Rheological Properties of Hydroxyl-Terminated and End-Capped Aliphatic Hyperbranched Polyesters

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ABSTRACT: The rheological behavior of two series of aliphatic hyperbranched (HB) polyesters, based on 2,2-bis(hydroxymethyl)propionic acid (bis-MPA) and di-trimethylol propane (Di-TMP) as a tetrafunctional core, was studied. The effect of the size (pseudo-generation number, from second to eight) and structure on the melt rheological properties was investigated for a series of hydroxyl-terminated HB polyesters. In addition, the influence of the nature and degree of modification of the terminal OH groups in a series of fourth-generation polyesters end-capped with short and long alkyl chains and some aryl groups on the rheological properties was analyzed. The time–temperature superposition procedure was applied for the construction of master curves and for the analysis of the rheological properties of HB polyesters. The data obtained from WLF analysis of the HB polyesters showed that the values of the thermal coefficient of expansion of free volume α_f and the fractional free volume at the glass transition temperature, f_g, increase with increasing size of the HB polyesters. It was shown that the modified HB polyesters exhibited lower T_g and $T_{G'=G''}$ temperatures, above which viscous became dominant over elastic behavior. From an analysis of the master curves of the modified HB polyesters, it was observed that with increasing degree of modification, both storage and loss modules and complex dynamic viscosity and apparent energy for viscoelastic relaxation decrease, because of reduced intermolecular hydrogen interactions. They do not exhibit a plateau of rubbery behavior, which confirms that no entanglements are present and that the molar masses are below the critical molar mass. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41479.

INTRODUCTION

Dendritic polymers, including dendrimers and hyperbranched polymers, because of their highly branched molecular structure with high surface functionality and distinctive properties, have attracted large interest in the last 30 years.[1–5] Their three-dimensional molecular, highly branched and open structure at lower generation changes to more closed, essentially globular structure at sufficiently high molar masses, i.e., higher generation. Dendrimers are defined as monodisperse highly branched polymers, with regular and uniform molar mass and structure, whereas HB polymers are polydisperse in terms of molar mass, degree of branching, and segment length between the branch points. HB polymers exhibit properties that are between those of perfect dendrimers and linear polymers. Although the synthesis of dendrimers requires absolute control of all synthesis steps, the synthesis of HB polymers can be realized in one-pot or pseudo-one-pot polycondensation reactions. Therefore, the

low production cost of HB polymers makes them more commercially available than dendrimers.

Among HB polymers, polyesters based on 2,2-bis(hydroxymethyl)propionic acid (Bis-MPA) are one of the most extensively studied. A few excellent reviews on these hyperbranched polyesters have been published, including the synthesis, physical and rheological properties, modification and their application.[6–8] These aliphatic HB polyesters based on bis-MPA are commercially available from Perstorp under the trade name Boltorn®.

HB polyesters exhibit good solubility in common organic solvents and low melt viscosity because of their compact and less flexible structure. Furthermore, the terminal groups of HB polyesters could be modified to change their properties, such as hydrophobicity, wetting, adhesion, and solubility in different solvents, or to introduce reactive groups. HB polyesters and their derivatives have found application in coatings, drug delivery systems, as macromolecular

Table I. Physical Properties of the Hydroxyl-Terminated HB Polyesters

Sample	Z^a	DB^b (%)	Terminal OH-groups (%)	$w(OH)^{c)}$ (%)	Hydroxyl number^d (mg KOH/g)	$[\eta]$ (cm^3/g)	$M_{n-theor}$ (g/mol)
HBP(G#2)-OH	16	44.6	54.9	16.6	(546)	4.03	1642
HBP(G#3)-OH	32	44.1	50.9	15.6	517 (513)	4.81	3498
HBP(G#4)-OH	64	44.5	46.3	15.1	494 (498)	5.66	7210
HBP(G#5)-OH	128	45.0	47.7	14.9	494 (491)	5.45	14634
HBP(G#6)-OH	256	43.9	44.0	14.7	480 (487)	5.89	29482
HBP(G#8)-OH	1024	44.6	51.6	14.7	476 (484)	5.79	118570

^{a} Z, theoretical number of functional OH groups per molecule.
^{b} DB, degree of branching, determined by ^{13}C NMR spectroscopy (calculated by the Fréchet definition.
^{c} Weight fraction of terminal OH groups.
^{d} Theoretical value of the hydroxyl number is given in parenthesis.

initiators, crosslinking agents and as melt viscosity modifiers or blend components.

In general, the rheological properties of dendritic polymers depend on their structure, dimensions, and type of intermolecular and intramolecular interactions. It was shown that dendritic polymers exhibit Newtonian behavior in the molten state and concentrated solutions, which suggests that no entanglements are formed.[9,10] It was also shown that their melt behavior is mainly determined by surface interactions and is highly sensitive to the chemical nature of the terminal groups.[11] Dendritic polymers are amorphous materials with a well-defined glass transition temperature, T_g. Kim and Webster[12] proposed that the glass transition temperature for dendritic macromolecules has its origin in translation motions, and should, consequently, be more sensitive to the nature of the terminal units and less to molar mass.

The rheological behavior of HP polyesters and especially of commercial products was the subject of several articles.[11,13–20] Plummer et al.[11] reported that the rheological behavior of a HB polyester melt depends on its thermal prehistory. Therefore, it is possible to distinguish between entanglements and other physical interaction between chains by thermal treatment, because hydrogen bonds could be removed by thermal treatment while entanglements not. Although primary HB polyesters exhibited viscoelastic behavior in the molten state, as a consequence of the formation of hydrogen bonds between functional groups, preheated HB samples, on the contrary, showed Newtonian behavior in the melt. It was reported that dendrimers[9,21] and hyperbranched polymers[21] in molten state follow the Cox–Merz rule, which states that the complex viscosity, $\eta^\star(\omega)$ and steady shear viscosity $\eta(\gamma)$ are equal at the same rate of deformation. In general, this rule holds for linear isotropic polymers and has a great industrial impact, because oscillatory measurements are easier to perform. On the contrary, in series of commercial aliphatic HB polyesters, Boltorn®,[14] and synthesized HB polyesters,[22] it was reported that the Cox–Merz rule does not apply with the possible explanation that the polymer melts exhibited a certain microstructure because of the higher hydrogen bonding interactions, which respond differently upon the application of steady or oscillatory shear.

In this article, the structure and rheological properties of aliphatic HB polyesters based on bis-MPA as the repeating unit and di-trimethylol propane (Di-TMP) as the tetrafunctional core are presented. The HB polyesters were synthesized by a pseudo-one-step reaction (also called an incremental reaction) where the stoichiometric amount of bis-MPA corresponding to each theoretical dendrimer generation was added successively. Because the produced polymers were polydisperse and had an imperfect branched structure, the term pseudo-generation[6,23] was already suggested to distinguish hyperbranched polymers from ideally branched dendrimers. Synthesized and commercial hyperbranched aliphatic polyesters resemble dendrimers, i.e., they consist of a core from which branches extend giving a structure with a degree of branching of around 43%. Two different series of HB polyesters were prepared. The first one was a series of hydroxyl-terminated HB polyesters with different molar masses or pseudo-generations from second to eight. The second one was a series of HB polyesters of fourth pseudo-generation modified to different extent by propionyl chloride, and additionally by benzoyl chloride and neodecanoyl chloride, without altering the basic molecular structure. The aim of this study was to investigate the influence of the structure, i.e., number of pseudo-generation or molar mass and the nature of functional end groups on the melt rheology and on some physical properties of the HB polyesters. Dynamic mechanical spectroscopy was used for the analysis of the rheological behavior of these HB polyesters. The changes in the rheological parameters, such as the storage modulus (G') and loss modulus (G''), the complex dynamic viscosity ($\eta^\star$), and tanδ with frequency and temperature were followed. The insight into the rheological behavior of hydroxyl terminated and end-capped HB polyesters at different temperatures and deformations, allows one to tailor rheological properties with simple end-group modification, and to define the potential application of these functionalized materials, especially in the field of coatings.[24–27]

EXPERIMENTAL

Materials

2,2-Bis(hydroxymethyl)propionic acid (bis-MPA) and di-trimethylol propane (Di-TMP) were supplied by Perstorp

Table II. Physical Properties of the Modified Fourth Generation HB Polyesters

| Sample | Hydroxyl Number[a] (Mg KOH/g) | Degree of modification (%) | Residual OH groups | | $[\eta]$ (cm^3/g) | $M_{n\text{-theor}}$ (g/mol) | GPC | | |
			Terminal	Linear			M_n (g/mol)	M_w (g/mol)	M_w/M_n
HBP(G#4)-OH	494 (498)	–	46.3	53.7	5.66	7210	3330	5080	1.50
HBP(G#4)-C1	365 (372)	15	31.4	53.6	5.93	7721	4840	6620	1.37
HBP(G#4)-C2	244 (257)	32	20.4	47.6	5.40	8377	4590	7760	1.69
HBP(G#4)-C3	206 (146)	70	0	30	5.43	9837	4460	6920	1.55
HBP(G#4)-C4	83.3 (71)	75	0	21	5.44	10092	3910	6800	1.74
HBP(G#4)-NeoC10		26	31.2	42.6	5.03	15146	4610	6670	1.45
HBP(G#4)-BA		35	17.3	42.7	5.10	11242	3830	6340	1.66

[a] The number in the parentheses is the theoretical hydroxyl number.

Polyols AB, Sweden. All other chemicals were from Aldrich and used as received without further purification. The commercial fourth generation HB polyester, BoltornH40, based on bis-MPA and with ethoxylated pentaerythritol as a core, was supplied by Perstorp AB, Sweden.

Synthesis of Hydroxyl-Terminated HB Polyesters
A series of hydroxyl-terminated aliphatic HB polyesters based on bis-MPA as an AB$_2$ monomer and a tetrafunctional polyol, Di-TMP, as the core, was synthesized by acid-catalyzed polyesterification in bulk, without further purification. By changing the core to monomer ratio, HB polyesters of different pseudo-generation numbers were obtained. The HB polyesters were synthesized using the pseudo-one-step procedure previously described in the literature.[28] Samples in the series of hydroxyl-functional HB polyesters from second to eight generation, were denoted HBP(G#2–8)-OH, whereby the number indicates the pseudo-generation number. The molar masses and structural characteristics of the hydroxyl-terminated HB polyesters are summarized in Table I.

Modification of HB Polyesters
Partially modified HB polyesters of the fourth pseudo-generation were obtained in the reaction with corresponding alkyl(aryl)-acyl chlorides. The modification of HB with propionyl chloride (80% modification of hydroxyl groups) is described below, as an example. To a solution of 12 g (1.66 mmol, with 0.1065 mol OH group) of the sample HBP(G#4)-OH in 25 g of THF, 6.8 g (0.086 mol) of pyridine was added. The flask was cooled in an ice bath to a temperature of 2–4°C. A solution of 7.88 g (0.085 mol) of propionyl chloride in 20 g of THF was added drop-wise over 3 h to the solution of the HB polyester. The reaction mixture was stirred at room temperature overnight. The product, modified HB polyester, was twice precipitated in water, dissolved in THF and precipitated in petroleum ether.

Hydroxyl-terminated polyester of the fourth pseudo-generation was modified (end-capped) with different groups: propionic, benzoic and neodecanoic, by using corresponding acid chloride. The series modified with different amounts of propionyl chloride (from 25 to 100%) is denoted as HBP(G#4)C3. The sam-

ples modified with the other acid chlorides are denoted as follows: with benzoate end-groups - HBP(G#4)-BA and with neodecanoate end-groups HBP(G#4)-neoC10. In this way, HB polyesters with various length and flexibility of the lateral branches were obtained. The molar masses and structural characteristics of the modified fourth pseudo-generation HB polyesters are given in Table II. The structural formulas of the modified fourth generation HB polyesters are shown in Figure 1.

Degree of Branching
The degree of branching was determined using ^{13}C NMR spectroscopy in accordance with the procedure described by Fréchet et al.[29] The samples were dissolved in deuterated DMSO and the solvent signal was used as a reference.

The average degree of branching of HB polyesters was calculated using the Fréchet equation:

$$DB = \frac{D+T}{D+L+T}$$

where the contents of dendritic (D), linear (L), and terminal (T) units were obtained by integration of corresponding peaks in the ^{13}C-NMR spectra.

Viscosity Measurements of Dilute Solutions
The intrinsic viscosities ($[\eta]$) of the HB polyesters were measured in an Ubbelohde viscometer at 25°C using THF as the solvent.
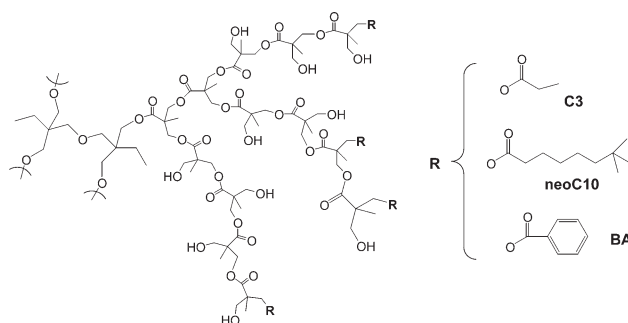

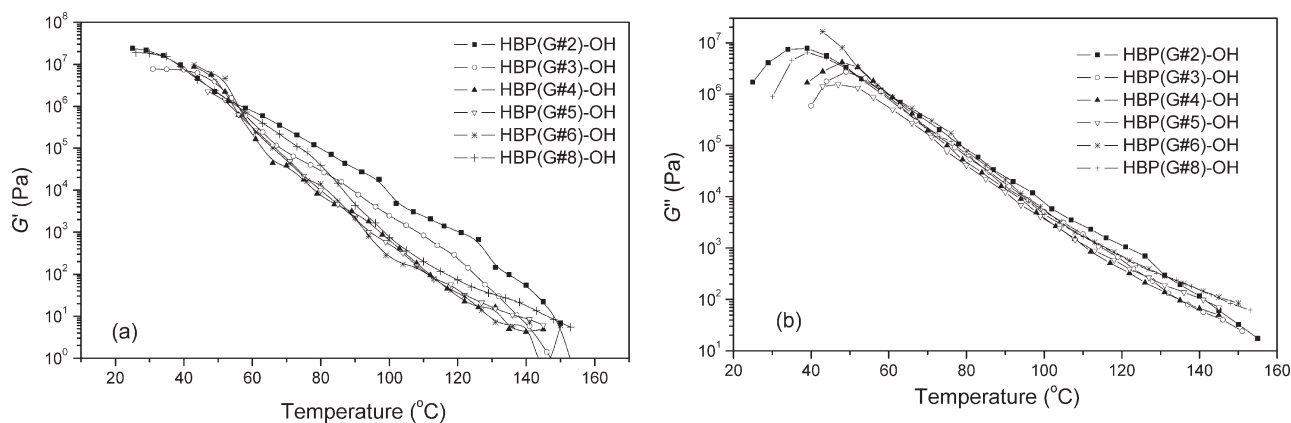**Figure 1.** The structural formulas of modified HB polyesters.

Figure 2. The dependence of storage (a) (G') and loss (b) (G'') modulus on temperature at a frequency of 1 Hz for the hydroxyl-terminated HB polyesters.

GPC Measurements of Molar Mass

The molar masses and molar mass distribution of the modified HB polyesters were measured using a Varian 9010 GPC system consisted of five TSK–GEL H columns (Tosoh Corporation) connected in series and a refractive index detector. THF was used as mobile phase at a flow rate of 1.0 mL/min. The system was calibrated with a number of polystyrene standards of known molar mass and low polydispersity.

Dynamic Mechanical Analysis

Dynamic rheological data, i.e., the dynamic storage modulus (G'), loss modulus (G'') phase angle ($\tan\delta$), and complex dynamic viscosity ($\eta^\star$), were obtained using a Rheometrics RMS 605 mechanical spectrometer. The parallel plate geometry was used in the temperature range 25–150°C. The temperature was increased stepwise in 5°C interval with a soak time of 0.5 min. A frequency range from 0.1 to 100 rad/s was scanned through 16 values equidistant on a logarithmic scale. The plate diameter was 25 mm and the gap between the plates was between 2 and 4 mm. The strain range was from 0.1% at the lowest temperature up to 30% at the highest temperature, to obtain an optimum response of the transducer. Some values of rheological parameters were omitted at higher temperatures and lower frequencies because they were outside the sensitivity range.

Samples of the HB polyesters were molded in the form of discs by pressing the powdered polymers in a three-part metal mold after heating for 90 min at a temperature of 140°C. After cooling, the samples were placed in a desiccator, because the HB polyesters were hygroscopic.

The results of the mechanical spectroscopic analysis are presented as master curves of the G', G'', and $\eta^\star$ *versus* shifted shear frequency. A standard procedure was used to reduce the rheological data and to construct the master curves at reference temperature of 100°C, by application of time–temperature superposition.

RESULTS AND DISCUSSION

Rheological Behavior of the Series of Hydroxyl-Terminated HB-Polyesters

Rheological tests were performed on the synthesized hydroxyl-terminated HB polyesters, of 2, 3, 4, 5, 6, and 8 pseudo-generations with 16, 32, 64, 128, 256, and 1024 hydroxyl groups per molecule. The theoretically predicted molar mass of these HB polyesters were in the range from 1642 to 118,000 g/mol. The degree of branching (calculated according to Freshet's definition) of the hydroxyl-terminated HB polyesters, synthesized by a pseudo-one-step procedure, was in the range from 44 to 45%, indicating it was not dependent on the number of generations or molar mass.

The viscosity measurements of dilute solutions of hydroxyl-terminated HB polyesters in THF showed that they exhibited low intrinsic viscosities [η], which only slightly increased with pseudo-generation (Table I). It was already reported that HB polyesters follow the Mark–Houwink equation with low values of the α coefficient, between 0.2 and 0.3, indicating a compact molecular conformation.[11]

Rheological properties of the synthesized HB polyesters are first presented as mechanical spectra in Figure 2. From these mechanical spectra (performed on samples that had not been thermally preheated), the glass transition temperatures were obtained and the temperature dependence of the storage modulus and complex dynamic viscosity of hydroxyl-terminated HB polyesters are compared.

Hydroxyl-terminated HB polyesters are amorphous materials in the glassy state at room temperature (Table III). The glass transition temperature, T_g, of the HB polyesters was determined through different rheological parameters. Thus, the T_g determined from the maximum of the loss modulus G'' (corresponding to the DSC measurements) was in the range of 40–49°C. T_g determined as the inflection point of G' was in the range from 33 to 56°C, whereas the values of T_g based on the maximum of $\tan\delta$ were up to 10 degrees higher (50–76°C).

Through increasing of the temperature, the drastic drop of the storage modulus and complex dynamic viscosity over 4.5–5 decades was observed. This could be attributed to the greater mobility of the molecules as a result of a weakening of the existing hydrogen bonds with increasing temperature, and to the highly branched molecular structure and the lack of entanglements, even for the HB polyesters of 6 and 8 pseudo-generations. It is well known that HB polyesters are brittle

Table III. The Influence of the Size of Molecules on the Rheological Properties the HB Polyesters

Sample	T_g (°C)			$T_{G'=G''}$ (°C)	$\eta^\star$ (Pa s) 0.1 rad/s, 110°C	λ (s) 110°C, 1 Hz
	G''_{max}	$G'_{inflect}$	$\tan\delta_{max}$			
HBP(G#2)-OH	39	33	50	123	6340	9.6
HBP(G#3)-OH	49	49	66	67	2470	2.7
HBP(G#4)-OH	48	48	65	52	511	1.0
HBP(G#5)-OH	46	52		52	473	0.54
HBP(G#6)-OH	42	56	76	52	585	0.36
HBP(G#8)-OH	39	40	58	44	416	0.77

materials with poor mechanical properties because of their non-entangled state.[5] This brittleness and their poor mechanical properties restrict the use of HB polyesters as thermoplastics and they are mainly suitable as additives to thermoplastic polymers (as flow modifiers to reduce the blend viscosity), blend components or as components in thermosetting resins.

In a molten state, the hydroxyl-terminated HB polyesters behaved as Newtonian liquids, i.e., the viscosity was independent of frequency, except for the second and third pseudo-generation HB polyesters (Figure 3). A similar behavior was reported for commercially available HB polyesters, Boltorn®, of different generations, where the lower generations (2 and 3) exhibited different melt rheology behavior in comparison to the Boltorn® polyesters of higher generations.[14] The polyester of the fourth generation, HBP(G#4)-OH, as a sample of a special interest in the current study (being the starting polyester for the second series of modified samples), was compared with the commercially available polyester with a similar structure, BoltornH40. The curve of the viscosity frequency dependence for BoltornH40 is also presented in Figure 3. The BoltornH40 polyester and the HBP(G#4)-OH were similar in their melt viscosity behavior, with slightly lower values being observed for the commercial polyester, indicating a low impact of the core structure on the rheological behavior.

The values of the complex dynamic viscosity, $\eta^\star$, at a frequency of 0.1 rad/s at a temperature of 110°C for the hydroxyl-terminated HB polyesters are also presented in Table III. These HB polyesters exhibited special behavior in the dependence of the melt viscosity at 0.1 rad/s (taken as the closest to the zero shear viscosity) on molar mass. Generally, a linear increase in melt viscosity with molar mass is observed for most linear polymers, with transition to the 3.4 power low beyond the critical molar mass, due to the onset of entanglements.[4] For the series of hydroxyl-terminated HB polyesters, the melt viscosity at 0.1 rad/s passed through a minimum at the fifth pseudo-generation, and leveled off at higher generations. Notably, a similar behavior was previously observed for polyamidoamine (PAMAM) dendrimers and aliphatic HB polyesters, which was explained by the transition from the open spherical structure of the lower dendritic generations into a more closed globular structure of the higher generations.[9,10] The absence of significant changes in the melt viscosity at 0.1 rad/s, i.e., its insensitivity to the molecular weight increase of the hydroxyl-terminated HB polyesters from the third to the eighth pseudo-generation indicates that entanglements were not present.

Characteristic relaxation times for the series of hydroxyl-terminated HB polyesters at a frequency of 1 Hz were calculated using the empirical equation:

$$\lambda = G'/(\eta^* \times \omega^2)$$

where G' is the storage modulus, $\eta^\star$ the complex viscosity, and ω is the applied frequency. The relaxation times of HB polyesters at a frequency of 1 Hz at 110°C are given in Table III. The HB polyesters of lower pseudo-generation (2 and 3 pseudo-generation) and with a higher content of terminal-hydroxyl groups (w(OH) or OH number in Table I) exhibited higher relaxation times compared with samples of higher generations (5 and 6). These results are in agreement with those previously reported by Hsieh et al.,[14] who showed that commercial HB polyesters of lower generation showed larger relaxation times of the same order of magnitude as rigid macromolecules, such as, for example, liquid crystalline polymers (LCPs) or grafted polystyrenes. Generally, linear flexible polymers exhibit relaxation times a few orders of magnitude smaller than rigid macromolecules and LCPs, and the behavior of HB polyesters is more similar to
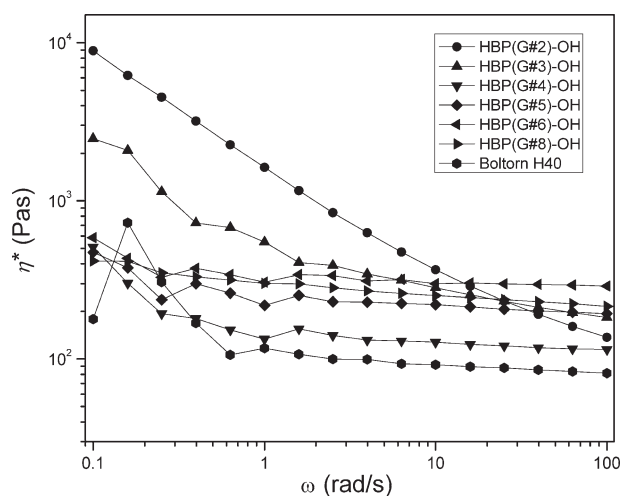

Figure 3. The change of the complex dynamic viscosity, $\eta^\star$, with frequency at 110°C for a series of the hydroxyl-terminated HB polyesters and BoltornH40, a commercial HB polyester of the fourth pseudo-generation.
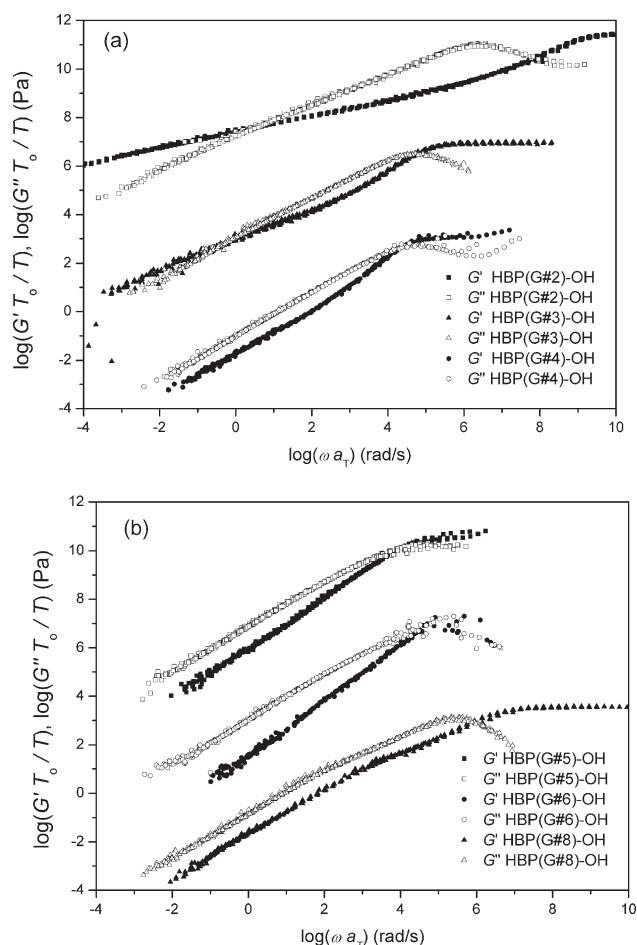
Figure 4. Master curves of the storage modulus and loss modulus for the series of hydroxyl-terminated HB polyesters ($T_o = 100°C$) (a) HBP(G#2–4) and (b) HBP(G#5–8). The data sets were shifted for clarity.

such molecules. In addition, for linear flexible polymer it is typical that the relaxation times increase with an increase in molar mass, due to the presence of entanglements. This phenomenon was not observed at higher HB generations presented in this article. Only an increase in relaxation time for the sample of eighth pseudo-generation (HBP(G#8)-OH) was observed, which could be a consequence of an increase in the concentration of hydroxyl groups (w(OH) or OH number in Table I).

Time–Temperature Superposition for the Series of Hydroxyl-Terminated HB-Polyesters

Using the dynamic mechanical analysis master curves of the reduced storage and loss modulus and the complex dynamic viscosity on frequency were obtained. For the construction of master curves, the time–temperature superposition principle was used. A standard procedure of reducing the rheological parameters with temperature, at an arbitrary chosen reference temperature, $T_o = 100°C$, was applied. The superposition procedure was accomplished by multiplying the experimental values of dynamic parameters G' and G'' with the factor T_o/T without a vertical shift, and multiplying the frequency with a shift factor, a_T. The shift factor was selected so as to achieve good superposition by translating reduced isotherms of G' and G'' horizon-

tally *vs.* ω. In this way, the frequency dependence of the dynamic moduli G' and G'' were expanded from three to 10–14 decades of frequency.

Master curves for the storage and loss moduli of all the examined hydroxyl-terminated HB polyesters at the reference temperature $T_o = 100°C$ are presented in Figure 4. As in the case of the $\eta^\star(\omega)$ dependence, the samples HBP(G#2)-OH and HBP(G#3)-OH showed different behavior compared with the other HB polyesters in the series. These HB polyesters exhibited two crossovers of G' and G'', one in the low-frequency region and the other in the high-frequency region, whereas for the other samples of higher generation, a crossover appeared only in the high-frequency region. They exhibited a solid-like viscoelastic response with $G' > G''$ and with a weak frequency dependence (a slope of G' of about 0.3) in the low frequency region. These results suggest a gel-like behavior characteristic for stiff network-like materials, which is a consequence of pronounced hydrogen bonding. It should be noted that none of the HB samples exhibited a plateau of their elastic or storage modulus at intermediate frequencies, which suggests that entanglements were not present.

In contrast to the behavior of the melt of HB polyesters of lower generations (2 and 3 pseudo-generation), the behavior of the higher generation HB polyesters (from 4 to 8 pseudo-generation) were characterized by near parallel changes of G' and G'' in the range from low to high frequencies.

The high-frequency crossovers of G' and G'' appeared at higher values of frequency for the HB samples with higher concentration of OH end-groups (HBP(G#2)-OH, HBP(G#3)-OH and HBP(G#8)-OH), due to significant contributions of intermolecular interactions, i.e., hydrogen bonding.

In the low-frequency (terminal) region, none of the examined HB polyesters exhibited a classical terminal behavior, i.e., both moduli deviated from a typical Rouse-like terminal behavior with $G' \sim \omega^2$ and $G'' \sim \omega^1$. This behavior was more pronounced in the G' than in the G'' dependence on frequency. The highest deviation in the scaling exponent for G' was observed for the samples of the second and third generation. With increasing generation number, the behavior slowly approached a terminal behavior with $G'' \sim \omega^{0.9}$, i.e., close to the terminal scaling, whereas the scaling exponent for G' was around one. These results are in agreement with non-terminal G' and G'' scaling that was previously reported for dendritic polymers and for HB polyesters.[13,17,23,30] These results indicate that synthesized HB polyesters exhibited slower relaxation modes compared with those for most linear polymers as a consequence of the high branch density and intermolecular interactions.

WLF Equation—Dependence of Shift Factor a_T on Temperature for the Hydroxyl-Terminated HB Polyesters

The temperature dependences of the shift factors, a_T, used to create the master curves of the dynamic parameters (G', G'' and $\eta^\star$) in the investigated temperature range, for all hydroxyl-terminated HB polyester, were well described by the Williams–Landel–Ferry (WLF) equation[31]

Table IV. Rheological Parameters of the Hydroxyl-Terminated HB Polyesters

Sample	C_1	C_2	E_a (kJ/mol) 80/110°C	f_g (10^2)	α_f, (10^4 K^{-1})
HBP(G#2)-OH	39.8	560.0	182/193	0.00971	0.195
HBP(G#3)-OH	23.9	347.6	185/182	0.0155	0.324
HBP(G#4)-OH	19.6	316.4	168/163	0.0185	0.722
HBP(G#5)-OH	12.9	232.5	158/143	0.0258	1.448
HBP(G#6)-OH	9.85	174.6	172/142	0.0294	2.525
HBP(G#8)-OH	8.10	150.7	170/133	0.0319	3.557

WLF constants, C_1, C_2, and the apparent activation energy for viscoelastic relaxation, E_a, fractional free volume, f_g, and the thermal expansion coefficient of the free volume, α_f.

$$\log a_T = -C_1(T-T_o)/(C_2+T-T_o)$$

where T_o is the reference temperature (100°C), and C_1 and C_2 are fitting constants. The WLF theory was developed to describe the temperature dependence of rheological properties close to the polymer glass transition temperature (in the temperature range from T_g to $T_g + 100$°C).

The values of the constants C_1 and C_2 obtained for the HB polyesters are listed in Table IV. Based on the values of the constants C_1 and C_2, the apparent activation energy for viscoelastic relaxation, E_a, was determined using the equation:

$$E_a = R\left(\frac{\mathrm{d}\ln a_T}{\mathrm{d}(1/T)}\right) = 2.303R\left[\frac{C_1 C_2 T^2}{(C_2+T-T_0)^2}\right]$$

The obtained values of E_a for the two temperatures (80 and 110°C) are presented in Table IV. The apparent activation energy for viscoelastic relaxation of HB polyesters ranged from 133 to 193 kJ/mol (at 110°C) and had a decreasing trend with increasing pseudo-generation number, which was more pronounced at higher temperatures. This implies increased chain mobility within the series that could be a consequence of decreased polar interactions in the higher generations that possess a smaller number of OH groups in their structure. Furthermore, in the higher pseudo-generations, the peripheral branches become more flexible and could be able to fold back into the interior of the globular molecules and thus decrease the extent of intermolecular hydrogen bond interactions. Relatively high values of the activation energies for the HB polyesters modeled by either the Arrhenius[10,14,15] or the WLF approach[23] were previously reported. The relatively high flow activation energies of branched and hyperbranched polymers were attributed to the increase in size and rigidity of the molecular structure.

The constants of the WLF equation varied with the structure, i.e., size and number of pseudo-generation of the HB polyesters, because of different contributions of the free volume, which is expected to depend on the mobility of the molecules. The fractional free volume in the temperature range above the glass transition temperature, T_g, is a linear function of temperature:

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

where f is the fractional free volume at temperature T, and f_g is the fractional free volume at T_g, whereas α_f is the thermal expansion coefficient of the free volume above T_g. The values of

f_g and α_f can be calculated from WLF equation based on the concept of free volume and are related to the constants C_1 and C_2 by the following equations:

$$f_g = B\left[1+\left(T_g-T_o\right)/C_2\right]/2.303C_1$$

$$\alpha_f = B/2.303C_1 C_2$$

where B is the empirical constant of the Doolittle equation, the value of which is close to 1. In these transformations, the lowest determined value of the T_g was used, i.e., the one determined as the maximum in the temperature dependence of G''. The calculated values of f_g and α_f for the hydroxyl-terminated HB polyesters are given in Table IV, being different from published values for most linear polymers ($f_g = 0.025$ and $\alpha_f = 4.8$ 10^{-4} K^{-1}). These differences could be explained by the fact that the free volume is directly controlled by the structure of the HB polyesters. It was observed that the values of the thermal coefficient of expansion, α_f, and the fractional free volume, f_g, increase with increasing size or pseudo-generation of the HB polyesters due to the increasing freedom of movement of the existing branches. This trend was identical and the values of α_f and f_g were similar to those found earlier for other HB polyesters.[23] Such a trend is in accordance with the observed decrease in E_a with generation number and suggests that the flexibility is increased because the hydrogen bonding is less pronounced. Simultaneously, these findings are in contradiction with some previously reported results, i.e., that the fractional free volume for HB polyesters did not change considerably with the molar masses,[10] or that f_g decreased with increasing M_w.[15]

Rheological Behavior of the Series of Modified HB Polyesters
Physical properties of modified HB polyesters are given in Table II. The structures of the modified HB polyesters of the fourth generation are given in Figure 1. The values of degree of modification were calculated from the hydroxyl numbers, whereas the percentage of terminal and linear hydroxyl groups were determined from ^{13}C NMR data. Four samples of HB polyesters modified with propionyl chloride, with different degree of modification (from 15 to 75%) were prepared in solution using a reactive acid chloride. It was observed that the degree of modification was lower than that theoretically predicted. In addition, samples modified with different structural groups: benzoate and neodecanoate, with a single degree of modification were also
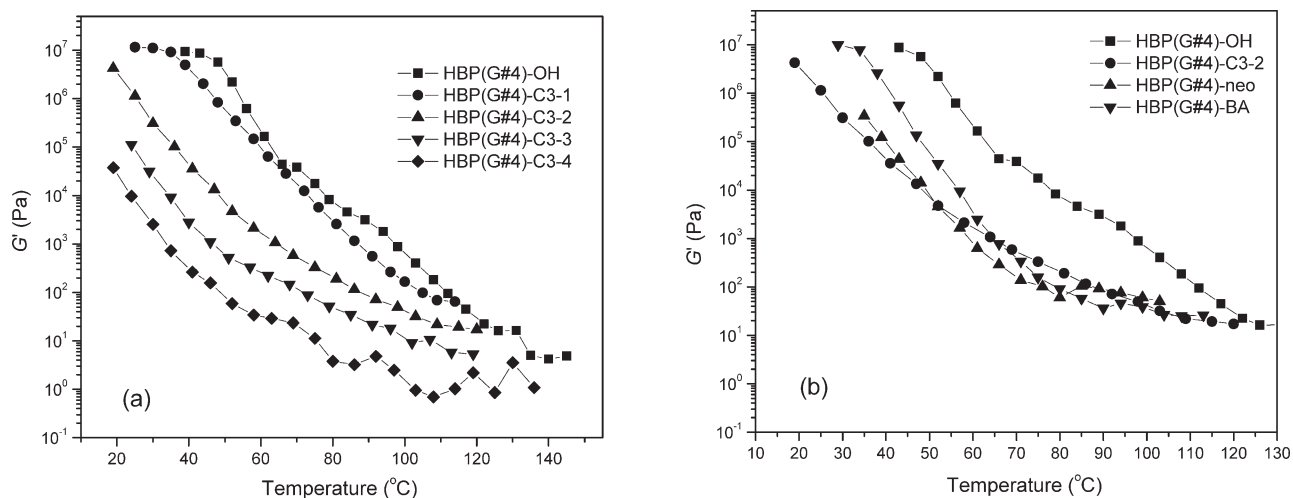
Figure 5. The storage G' modulus as a function of temperature at a frequency of 1 Hz for partially modified HB polyesters having (a) different contents of propionate end-groups and (b) different types of end-groups.

synthesized. The extent of modification was 26 and 35% for the samples with neodecanoate and benzoate groups, respectively. Through comparison of the type of hydroxyl groups (linear or terminal) present in the unmodified and modified HBP, it can be concluded that the modifications generally occurred at terminal or outer OH groups, due to the low reactivity of the linear OH groups. Another reason for the difference in reactivity of terminal and linear OH groups could be steric hindrance resulting from the highly-branched molecular structure of the HB polyesters. Only a large excess of acid chloride could lead to higher degrees of modification.

The alkyl-terminated and hydroxyl-terminated HB polyesters of the fourth generation were analyzed by gel permeation chromatography (GPC) using THF as the solvent. The GPC values of the molar masses were smaller than those theoretically predicted as a result of using linear polystyrene calibration standards. This is due to the specific branched structure of HB polyesters that have a smaller hydrodynamic volume compared with a linear polymer of the same molar mass and/or the interaction of a large number of polar functional groups with the column packing, especially in THF.[28,32] In addition, the presence of side reactions, such as cyclization, ether formation, decarboxylation and deactivation of carboxylic groups, and the self-condensation of bis-MPA, during melt polycondensation led to a broadening of the molar mass distribution and limits the attainable molar mass.[33–37] The number-average molar mass, M_n, of the starting hydroxyl-terminated fourth generation HB polyesters was 3330 g/mol, whereas it ranged from 3830 to 4840 g/mol for the modified polyesters. The degree of polydispersity was not significantly changed in the series of modified HB polyesters and ranged from 1.37 to 1.74.

The results obtained from dilute solution viscosity measurements showed that there was no significant change in the intrinsic viscosities $[\eta]$ in the series of HB polyesters modified with different amounts of propionate end-groups or with benzoate or neodecanoate end-groups. This suggests that there was no considerable increase in the hydrodynamic volume of the

modified polymers in the solvent compared to that of the unmodified HB polyester.

In the first part of the article, it was demonstrated that intermolecular hydrogen interactions (beside size and molecular structure) strongly affect the rheological properties of hydroxyl-terminated HB polyesters through changes of the dynamic modules, melt viscosities and the thermal transition temperatures. Thus, the end-group modification could be used for adjusting the rheology and melt viscosity, solubility and thermal transition temperatures and the thermal properties of HB polyesters.[5,10,23,38] The significant decrease in the T_g of the HB polyesters end-capped with short alkyl chains (C3–C6) is mainly attributable to a reduced extent of the hydrogen bonding.[5] The HB polyesters terminated with sufficiently long alkyl chains (C12 –C16), beside a lower T_g, exhibited a tendency to crystallize.[38] It was emphasized that the melt viscosity of the modified HB polyesters decreased with increasing degree of end-capping due to a reduction in the formation of hydrogen bonds and also depended on the chemical composition of the end-groups. In the molten state, the end-capped HB polyesters behave as Newtonian liquids and follow the empirical Cox–Merz rule.[15] The aim of the current study was to perform a thorough rheological analysis, and to compare the rheological behavior of partially modified or end-capped HB polyester of the fourth pseudo-generation having different degrees of modification and end-groups with different structures.

The rheological properties of the modified fourth pseudo-generation HB polyesters are presented as mechanical spectra, i.e., change of G' with temperature at a constant frequency of 1 Hz, in Figure 5(a) for the samples with different contents of propionate end-groups and in Figure 5(b) for the samples with different end-groups, but with a similar degree of end-capping.

The hydroxyl-terminated HBP(G#4)-OH polyester is amorphous and in the glassy state at room temperature (T_g (G''_{max}) = 48°C). In this series of HB polyesters end-capped with propionate groups, only the first two in the series have a

Table V. The Influence of the Nature of the End-Groups and Degree of End-Capping on the Rheological Properties of the Modified HB(G#4) Polyesters

Sample	Degree of modification (%)	$T_g(G''_{max})$ (°C)	$T_{G'=G''}$ (°C)	η^* (Pa s) 1 Hz, 110°C	λ (s) 110°C, 1 Hz
HBP(G#4)-OH	–	48	50	112	1.00
HBP(G#4)-C3-1	15	39	42	64.7	1.04
HBP(G#4)-C3-2	32	19	22	16.3	1.27
HBP(G#4)-C3-3	70	–	–	5.0	1.66
HBP(G#4)-C3–4	75	–	–	2.2	0.35
HBP(G#4)-neoC10	26	–		–	–
HBP(G#4)-BA	35	37	37	20	1.28

$T_g(G''_{max})$ above 20°C (Table V), and their values decreased with increasing degree of modification. This confirms that the T_g of HB polyesters partially modified with propionate end-groups is sensitive to the modification of the end-groups and its extent, due to a reduction in the number of hydroxyl groups per molecule. Therefore, it was shown that the reduction of hydrogen interactions between the molecules has a significant influence on the T_g of HB polyesters. An influence of the type of end-group on the T_g was clearly observed from the difference in $T_g(G''_{max})$ for the samples with a similar degree of modification, but with a different structure of the end-group: HBP(G#4)-C3–2 and HBP(G#4)-BA, whereby the latter has a higher $T_g(G''_{max})$ because of its structural rigidity.

Figure 5 shows that the storage modulus of the modified HB polyesters monotonically decreased with increasing temperature, with no rubbery plateau within which the material could support higher deformation. In addition, it could be noticed that the values of G' were smaller for the modified samples over the whole investigated temperature range, with the G' shifted to lower values with increasing degree of modification. This again confirms that the introduction of short alkyl end-groups into the molecular structure reduced the extent of the hydrogen bonding, and also contributed to chain flexibility and therefore to decreases in the dynamic storage moduli.

A comparison of the G' modulus of HBP(G#4)-C3–2, HBP(G#4)-neoC10 and HBP(G#4)-BA with approximately same degree of modification showed that the structure of the end-groups also significantly affected the rheological properties. It can be seen that the benzoate-terminated (HBP(G#4)-BA) exhibited the largest values of the storage modulus at low temperatures, followed by the neodecanoate-terminated polyester (HBP(G#4)-neoC10) and finally the propionate-terminated (HBP(G#4)-C3–2). This could be explained by the size and rigidity of the ester end-capped groups. The aromatic nucleus in the benzoic group contributes to the stiffness of the chain, thus increasing the storage and loss modulus, and the T_g. At higher temperatures, the differences between the HP polyesters modified with different structural units were less pronounced, although their corresponding values of G' were all lower compared with the unmodified HB polyester, indicating that hydrogen bonding was still dominant at these temperatures (in the case of HBP(G#4)-OH) within the time of the experiment.

Another important rheological parameter is the temperature at which the modulus G' and G'' are the same ($T_{G'=G''}$ in Table V) and at this temperature, the elastic and viscous response of the material are the same. At temperatures lower than this temperature, G' is greater than G'', which means that the elastic response to the deformation of the sample dominates, and
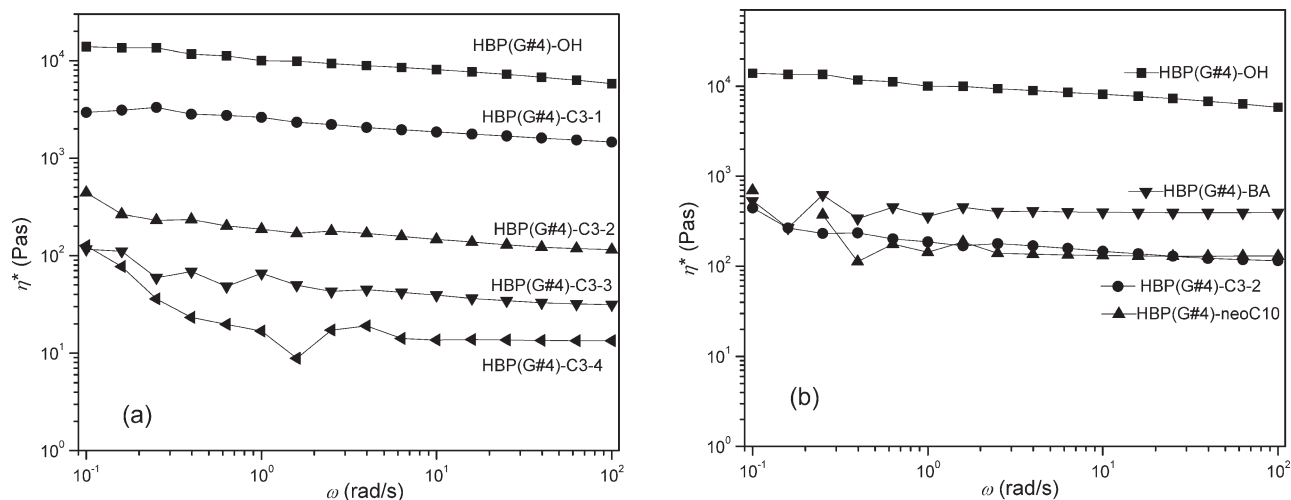
Figure 6. The change of the complex dynamic viscosity, η^*, with frequency at 80°C for the partially modified HB polyesters (a) with different contents of propionate end-groups and (b) with different types of end-groups.
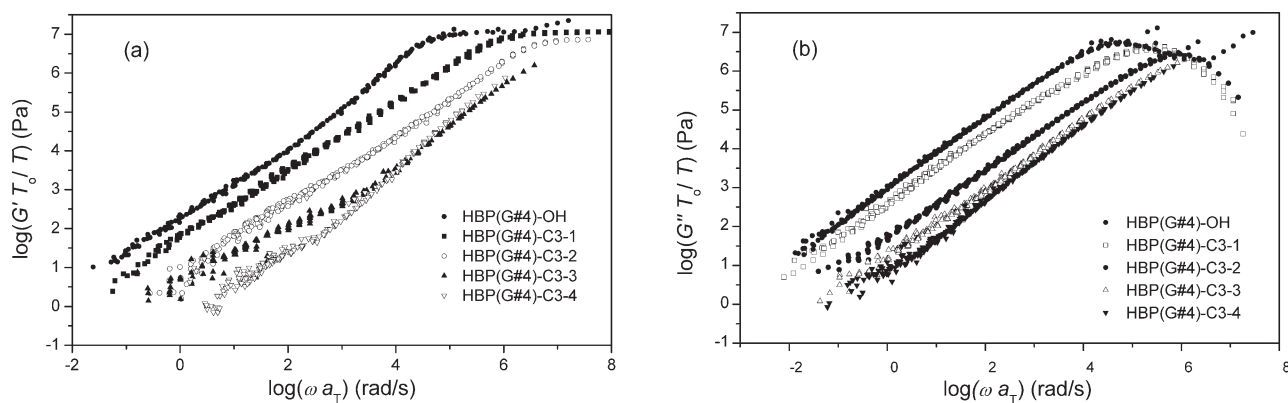
Figure 7. Master curves of the (a) storage and (b) loss modulus as a function of frequency for HBP(G#4)-C3 modified with propionate end-groups at a reference temperature of 100°C.

above this temperature, G'' is greater than G', i.e., the viscous response dominates. Polymers with higher content of propionate groups have a lower $T_{G'=G''}$ temperature compared with the unmodified HB polyester, whose temperature $T_{G'=G''} = 50°C$. This means that the modified HB polyesters softened and began to flow at lower temperatures. An influence of the type of end-group was also observed in the trend of $T_{G'=G''}$ among HBP(G#4)-C3–2, -neoC10 and -BA. The introduction of the more rigid benzoic group increased the $T_{G'=G''}$ value, whereas the more flexible long alkyl chain had the opposite effect.

The complex dynamic viscosity of HB polyesters greatly depends on the type and degree of modification, implying that this rheological parameter is sensitive to any change in the chemical structure of HB molecules. The values of the complex dynamic viscosities at 110°C and 1 Hz for the modified HB polyesters are given in Table V. The complex dynamic viscosity of HB polyesters decreases by two to three orders of magnitude (almost shifting out of the range of the instrument sensitivity) on incorporation of the propionate end-capping groups, which could be of great importance in processing applications, where low viscosities are required. To capture the rheological behavior of the complex viscosity, the viscosity curves of the modified HB polyesters at 80°C are compared in Figure 6. At 80°C, the unmodified HB polyester of fourth generation still exhibit pseudoplastic behavior in contrast to its behavior at 110°C (Figure 2). For the propionate modified polyesters, along with the decrease in the viscosity (as a consequence of reduced hydrogen bonding), the behavior is approaching Newtonian with increasing degree of modification.

The influence of the type of end-group on the magnitude of the complex viscosity is not as pronounced as the influence of the degree of modification [Figure 6(b)]. As expected, among the HB polyesters with different end-groups, the highest viscosities were observed for the HB polyesters with rigid benzoate end-groups. In contrast to the corresponding propionate functionalized HB polyesters, benzoate functionalized polyester exhibited Newtonian behavior, indicating less hydrogen bonding in the latter case. Although these two polyesters have a similar degree of modification, the relative amount of residual terminal and

linear OH groups in these samples were different (Table II). The benzoate modified polyester possessed fewer terminal OH groups that contribute more to the hydrogen bonding.

The relaxation times of the partially modified HB(G#4) polyesters at a frequency of 1 Hz at 110°C are given in Table V. It could be observed that all the modified HB polyesters of fourth pseudo-generation, except for the sample HB(G#4)-C3–4 with the highest extent of propionate modification, exhibited larger relaxation times compared with the hydroxyl-terminated starting HB polyester. The observed increase in the relaxation times for the modified HB polyesters could be attributed to the synergistic effect of reduced flexibility of chain segments and the presence of bulky end-groups.

Time–Temperature Superposition for the Series of Partially Modified HB Polyesters
The results of the mechanical spectrometric analysis of the partially modified HB polyesters of the fourth generation are presented as master curves of the dependence of the modulus G' and G'' and complex dynamic viscosity on the shifted shear frequency at the reference temperature of 100°C (Figures 7–10).
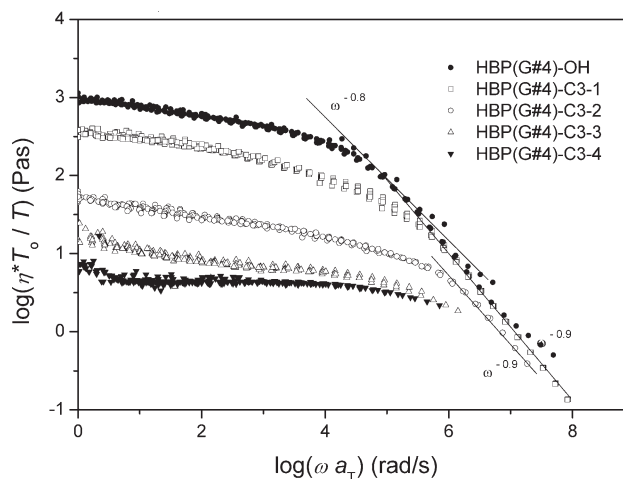

Figure 8. Master curves of the complex viscosity vs. frequency for the HBP(G#4)-C3 with different degrees of propionate end-groups at a reference temperature of 100°C.
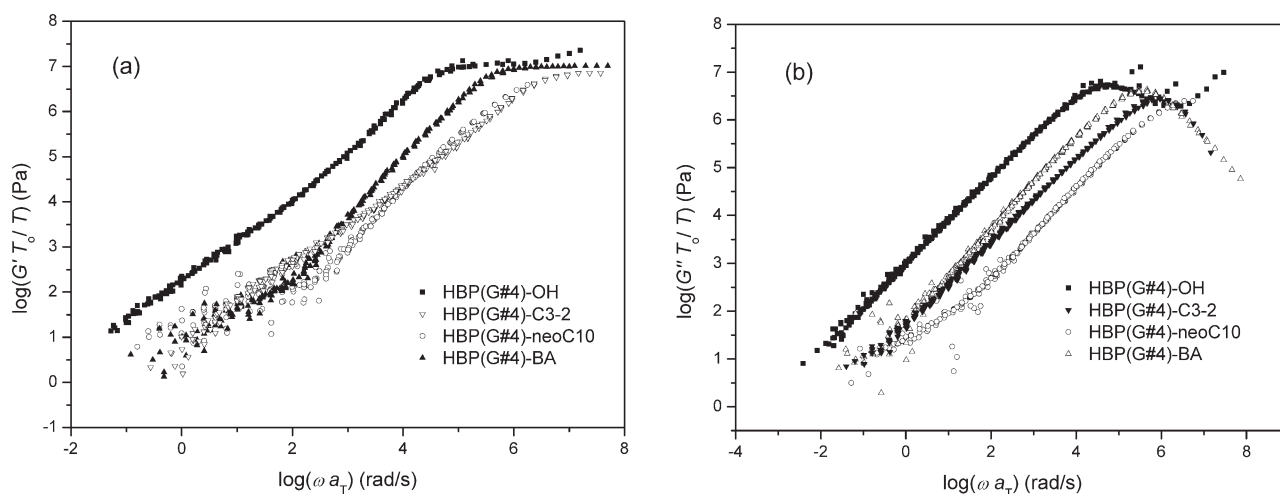
Figure 9. Master curves of the (a) storage and (b) loss modulus *vs.* frequency for the HBP(G#4) modified with approximately 30% of propionate, benzo-ate and neodecanoate groups at the reference temperature of 100°C.

In the HBP(G#4)-C3 series, the values of the storage modulus decreased with increasing degree of modification. At intermediate frequencies, no rubbery plateau of the storage modulus was observed for any of the modified HBP, which means that entanglements were not present and the molar masses were below the critical values. The maximum values of the modulus G'' were shifted to a higher frequency because the chains were more flexible and the impact of hydrogen bonding was less pronounced. At higher temperatures, there was scattering of the results, which became increasingly prevalent as the degree of modification increased; therefore, the low-frequency region was omitted from Figure 7. All modified HB polyesters, similar to their parent polyesters, exhibited non-terminal behavior. The divergence from Rouse-like behavior was more visible in the $G'(\omega)$ dependence, where the scaling exponent was found to range from 0.61 to 0.87, whereas the terminal slope of the $G''(\omega)$ dependence ranged from 0.61 to 0.97. These results imply that the modification of the end groups, either to a different extent or with a different architecture, could not prevail over the influence of the overall branched architecture and broad molecular weight distribution, which determine the behavior of HB polyesters in the terminal zone. Simultaneously, in the low frequency region, the values of G' lay below the corresponding G'' values. Another parameter that could be used for the detection of entanglements is the crossover of the G' and G'' master curves at frequencies just above the terminal zone, present in the case of entangled polymers. This criterion confirmed that entanglements were absent from the hydroxyl-terminated and end-capped HB polyesters of the fourth generation (not presented here).

The complex dynamic viscosity of the modified HBP samples decreased with increasing fraction of propionate end-groups in the molecular structure (Figure 8). Only the sample HBP(G#4)-C3–4 with the highest degree of propionate modification exhibited a pronounced plateau in the master curves, as a result of Newtonian behavior. The other HBP(G#4)-C3 (1–3) with lower degrees of modification exhibited a quite pronounced frequency dependence of the complex viscosity, i.e., complex viscosity

thinning. At the high-frequency end, the complex dynamic viscosity of the partially modified HB polyesters exhibited a characteristic frequency dependence for the glassy range where the exponent will approaches the value of -1 ($\eta^\star \sim \omega^{-1}$).

In addition, the influence of the structure of the terminal groups in series of polyesters of fourth generation end-capped with neodecanoate branched chains or rigid benzoate groups on the rheological properties was analyzed. It can be seen from Figure 9. that the benzoate-terminated polyester HBP(G#4)-BA showed a more elastic behavior (higher G' values) than other two modified HB polyesters with the similar degree of modification, but with different structures of the end groups. Additionally, its storage modulus G' declined significantly faster, i.e., it lost elasticity the fastest, with shifting shear frequency. Polymers HBP(G#4)-neoC10 and HBP(G#4)-C3–2 exhibited similar modulus values in the high-frequency range. The maximum value of the loss modulus G'' for the benzoate-terminated
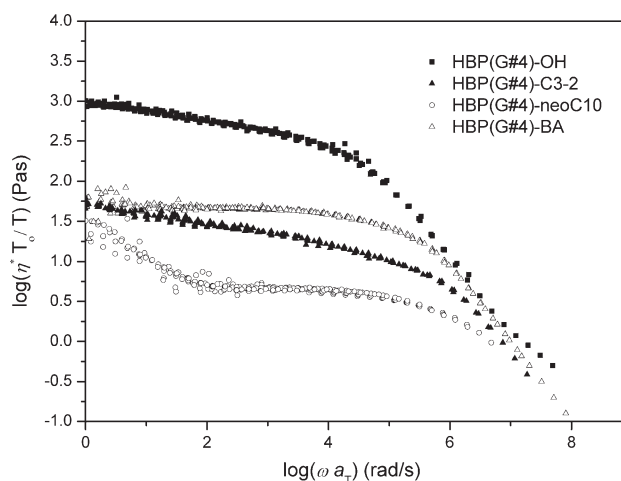

Figure 10. Master curves of the complex dynamic viscosity *vs.* frequency for the HBP(G#4) modified with approximately 30% of propionate, benzoate and neodecanoate groups at a reference temperature of 100°C.

Table VI. Rheological Parameters of End-Capped HB(G#4) Polyesters

Sample	C_1	C_2	E_a, (kJ/mol)		
			60°C	80°C	110°C
HBP(G#4)-OH	19.6	316.4	172.3	168	163.5
HBP(G#4)-C3-1	7.3	148.6	195.8	156.9	121.5
HBP(G#4)-C3-2	9.3	240.6	117.6	109.2	99.6
HBP(G#4)-C3-3	9.0	240.6	114.7	106.6	97.3
HBP(G#4)-C3–4	8.0	290.5	78.4	75.6	72.1
HBP(G#4)-neoC10	19.0	326.2	160.7	157.7	154.0
HBP(G#4)-BA	7.0	166.5	155.5	130.3	105.7

WLF constants, C_1, C_2, and the apparent energy for viscoelastic relaxation E_a.

polyester HBP(G#4)-BA was shifted to a lower frequency because of the segmental rigidity of the benzoate group.

The master curves of the complex dynamic viscosity for the HB polyesters modified with different groups are presented in Figure 10. The lowest viscosity was exhibited by the polymer modified with neodecanoic groups HBP(G#4)-neoC10, whereas the highest was demonstrated by the benzoate-terminated HBP(G#4)-BA. In addition, it could be seen that the HBP(G#4)-neoC10 and HBP(G#4)-BA samples exhibited a plateau of Newtonian behavior, whereas HBP(G#4)-C3–2 showed viscoelastic behavior, i.e., dynamic shear thinning over the whole frequency range. As in the case of the viscosity dependence at 80°C, this could also be a consequence of the different amounts of hydrogen bonds originating from the terminal and linear OH groups present in the samples after modification.

The WLF equation was used to fit the temperature dependence of the shift factor a_T. The corresponding constants, C_1 and C_2, and the apparent energies for viscoelastic relaxation, E_a, at different temperatures for the series of partially modified HB(G#4) polyesters are summarized in Table VI. The apparent energy for viscoelastic relaxation, which is a quantitative measure of molecular mobility and intermolecular interactions, decreased with increasing extent of modification in the HBP(G#4)-C3 series. This is a direct consequence of reduced hydrogen bonding, which hindered molecular mobility in the unmodified hydroxyl-terminated HB polyesters. Moreover, judging by the values of the apparent energy for viscoelastic relaxation, the structure had a significant influence on molecular mobility. For example, the polyesters terminated with the branched neodecanoate and the rigid benzyl groups exhibited higher E_a values when compared with HBP(G#4)-C3.

To summarize, the properties of HB polyesters can be easily tailored by modification of their end terminal groups, thus leading to many applications. The rheological behavior of HB polyesters in the solid, and in the molten state, is important from both fundamental and applied aspects, because it could give information concerning their structure and macroscopic properties.

CONCLUSIONS

In the first part of the current study, the rheological properties of hydroxyl-terminated HB polyesters based on bis-MPA with different pseudo-generations (from 2 to 8 generation) were presented. All the HB polyesters are amorphous with a T_g from 39 to 48°C, whereas the modules G' and G'', and $\eta^\star$, drastically decreased with increasing temperature. The investigated HB polyesters, except the HB polyesters of second and third generation, behaved as Newtonian fluids in the molten state above 110°C. The values of characteristic constants of the WLF equation and the apparent activation energy for viscoelastic relaxation were determined. The fact that values of E_a decrease with increasing pseudo-generation number could be explained by the decreased intermolecular hydrogen interactions and the formation of a more closed globular structure. In addition, it was found that the values of the thermal coefficient of expansion, α_f and fractional free volume, f_g, increased with increasing size, i.e., pseudo-generation, because of the increased freedom of movement of the existing branches.

In the second part of the article, it was shown that the structure and degree of end-capping influenced the rheological behavior of the HB polyester of the fourth generation. The introduction of functional groups into the HB polyester decreased the number of terminal hydroxyl groups and reduced the hydrogen bonding, which led to the following:

HB polyesters with a low degree of modification with propionate end-groups and benzoate and neodecanoate groups were amorphous and glassy with a T_g above room temperature, whereas the HB polyesters with a high degree of modification with propionate groups were viscous liquids at room temperature. The rheological parameters, such as modulus G' and G'' and the complex dynamic viscosity of the modified HB polyesters were lower compared with the parent hydroxyl-terminated HB polyester. The polyesters with benzoate functional end-groups, which are the largest and least flexible, exhibited the highest modulus and viscosity, and T_g and $T_{G'=G''}$ values.

Analyses of the master curves of the partially modified HB polyesters showed that with increasing degree of modification, both the moduli and complex dynamic viscosity and apparent energy for viscoelastic relaxation decreased, because the chains were more flexible and the impact of hydrogen bonding was less pronounced. They did not exhibit a plateau of rubbery behavior, which confirmed that no entanglements were present and that the molar masses were below the critical molar mass. HB

polyesters with a higher degree of modification and the benzoate- and neodecanoate–terminated polyesters exhibited pronounced Newtonian behavior on master curves in the molten state. The HB polyesters with a lower degree of modification showed complex viscosity dependence on frequency, i.e., dynamic shear thinning.

The presented results showed that either the type of end-group or the degree of end-capping could be chosen as an effective means to finely tune the rheological properties of HB polyesters to fit the desired application.

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