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Characterization of commercial aliphatic hyperbranched polyesters

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Abstract

Commercially available Boltorn Hx ($x=20$, 30) hyperbranched (HB) polyesters of different theoretical core/monomer ratio (1/12 for H20 and 1/28 for H30) were characterized with respect to molar mass, composition, and structure. The results were compared to those obtained for the Boltorn H40 with a core/monomer ratio of 1/60 [Žagar E, Žigon M. Macromolecules 2002;35:9913 [11]]. The main side reaction in the pseudo one-pot synthesis of Boltorn polymers is a self-condensation of bis-MPA leading to the formation of HB structures without a core molecule. These are actually branches containing an unreacted carboxyl group. The fraction of HB structures without a core molecule increases with decreasing core/monomer ratio due to the decreasing fraction of HB structures with a core molecule. Since HB structures without a core molecule are of lower molar masses than HB structures with a core molecule, they particularly decrease the number average molar masses of the samples compared to the theoretically calculated ones. The polydispersity of Boltorn Hx increases with decreasing core/monomer ratio. Some of the hydroxyl groups were found to react intramoleculary forming ether bonds. Boltorn Hx polyesters have low degrees of branching due to the limited carboxyl group conversions, low DP_n values, the presence of the core unit, and lower reactivity of hydroxyl groups in linear repeat units compared to those in terminal ones. The degree of branching according to Frey increases with decreasing core/monomer ratio.

Keywords: Dendritic; Hyperbranched; Polyesters

1. Introduction

Hyperbranched (HB) polymers with dendritic architecture contain a large number of branching points and functional end groups. They can be synthesized by simple one-step polymerizations [1]. Such synthetic routes result in extremely polydisperse products in terms of both molar mass and molecular structure [2]. Both theoretical and real systems reveal that control over molar mass averages (MMA) and molar mass distribution (MMD) of HB polymers can be achieved by the addition of a small amount of multifunctional core molecules to the reaction system [3]. In the case of AB_x polycondensation, the core molecule is of type B_f. The most effective polymerization procedure involves the slow addition of monomers to core molecules [3f,4]. This favors the growth of HB polymers by reacting the monomers with growing molecules containing the core unit, whereas the reaction between monomers is negligible. The molar mass of the resulting polymer is controlled by the core/monomer ratio and the polydispersity (PDI) by the functionality f of the core molecule B_f. The degree of branching ($\overline{DB}$), a parameter describing the perfectness of the HB structure, is enhanced where the slow monomer addition strategy is used.

Control over the molar mass and PDI of the HB polymer by using a multifunctional core moiety in the polycondensation of AB_2 monomers has been demonstrated in the synthesis of HB aliphatic polyesters from 2,2-bis(methylol)propionic acid (bis-MPA) and various core molecules [3a,5–7]. Hult et al. reported a pseudo-one-step reaction where stoichiometric amounts of bis-MPA monomer, corresponding to each theoretical dendrimer generation, were added successively to the core molecules in bulk under acidic catalysis. The incremental addition mode of adding bis-MPA to ethoxylated pentaerythritol (PP50) as the core molecule was used for the synthesis of the commercially available Boltorn® aliphatic HB polyesters (Perstorp Specialty Chemicals AB, Sweden), which have been examined by several research groups for potential applications [8]. In our previous studies we investigated the structure of the H-bond network of the fourth generation HB polyester Boltorn H40 [9] and developed a procedure for the determination of its MMA and MMD [10]. Boltorn H40 was characterized in detail with respect to molar mass,

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composition, structure, the presence of side-products [10,11], and the relationship between the structure, thermal, and rheological properties [12]. These studies reveal that Boltorn H40 is highly polydisperse in terms of molar mass, composition (the content of dendritic, linear, terminal repeat units), and structure (with or without core molecule). The main side reaction in its synthesis is a self-condensation of bis-MPA leading to HB structures without a core molecule. This side reaction mainly influences the sample number average molar mass ($\bar{M}_n$), and to a lesser degree its weight average molar mass ($\bar{M}_w$). Due to bis-MPA self-condensation the fraction of HB macromolecules without a core molecule in H40 increases with decreasing degree of polymerization due to the decreasing fraction of HB macromolecules with a PP50 core molecule. A comparison of the $\bar{M}_n$ value calculated from its ^{1}H NMR spectrum with that experimentally determined by SEC-MALS measurements, as well as its mass spectrum [11], reveal that cyclization through intramolecular esterification as a side reaction did not take place during the synthesis of H40. Some of the hydroxyl groups (below 1%) reacted intramolecularly to form cyclic structures through ether bonds.

The aim of this work was to characterize Boltorn H*x* HB aliphatic polyesters with a theoretical core/monomer ratio of 1/12 for H20 and 1/28 for H30 in detail and compare the obtained results with those of Boltorn H40 (core/monomer ratio 1/60), which were presented in our previous paper [11]. The MMA and MMD of the samples were determined by size exclusion chromatography coupled to a multi-angle laser light scattering photometer (SEC-MALS) in a 0.7% solution of LiBr in solvent *N*,*N*-dimethyacetamide (DMAc) according to a procedure recently described [10]. The composition and structure were determined by ^{1}H and ^{13}C NMR spectroscopy under quantitative experimental conditions [11]. The fractions of unreacted bis-MPA carboxyl groups as well as ether groups were determined from the ^{1}H NMR spectra. The extent of cyclization through the ester bonds was evaluated by comparing experimentally determined $\bar{M}_n$ using SEC-MALS to the values calculated from the ^{1}H NMR spectra of the samples, and experimentally by mass spectrometry.

2. Experimental section

2.1. Materials

The HB polymers studied in this work are commercially available hydroxy-functional aliphatic polyesters of the 2nd, 3rd, and 4th pseudo-generation synthesized from 2,2-bis (methylol)propionic acid (bis-MPA) as the tri-functional AB_2 monomer and ethoxylated pentaerythritol (PP50) as the tetra-functional B_4 core molecule. The samples were supplied by Perstorp Specialty Chemicals AB, Sweden, under the tradename Boltorn H*x* ($x=20$, 30, 40) polymers, where *x* denotes pseudo-generation. The term pseudo-generation was suggested by Hult et al. [5] according to the stepwise addition of bis-MPA to PP50 in portions that represent the theoretical dendrimer generations. Our denotation of the samples is H20, H30, and H40. Details of the synthesis of materials are referred in the literature [5,6]. The theoretical core/monomer ratios, theoretical molar masses, weight average molar masses, polydispersities, hydroxyl and acid numbers per gram of material, and their glass transition temperatures (T_g) were obtained by Perstorp and are summarized in Table 1. The samples were dried at ambient temperature under vacuum for 24 h before measurements took place.

2.2. Characterization

The SEC-MALS measurements were performed at 25 °C using a Hewlett Packard pump series 1100 coupled to a Dawn-DSP laser photometer equipped with an He–Ne laser ($\lambda_0=$ 633 nm) and to an Optilab-DSP interferometric refractometer (DR) (both instruments are from Wyatt Technology Corp., USA). Separations were carried out using a PLgel 5 μm Mixed-D column (300 mm length and 7.5 mm ID, Polymer Laboratories, Ltd) with a precolumn in a 0.7% solution of LiBr (Aldrich) in DMAc (Aldrich). The PLgel Mixed-D column contains a mixture of individual pore size materials that cover a range of molar masses from 200 to 400, 000 g mol^{-1}. The nominal flow rate of the eluent was 0.9 mL min^{-1}. The mass of HB polyester injected onto the column was typically (1–2)$\times10^{-3}$ g, whereas the solution concentration was (1–2)$\times10^{-2}$ g mL^{-1}. A detailed description of the sample dissolution procedure is given in our previous paper [10]. The calculation of $\bar{M}_w$ from MALS requires a sample specific refractive index increment (d*n*/d*c*= 0.065), which was determined from the DRI response assuming a sample mass recovery from the column of 100%. Data acquisition and evaluation utilized Astra 4.73.04 software (Wyatt Technology Corp.). Since a MALS detector is not particularly sensitive toward low molar mass species, the sample molar mass averages were recalculated using Corona 1.40 software (Wyatt Technology Corp.), where the scattered

Table 1
Characteristics of HB polyesters Boltorn H*x* ($x=20$, 30, 40)

Boltorn H*x*	Theoretical core/ monomer ratio	M_{theor}[a] (g mol^{-1})	$\bar{M}_w$[b] (g mol^{-1})	$\bar{M}_w/\bar{M}_n$	Hydroxyl number (mg KOH g^{-1})	Acid number (mg KOH g^{-1})	T_g (°C)
H20	1/12	1748	2100	1.3	490–520	5–9	25
H30	1/28	3604	3500	1.5	480–510	6–10	35
H40	1/60	7316	5100	1.8	470–500	7–11	40

Data from Perstorp Specialty Chemicals AB.

[a] $M_{theor.}$ is a dendrimer-equivalent molar mass in which all the repeat units are attached to a core molecule.

[b] $\bar{M}_w$ was determined by SEC in 0.2% LiBr/DMF using linear PEO standards.

data points at the end of the chromatogram were fitted by regression.

The ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian Unity Inova 300 MHz NMR spectrometer using DMSO-d_6 as the solvent and tetramethylsilane (TMS) as the internal reference. Integrals in the ^{13}C NMR spectra were obtained from 10% solutions using an inverse gated decoupling mode with a suppressed NOE effect (a relaxation delay of 20 s, an acq. time of 5 s and up to 20,000 repetitions). ^{1}H NMR spectra were obtained from a 0.5% solution at room temperature and at 75 °C (a relaxation delay of 20 s, an acq. time of 5 s and up to 500 repetitions). The procedure for dissolution of Boltorn Hx in DMSO-d_6 involved thermal pretreatment (annealing at 140 °C for 20 min with subsequent quenching), as was also the case in SEC-MALS measurements [10]. By this means the H-bonding of hydroxyl groups was completely disrupted allowing well-resolved signals for –OH groups in terminal (4.6 ppm) and linear (4.9 ppm) repeat units. The signal for –OH groups in polyester terminal repeat units is well separated from the signal for –CH_2OR groups (4.2 ppm) [11]. Moreover, in the case of thermally pretreated samples, the intensities of the signals for –OH groups relative to the signal of methyl groups are higher, whereas those for –CH_2OR groups are lower when compared to the corresponding relative intensities of signals in the ^{1}H NMR spectra of the original samples.

Electrospray ionization-mass spectrometry (ESI-MS) measurements were performed on an LCQ ion trap mass spectrometer (Finnigan, MAT) with an electrospray ionization (ESI) interface. A mixture of 0.1 vol% ammonia in methanol/water (0.8:0.2, v/v) was used as the mobile phase with a flow rate of 0.5 mL min^{-1}. The injection volume was 50 μL. The ESI-MS conditions were as follows: capillary temperature 250 °C, ion time 5.00 ms, sheath gas flow pressure (N$_2$) 0.2 MPa, source voltage 4.50 kV, source current 1.60 μA, capillary voltage 10.00 V, and tube lens offset 10.00 V. A negative scan was obtained at m/z values from 150.0 to 2000.0.

Table 2
SEC-MALS results of Boltorn Hx (x=20, 30, 40) in 0.7% LiBr/DMAc

Injected mass (g)	$\bar{M}_w$ (g mol^{-1})	$\bar{M}_n$ (g mol^{-1})	$\bar{M}_w/\bar{M}_n$
Boltorn H20 ($M_{theor.}$=1748 g mol^{-1})			
1.530×10^{-3}	1890	915	2.06
1.793×10^{-3}	1880	940	2.00
2.066×10^{-3}	1810	920	1.97
Average	1860	920	2.01
Boltorn H30 ($M_{theor.}$=3604 g mol^{-1})			
1.539×10^{-3}	3370	1400	2.41
1.845×10^{-3}	3310	1420	2.33
2.072×10^{-3}	3340	1400	2.39
Average	3340	1410	2.38
Boltorn H40 ($M_{theor.}$=7316 g mol^{-1})[a]			
1.532×10^{-3}	6620	2430	2.72
1.800×10^{-3}	6560	2660	2.47
2.079×10^{-3}	6730	2650	2.54
Average	6640	2580	2.57

Molar mass averages were calculated using Corona software.

[a] Results for Boltorn H40 are presented in Ref. [11].

3. Results and discussion

The obtained MMA and MMD of Boltorn polyesters are independent of solution concentration indicating that H-bonds between polar groups are completely disrupted and the samples are actually dissolved on a molecular level (Table 2, Fig. 1(a)). The dissolution procedure involves thermal pretreatment of the samples at 140 °C for 20 min, subsequent quenching of samples to the temperature of liquid nitrogen, and the addition of solvent (0.7% LiBr/DMAc) to the frozen samples. Intermolecular H-bonding is prevented by complex formation of hydroxyl, carboxyl, and ester polar groups with Br$^-$ and/or [Li(DMAc)$_n$]$^+$ ions [10].

All three Boltorn HB polyesters have $\bar{M}_w$ values close to their theoretical molar masses, $M_{theor.}$, while the $\bar{M}_n$ values obtained with the regression of the points at the end of the chromatograms are considerably lower (Table 2). The MMA increases with decreasing core/monomer ratio, but the increase is lower than expected, especially in $\bar{M}_n$. The $\bar{M}_n$ of H20

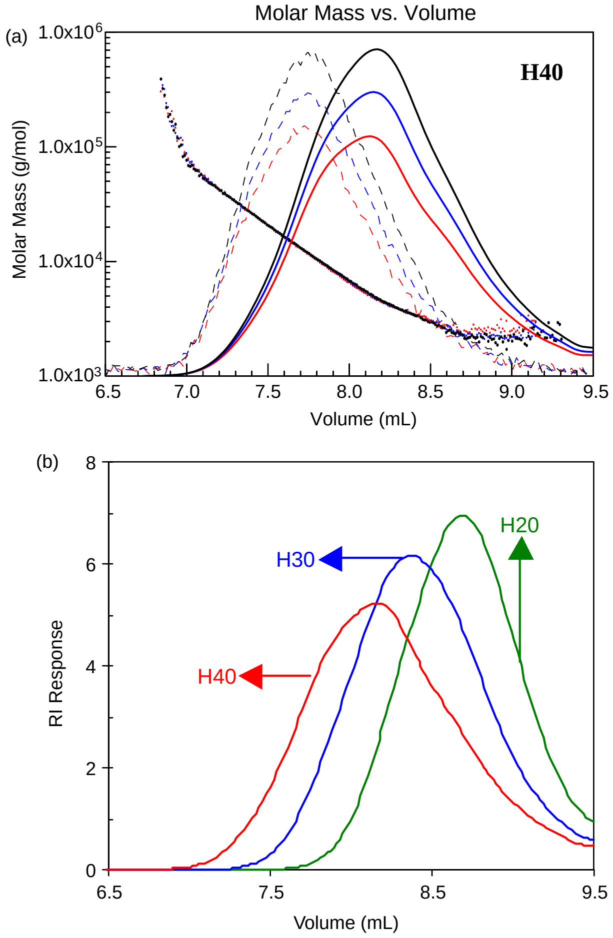


Fig. 1. (a) SEC-MALS chromatograms ((—) DRI response, (– – –) LS response at 90° angle), and molar mass vs. elution volume curves for thermally pretreated (140 °C, 20 min) Boltorn H40 polyester in 0.7% LiBr/DMAc (injection volume = 100 μL) at three different injected concentrations (Table 2). (b) RI chromatograms of thermally pretreated (140 °C, 20 min) Boltorn Hx (x=20, 30, 40) HB polyesters (injected mass $\sim2\times10^{-3}$ g, injection volume = 100 μL).

Table 3
Integrals of the ^{1}H NMR signals of individual protons for Boltorn Hx (x = 20, 30, 40)

Assignation	H20	H30	H40[a]
Experimental values			
$I\,(CH_3)$	55.84	52.95	54.11
$I\,(CH_2\mathrm{OR})$	34.71	33.44	35.00
$I\,(CH_2\mathrm{OH})$	88.96	60.89	46.08
$I\,(OH)$	25.28	21.10	19.77
Calculated values			
$I\,(CH_2)_{\mathrm{Penta}}$ (Eq. (1))	14.06	6.78	2.55
$I\,(CH_2)_{\mathrm{EO}}$ (Eq. (2))	35.16	16.95	6.38
$I\,(OH)_{\mathrm{theor.}}$ (Eq. (3))	25.64	21.04	19.31
$N_{\mathrm{B_2}}$ (Eq. (4))	1.26	0.93	0.54
$I\,(OH)_{\mathrm{calcd.}}$ (Eq. (5))	26.90	21.97	19.85

[a] Results for Boltorn H40 are presented in Ref. [11].

$$I(CH_2)_{\mathrm{Penta}} = \frac{2I(CH_2)_{\mathrm{B_4}}}{7} \tag{1}$$

and

$$I(CH_2)_{\mathrm{EO}} = \frac{5I(CH_2)_{\mathrm{B_4}}}{7} \tag{2}$$

where $I(CH_2)_{\mathrm{B_4}} = I(CH_2) - I(CH_2)_{\mathrm{calcd.}}$ and $I(CH_2)_{\mathrm{calcd.}} = (4/3)I(CH_3)$.

$$\begin{aligned} I(\mathrm{OH})_{\mathrm{theor.}} &= 4N_{\mathrm{B_4}} + N_{\mathrm{bis-MPA}} \\ &= \left(\frac{I(CH_2)_{\mathrm{Penta}}}{2} + \frac{I(CH_3)}{3}\right) \end{aligned} \tag{3}$$

where $N_{\mathrm{B_4}} = I(\mathrm{CH_2})_{\mathrm{Penta}}/8$ is the fraction of PP50 core molecules and $N_{\mathrm{bis-MPA}} = I(CH_3)/3$ the fraction of monomer units.

$$\begin{aligned} N_{\mathrm{B_2}} &= I(\mathrm{OH}) - I(\mathrm{OH})_{\mathrm{theor.}} \\ &= I(\mathrm{OH}) - \left(\frac{I(CH_2)_{\mathrm{Penta}}}{2} + \frac{I(CH_3)}{3}\right) \end{aligned} \tag{4}$$

$$I(\mathrm{OH})_{\mathrm{calcd.}} = \frac{1}{2}(I(CH_2\mathrm{OH}) - I(CH_2)_{\mathrm{EO}}) \tag{5}$$

represents only 53%, that of H30 39%, and that of H40 35% of their theoretical molar masses. As a consequence, the value of PDI also increases with decreasing core/monomer ratio (Table 2). Since the samples have broad MMDs the light scattering (LS) responses are skewed toward high molar masses, while the RI responses are of asymmetrical shape (Fig. 1(a) and (b)). Higher molar mass samples show more skewed LS responses as well as a more pronounced shoulder at a larger elution volume, although the amounts of injected samples onto the column were equal. This is in agreement with increasing sample PDI with lower core/monomer ratio.

Experimentally determined $\bar{M}_{\mathrm{n}}$ values of Boltorn polyesters by SEC-MALS are in good agreement with those calculated from the ^{1}H NMR spectra (Tables 3 and 4) as well as with the $\bar{M}_{\mathrm{n}}$ values determined experimentally by vapor pressure osmometry (VPO) [13], particularly in the case of H20 and H30.

Table 4
The number average degree of polymerization ($\overline{\mathrm{DP}}_{\mathrm{n}}$), average number of bis-MPA molecules per one core molecule (X), number average molar mass ($\bar{M}_{\mathrm{n}}$), fraction of macromolecules with and without core molecule ($x_{\mathrm{B_4}}$, $x_{\mathrm{B_2}}$), proportion of B$_4$ core molecules (%B$_4$), average number of hydroxyl groups per one HB macromolecule (OH), fraction of ether groups (%OH ether), and conversion of bis-MPA carboxyl groups (p_{A}) for Boltorn Hx (x = 20, 30, 40), as determined by ^{1}H NMR spectrometry [11].

Parameter	H20	H30	H40[a]
$\overline{\mathrm{DP}}_{\mathrm{n}}$ (Eq. (6))	6.76	10.41	21.44
$\overline{\mathrm{DP}}_{\mathrm{n}}$ (Eq. (7))	6.75	10.41	21.37
X (Eq. (8))	6.17	9.93	21.00
$\bar{M}_{\mathrm{n}}$ (Eq. (9))	930	1323	2579
$x_{\mathrm{B_4}}$ (Eq. (10))	0.58	0.48	0.37
$x_{\mathrm{B_2}}$ (Eq. (10))	0.42	0.52	0.63
%B$_4$ (Eq. (11))	8.59	4.6	1.73
OH (Eq. (12))	8.91	12.37	22.37
%OH$_{\mathrm{ether}}$ (Eq. (13))	6.0	4.0	0.4
p_{A} (Eq. (14))	0.93	0.95	0.97

[a] Results for Boltorn H40 are presented in Ref. [11].

$$\overline{\mathrm{DP}}_{\mathrm{n}} = \frac{2I(OH) + I(CH_2\mathrm{OR}) - (1/2)I(CH_2)_{\mathrm{Penta}}}{2I(OH) - I(CH_2\mathrm{OR}) - (1/2)I(CH_2)_{\mathrm{Penta}}} \tag{6}$$

The fact that experimentally determined SEC-MALS $\bar{M}_{\mathrm{n}}$ of Boltorn polyesters are accurate values is also confirmed by the calculation of the number of hydroxyl groups per mol (H20: 8–8.5; H30: 12.1–12.8; H40: 21.6–23.0) from the hydroxyl numbers values stated in Table 1, which are consistent with the number of hydroxyl groups calculated from the ^{1}H NMR

Table 5
Contents of dendritic (D), linear (L), and terminal (T) repeat units, degree of branching ($\overline{\mathrm{DB}}$), coefficient of branching (α), average number of core reacted hydroxyl groups (f''_{PP50}, and the number average degree of polymerisation ($\overline{\mathrm{DP}}_{\mathrm{n}}$) of Boltorn H$x$ (x = 20, 30, 40) determined by ^{13}C NMR spectrometry

Parameter	H20	H30	H40[a]
D (%)	10.0	14.0	16.5
L (%)	56.5	57.0	57.0
T (%)	33.5	29.0	26.5
$\overline{\mathrm{DB}}_{\mathrm{Frey}}$	26.1	32.9	36.7
$\overline{\mathrm{DB}}_{\mathrm{Fréchet}}$	43.5	43.0	43.0
$\alpha = p_{\mathrm{A}}/2$	46.5	47.5	48.5
$\overline{\mathrm{DP}}_{\mathrm{n}}$[b]	11.6	16.3	21.1
f''_{PP50}	1.8	2.4	3.3
$\overline{\mathrm{DP}}_{\mathrm{n}}$[c]	6.2	11.2	18.5

D, L, T are fractions of dendritic, linear, and terminal repeat units determined from ^{13}C NMR spectra. $\overline{\mathrm{DB}}_{\mathrm{Frechet}} = (D+T)/(D+T+L)$ is the degree of branching according to Fréchet [22]. $\overline{\mathrm{DB}}_{\mathrm{Frey}} = (2D)/(2D+L)$ is the degree of branching according to Frey [17]. $\overline{\mathrm{DP}}_{\mathrm{n}}$ is the number average degree of polymerization calculated from the fractions of D, L, T structural units according to equation $\overline{\mathrm{DP}}_{\mathrm{n}} = (T+L+D)/(T-D)x_{\mathrm{B_4}}f + (T+L+D)/(T-D)x_{\mathrm{B_2}}$, where f is the functionality of the core molecule (f = 4 for fully reacted PP50 hydroxyl groups), and $x_{\mathrm{B_4}}$, $x_{\mathrm{B_2}}$ are the fractions of B$_4$ and B$_2$ core molecules [11].

[a] Results for Boltorn H40 are presented in Ref. [11].

[b] $\overline{\mathrm{DP}}_{\mathrm{n}}$ is calculated considering core functionality, f_{PP50}, of four.

[c] $\overline{\mathrm{DP}}_{\mathrm{n}}$ is calculated considering only the reacted hydroxyl groups of PP50 core, f''_{PP50}.

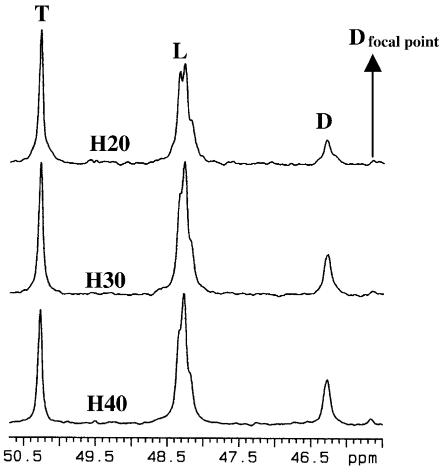


Fig. 2. ^{13}C NMR spectra of Boltorn H*x* ($x=20$, 30, 40) in DMSO-d_6. The quaternary carbon region of the spectra has been magnified: *T*, terminal repeat units (50.25 ppm); *L*, linear repeat units (48.25 ppm); *D*, dendritic repeat units (46.25 ppm); $D_{\text{focalpoint}}$: focal point dendritic units with –COOH group (45.65 ppm).

spectra (H20: 8.9; H30: 12.4; H40: 22.4, Table 4). The increase in molar mass from H20 to H40 HB polyester is also reflected in an increasing glass transition temperature (T_g) due to the skeleton buildup (Table 1).

The $\overline{\text{DP}}_n$ of Boltorn polyesters were also calculated from the intensities of the quaternary carbon signals for individual structural units in their ^{13}C NMR spectra (Fig. 2) according to the equation given in Table 5. These $\overline{\text{DP}}_n$ also increase with decreasing core/monomer ratio but the values are somewhat higher than those determined from the ^1H NMR spectra, especially in the case of H20 and H30. The reason is that only a part of hydroxyl groups of the PP50 core had reacted with bis-MPA. The average number of reacted core hydroxyl groups (f''_{PP50}) was estimated from the ^{13}C NMR spectra by comparison of the integrals for the –CH_2OCH_2– groups of PP50 core (chemical shift between 67.5 and 71 ppm) and unreacted core –CH_2OH groups at ~60.2 ppm, taking into consideration that their ratio in the original compound is 10/4. The average number of reacted hydroxyl groups per core increases with decreasing core/monomer ratio f''_{PP50}: H20: 1.8, H30: 2.4, H40: 3.3, Table 5). If only the reacted core hydroxyl groups are taken into account in the calculation of $\overline{\text{DP}}_n$, the obtained samples' $\overline{\text{DP}}_n$ are lower than those calculated with the supposition that all core hydroxyl groups were reacted ($f=4$), and consequently are in better agreement with those calculated from ^1H NMR spectra (Tables 5 and 4).

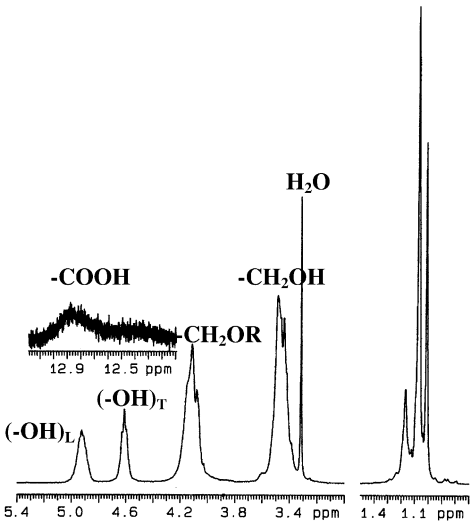


Fig. 3. ^1H NMR spectrum of Boltorn H20 HB polyester in DMSO-d_6. The carboxyl group region of the spectra has been magnified.

Significantly lower $\bar{M}_n$ values of Boltorn polyesters compared to their $M_{\text{theor.}}$ are a consequence of a self-condensation of bis-MPA. This side reaction leads to the formation of HB structures without a core molecule. They are actually branches with one carboxyl group in focal point dendritic or linear units. The quaternary carbon regions of the samples' ^{13}C NMR spectra reveal that the carboxyl groups in Boltorn polyesters are present mainly as focal point dendritic units (two reacted hydroxyl groups and unreacted carboxyl groups) as indicated by a quaternary carbon signal at 45.65 ppm (Fig. 2). In the ^1H NMR spectra the presence of carboxyl groups in HB polyesters can be seen as a broad signal between 12 and 13 ppm (Fig. 3).

The branches with unreacted carboxyl groups are present in poly(bis-MPA) polyesters due to the poor accessibility of carboxyl groups in the bulky HB structure, reduced reactivity since carboxyl groups can participate in H-bonding with H-bond acceptor groups [3a], or rather low extent of the reaction, which was ended before its completion in order to avoid undesirable side reactions (etherification, cyclization), which tend to occur at higher degrees of conversion [13–15].

The relative amounts of HB macromolecules with and without the core molecule were calculated from the ^1H NMR spectra (Tables 3 and 4). In spite of the fact that the carboxyl group conversion rises with decreasing core/monomer ratio (p_A: H20: 0.93, H30: 0.95, H40: 0.97, Table 4), the fraction of HB species without the core molecule, x_{B_2}, increases in the same order (x_{B_2}: H20 < H30 < H40) due to decreasing fraction of HB species with the PP50 core molecule, x_{B_4} (Table 4). The reason for this is that the probability for a self-condensation of bis-MPA increases when step by step larger amounts of bis-MPA are added to the reaction mixture for the synthesis of higher molar mass Boltorn polyesters.

PDI of Boltorn polyesters (PDI: H20: 2.01, H30: 2.38, H40: 2.57, Table 2) increases with decreasing core/monomer ratio, which is in agreement with PDI dependence on the core/monomer ratio for HB polymers synthesized in the batch system where all reactants are simultaneously mixed together [3d–3h,4j]. The exact influence of individual parameters (core/monomer ratio, carboxyl group conversion, reactivity of core functional groups, the average number of reacted B groups on the core molecule, step-wise monomer addition mode) on sample PDI is difficult to evaluate since each of them differently effects the $\bar{M}_w$ and $\bar{M}_n$ values. Nevertheless, the PDIs of Boltorn polyesters are unexpectedly low as compared to the theoretical calculation of PDI for HB polymers synthesized via batch polymerization process with the supposition that hydroxyl functional groups of the monomer and core molecule are of equal reactivities [3d–3h,4j]. In addition, our results on fractions of H40 indicate that the core molecule is not uniformly distributed in species over the entire molar mass distribution that would be expected for random batch polymerization of AB_2 and B_f. Its relative amount decreases with decreasing DP_n on account of the increasing fraction of coreless molecules [11].

Eqs. (1) and (2) represent the fraction of the core $–CH_2–$ groups belonging to the pentaerythritol (Penta) and ethoxylated (EO) part of PP50 core molecule, respectively.

$$\overline{\mathrm{DP}}_n = \frac{N_{\text{bis-MPA}}}{N_{B_4}+N_{B_2}} + \frac{N_{B_4}}{N_{B_4}+N_{B_2}} = \frac{8I(CH_3)+3I(CH_2)_{\text{Penta}}}{24I(OH)-9I(CH_2)_{\text{Penta}}-8I(CH_3)} \tag{7}$$

$$X = \frac{N_{\text{bis-MPA}}}{N_{B_4}+N_{B_2}} = \frac{I(CH_3)/3}{(I(CH_2)_{\text{Penta}}/8)+I(OH)-((I(CH_2)_{\text{Penta}}/2)+(I(CH_3)/3))} \tag{8}$$

$$\bar{M}_n = (\overline{\mathrm{DP}}_n-1)(M_{\text{bis-MPA}}-M_{H_2O}) + x_{B_4}M_{B_4} + x_{B_2}M_{B_2} = 116(\overline{\mathrm{DP}}_n-1) + 356x_{B_4} + 134x_{B_2} \tag{9}$$

$$x_{B_4} = \frac{N_{B_4}}{N_{B_4}+N_{B_2}} \text{ and } x_{B_2} = \frac{N_{B_2}}{N_{B_4}+N_{B_2}} = 1-x_{B_4} \tag{10}$$

$$\%B_4 = \left(\frac{x_{B_4}}{x_{B_4}+X}\right)100 \tag{11}$$

$$OH = X + 4x_{B_4} + x_{B_2} \tag{12}$$

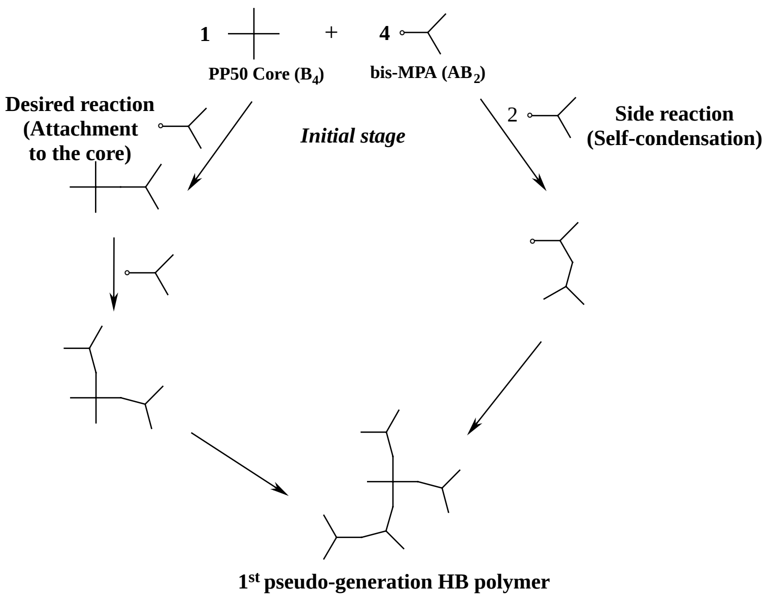
$$\%OH_{\text{ether}} = \left(\frac{I(OH)}{I(OH)_{\text{calcd}}}\right)100 \tag{13}$$

$$p_A = \frac{(X-x_{B_2})}{X} \tag{14}$$

If we consider the batch polymerization of AB_2 monomers with a small amount of B_f core molecules, the reaction mixture above a certain conversion will consist of species with an unreacted carboxyl group and of species with a core unit. The molecules with a focal unit can react with each other, or with the others containing a core unit to form a larger molecule. On the other hand, no reaction occurs among the molecules with a core unit, which leads to a lowering of sample DP_w and, consequently, to a narrowing of its molar mass distribution (MMD) compared to the MMD of the sample synthesized by batch polymerization of AB_2 monomers only. Taking into account that the rate at which a given molecule reacts with another is proportional to the number of its functional groups, which again is proportional to its degree of polymerization, it is obvious that a decrease in M_w and consequently PDI would be more efficient if there are a larger number of HB molecules with a core unit formed in the early stage of the reaction. The number of molecules with a core unit formed at the beginning of the reaction will be higher at higher core/monomer ratios resulting in lower MMA, higher reactivity of core B groups, and/or higher core functionality [3d–3h,4j]. By this means, the DP_w is considerable lowered, whereas the DP_n is only affected by the core/monomer ratio and the A group conversion. An even more efficient synthetic procedure for narrowing the MMD of the HB polymer is a core dilution/slow addition method, which allows the preparation of HB polymers with controlled molar masses and an enhanced degree of branching [4a]. In this procedure, the monomers are slowly added to the core molecules in solution leading to a preferential reaction between the core or growing core molecule and the AB_2 monomer. Therefore, coupling between growing HB molecules cannot occur.

The results obtained for Boltorn polyesters cannot be explained by either the higher reactivity of the core hydroxyl groups, since the reaction rate of bis-MPA polycondensation is comparable to that of PP50 and bis-MPA [3a], or by the chain growth type of kinetics that characterizes the slow monomer addition mode [4a], since a step-wise monomer addition used in the synthesis of Boltorn polyesters is actually a repeated one-pot procedure. Obviously, the reason for the greatly reduced PDIs of Boltorn polyesters has to be a consequence of their synthetic procedure [3a–3b,5,6]. In the first stage of a step-wise monomer addition an equivalent number of core hydroxyl groups and bis-MPA carboxyl groups react (core/monomer ratio = 1:4), Scheme 1 [16]. The polymerization proceeds via two reactions, the reaction of bis-MPA with the core, which is a desired reaction, and the self-condensation of bis-MPA, which competes with the attachment to the core. Statistically it is more probable that two bis-MPA react with each other than a bis-MPA with a core molecule ($OH_{\text{bis-MPA}}:OH_{\text{core}} = 2:1$). However, at higher conversions, the branches with carboxyl groups formed by AB_2 self-condensation will react with the core containing HB species. Hult et al. [3a] reported that an additional reason for the favored growth from the core is the solubility phenomena. The reaction mixture is, in the case of the PP50 core molecule, a two-phase system in the first stage of the reaction. Solid bis-MPA slowly dissolves in a low viscosity melt of PP50 at temperatures below the melting temperature of bis-MPA. Therefore, the reaction is diffusion controlled, leading to improved statistics for bis-MPA attachment to the core. A combination of step-wise monomer addition together with the two-phase system enables the formation of a large number of core containing HB macromolecules in the first stage of polycondensation reaction, which consequently results in effectively reduced M_w and PDI of Boltorn HB polyesters.

In the next steps, successively larger amounts of bis-MPA are added to the reaction mixture. The growth of the HB polymer is dominated by the reaction of already formed HB species containing a core unit. In addition, the self-condensation of bis-MPA proceeds as a competitive reaction to the attachment of bis-MPA to the core. During the synthesis



Scheme 1. Schematic illustration of hyperbranched polyester growth.

of higher molar mass Boltorn HB polyesters gradually greater amounts of bis-MPA are added to the reaction mixture, which increases the probability of a self-condensation reaction taking place. As a consequence, the fraction of HB structures without the core unit, as well as the total number of macromolecules in the reaction mixture, increases with decreasing core/monomer ratio. Since new branches with carboxyl groups continue to be formed during the step-wise monomer addition and are simultaneously consumed in the reaction with the core containing species, their growth is limited in comparison to the HB species containing core units. Therefore, the branches are of lower molar masses, and, consequently, especially affect the samples $\bar{M}_n$ values. On the contrary, the samples' $\bar{M}_w$ are influenced predominantly by higher molar mass species, i.e. HB species containing a core unit, which have been growing continuously from the beginning of the reaction. The self-condensation of bis-MPA thus has a more pronounced effect on the samples' $\bar{M}_n$, whereas its influence on the samples' $\bar{M}_w$ values is less significant.

Experimentally determined $\bar{M}_n$ values of Boltorn polyesters using SEC-MALS along with the regression analysis are comparable to those calculated from the ^{1}H NMR spectra (Tables 2 and 4), indicating that carboxyl and hydroxyl groups did not react intramolecularly into the cyclic structures. The absence of cyclic structure in Boltorn H*x* polyesters was confirmed by mass spectrometry, which distinguishes between the molecular ions of HB species with and without the core, as well as between acyclic species with –COOH groups and cyclic structures in the case of HB macromolecules without the core molecule. Molar masses of the acyclic and cyclic species without the core molecule can be calculated according to the following equations:

$$M = M_{\text{bis-MPA}} + (\text{DP}_n - 1)(M_{\text{bis-MPA}} - 18) \tag{15}$$

and

$$M = \text{DP}_n(M_{\text{bis-MPA}} - 18) \tag{16}$$

respectively.

The mass spectra of Boltorn H*x* polyesters show intense peaks of molecular ions of acyclic species with carboxyl groups and without a core molecule (Fig. 4 and Ref. [11]). A distance of 116 between two peaks corresponds to the repeat unit $M_{\text{bis-MPA}}$-H_2O. The peaks due to the molecular ions of cyclic structures without a core molecule are of very low intensity and may also originate from intramolecular etherification as a side reaction. Beside the main distribution, signals of lower intensity also appear in mass spectra and are ascribed to the species containing core molecule. These results and the fact that $\bar{M}_n$ obtained by SEC-MALS and ^{1}H NMR are comparable indicate that the content of cyclic structures in Boltorn H*x* polyesters is low and that they were most probably formed through an intramolecular etherification reaction, especially in the case of Boltorn polyesters with higher core/

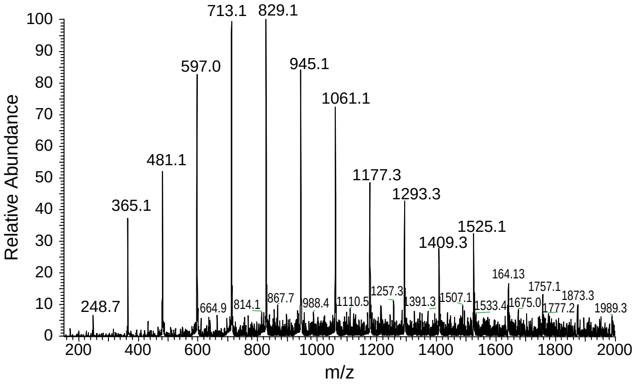


Fig. 4. ESI/MS spectrum of HB polyester Boltorn H20, negative ionization.

monomer ratios (H20, H30) as indicated by their ^{1}H NMR spectra (Table 4).

The role of cyclization through ester bonds in poly (bis-MPA) HB polyesters without the core molecule was studied theoretically and experimentally by Dušek et al. [14] using ESI-MS spectroscopy, and through ether bonds by Komber et al. [15] using NMR spectroscopy. Cyclization in poly(bis-MPA) with a core molecule (1,1,1-tris(hydroxymethyl)propane, TMP, PP50: Boltorn polyesters) was studied by Frey et al. [13] by comparing the samples' $\bar{M}_n$ values calculated from ^{1}H NMR spectra with those determined by the absolute VPO method. In the case of poly(bis-MPA) with a TMP core molecule, the authors also used the MALDI-TOF technique.

The above authors found that cyclic structures are present in poly(bis-MPA) regardless of the presence of a core molecule. Intramolecular cyclization through ester bonds competes with the desired intermolecular reaction, which is, in the authors' opinion, the reason for the drastically limited molar mass averages of poly(bis-MPA) HB polyesters. In poly(bis-MPA) without a core molecule, Dušek et al. [14] found that the fraction of cyclic structures increased with increasing carboxyl group conversion and converged to 100% at $p_A = 1$; they also found that, at a given conversion, the fraction of cyclic structures increases with increasing degree of polymerization and converges to a certain value. Frey et al. [13] reported that the fraction of cyclic species in poly(bis-MPA) with a TMP core molecule at a given core/monomer ratio increases with decreasing core/monomer ratio, while, at a given core/monomer ratio, it decreases with increasing degree of polymerization, which is the opposite of the results reported by Dušek et al. [14].

The presented results on Boltorn HB polyesters together with those presented in Ref. [11] show that the fraction of HB species without a core molecule increases with decreasing core/monomer ratio, and, at a given core/monomer ratio, it increases with decreasing degree of polymerization [11]. Such dependences are similar to the dependence of degree of cyclization on core/monomer ratio and degree of polymerization reported by Frey et al. [13]. The disagreement between our results and those obtained by Frey et al. [13] could be explained by a higher extent of AB_2 self-condensation in the case of poly(bis-MPA) with a TMP core molecule and/or the fact that the fraction of cyclic structures increases with increasing carboxyl group conversion, meaning that conversion in Boltorn polyesters is most probably lower than in poly(bis-MPA) with a TMP core molecule. Unfortunately, the carboxyl group conversion in the case of poly(bis-MPA) with a TMP core molecule is not given in the paper of Frey et al. [13] We also believe that for a given degree of cyclization the carboxyl group conversion in the poly(bis-MPA) HB polyesters synthesized from AB_2 and B_f have to be higher than in the poly(bis-MPA) HB polyester obtained by polycondensation of only AB_2. The reason is that during polymerization of AB_2 and B_f a certain amount of carboxyl groups of bis-MPA and branches is consumed in the reaction with the core or growing core molecules, which predominate at a higher DP_n. On the other hand, HB species without core molecule are more abundant at lower DP_n [11]. The lower degree of cyclization in the case of Boltorn polyesters with a carboxyl group conversion of 93–97%, compared to poly(bis-MPA) polyesters synthesized from AB_2 in the same range of carboxyl group conversion, can be explained by the fact that the probability for cyclization is lower for HB species of lower DP_n, [14].

The ether carbon was detected in the samples' ^{13}C NMR spectra as a broad signal of low intensity, at a chemical shift around 72–73 ppm. The calculations from the ^{1}H NMR spectra indicate that at a conversion of 93–97% the content of ether groups is 1–6%, and that they were mainly formed in an intramolecular reaction, resulting in cyclic structures. These results are in good agreement with those published by Komber et al. [15], who reported that at carboxyl group conversions below ~96%, depending on experimental conditions, 1–12% ether groups are formed mainly in intramolecular reactions.

The composition and $\overline{DB}$ of Boltorn H*x* polyesters were determined from the integrals of the quaternary carbon signals in their ^{13}C NMR spectra for terminal, linear, and dendritic repeat units (Table 5, Fig. 2). With decreasing core/monomer ratio the fraction of dendritic units increases, whereas the fraction of terminal repeat units decreases. The linear repeat units do not show any specific trend. Consequently, the relative amount of hydroxyl groups in linear repeat units increases and the amount in terminal ones decreases in the same order. These results are consistent with the relative intensities of the ^{1}H NMR signals for linear and terminal hydroxyl groups; $OH_{terminal}:OH_{linear}$: H20: 60:40, H30: 53:47, H40: 49:51 (Fig. 5).

All Boltorn H*x* polyesters show far larger fractions of linear repeat units (~57%) compared to fractions of dendritic ones (H20: 10%, H30: 14%, and H40: 16.5%, Table 5). The content of linear repeat units is larger, whereas that of dendritic repeat units lower than the calculated values for HB polymers obtained by a random batch polymerization of AB_2, which assumes equal reactivity of both kinds of B groups in the AB_2 monomer [17,18].

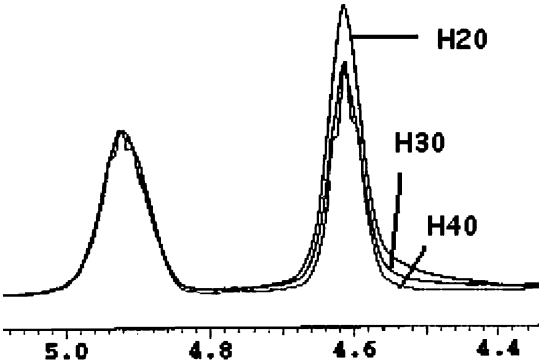


Fig. 5. The magnified hydroxyl region of ^{1}H NMR spectra of Boltorn H*x* (x= 20, 30, 40) in DMSO-d_6. The signal at 4.61 ppm is due to the –O*H* groups in terminal repeat units, whereas the signal at 4.93 belongs to the –O*H* groups in linear repeat units.

At conversions of 0.93, 0.95, and 0.97 the coefficient of branching, α, defined by Flory [19] is 0.465, 0.475, and 0.485 for H20, H30, and H40, respectively (Tables 4 and 5). The $\overline{\mathrm{DB}}$ according to Frey [17], which has been suggested to be more accurate for lower molar mass polymers, are much lower than the α values and increase with decreasing core/monomer ratio from H20 to H40 (Table 5). The reason is that Frey's $\overline{\mathrm{DB}}$ increases from zero to the limiting value (0.5 for random polycondensation) with increasing $\mathrm{DP_n}$. Due to the low $\mathrm{DP_n}$ of Boltorn polyesters and limited carboxyl group conversion, the $\overline{\mathrm{DB}}$ is additionally reduced due to the presence of a core molecule in the HB structure [20]. Namely, the $\overline{\mathrm{DB}}$ is lower at a higher content and functionality of the core molecule [3g–3h,4j]. Nevertheless, the reduction in $\overline{\mathrm{DB}}$ due to the presense of the core molecule is compensated for, in the case of lower molar mass polyesters, by the actual functionality of the core, which is much lower than four (Table 5). On the other hand, the reduction in $\overline{\mathrm{DB}}$ due to the formation of low molar mass HB species in the self-condensation reaction is compensated for by the lower functionality of AB_2 compared to that of the PP50 core molecule. Even if we take all of the above mentioned parameters (incomplete conversion, low $\mathrm{DP_n}$ values, the presence of a core unit) into account, they cannot explain such low experimentally determined $\overline{\mathrm{DB}}$ values for Boltorn polyesters. Another thing that may also reduce the $\overline{\mathrm{DB}}$ is the lower reactivity of the hydroxyl groups in the linear repeat units compared to those in the terminal ones [3h,17,21]. This is supported by the evolution of individual repeat units in poly(bis-MPA) during polycondensation of bis-MPA. At conversions above around 0.7 the fraction of linear units became larger, whereas the fraction of dendritic units smaller than predicted for random polycondensation [7]. This effect further increased with increasing conversion and was explained by slowed diffusion of the molecules due to the high viscosity of the reaction mixture.

According to Fréchet [22], the $\overline{\mathrm{DB}}$ are higher (around 0.43, Table 5) and do not change substantially with the core/monomer ratio. The reason is that the $\overline{\mathrm{DB}}$ according to Fréchet decreases from one at low $\mathrm{DP_n}$ and reaches the limiting value with increasing $\mathrm{DP_n}$. Therefore, the reduction in $\overline{\mathrm{DB}}$ for the above mentioned reasons is compensated for by the over-estimated Fréchet $\overline{\mathrm{DB}}$ values, especially in the case of Boltorn polyesters of lower $\mathrm{DP_n}$.

4. Conclusion

Boltorn polyesters are polydisperse products not only with respect to molar mass, but also to structure. They consist of HB structures with a polyol core from which branches extend, while the HB structures without a core unit consist of tree-like branches that contain a focal point unit (unreacted carboxyl group), mainly in the dendritic focal point repeat units.

The molar mass averages and molar mass distributions of Boltorn H*x* HB polyesters are independent of solution concentration, thus indicating that thermally pretreated (140 °C, 20 min) and quenched samples are dissolved in 0.7% solution of LiBr in DMAc on a molecular level. The samples weight average molar masses are close to their theoretical molar masses, whereas the number average molar masses are significantly lower. This is a consequence of the self-condensation of bis-MPA during their synthesis. This side reaction results in the formation of HB structures without a core molecule. The fraction of HB structures without a core molecule increases with decreasing core/monomer ratio. Since they are of lower molar masses they particularly influence the samples' number average molar masses. The reduction in the number average molar mass is more pronounced at lower core/monomer ratios and, consequently, the polydispersity index increases in the same order. Self-condensation of bis-MPA was found to be the main side reaction in the pseudo one-pot synthesis of Boltorn H*x* polyesters.

The experimentally determined SEC-MALS number average molar masses of Boltorn H*x* are comparable to those calculated from the ^{1}H NMR spectra, indicating that cyclization through intramolecular esterification reaction is not an important side reaction in the synthesis of Boltorn HB polyesters. This conclusion was also confirmed by mass spectrometry. Based on ^{1}H NMR spectroscopy of Boltorn H*x* it was found that a small amount of cyclic structures are formed through intramolecular etherification reaction.

The degrees of branching for Boltorn H*x* polyesters are low due to limited carboxyl group conversion, low $\mathrm{DP_n}$ values, the presence of the core unit, and most probably also due to lower reactivity of hydroxyl groups in linear repeat units compared to those in terminal ones. The degree of branching according to Frey increases with decreasing core/monomer ratio.

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