	62.5	459.4	298.5	66.5	432.0	0.006	0.15
AHBP-3I	0.010	21.4	194.0	216.1	24.1	171.7	0.018	1.05
AHBP-4I	0.011	25.5	240.3	215.9	28.3	216.5	0.015	0.71
AHBP-5I	0.011	22.6	212.6	212.5	25.4	189.2	0.017	0.90
AHBP-6I	0.016	21.3	218.1	195.6	23.3	198.9	0.019	0.93
AHBP-8I	0.014	19.7	192.5	201.0	22.0	172.5	0.020	1.14
AHBP-10I	0.004	36.4	285.3	266.3	39.9	260.4	0.011	0.42
AHBP-4II	0.015	30.7	322.9	201.1	32.5	304.7	0.013	0.44
AHBP-6II	0.014	27.7	276.3	208.0	29.4	260.3	0.015	0.57
AHBP-8II	0.027	9.55	103.4	154.9	11.3	87.4	0.038	4.40
BH-3	0.012	28.4	275.3	214.0	31.4	246.3	0.014	0.56
BH-4	0.020	18.3	199.7	180.4	21.4	170.3	0.020	1.19

clearly seen from the results presented in Figure 9. The non-Newtonian behavior of the AHBP-3ISA up to the 40°C [Fig. 9(a)] is probably due to the interpenetration of end alkyl groups from the surrounding molecules.⁴⁰ Beside that, from the frequency and temperature dependence of the complex viscosity of AHBP-3ISA, a significant decrease of the η^* values at around 37°C can be observed. Values of the complex viscosity for the AHBP-3ISA are lower in comparison with η^* obtained for the AHBP-3I, especially at temperatures higher than 30°C [Fig. 9(b)]. This indicates that the presence of long alkyl chain ends instead of polar -OH groups, reduces to a certain amount the possibility for the hydrogen bonding, leading also to the glass transition temperature decrease. From the C_2^g , it was obtained that T_g for the AHBP-3ISA is 29°C, whereas glass transition temperature of the sample AHBP-3I is 38°C (Table II). However, the presence of such long terminal alkyl chains (C18) can induce crystallinity in the AHBP samples and in this manner limit the reduction of the glass transition temperature.⁴⁰ Therefore, the sudden decrease of the η^* values for the AHBP-3ISA is ascribed to the melting of this sample.

CONCLUSIONS

Results obtained from the rheological investigation of aliphatic hyperbranched polyesters indicate that depending on the number of pseudo generation and applied temperature, investigated AHBP samples can show Newtonian or non-Newtonian behavior. Even beside the fact that they were not thermally pretreated, samples AHBP-4I, AHBP-5I, AHBP-6I, AHBP-4II, and BH-4 show Newtonian behavior at temperatures higher than 70°C, which indicates lower extent of polar interactions between molecules

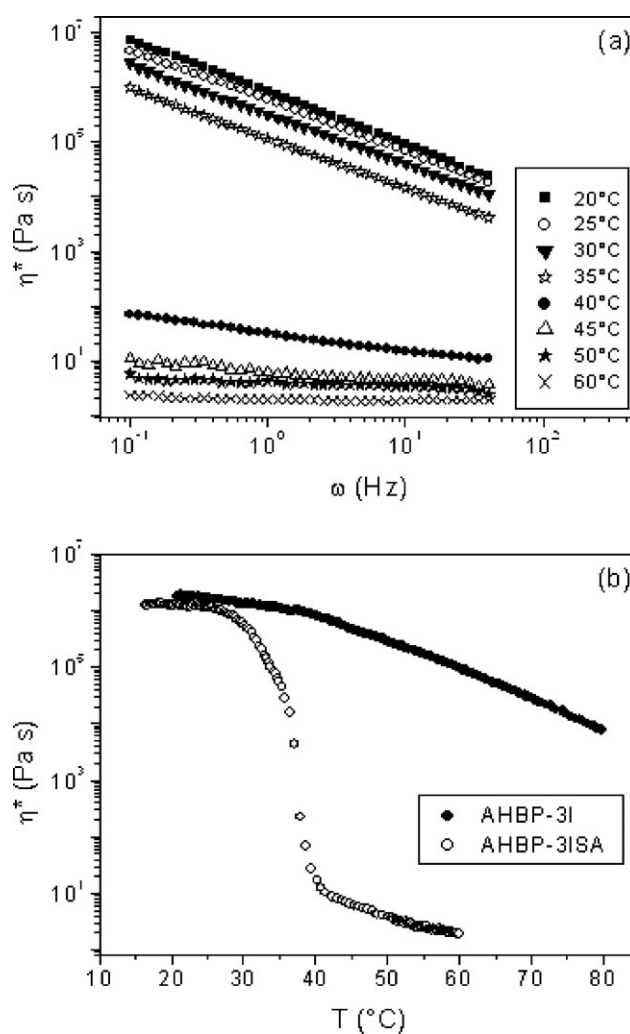


Figure 9 (a) Frequency dependence of the complex viscosity for the sample AHBP-3ISA, determined at different temperatures and (b) temperature dependence of the complex viscosity of the samples AHBP-3I and AHBP-3ISA, obtained at frequency of 1 Hz.

in comparison to the non-Newtonian behavior of samples AHBP-3I, AHBP-6II, AHBP-8I, and AHBP-8II. For these last four samples, complex viscosity is constant at temperatures higher than 65°C and at lower frequencies. Samples of lower generation number (AHBP-2I, BH-2, and BH-3), as well as the sample of tenth pseudo generation, show non-Newtonian behavior with significant frequency dependence of the complex viscosity in entire investigated temperature and frequency region. AHBP samples synthesized using one-step procedure have slightly higher values of complex viscosity than adequate samples synthesized by pseudo-one-step procedure, as a consequence of greater amount of linear units. The presence of strong hydrogen bonds in samples of lower generation number and in the sample AHBP-10I was confirmed from the values of melt flow activation energy and fractional free volume.

Modification of the end —OH groups with stearic acid leads to the significant change of rheological properties of third generation AHBP sample from the series I. At temperatures higher than 30°C, value of the complex viscosity is quite lower for the modified sample than for the nonmodified, which indicates that the presence of long chains instead polar —OH groups decreases the possibility of hydrogen bonds formation.

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