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Aliphatic hyperbranched polyesters based on 2,2-bis(methylol)propionic acid—Determination of structure, solution and bulk properties

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ABSTRACT

Due to their highly branched structure and the large number of functional groups hyperbranched polymers possess unique properties that make them interesting for uses in a wide variety of applications. Some of the most widely investigated hyperbranched polymers are the polyesters based on 2,2-bis(methylol)propionic acid. In this paper we present the results of characterization studies of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid which show that they are very complex products with a multidimensional distribution of various properties. The influence of the synthesis conditions on the structure and molar-mass characteristics of hyperbranched polyesters as well as the findings that allow a thorough understanding of the structure–property relationships are reviewed in detail.

Contents

1. Introduction

Changing the polymer architecture from that of conventional linear to partially or highly branched is one of the methods available to tailor a material's properties for a specific application where high performance or a specific functionality is required. Highly branched polymers, i.e., dendritic polymers, include dendrimers with a perfectly branched, monodisperse structure and imperfectly branched, hyperbranched polymers. The first hyperbranched polymers were synthesized about 30 years ago, although a theoretical description of the random polycondensation of multifunctional AB_x monomers with equal reactivity of the B functions, leading to statistical hyperbranched polymers, was reported by Flory as early as 1952 [1,2]. The polycondensation of multifunctional AB_x and a combination of the A_2 and B_y monomers is based on a step-growth reaction mechanism. These reactions dominate the preparation of hyperbranched polymers, particularly during the early stage of their development. Later on, other synthetic approaches based on a chain-growth mechanism were applied in order to prepare hyperbranched polymers with a versatile structure, e.g., self-condensing vinyl polymerization (SCVP) and ring-opening multi-branching polymerization (ROMBP), which is also called self-condensing ring-opening polymerization (SCROP), or proton-transfer

polymerizations, etc. The reported polymerization strategies for hyperbranched polymer preparation more closely resemble the polymerization reactions employed in the preparation of classical linear polymers rather than dendrimers, which require time-consuming and elaborate synthetic procedures involving many protection, deprotection and purification steps. For this reason the synthesis of dendrimers is far too complex and costly for large-scale industrial production and use as engineering materials. On the other hand, hyperbranched polymers are prepared in large quantities much more easily and cheaply than dendrimers by one-pot or pseudo-one-pot synthetic procedures, but at the expense of losing control over their structure and molar mass. Nevertheless, hyperbranched polymers are, because of their simple and, consequently, relatively cheap preparation, very attractive from the industrial point of view.

It is generally accepted that hyperbranched polymers possess very complex structures with a broad multi-dimensional distribution of their various parameters, such as molar mass, degree of branching and, in the case of side reactions, also chemical structure. In addition, a large number of geometrical isomers can be formed for a given molar mass and degree of branching, complicating the characterization of hyperbranched polymers. At present,

an exact determination of the structural and molar-mass characteristics of hyperbranched polymers using the available characterization techniques is not completely feasible and, therefore, establishing and understanding the structure–property relationship of hyperbranched polymers are challenges to be faced in the future. Recently, many theoretical and computational studies focused on the structure–property relation of hyperbranched polymers have appeared in the literature and are of great help in the understanding of these relations.

Despite the complex characterization, hyperbranched polymers are, in general, considered to have unique solution and bulk properties, which differ significantly from those of their linear counterparts, e.g., they exhibit a compact structure, less flexibility, a low degree of entanglement, a significant chain-end effect, a low solution and melt viscosity, a high solubility in common solvents, and a different origin of the glass-transition temperature. In contrast to polymerization reactions, from the property-profile viewpoint hyperbranched polymers more closely resemble dendrimers than conventional linear polymers. The modification of a large number of functional groups of hyperbranched polymers makes it possible to tailor their thermal, rheological and solution properties, solubility, reactivity, compatibility, adhesion to various surfaces, self-assembly, chemical recognition as well as electrochemical and luminescence properties, and thus provides a powerful tool for the design of hyperbranched polymers for a wide variety of applications.

Because of their simple one-pot or pseudo-one-pot preparation procedures, hyperbranched polymers were initially developed for large-scale industrial applications as blend components, additives for linear polymers, and above all as reactive components in coating and resin formulations, where they enhance specific material properties in spite of their imperfectly branched structure and highly dispersed molar mass. Subsequent literature indicated the much wider applicability of hyperbranched polymers, i.e., in high-tech fields like microelectronics, sensorics, non-linear optics, molecular imprinting, catalysis, biomedicine, etc. In recent years huge progress has been made with regard to the synthesis, characterization, theory, modeling, and potential applications of hyperbranched polymers, as demonstrated by the many excellent, comprehensive reviews on this topic [3–19].

In this review we focus on aliphatic hyperbranched polyesters prepared by the polycondensation of 3-hydroxy-2-(hydroxymethyl)-2-methylpropanoic acid (or 2,2-bis(methylol)propionic acid, bis-MPA) as the AB$_2$ monomer that contains one carboxyl (A = COOH) and two hydroxyl (B = OH) functional groups. The synthesis of hyperbranched polymers based on bis-MPA can be performed with or without various B$_f$ core molecules (f is the number of core hydroxyl functional groups). Hyperbranched polyesters based on bis-MPA were some of the first hyperbranched polymers to be synthesized and have been commercially available for many years. For this reason they have been widely investigated for possible applications as well as being the subject of detailed characterizations. The objective of this review is to present the recent progress in the characterization of the structural

and molar-mass characteristics of poly(bis-MPA) hyperbranched polyesters with respect to the experimental conditions used for the polymerization. Special emphasis is placed on the effects of these parameters on the solution and bulk properties. Thus, hyperbranched polyesters based on bis-MPA are a representative example of the complexity of the structure-to-property relationship for hyperbranched polymers and their complete characterization using advanced instrumental techniques. In addition, the variety of their fields of application is reviewed.

2. Synthesis of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid

2.1. Theoretical aspects of AB$_{f-1}$ condensation

The polycondensation of AB$_{f-1}$ monomers ($f \geq 3$ is the total number of monomer functional groups) was theoretically considered by Flory [1,2]. He predicted that the polycondensation of multifunctional AB$_{f-1}$ monomers would give randomly branched molecules without any crosslinking. The reaction involves the typical features of a step-growth reaction of multifunctional monomers. The theoretical consideration was simplified by assuming that the only allowed reaction is between the A function and the B function of another molecule and that both B functions have equal reactivity. Flory anticipated that the product should have a highly branched structure, containing dendritic (fully reacted B functions), terminal (no reacted B function), linear (one reacted B function if $f = 3$) units, and a single focal unit with an A function. Theoretically, the number of B functions should be $fn - 2n + 1$ (where n is the degree of polymerization) placed not only in terminal units at the periphery but also in linear units in the interior of the branched structure. The reacted A and B functions are equal to the probabilities that arbitrarily chosen A and B functions are reacted, i.e., p_A and $p_B = p_A(f-1)$, respectively. If p_A is replaced with the conversion (p), the branching coefficient (α), the number-average degree of polymerization (X_n), the mass-average degree of polymerization (X_w), and the degree-of-polymerization dispersity ($D_X = X_w/X_n$) can be expressed using Eqs. (1)–(4) [1,2]:

$$\alpha = \frac{p}{f-1} \tag{1}$$

$$X_n = \frac{1}{1-p} = \frac{1}{1-\alpha(f-1)} \tag{2}$$

$$X_w = \frac{1-\alpha^2(f-1)}{[1-\alpha(f-1)]^2} \tag{3}$$

$$D_X = \frac{X_w}{X_n} = \frac{1-\alpha^2(f-1)}{1-\alpha(f-1)} = \frac{1-\alpha p}{1-p} \tag{4}$$

Because of the statistically driven polymerization process, hyperbranched polymers based on AB$_{f-1}$ monomers exhibit very broad molar-mass distributions. The distribution broadens with the conversion since the probability that larger molecules will react increases as they contain a larger number of B functions. Eq. (4) indicates that when the conversion is driven towards completion, i.e., p is close to unity, the degree-of-polymerization disper-
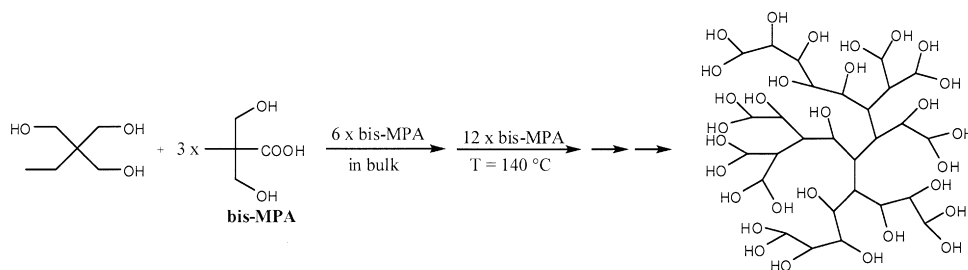
Fig. 1. Schematic presentation of poly(bis-MPA) synthesis from bis-MPA as an AB$_2$ monomer and trifunctional B$_3$ core molecule.

sity approaches infinity. Theoretically, this means that the polycondensation of AB$_{f-1}$ monomers results in an infinite molecule. In practice, the polycondensation reaction of AB$_{f-1}$ monomers is accompanied by undesired side reactions, which lead to a deviation of the product's molar mass from the theoretical values (Eqs. (2) and (3)). If intramolecular side reactions occur (e.g., cyclization) the polymerization is terminated, resulting in a reduced molar mass of the hyperbranched polymer when compared to the theoretical one. On the other hand, intermolecular side reactions lead to the formation of high-molar-mass species and, consequently, to an overestimated molar mass. Eventually, intermolecular side reactions result in the formation of an infinite network, i.e., product gelation.

Control over the molar mass and the molar-mass distribution of hyperbranched polymers prepared by the polycondensation reaction can be achieved by using a small amount of core molecules, B$_f$, with the functionality f, as supported by both theoretical treatments and experimental results [20–28]. The most effective polymerization procedure involves the slow addition of AB$_x$ monomers to B$_f$ core molecules in a dilute solution [20–23]. This favors the growth of hyperbranched polymers by reacting the monomers with core molecules or growing hyperbranched molecules containing the core units, whereas the undesired reaction between monomers leading to branches is negligible. Thus the polymerization reaction approaches chain-growth-type kinetics. The molar mass of the resulting polymer is controlled by the monomer/core ratio and the molar-mass distribution by the functionality f of the core molecule B$_f$ according to the following equation: $D_M = 1 + 1/f$. The average degree of branching (*DB*), a parameter describing the branching perfection of the hyperbranched structure, is also enhanced if the slow-monomer-addition strategy is used. The procedure of core addition has also been applied in the polymerization of AB$_x$ monomers in a melt, giving hyperbranched polymers with a narrower molar-mass distribution compared to that of hyperbranched polymers polymerized without the core molecules [24–28].

2.2. Synthesis of poly(bis-MPA) without a core molecule—self-condensation of bis-MPA

The use of bis-MPA as an AB$_2$ monomer for the synthesis of hyperbranched polymers was described early in the literature [3,4,24,25,29,30]. The reason for this is that the bis-MPA monomer is easily available and relatively stable with respect to decarboxylation and dehydration. Hyperbranched polyesters based on bis-MPA, i.e., poly(bis-MPA), can be prepared by an acid-catalyzed self-condensation of the bis-MPA without any core molecule. As is usually required for polycondensation reactions, the low-molar-mass condensation side products have to be removed, e.g., by applying a vacuum in order to drive the reaction toward high conversions. The self-condensation reaction of bis-MPA in the bulk, catalyzed by sulphuric acid, results in products with broad molar-mass distributions (M_w/M_n up to 10), as was proposed by Flory [1,2], while the molar mass depends to a large extent on the conversion and polymerization conditions used [29]. In the absence of the core moiety, bis-MPA forms an insoluble lump after a conversion of approximately 90–92%. Even at conversions lower than the gel point, insoluble particles are present in the reaction mixture [29]. Therefore, most scientific efforts have been devoted to the synthesis of poly(bis-MPA) with a core moiety.

Poly(bis-MPA) without the core molecule was also prepared from a preformed AB$_4$ trimer of bis-MPA in a melt at 160 °C. Unfortunately, the reaction rate of the trimer polymerization is very slow, which was explained by the less-accessible carboxyl group of the trimer than that of the bis-MPA [31].

2.3. Synthesis of poly(bis-MPA) with a core molecule: AB$_2$ + B$_f$ copolymerization

In 1995, Hult et al. [24] reported on the polymerization of bis-MPA in a melt in the presence of a B$_3$ core molecule, 2-ethyl-2-(hydroxymethyl)propane-1,3-diol (or tris(methylol) propane, TMP). The polymerization was carried out at 140 °C in the bulk, which is below the melting point of bis-MPA (190 °C). The esterification reaction was acid catalyzed by p-toluenesulphonic acid (p-TSA). The synthesis was performed in a pseudo-one-step reaction (also called the incremental or step-wise addition mode) where stoichiometric amounts of bis-MPA, corresponding to each theoretical dendrimer generation, were added in succession: first, the portion to the B$_f$ core molecules, and, next, the portions to the resulting reaction mixture (Fig. 1). Since such prepared polycondensation products have an imperfectly branched structure with control lost over the generations and molar mass, the term pseudo-generation was suggested in order to distinguish the hyperbranched
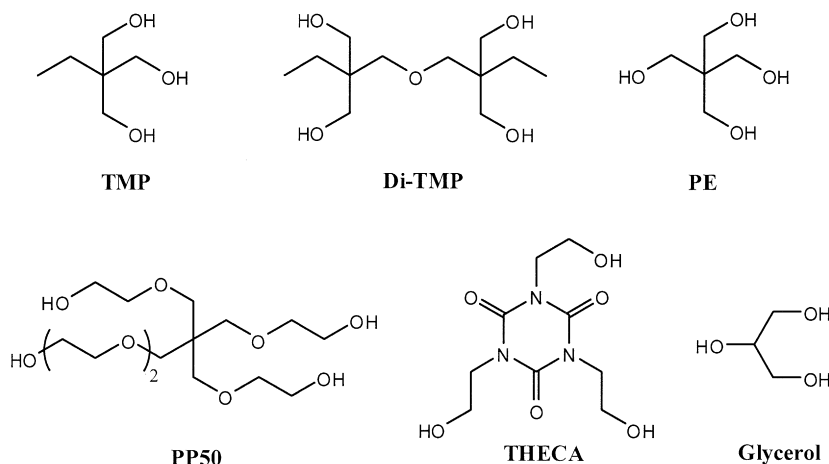
Fig. 2. Polyol core molecules used in the synthesis of poly(bis-MPA).

polymers from the ideally branched dendrimers with precisely defined radial–symmetrical generations around the core molecule.

The reaction mixture composed of the bis-MPA and TMP is a two-phase system at 140 °C, where bis-MPA slowly dissolves in a low-viscosity core melt instead of melting by itself. The melt initially consists of the core and, during later stages, of the formed polyester. The combination of an incremental addition and a two-phase system was believed to improve the statistics for the attachment of the bis-MPA to the core or the growing hyperbranched polymer containing the core molecule, which results in a hyperbranched polyester with a narrower molar-mass distribution than that of the hyperbranched polyester prepared solely by bis-MPA self-condensation [29]. The molar masses of the resulting hyperbranched polyesters increase with the increasing monomer/core ratio; however, to a lesser extent than was predicted. The use of the core molecule in the polycondensation of bis-MPA greatly reduces the risk of product gelation [24].

In addition to TMP, other polyols have been used as the core molecules in the polycondensation of bis-MPA in the melt, e.g., 2,2′-(2,2-bis((2-hydroxyethoxy)methyl) propane-1,3-diyl)bis(oxy)diethanol (or ethoxylated pentaerythritol; PP50, which is a mixture of molecules with various arm lengths; it contains an average of five ethylene oxide units per pentaerythritol, 5EO/PE), 2,2′-oxybis (methylene)bis(2-ethylpropane-1,3-diol) or di(trimethylolpropane; Di-TMP), 2,2-bis(hydroxymethyl)propane-1,3-diol (or pentaerythritol; PE), 1,3,5-tris(2-hydroxyethyl)-1,3,5-triazinane-2,4,6-trione (or 1,3,5-tris(2-hydroxyethyl)cyanuric acid; THECA), and propane-1,2,3-triol (or glycerol) [25,29,32,33] (Fig. 2). The polycondensation reaction was, in most cases, catalyzed by p-TSA; however, sulphuric acid or titanium tetraisopropoxide (TTIP) were also used as the catalysts [29,31,33]. No other modification of the polymerization conditions has been reported since then; except that the copolymerization of bis-MPA with PE or THECA was performed at 160 °C using one-pot and pseudo-one-pot

procedures [32,34], and with various core molecules at 190–200 °C using TTIP as a catalyst.

The poly(bis-MPA) hyperbranched polyesters synthesized from the bis-MPA monomer and the PP50 core molecule (Fig. 2) using the pseudo-one-step synthetic procedure have been commercially available for more than 10 years under the trade name Boltorn® Hx hyperbranched polyesters (x denotes the pseudo-generation number, Perstorp Specialty Chemicals AB, Sweden).

2.4. Kinetics of hyperbranched structure formation

A kinetic study of the polymerization of bis-MPA and various core molecules, i.e., TMP, PP50, Di-TMP, and PE (Fig. 2), indicates that the melting temperature of the polyol core with respect to that of bis-MPA, as well as miscibility of the bis-MPA monomer and polyol core, defines the mechanism and the kinetics of the reaction [29]. For the reactions where the core molecule has a lower or higher melting temperature compared to that of the bis-MPA the following kinetic equations were proposed, Eqs. (5) and (6):

$$-\frac{d[COOH]}{dt}$$
$$= [COOH]_t([COOH]_0+[COOH]_t+[OH]_{core,0})[H^+]k \quad (5)$$

$$-\frac{d[COOH]}{dt} = k'[COOH]^2 \quad (6)$$

In the case of the polymerization of bis-MPA with the TMP or PP50 core the best linear fit for the experimental data was achieved with Eq. (5), whereas the polymerization of pure bis-MPA, and the copolymerization of bis-MPA with PE was better described with Eq. (6), which is of the second order with respect to the carboxyl groups. These results indicate a shift in the reaction mechanism when bis-MPA is copolymerized using TMP or PP50 with melting points below that of bis-MPA, as compared to PE with a melting point above that of bis-MPA. It is believed that the phase-separated reaction mixture, consisting of the

solid bis-MPA and polyol core melt, in which bis-MPA slowly dissolves, improves the statistics for the reaction of the carboxyl groups with the hydroxyl groups of the core or of the growing hyperbranched polymer containing the core. For the copolymerization of bis-MPA with Di-TMP both rate equations gave good linear fits, indicating that the Di-TMP core represents a borderline where the core molecules no longer affect the reaction mechanism [29]. We should mention that the kinetic equations governing a homogeneous system are not fully consistent for use with a non-homogeneous system, an example of which is the system of bis-MPA and one of the above-mentioned core molecules.

3. Structural characterization of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid

3.1. Average composition and average degree of branching

The composition of the hyperbranched polymers based on bis-MPA has been determined by ^{13}C nuclear magnetic resonance (NMR) spectroscopy from the quaternary carbon signals representing the fractions of the individual structural units (Fig. 3); dendritic (D; $\delta_D = 46.7$ ppm), linear (L; $\delta_L = 48.7$ ppm), and terminal (T; $\delta_T = 50.7$ ppm) [24,42,44]. The branching perfection of the hyperbranched structure is characterized by the average degree of branching (DB) and is one of the most important parameters of hyperbranched polymers, since it is correlated with the density of the hyperbranched structure and the location of the functional groups. DB was defined by Fréchet [35] and Frey [36] as:

$$DB_{\text{Fréchet}} = \frac{D+T}{D+L+T} \tag{7}$$

$$DB_{\text{Frey}} = \frac{2D}{2D+L} \tag{8}$$

The DB by Frey (Eq. (8)), which is based on a comparison of the actually existing growth directions with the maximum possible number of growth directions, has been suggested to be more accurate for lower-molar-mass hyperbranched polymers. In the case of an ideal, statistical self-condensation of an AB$_2$ monomer with an equal reactivity of B functions and the absence of side reactions, the content of the linear units should be 0.5 and that of the dendritic and terminal units should each be equal to 0.25, thus leading to a DB of 0.5 [1,2]. Experimentally and theoretically it was shown that the DB of the hyperbranched polymer can be enhanced by (i) the slow addition of AB$_x$ monomers to the B$_f$ core molecules in a dilute solution [20,37], (ii) the activation of the second B group of AB$_2$ monomers after the reaction of the first B group [36], and (iii) the polymerization of the prefabricated perfect dendrons [22], which is in the case of the polymerization of the AB$_4$ trimer of bis-MPA an ineffective route due to the very slow reaction rate [31].

The DB of a hyperbranched polyester prepared solely from bis-MPA was reported to be 0.35 and 0.32, according to definitions by Fréchet and Frey, respectively [31]. For a hyperbranched polymer prepared from a dendritic bis-MPA trimer these values reach 0.76 and 0.70, whereas the

Table 1
The contents of dendritic (D), linear (L), and terminal (T) repeat units, the degree of branching (DB), the average number of core-reacted hydroxyl groups (f_{PP50}), the fractions of hyperbranched species with and without the core molecule (x_{B_4}, x_{B_2}), the content of ether groups, and the glass-transition temperatures (T_g) of Boltorn® Hx ($x = 20, 30, 40$) hyperbranched polyesters [38,43].

Parameter		H20	H30	H40
D (%)		10.0	14.0	16.5
L (%)		56.5	57.0	57.0
T (%)		33.5	29.0	26.5
DB_{Frey}	Eq. (8)	26.1	32.9	36.7
$DB_{\text{Fréchet}}$	Eq. (7)	43.5	43.0	43.0
f_{PP50}		1.8	2.4	3.3
x_{B_4}	Eq. (15)	0.58	0.48	0.37
x_{B_2}	Eq. (14)	0.42	0.52	0.63
% OH$_{\text{ether}}$	Eq. (18)	6.0	4.0	0.4
T_g (°C)		25	35	40

[a]Data for T_g are from Perstorp Specialty Chemicals AB [38].
[38] Copyright 2006, Elsevier Ltd.
[43] Copyright 2002, American Chemical Society.

DB of a hyperbranched polymer prepared from bis-MPA and TMP core molecules was 0.47 and 0.44, respectively, indicating a somewhat increased DB due to the applied pseudo-one-step synthetic procedure [31]. The DB of the Boltorn® products is, according to Fréchet, around 0.43, and this does not change substantially with the monomer/core ratio, whereas the DB according to Frey increases from 0.26 to 0.37 when going to a higher pseudo-generation (Table 1) [38]. The lower DB of the Boltorn® hyperbranched polyesters, as compared to those of poly(bis-MPA) prepared from bis-MPA and TMP, are ascribed to the higher functionality of PP50 ($f = 4$) than TMP ($f = 3$), since the DB decreases with the increasing core functionality [23,27,28]. All the hyperbranched polyesters based on bis-MPA thus have a lower DB than would be predicted for a random polycondensation, i.e., 0.5 [1,2], which assumes the equal reactivity of both B functions. This is mainly due to the lower reactivity of the hydroxyl functions in linear units as compared to those in the terminal ones, which was supported by following the evolution of individual structural units during the polycondensation of bis-MPA. During the conversions of carboxyl groups above $p > 0.7$, the fraction of linear units is higher, whereas the fraction of dendritic units is lower than predicted for a random polycondensation (Fig. 4). This effect was explained by a slower diffusion of the molecules due to the high viscosity of the reaction mixture [31].

3.2. Side reactions in polycondensation of 2,2-bis(methylol)propionic acid

3.2.1. Monomer self-condensation in the copolymerization of 2,2-bis(methylol)propionic acid and core molecules

In the copolymerization of the bis-MPA and the core molecules, the bis-MPA molecules not only react with the core or growing core molecules, but also self-condensate into low-molar-mass hyperbranched structures without a core molecule. They are actually branches containing one carboxyl group situated in focal linear units or, especially during higher conversions, in focal dendritic units.

The self-condensation of bis-MPA is a consequence of the lower reactivity of the carboxyl groups in branches, since their accessibility is hindered either due to the bulky hyperbranched structure or the participation in H-bonds [29]. Another reason could be the rather limited extent of the reaction in order to avoid undesirable side reactions (etherification, cyclization), which are known to take place especially at higher degrees of conversion [39–41]. The lower reactivity of the carboxyl groups in branches was explained theoretically by a negative A−B substitution effect, i.e., the decreased reactivity of the carboxyl group after the hydroxyl group(s) of the same monomer unit reacted [42,55]. The presence of branches in poly(bis-MPA) is evidenced by the signals of the focal units in the quaternary carbon region of the ^{13}C NMR spectra (focal dendritic units at $\delta = 46$ ppm, Fig. 3, and
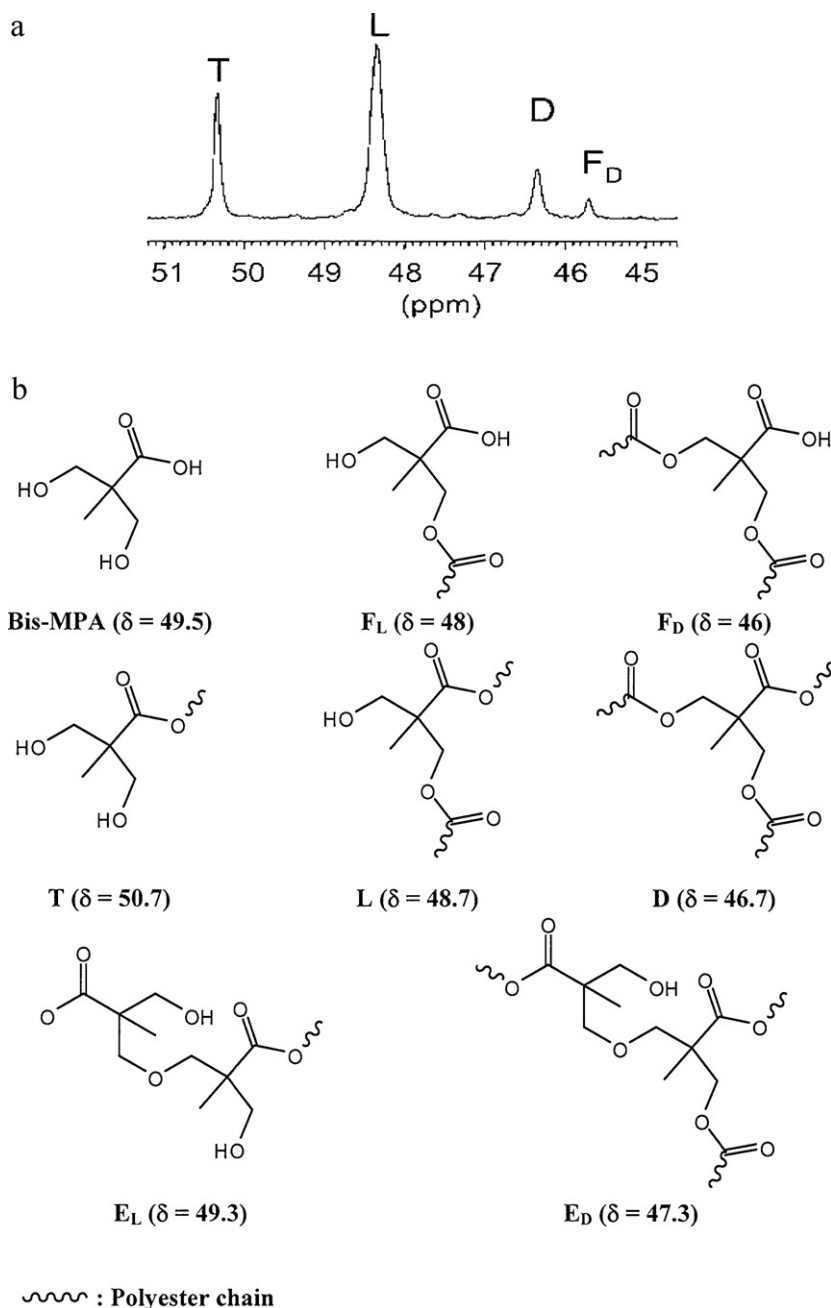
Fig. 3. (a) Magnification of the quaternary carbon region of the ^{13}C NMR spectrum of the poly(bis-MPA) hyperbranched polyester, representing the signals for the terminal (T), linear (L), dendritic (D), and focal dendritic (F$_D$) units. (b) Structural units in poly(bis-MPA) hyperbranched polyesters. Esterification reaction leads to the focal linear (F$_L$), focal dendritic (F$_D$), terminal (T), linear (L), and dendritic (D) structural units, whereas the etherification reaction leads to the linear ether (E$_L$) and dendritic ether (E$_D$) structural units. In brackets are the quaternary carbon chemical shifts (δ in ppm) of the individual structural units in the ^{13}C NMR spectra of poly(bis-MPA) hyperbranched polyesters [24,42,44].
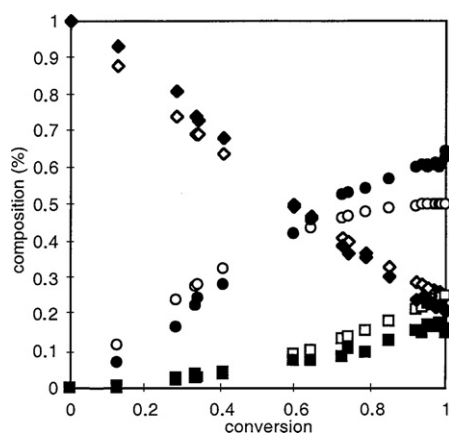
Fig. 4. Composition of the hyperbranched structure as a function of conversion. The fractions of the terminal (◆), linear (●) and dendritic (■) units are calculated from the ^{13}C NMR spectra of the AB$_2$ polycondensate. Empty symbols represent the theoretical values [31]. Copyright 2000, American Chemical Society.

focal linear units at $\delta = 48$ ppm, Fig. 3b), and by the signal of the carboxyl groups in the low magnetic field of the ^{1}H NMR spectra (between 12 and 13 ppm) of poly(bis-MPA). In the case of Boltorn® hyperbranched polyesters, the molar fractions of the hyperbranched species with and without the core molecule were calculated from their ^{1}H NMR spectra [38,43]. The fraction of hyperbranched species without the core molecule increases with pseudo-generation on account of the decreasing fraction of hyperbranched species with the core molecule (Table 1). This was ascribed to the higher probability of the bis-MPA self-condensation reaction taking place when increasingly larger amounts of bis-MPA are added to the reaction mixture for the synthesis of higher-molar-mass hyperbranched

polyesters (Fig. 5) [25,38]. Due to the increasing extent of the bis-MPA self-condensation with pseudo-generation the fraction of branches as well as the total number of macromolecules increases in the reaction mixture. Since new branches 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 hyperbranched species containing the core moiety. Therefore, the branches have lower molar masses, and, consequently, particularly affect the samples' M_n values. In contrast, the samples' M_w values are influenced predominantly by higher-molar-mass species, i.e., hyperbranched structures containing a core unit, which have been growing continuously from the beginning of the reaction. Thus, the self-condensation of the bis-MPA in the copolymerization of the bis-MPA with the core molecules has a more pronounced effect on the samples' M_n, whereas its influence on the samples' M_w is less significant.

3.2.2. Cyclization reactions: intramolecular esterification, intramolecular etherification and intramolecular hydroxy-ester interchange

The role of cyclization in poly(bis-MPA) was extensively studied by mass spectrometry (MS) and NMR spectroscopy [33,39–45]. Cyclic structures can be formed by the intramolecular esterification reaction of the carboxyl group in the focal unit with a hydroxyl group of the same hyperbranched molecule, leading to the cycle containing hyperbranched structures without the core molecule (Fig. 6A). Cyclic structures with or without the core molecule can also form in the intramolecular etherification reaction between two hydroxyl groups and the hydroxy-ester intramolecular interchange reaction (Figs. 6 and 7). The mass spectra of poly(bis-MPA) show peaks that are characterized by a mass of 18 g/mol less
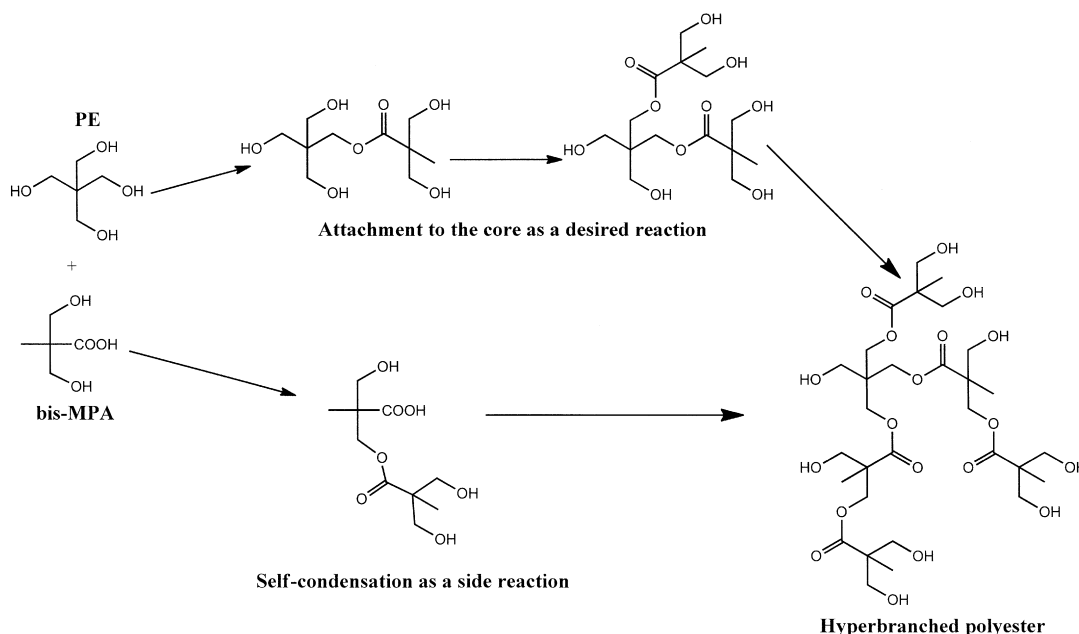
Fig. 5. Schematic representation of hyperbranched polyester growth [25,38].
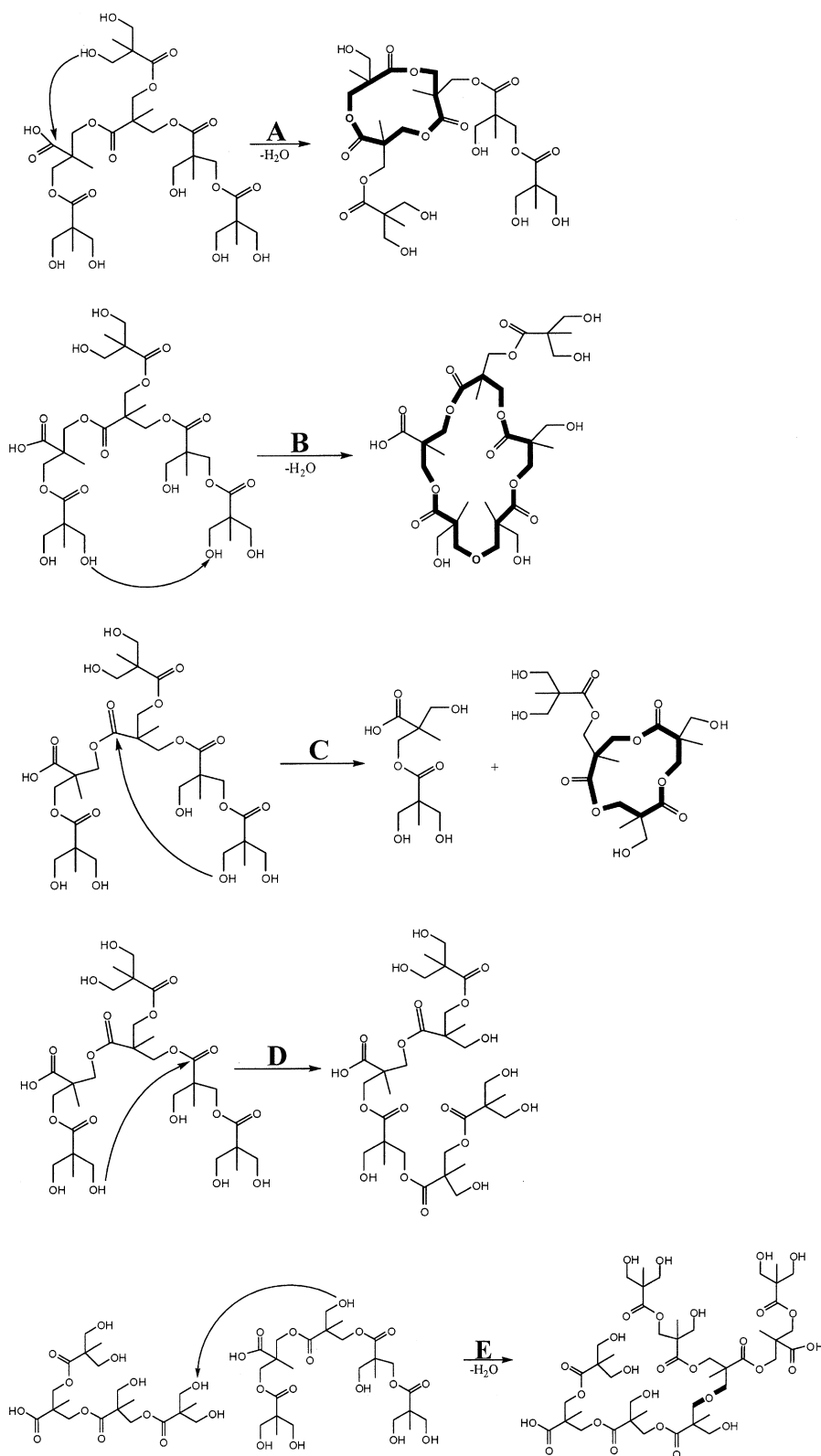
Fig. 6. Possible side reactions in poly(bis-MPA) without the core unit: A – intramolecular esterification reaction; B – intramolecular etherification reaction; C – intramolecular hydroxyl-ester interchange between groups of the same branch; D – intramolecular hydroxyl-ester interchange between groups of different branches; and E – intermolecular etherification reaction [44].
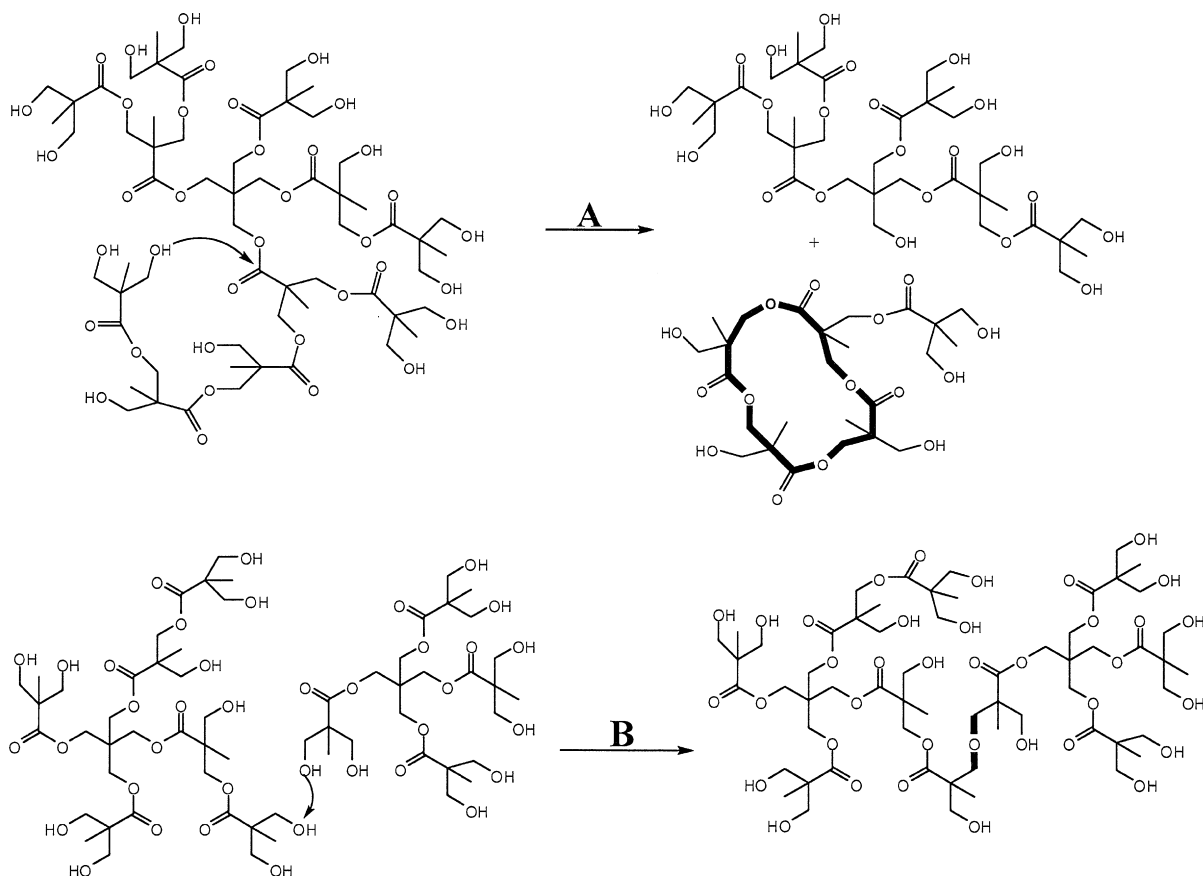
Fig. 7. Side reactions of poly(bis-MPA) containing a core unit: A – intramolecular hydroxyl-ester interchange between groups of the same hyperbranched polyester; and B – intermolecular etherification between two hyperbranched molecules containing a core unit [44].

than the set of peaks originating from the regular hyper-branched polymer structure. However, mass spectrometry cannot distinguish between the cyclic structures formed by the intramolecular esterification or etherification reaction and the hydroxy-ester intramolecular interchange reaction, nor can it distinguish between the structures originating from the intermolecular etherification or ester-ification (Figs. 6 and 7), since both types of reactions lead to the same molar-mass increase. In the ^{13}C NMR spectra of poly(bis-MPA) the signal of the oxyalkylene methylene carbons ($-CH_2-O-CH_2-$) is detected at a chemical shift around 72–73 ppm, whereas ether-containing linear and dendritic structural units are also detected in the quaternary carbon regions at 49.3 ppm and 47.3 ppm, respectively (Fig. 3) [38,41,44].

The role of cyclization through ester bonds in poly(bis-MPA) hyperbranched polyesters without the core molecule was studied theoretically and experimentally by Dušek et al. [40] using electrospray ionization mass spectrometry (ESI-MS), whereas Komber et al. [41] studied cyclization through ether bonds by using high-resolution magic-angle spinning (HR-MAS) NMR spectroscopy. The cyclization in poly(bis-MPA) with a core molecule (TMP, PP50, i.e., Boltorn® polyesters) was studied by Frey et al. [39] by comparing the samples' M_n values calculated from ^{1}H NMR spectra with those determined by the absolute vapor-

pressure osmometric (VPO) method. For poly(bis-MPA) with a TMP core molecule, the authors also used matrix-assisted laser-desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). Boltorn® hyperbranched polyesters were studied by Žagar et al. [38,43] by comparing the calculated M_n values from the ^{1}H NMR spectra with those determined by the absolute method, i.e., size-exclusion chromatography coupled to a light-scattering detector (SEC-MALS) and by using ESI-MS. The structure of poly(bis-MPA) with and without the core molecule was studied by MALDI-TOF also by Fradet et al. [42,44,45] and Aminabhavi et al. [33]. All these studies show that cyclic structures are present in poly(bis-MPA), regardless of the presence of a core molecule. The presence of the core moiety only reduces the extent of the cyclization.

In poly(bis-MPA) without a core molecule, the molar ratio of the cyclic structures ($x_{cyc,n}$, Eq. (9)) increases with the increasing conversion and converges to unity at $p_{COOH} = 1$ [40].

$$x_{cyc,n} = \frac{[\text{cyclic } n\text{-mer}]}{[\text{cyclic } n\text{-mer}][\text{acyclic } n\text{-mer}]} \tag{9}$$

For a given conversion, the molar ratio of the cyclic structures increases with the increasing degree of polymerization and converges to a certain value [40]. These results are in agreement with the dependence of the number-
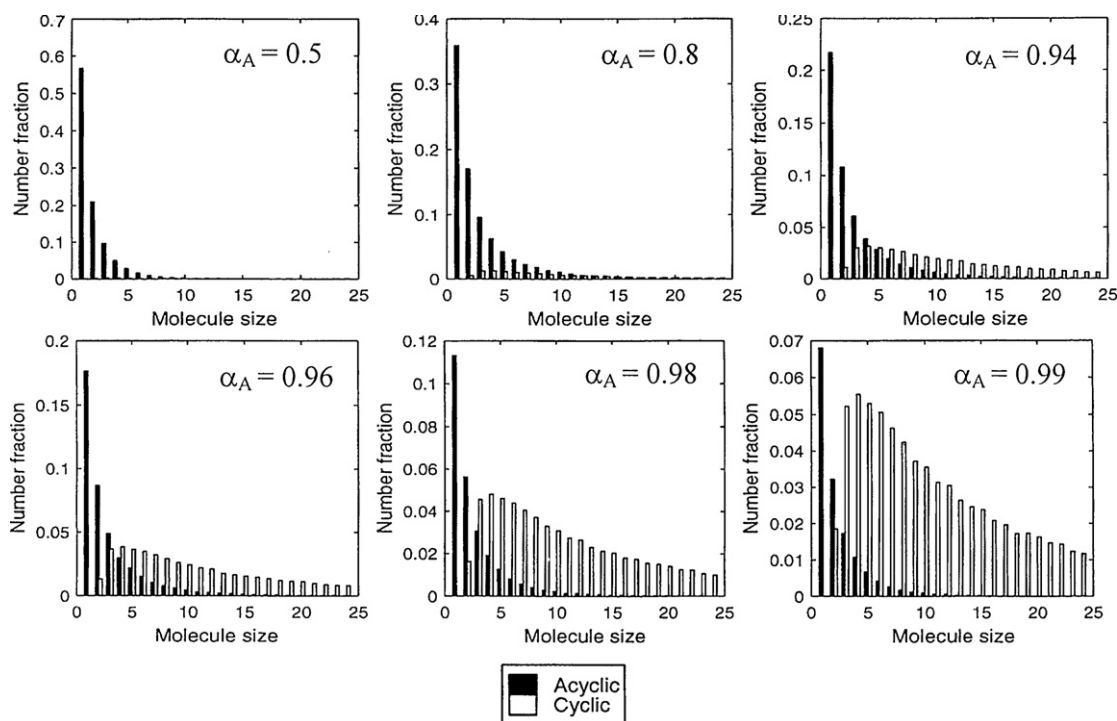
Fig. 8. Distributions of acyclic (full bars) and cyclic (open bars) fractions in n-mers of AB_2 as a function of A-group conversion, p_A [40]. Copyright 1999, Springer – Verlag.

fraction distribution of the cyclic species on the molecular size and conversion, as was predicted by a simulation using a kinetic model [40] (Fig. 8). Komber et al. [41] reported that during carboxyl group conversions below about 0.96, depending on the experimental conditions, 1–12% of ether groups are formed, mainly in intramolecular cyclization reactions.

In poly(bis-MPA) with a TMP core molecule the extent of the cyclization (ξ), i.e., the number of cyclic molecules N_{cycles} compared to the number of molecules in the mixture N (Eq. (10)), increases with the increasing monomer/core ratio (i.e., pseudo-generation), while, at a given monomer/core ratio, it decreases with the increasing degree of polymerization (Fig. 9) [39], which is the opposite of the results reported for poly(bis-MPA) without a core molecule [40], but is consistent with the content of the branches in the Boltorn hyperbranched polyesters [38].

$$\xi = \frac{N_{cycles}}{N} = 1 - \frac{X_n}{X_{n,app}} \tag{10}$$

where X_n is the actual number-average degree of polymerization determined by the absolute technique, e.g., VPO, $X_{n,app}$ is the apparent number-average degree of polymerization calculated from the proton NMR spectra.

The extent of the cyclization in poly(bis-MPA) with a PP50 core molecule (Boltorn® polyesters) is lower than that of poly(bis-MPA) with a TMP or poly(bis-MPA) without the core molecule. Intramolecular cyclization through ester bonds is not extensively involved in their synthesis, as is indicated by the comparable experimentally determined absolute M_n values by SEC-MALS or the VPO method and those calculated from ^{1}H or ^{13}C NMR spectra, although

some of the cyclic structures are formed by intramolecular etherification as a side reaction [38,39,43]. The low content of the cyclic species in Boltorn® hyperbranched polyesters was also evidenced by ESI-MS and was ascribed to the rather low carboxyl-group conversion compared to other poly(bis-MPA) hyperbranched polyesters. The content of ether groups in poly(bis-MPA) with a PP50 or PE core increases with increasing core content (Table 1.) [38,44], which was in the latter case ascribed to the higher reactivity of the core hydroxyl groups with respect to bis-MPA towards etherification [44]. The fraction of cyclic structures in poly(bis-MPA) with a PE core is the lowest for the hyperbranched polyester with the lowest monomer/core ratio [44], which is in agreement with other poly(bis-MPA) containing the core moiety.

3.2.3. Intermolecular etherification

An etherification reaction may also take place intermolecularly, especially at high reaction temperatures, high carboxyl-group conversions, and for long reaction times [41,44]. In the case when two branches react intermolecularly through the ether bond the resulting hyperbranched molecule contains two or more focal groups (Fig. 6E), which can form cross-linked structures during a high degree of carboxyl-group conversion. Eventually, the point of the product's gelation could be reached. As reported by Fradet et al. [44], the risk of poly(bis-MPA) gelation is higher when bis-MPA is copolymerized with PE as a core, as compared to polymerization without the core. The higher reactivity of the hydroxyl groups of the PE core towards etherification leads to a greater extent of the intermolecular etherifi-
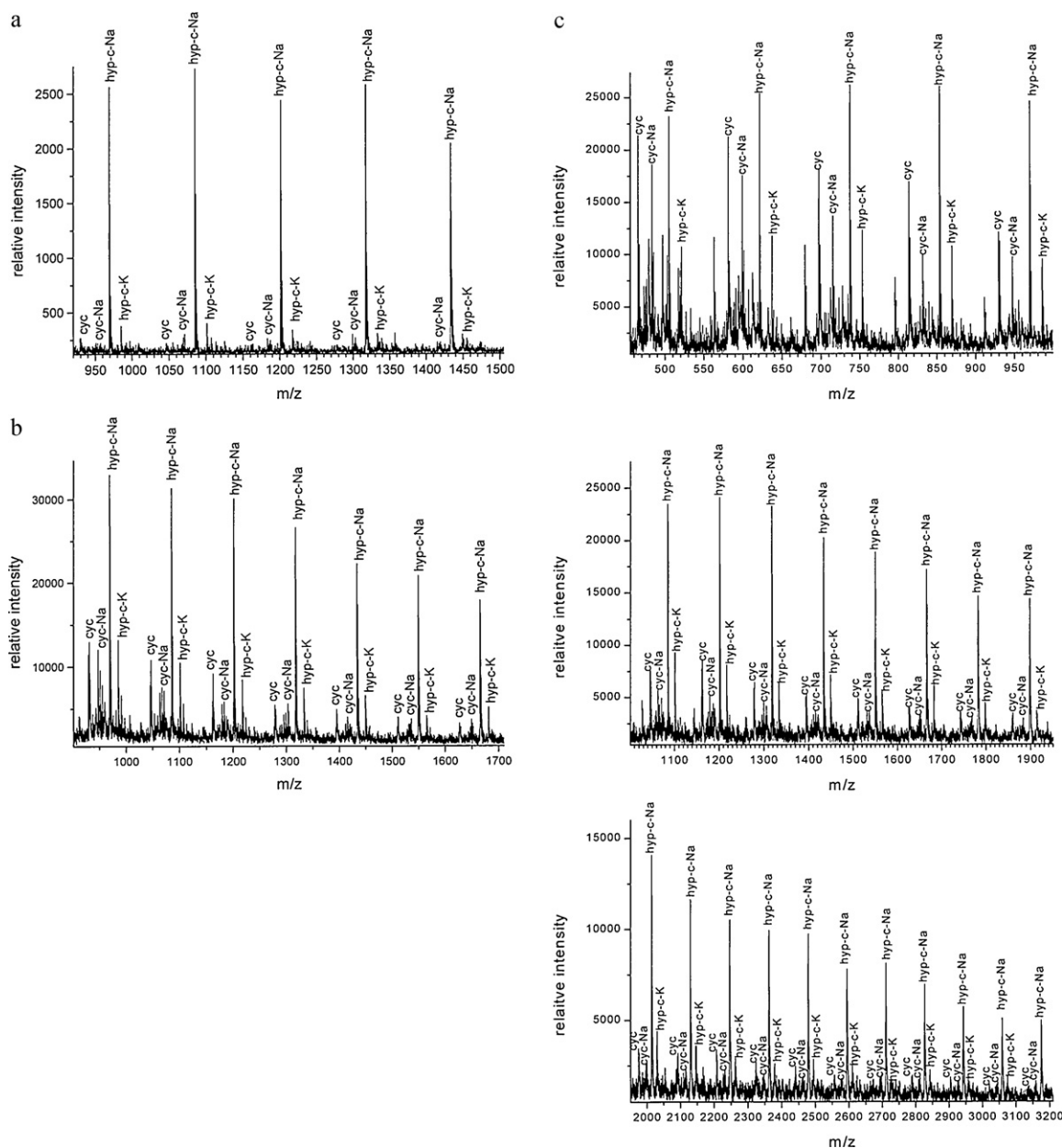
Fig. 9. Enhanced part of the MALDI-TOF mass spectra for (a) 2nd, (b) 3rd, and (c) 4th pseudo-generation poly(bis-MPA) containing the TMP core moiety [39]. Copyright 2000, Wiley-VCH Verlag GmbH, D-69451 Weinheim.

cation reaction and an increased probability of product gelation. However, when TMP or PP50 was used as a core molecule in the polycondensation of bis-MPA the opposite was observed, i.e., the risk of product gelation was to a large extent reduced [24].

All these results indicate that the content and type of the cyclic structures formed, as well as the extent of the intermolecular etherification in poly(bis-MPA), greatly depend on the reaction conditions used (reaction temperature, reaction time, type of catalyst used), the degree of carboxyl-group conversion as well as the presence and the type of the core molecule used. The intramolecular

cyclization through ester bonds competes with the desired intermolecular reaction, whereas the intramolecular interchange reaction can result in the formation of two species of lower molar masses. The cyclization and intramolecular interchange side reactions (Figs. 6 and 7) greatly reduced the number average molar mass of poly(bis-MPA) hyperbranched polyesters as compared to the theoretical molar mass. An exception is the intermolecular etherification reaction (Figs. 6E and 7B), which increases, in particular, the weight average molar mass and eventually may lead to gelation. The control over the molar-mass characteristics (M_n, M_w, molar-mass dispersity; D_M) of poly(bis-MPA)
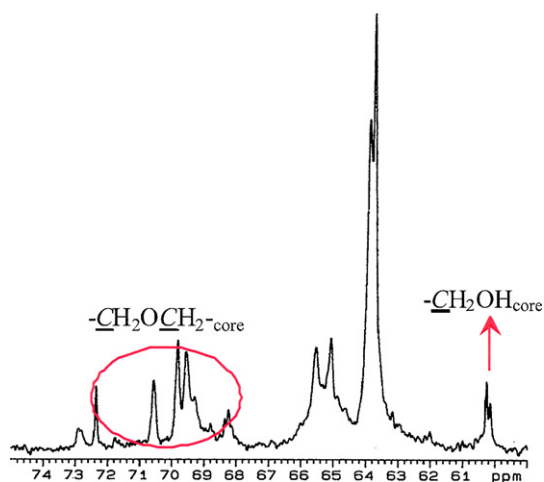
Fig. 10. Magnification of the methylene carbon region of the ^{13}C NMR spectrum of the 2nd pseudo-generation Boltorn® H20 hyperbranched polyester [38].

hyperbranched polyesters by the copolymerization of bis-MPA with a small amount of core molecules is thus quite complex due to the unavoidable presence of side reactions.

3.3. Core functionality

The number of reacted hydroxyl groups of the core molecule is usually lower than the theoretical core functionality [38,44,46]. In the case of Boltorn® hyperbranched polyesters the average number of reacted core hydroxyl groups was estimated by ^{13}C NMR spectroscopy by comparing the integrals of the oxyalkylene methylene carbons of the PP50 core ($\delta_{CH_2-O-CH_2}$, between 67.5 and 72.5 ppm) and the methylene groups near the unreacted core hydroxyl groups (δ_{CH_2OH}, 60.2 ppm, Fig. 10), taking into consideration that their ratio in the original compound is 10/4 [38]. The average number of reacted hydroxyl groups per core increases with the increasing monomer/core ratio (Table 1) [38,46]. A lower core functionality than the theoretical one ($f = 4$) was predicted and found also for poly(bis-MPA) hyperbranched polyesters with PE core molecules [44,46]. Partially reacted PE core molecules in poly(bis-MPA) were detected in the quaternary carbon region of the ^{13}C NMR spectra between 43 and 45.5 ppm (Fig. 11).

3.4. Molar-mass dependency of structural parameters

The molar-mass dependence of the structural parameters (average composition, DB, fractions of hyperbranched structures with and without the core, content of ether groups) of Boltorn® hyperbranched polyester of the fourth pseudo-generation was studied by fractionation of the sample according to molar mass by preparative size-exclusion chromatography (SEC), Fig. 12 [43]. With a decreasing molar mass the content of dendritic units decreases, that of terminal units increases, whereas the linear units do not show any specific trend (Table 2).
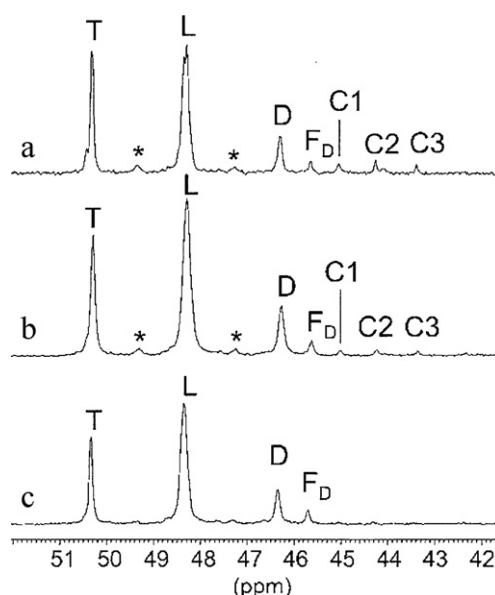
Fig. 11. Magnification of the quaternary carbon region of the ^{13}C NMR spectra of poly(bis-MPA) hyperbranched polyesters containing the PE core molecule: (a) 2nd pseudo-generation, (b) 3rd pseudo-generation, and (c) poly(bis-MPA) hyperbranched polyester without the core molecule. *The etherified linear and dendritic units. C1, C2, and C3 denote the quaternary carbon of PE with one, two, and three reacted hydroxyl groups, respectively [42]. For other notations see Fig. 3. Copyright 2008, American Chemical Society.

Consequently, the DB according to Frey decreases with a decreasing molar mass (Table 2). The fraction of hyperbranched species without the core molecule increases with a decreasing molar mass on account of the decreasing fraction of hyperbranched species containing the core (Table 2.). The lower molar mass of the branches than that of the hyperbranched species with the core moiety is a consequence of their successive formation during the incremental addition of bis-MPA to the reaction mixture. The increasing fraction of branches with a decreasing molar mass is also evidenced by the growing intensity of the signal for focal dendritic units at 45.6 ppm in the quaternary

Table 2
The number-average degrees of polymerization (X_n), the fractions of hyperbranched species with and without the core molecule (x_{B_4}, x_{B_2}), the content of individual repeat units (D, L, T), the average degree of branching (DB), and the content of ether groups (% OH$_{ether}$) determined by NMR spectroscopy for the 4th pseudo-generation Boltorn H40 hyperbranched polyester and its fractions [43].

Parameter	F1	F2	F3	H40
X_n	61.90	21.85	16.88	21.44
x_{B_4}	0.91	0.42	0.34	0.37
x_{B_2}	0.09	0.58	0.66	0.66
D	17.5	16.0	13.5	16.5
L	59.0	57.0	58.0	57.0
T	23.5	27.0	28.5	26.5
DB_{Frey}	37.2	36.0	31.8	36.7
$DB_{Fréchet}$	41.0	43.0	42.0	43.0
% OH$_{ether}$	2.1	0	0	0.4

[43] Copyright 2002, American Chemical Society.
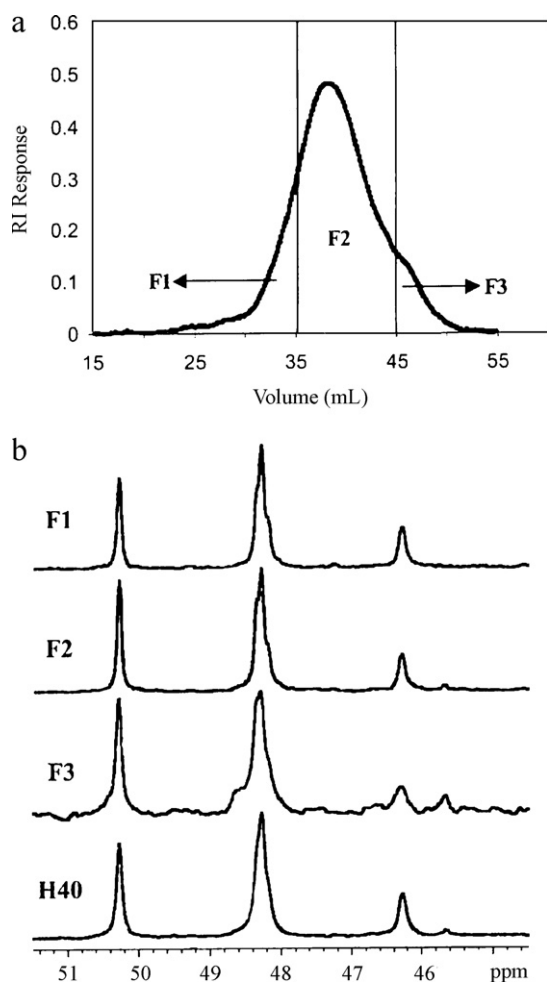
Fig. 12. RI chromatogram of the 4th pseudo-generation Boltorn® H40 hyperbranched polyester in DMAc obtained using a preparative SEC column (a) and quaternary carbon region of the ^{13}C NMR spectra of Boltorn® H40 and its fractions F1, F2, F3 in DMSO-d_6 (b) [43]. Copyright 2002, American Chemical Society.

carbon region of the fractions' ^{13}C NMR spectra (Fig. 12). The highest molar-mass fraction of the fourth pseudo-generation Boltorn® hyperbranched polyester contains the largest amount of ether groups (Table 2).

3.5. Hydrogen bonding network

A H-bond network strongly influences the properties of poly(bis-MPA), e.g., thermal, rheological and processing properties, dielectric relaxation properties, solubility, reactivity, blend formation, etc. The type, extent, and strength of the hydrogen bonds, i.e., the hydrogen-bond network, in poly(bis-MPA) was investigated by FTIR spectroscopy [33,47–53]. Since poly(bis-MPA) contains a large number of polar hydroxyl groups, they are liable to form H-bonds, not only between themselves and other groups in the hyperbranched polyester structure, but also with solvents, surfaces, etc. A comprehensive IR study, including hydration, H/D exchange, and temperature measurements, was performed on the fourth pseudo-generation Boltorn®

hyperbranched polyester in order to obtain information about the extent and the type of H-bonds. The majority of the hydroxyl groups are H-bonded and exist in four diverse assemblies, differing in terms of their strength. Besides the most frequently formed hydrogen-bonded pairs, i.e., between hydroxyl hydrogens and hydroxyl oxygens denoted as OH···OH, and between hydroxyl hydrogens and carbonyl oxygens denoted as C=O···HO, H-bonds of the type O=C-O···HO [33] and the double hydrogen bonds C=O···HO···HO were also detected [47] (Fig. 13). The existence of such double hydrogen bonds was hypothesized on the basis of IR spectroscopic experiments [47] and simulation studies [48], which support the existence of these types of H-bonds exclusively on the intramolecular level. The type and the extent of the H-bonds formed depend on the structural and molar-mass characteristics as well as on the thermal prehistory of poly(bis-MPA) hyperbranched polyesters. A small number of the OH and C=O groups are not accessible and, therefore, they do not participate in the H-bonding, which was ascribed to a very compact globular structure of the aliphatic hyperbranched polyesters as a consequence of a small bis-MPA monomer and thus a high branching density [47].

3.6. Structure ordering through H-bonds

The reorganization of the H-bond network microstructure in Boltorn® poly(bis-MPA) induced by annealing the samples at different temperatures and for different times was investigated by FTIR and DSC measurements, applying heating–annealing–cooling cycles at temperatures above the glass transition (T_g) [49,50]. Heating the hyperbranched polyesters above T_g leads to a weakening of the existing H-bond network and, consequently, to the greater mobility of the molecules. The H-bond network rearranges itself so that H-bonds that are thermally more stable are formed, although the number of formed H-bonds decreases. The rate of H-bond formation during annealing as well as the kind of H-bond microstructure formed depends not only on the annealing conditions (temperature and time) but also on the specific structure and molar-mass characteristics of the poly(bis-MPA). Reorganization of the H-bond network results in a density increase due to the higher degree of structural ordering, as determined by the sharper amorphous halo of the annealed poly(bis-MPA) using X-ray diffractometry (XRD) [49–51,76] (Fig. 14a). This structural ordering was ascribed to the formation of multiple H-bonds between long linear sequences in the hyperbranched structure, which were proposed to be formed not only intermolecularly [49,50], but also intramolecularly via back folding of the branches into the interior of the hyperbranched structure [48,51–53]. The fact that the topology of the hyperbranched polyesters plays a significant role in their physical behavior down to the atomic level was confirmed by an unchanged XRD trace after annealing of the ideally branched dendrimer analogue based on bis-MPA (Fig. 14b). In other words, annealing does not induce ordering of the dendrimer structure since it does not contain linear units.
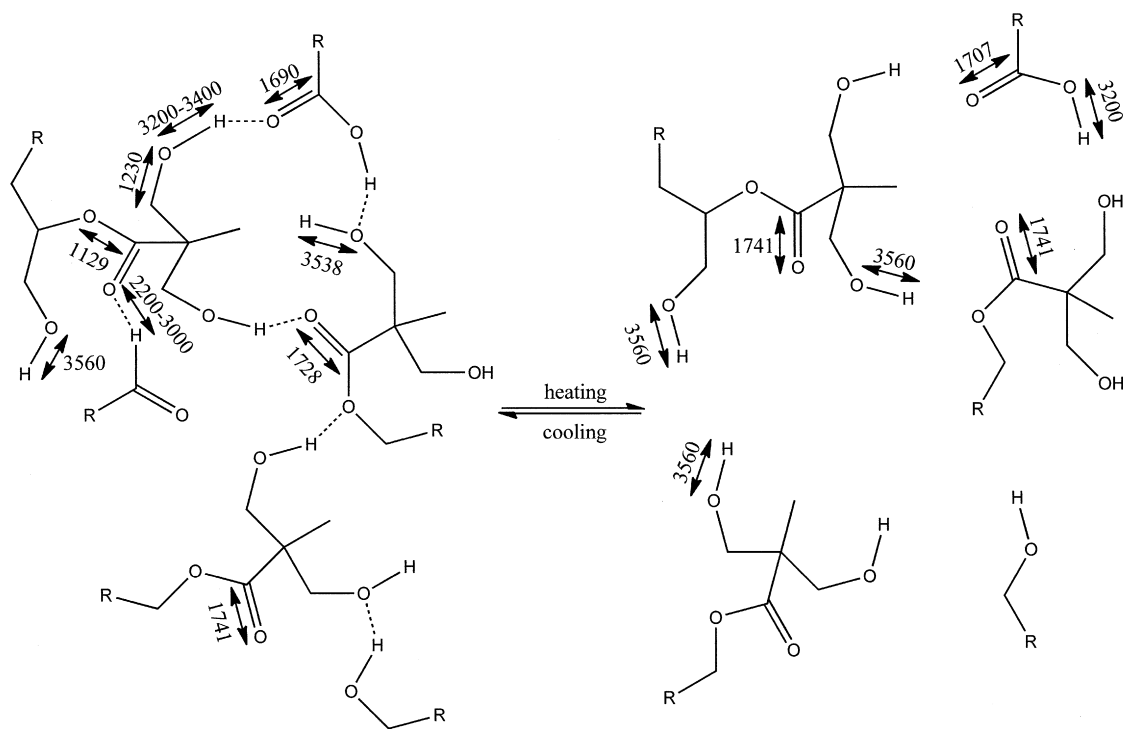
Fig. 13. Schematic structure of H-bond network in Boltorn® H*x* hyperbranched polyesters [47].

4. Solution characterization of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid

4.1. Molar-mass averages (MMA) and molar-mass distribution (MMD)

Statistically, hyperbranched polymers prepared by the polycondensation of AB_{f-1} monomers exhibit a very broad degree-of-polymerization distribution (D_X), which broadens with the increased degree of polymerization. The theoretical average degrees of polymerization (X_n, X_w) and degree-of-polymerization dispersity of such statistical hyperbranched polymers prepared by the polycondensation of AB_{f-1}, were proposed by Flory, based on Eqs. (2)–(4) [1,2]. At a high A group conversion (p is close to unity) Eq. (4) anticipates that the D_X of the hyperbranched polymer made of AB_2 ($f=3$) depends on the number-average degree of polymerization (X_n) according to $D_X \sim X_n/2$ [2,54,55].

Experimentally and theoretically it was shown that the broad molar-mass distribution of the hyperbranched condensation products can be influenced by the addition of a small amount of multifunctional core molecules in the reaction mixture, which to a large extent prevents the coupling of the polymeric species with themselves [22,25,29,31–34].

Frey et al. [39] showed that the number-average degrees of polymerization (X_n) and the number-average molar masses (M_n) of the hyperbranched polymers prepared from a AB_x/B_f monomer/core combination can be, in the ideal case (polymerization without side reactions), calculated

from the conversion of A-groups (A = COOH) and the stoichiometric ratio of AB_x/B_f according to Eq. (11).

$$(X_n)_{NMR} = \frac{N(B) + N(AB) - (f-2)N_{core}}{N(B) - N(AB) - (f-2)N_{core}} \quad (11)$$

$N(B)$ and $N(AB)$ are the integrals of the signals for methylene groups near the unreacted and reacted hydroxyl groups, respectively, in the ^{1}H NMR spectra of poly(bis-MPA); f, core functionality; N_{core}, the number of core molecules, which is usually known from the experiment or the monomer/core ratio.

Žagar et al. [38,43] extended this calculation for Boltorn® hyperbranched polyesters further to show that the content of the core molecule can also be calculated from the ^{1}H NMR spectra of poly(bis-MPA) with the PP50 core molecule. The X_n were calculated from the samples' ^{1}H NMR spectra using the integrals of the signals for individual groups in the hyperbranched polyesters (Table 3) (Eq. (12)).

$$X_n = \frac{2I(OH) + I(CH_2OR) - (1/2)I(CH_2)_{PP50-Penta}}{2I(OH) - I(CH_2OR) - (1/2)I(CH_2)_{PP50-Penta}} \quad (12)$$

$$I(CH_2)_{PP50-Penta} = \frac{2I(CH_2)_{B_4}}{7} \quad (13)$$

$$I(CH_2)_{B_4} = I(CH_2) - I(CH_2)_{calcd.} \quad (14)$$

$$I(CH_2)_{calcd.} = \frac{4}{3}I(CH_3) \quad (15)$$

where $I(CH_2)_{calcd.}$ is the calculated integral corresponding to the poly(bis-MPA) methylene groups, taking into account that each methyl group of bis-MPA is surrounded
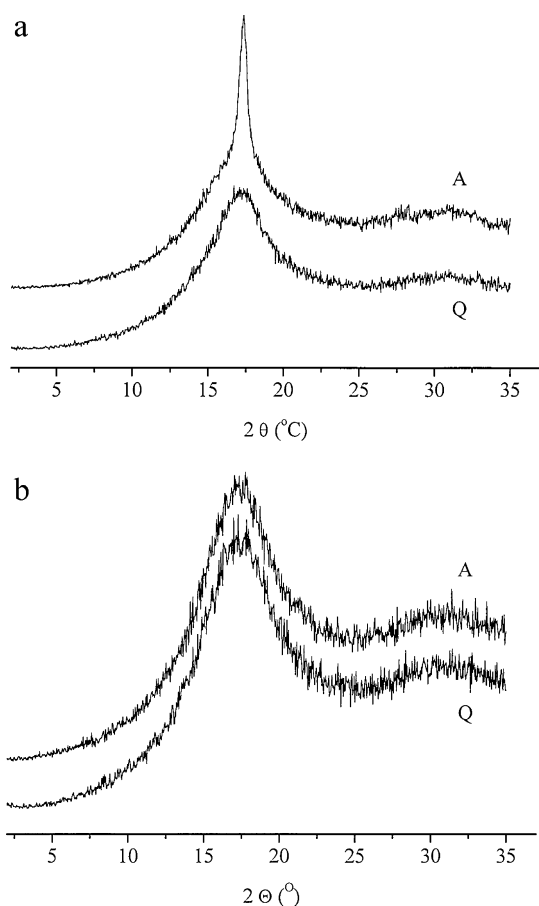
a

b

Fig. 14. X-ray diffractograms of quenched (Q) and annealed (A; 14 days at 50 °C) 4th pseudo-generation Boltorn® H40 hyperbranched polyester (a) and the dendrimer of the 4th generation based on bis-MPA (b) [49]. Copyright 2005, American Chemical Society.

by two methylene groups, either attached to the reacted (–CH$_2$OR) or uncreacted (–CH$_2$OH) hydroxyl groups (Eq. (15)). $I(CH_2)_{B_4}$ is the difference between the actual integral value and the calculated value for the methylene groups and represents the integral of the methylene groups of the PP50 core molecules (Eq. (14)). Since the PP50 core molecule contains an average of five ethylene oxide units per Pentaerythritol (5EO/Penta), the fraction of the core methylene groups belonging to Penta $I(CH_2)_{PP50-Penta}$ is calculated using Eq. (13).

The X_n values of the Boltorn® products were also calculated using another approach based on the fact that the number of molecules in the reaction mixture is, due to the bis-MPA self-condensation, equal to the sum of hyperbranched species containing the core moiety (N_{B_4}) and the hyperbranched species without the core moiety (N_{B_2}). The fraction of branches was calculated from the difference between the actual integral value of the signals for the hydroxyl groups and the calculated theoretical value of the hydroxyl groups for the ideal hyperbranched polyester containing the tetra-functional core moiety, i.e., $X + 4$, where X is the monomer/core ratio (Eq. (16)) [38,43].

$$N_{B_2} = I(OH) - I(4N_{B_4} + N_{bis-MPA})$$
$$= I(OH) - \left(\frac{I(CH_2)_{PP50-Penta}}{2} + \frac{I(CH_3)}{3} \right) \quad (16)$$

The fractions of hyperbranched structures with (x_{B_4}) and without the core moiety (x_{B2}) are calculated using Eq. (17):

$$x_{B_4} = \frac{N_{B_4}}{N_{B_4} + N_{B_2}} \text{ and } x_{B_2} = \frac{N_{B_2}}{N_{B_4} + N_{B_2}} = 1 - x_{B_4} \quad (17)$$

The X_n and M_n, which takes into account the fraction of B_4 core molecules, can be expressed by Eqs. (18) and (19):

$$X_n = \frac{N_{bis-MPA}}{N_{B_4} + N_{B_2}} + \frac{N_{B_4}}{N_{B_4} + N_{B_2}}$$
$$= \frac{8I(CH_3) + 3I(CH_2)_{PP50-Pemta}}{24I(OH) - 9I(CH_2)_{PP50-Penta} - 8I(CH_3)} \quad (18)$$

Table 3
The theoretical core/monomer ratio, the theoretical molar mass and molar mass characteristics (X_n, M_n, M_w, D_M) of Boltorn® Hx products calculated from their NMR spectra and experimentaly determined by VPO and SEC-MALS [38,39,43,57].

Parameter		Boltorn® H20	Boltorn® H30	Boltorn® H40
(core/monomer)$_{theor.}$		1/12	1/28	1/60
X_n[a]	Eq. (20)	6.2	11.2	18.5
X_n	Eq. (10)	6.76	10.41	21.44
X_n	Eq. (16)	6.75	10.41	21.37
M_{theor} (g mol^{-1})[b]		1748	3604	7316
M_n (g mol^{-1})	Eq. (17)	930	1323	2579
M_n (g mol^{-1})	VPO	827	1324	1727
M_n (g mol^{-1})	SEC-MALS	920	1410	2580
M_w (g mol^{-1})	SEC-MALS	1860	3340	6640
$D_M = M_w/M_n$	SEC-MALS	2.01	2.38	2.57

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[43] Copyright 2002, American Chemical Society.
[57] Copyright 2004, Elsevier B.V.
[a] X_n are calculated from ^{13}C NMR spectra considering only the reacted hydroxyl groups of the PP50 core (f_{PP50}).
[b] M_{theor} is a dendrimer-equivalent molar mass in which all the repeat units are attached to a core molecule.

$$M_n = (X_n - 1)(M_{\text{bis-MPA}} - M_{H_2O}) + x_{B_4}M_{B_4} + x_{B_2}M_{B_2}$$
$$= 116(X_n - 1) + 356x_{B_4} + 134x_{B_2} \qquad (19)$$

The content of ether groups in the Boltorn® hyperbranched polyesters was estimated using Eq. (20):

$$\%OH_{\text{ether}} = \left(\frac{I(OH)}{I(OH)_{\text{calcd.}}}\right) \cdot 100 \qquad (20)$$

where $I(OH)$ is the actual integral and $I(OH)_{\text{calcd.}}$ is the calculated integral for poly(bis-MPA) hydroxyl groups according to Eq. (21).

$$I(OH)_{\text{calcd.}} = \frac{1}{2}(I(CH_2OH) - I(CH_2)_{EO}) \qquad (21)$$

The content of the core molecules as well as the X_n and M_n of the poly(bis-MPA) hyperbranched polyesters prepared from the bis-MPA and the THECA core have also been calculated using ^{1}H NMR spectroscopy [32].

The X_n and M_n of the Boltorn® poly(bis-MPA) hyperbranched polyesters were also calculated from the intensities of the quaternary carbon signals of individual structural units in their ^{13}C NMR spectra according to Eq. (22), taking into account the fraction of hyperbranched species containing the core (x_{B_4}) and hyperbranched species without the core (x_{B_2}), as well as the average number of reacted hydroxyl groups of the core (f) [38,43]. These values were in fairly good agreement with those calculated from the ^{1}H NMR spectra (Table 3).

$$X_n = \left(\frac{T+L+D}{T-D}\right)x_{B_4}f + \left(\frac{T+L+D}{T-D}\right)x_{B_2} \qquad (22)$$

The equations for the calculation of the mass-average molar mass (M_w) and the molar-mass dispersity (D_M) of the hyperbranched polymers prepared from the AB$_x$ and B$_f$ monomer/core combination, as given by Fradet et al. [54,55] are based on a recursive probability approach and the structural information obtained from the ^{13}C NMR spectra. Calculations have been made for the case of the equal reactivity of the functional groups [54] as well as the existence of the first shell-substitution effects, i.e., assuming that the reactivity of a given reactive group depends on the status (reacted or nonreacted) of the other groups present on the same monomer unit [55]. The expressions for the mass- and the number-average degrees of polymerization of the hyperbranched polymer prepared from 1 mol of AB$_x$ monomer and n mol of B$_f$ core molecules, taking into account the equal reactivity of the functional groups, are given by Eqs. (23) and (24), respectively [54].

$$X_w = 1 + \frac{2p_A(x+fn)[x(1-p_A)+fn]+p_A^2[x(x-1)+fn(f-1)]}{(1+n)[x(1-p_A)+fn]^2} \qquad (23)$$

$$X_n = \frac{1+n}{1+n-p_A} \qquad (24)$$

Under the first shell-substitution effects the mass-average molar mass of the hyperbranched polymer prepared from 1 mol of AB$_x$ monomer and n mol of B$_f$ core

molecules is given by Eq. (25) [42,55].

$$M_w = \frac{M_w^0 M_n^0 - (p_A/(1+n))M_E^2}{M_n^0 - (p_A/(1+n))M_E} + \frac{(p_A/(1+n))}{M_n^0 - (p_A/(1+n))M_E}$$
$$\times \left[\frac{2(1-\delta_{AB})(M_0-M_E)(M_b-M_E)+\delta_B(M_0-M_E)^2}{(1-\delta_{AB})^2}\right] \qquad (25)$$

where $M_n^0 = ((M_0+nM_c)/(1+n))$, $M_w^0 = ((M_0^2+nM_c^2)/(M_0+nM_c))$, p_A is the conversion of A-groups (A = –COOH), M_0 is the molar mass of the AB$_2$ monomer, M_C is the molar mass of the core molecule, and M_E is the molar mass of the byproduct, which is water in this case. M_b is the expected molar mass of a monomer unit chosen by picking a reacted B-group at random in the polymer. Eq. (25) allows for the mass-average molar-mass calculation, taking into account the differences in the reactivity and the molar mass between the various types of monomer units. The δ's (branching factors) are average quantities that characterize the nature of the polymer branching. They extend the concept of the degree of branching, defined for hyperbranched polymers made of AB$_2$ monomers to any type of hyperbranched polymers, including those made of an AB$_2$/B$_f$ monomer/core combination. In the case of the equal reactivity of the functional groups, δ_B, δ_{AB} and M_b (Eqs. (26)–(28)) can be calculated from the conversion p_A and the monomer/core stoichiometry. For 1 mol of AB$_x$ monomer and n mol of B$_f$ core molecules:

$$\delta_{AB} = p_A\frac{x}{x+fn} \qquad (26)$$

$$\delta_B = p_A\frac{x(x-1)+fn(f-1)}{(x+fn)^2} \qquad (27)$$

$$M_b = \frac{xM_0+fnM_C}{x+fn} \qquad (28)$$

In the case of the first shell substitution effects, the branching factors δ_B and δ_{AB} as well as the average molar mass M_b can be calculated from the mole fractions of the various monomer units present in the polymer at a given reaction time (dendritic, linear, terminal, etc.), which in turn can be experimentally determined by NMR or chemical analysis or can be calculated by kinetic modeling. For the AB$_2$ + B$_3$ and AB$_2$ + B$_4$ systems, δ_B, δ_{AB} and M_b are given by Eqs. (29)–(31):

$$\delta_{AB} = \frac{2D+L}{T+L+D} \qquad (29)$$

$$\delta_B = \frac{2(D+F_D)+2C_2+6C_3+12C_4}{2(D+F_D)+L+F_L+C_1+2C_2+3C_3+4C_4} \qquad (30)$$

$$M_b = \frac{M_0[2(D+F_D)+L+F_L]+M_C(C_1+2C_2+3C_3+4C_4)}{2(D+F_D)+L+F_L+C_1+2C_2+3C_3+4C_4} \qquad (31)$$

where L and D are the molar fractions of the linear and dendritic units, F_D and F_L the molar fractions of the dendritic focal and linear focal units, and C_1–C_4 the molar fractions of the core unit with 1–4 reacted groups. In Eqs. (29)–(31), the molar fractions refer to the total number of monomer units, i.e., AB$_2$-type + B$_f$ type units, including residual monomers.

Fradet et al. [42] showed that the experimentally deter-mined molar-mass averages (MMA) and the molar-mass dispersities of poly(bis-MPA) with a PE or TMP core are much lower than the values calculated by the recursive approach for a random polycondensation of the AB_x/B_f monomer/core combination. However, calculations on the basis of a recursive approach, taking into account the existence of the negative first shell-substitution effects, i.e., the lower reaction rate of the given A or B groups after the reaction of the other group present on the same monomer unit, gave molar-mass values that were reason-ably close to the experimental ones, indicating that the A–B and B–B negative-substitution effects result in rather narrow molar-mass distributions experimentally observed for the poly(bis-MPA) hyperbranched polyesters. Even bet-ter agreement between the calculated and experimental values was obtained when side reactions were taken into account in the calculations. Intramolecular esterification and/or self-condensation, important side reactions in the case of poly(bis-MPA), led to a broadening of the molar-mass distribution, mainly due to a decrease in M_n with respect to theory. A similar effect was observed when inter-molecular etherification took place, mainly due to the M_w increase with respect to theory.

Since the physical properties of polymeric materi-als depend not only on the molecular architecture but also on the molar-mass characteristics (MMA and MMD), it is very important that these parameters are accu-rately determined experimentally. Usually, the MMA and MMD of poly(bis-MPA) hyperbranched polyesters are determined by a relative SEC method under various chro-matographic conditions (solvent, temperature, polymer standards for column calibration). However, the relative SEC in the solvent tetrahydrofuran (THF), using linear polystyrene (PS) standards for the column calibration, gives underestimated MMA and molar-mass dispersity val-ues ($D_M = M_w/M_n = 1.4$–1.9) when compared to the theory. This is due to the smaller hydrodynamic volume of the hyperbranched polymer in comparison to the linear PS standards of the same molar mass and/or the interac-tions of a large number of polar functional groups with the column-packing material, especially in the solvent THF [24,29,57]. Another problem when determining the molar-mass characteristics of poly(bis-MPA) is their strong tendency to associate through intermolecular H-bond interactions between the polar hydroxyl end-groups, even in polar organic solvents such as N,N-dimethylformamide (DMF) [56] or methanol. On the other hand, the incom-plete solubility of poly(bis-MPA) hyperbranched polyesters in the solvents THF and N,N-dimethylacetamide (DMAc) was attributed to the existence of an extensive H-bond net-work in bulk samples stored at room temperature, which could be completely destroyed only after a thermal heat treatment of the samples (Fig. 15) [38,57].

The absolute MMA and MMD of Boltorn® hyper-branched polyesters were determined by size-exclusion chromatography in combination with a multi-angle light-scattering detector (SEC-MALS) using a procedure of thermal pretreatment (140 °C, 10 min, quenching to liquid-nitrogen temperature and dissolution in an appropriate solvent) that allows the dissolution of hyperbranched
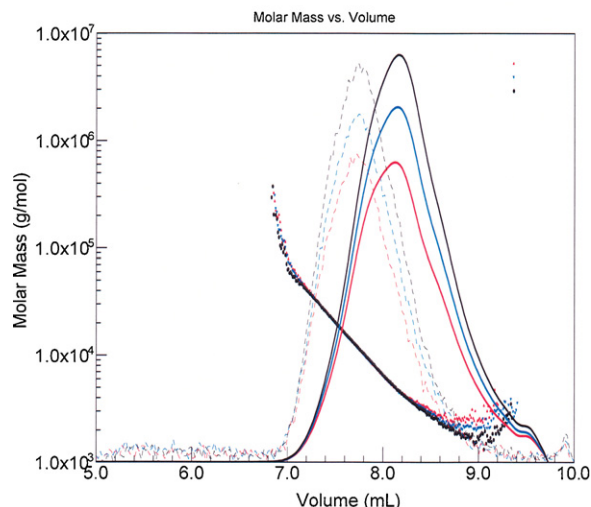
Fig. 15. SEC-MALS chromatograms (—— DRI response, – – – LS response at 90° angle), and molar mass vs. elution volume curves for the thermally pretreated 4th pseudo-generation Boltorn® H40 hyperbranched polyester in 0.7% LiBr/DMAc at three different injected concentrations [57]. Copy-right 2004, Elsevier B.V.

polyesters at the molecular level in a mixture of methanol/THF and a solution of LiBr in DMAc (Fig. 15), which is evidenced by the independence of the MMA on the solution concentration [38,57]. The absolute M_n values of poly(bis-MPA) with various core molecules (TMP and PP50 Boltorn® products) were assessed using vapor-pressure osmometry (VPO) in DMF at 90 °C [39]. Boltorn® hyperbranched polyesters have M_w values close to their theoretical dendrimer-equivalent molar masses, whereas their M_n values obtained by SEC-MALS using the regression procedure or by VPO are considerably lower (Table 3.) [38,39,43,57]. The MMA increase with the increasing monomer/core ratio, but the increase is lower than expected, especially in M_n. As a consequence, the molar-mass dispersity values of Boltorn® hyperbranched polyesters also increase with the increasing monomer/core ratio (Table 3.). The significantly lower M_n values, as compared to the theoretical dendrimer equivalents, are ascribed to the formation of lower-molar-mass branches formed in the self-condensation of bis-MPA. The proba-bility of self-condensation taking place increases when, step by step, larger amounts of bis-MPA, related to a higher pseudo-generation, are added to the reaction mix-ture, which results in a larger reduction in M_n, and, consequently, in a broader molar-mass distribution. The experimentally determined absolute M_n values were in good agreement with those calculated from the ^{1}H or ^{13}C NMR spectra (Table 3), indicating that intramolecular cyclization through ester bonds is not extensively involved in the synthesis of Boltorn® hyperbranched polyesters, although some cyclic structures are mainly formed by intramolecular etherification.

The off-line SEC/MALDI-TOF MS technique was also used to determine the absolute MMA and MMD of poly(bis-MPA) with PE or TMP core molecules [42]. The poly(bis-MPA) were fractionated by SEC in the solvent THF

into fractions with a narrow molar-mass distribution. The fractions were analyzed by off-line MALDI-TOF MS and used as narrow molar-mass standards to obtain a calibration curve for the MMA determination by SEC. The obtained MMA and MMD were in very good agreement with the values obtained by using a conventional calibration method and PS standards. This unexpected agreement was ascribed to two antagonist effects involved in the SEC of aliphatic hyperbranched polyesters: the molar-mass underestimation generally observed for highly branched polymers due to their compact globular shape, and the molar-mass overestimation generally observed for linear polyesters when using the PS calibration [42]. Comparable results for the molar-mass determination of poly(bis-MPA) with various core molecules using SEC with the PS calibration and the MALDI-TOF MS techniques were also obtained by Aminabhavi et al. [33].

The absolute MMA and MMD of poly(bis-MPA) containing a PP50 core molecule were also determined by SEC with differential viscometry using the universal calibration concept, with which the polymer hydrodynamic volume, proportional to the product of the intrinsic viscosity and the molar mass, $V_h \approx [\eta]M$, is correlated with its elution volume [58,59]. The universal calibration concept is only valid under conditions of strict size-exclusion separation, without the presence of secondary separation mechanisms, including adsorption, thermodynamic partition, ionic effects, etc. These requirements were met for poly(bis-MPA) in DMF and their trimethylsilylated derivatives in THF as SEC eluents [58,59].

4.2. Solution viscosity

Information about the molecular shape and density were obtained from the correlation of the molar mass and the intrinsic viscosity $[\eta]$ using the online coupling of SEC with viscometry. Poly(bis-MPA) hyperbranched polyesters containing various core molecules (TMP, PE, PP50 Boltorn® hyperbranched polyesters) follow the Kuhn–Mark–Houwink–Sakurada (KMHS) viscosity law (Eq. (32)) in the solvent DMF at 60 °C [58] and THF at 40 °C [42].

$$[\eta] = K_\eta M^\alpha \tag{32}$$

where K_η and α are system-specific constants dependent on the constitution, the configuration, and the molar-mass distribution of the polymer, as well as the solvent power and the system conditions.

All the viscosity–molar-mass curves of the hyperbranched polyesters exhibit a linear region where the KMHS coefficient α was determined. In both solvents the determined α values are very low, between 0.2 and 0.3, indicating a more compact molecular conformation than that of linear polymers, for which α is generally between 0.5 and 0.7. This compact conformation of the hyperbranched polyesters was ascribed to their highly branched structure. In the case of Boltorn® products the coefficient α increases somewhat with pseudo-generation (from 0.215 for the 2nd, 0.250 for the 3rd, 0.325 for the 4th pseudo-generation hyperbranched polyester) [58]. The low KMHS coefficient ($\alpha \approx 0.2$) was also obtained for
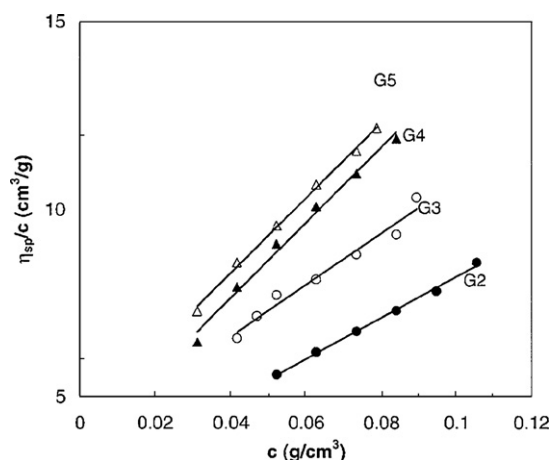

Fig. 16. Huggins plots for Boltorn® hyperbranched polyesters of different pseudo-generations (G2–G5) in NMP [61]. Copyright 2000, American Chemical Society.

hydroxyl-terminated Boltorn® hyperbranched polyesters in the solvent N-methyl-2-pyrrolidinone (NMP) at 25 °C by using an Ubbelohde capillary viscometer for the measurements of the solution viscosity [63].

The effects of the solvent and the type of end-groups (hydroxyl groups or alkyl chains) on the size of the Boltorn® hyperbranched polyesters in DMF, NMP and THF at 30 °C were studied by measuring the dependence of the reduced viscosity on the solution concentration according to the Huggins equation (Eq. (33)) [60,61]:

$$\frac{\eta_{sp}}{c} = [\eta] + k_H [\eta]^2 c \tag{33}$$

where η_{sp}/c is the reduced viscosity, $[\eta]$ is the intrinsic viscosity, and k_H is the Huggins coefficient.

Since these plots were linear, the authors exclude the presence of aggregated species of poly(bis-MPA) in the NMP (Fig. 16) [60,61], although metastable aggregates that do not dissociate during the time of dilution may still be present.

The intrinsic viscosity and viscometric (hydrodynamic) radius in good solvents (THF, NMP, DMF) smoothly increase with the molar mass, whereas in poor solvents the relation between the viscosity and the molar mass is more complicated [60]. Boltorn® hyperbranched polyesters readily expand or contract, depending on the solvent quality, creating large and small free volumes, respectively [60]. In contrast to the hydroxyl-terminated hyperbranched polyester, the hyperbranched polyester with alkyl end-groups does not swell or contract in a wide range of solvents as much and shows a lower overall free volume, similar to sterically stabilized particles [60].

The solution properties of poly(bis-MPA) hyperbranched polyesters with a PP50 core molecule and their acetyl derivatives in DMF [56] differ from those mentioned above [60]. The authors report that the intrinsic viscosities of hydroxyl-terminated poly(bis-MPA) do not reflect the real monomolecular hydrodynamic volume due to strong intermolecular interactions, limited to the surface layer rather than intermolecular entanglements, leading to the formation of stable clusters. Intermolecular association
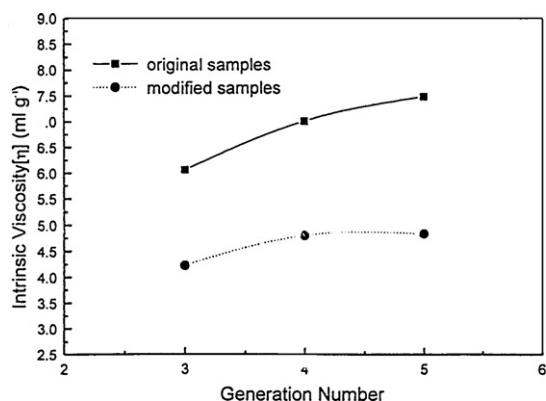
Fig. 17. Intrinsic viscosities [η] as a function of generation number for hydroxyl- and acetyl-terminated Boltorn® hyperbranched polyesters in DMF at 30 °C [56]. Copyright 2001, John Wiley and Sons, Inc.

is also an explanation for the higher intrinsic viscosities of hydroxyl-terminated poly(bis-MPA) in comparison to their acetyl derivatives (Fig. 17). In addition, the intrinsic viscosities of both types of poly(bis-MPA) hyperbranched polyesters do not change linearly with molar mass (Fig. 17), which was explained by the change of the flow model, from free-draining to non-draining, as a consequence of the increasing density of the hyperbranched structure with molar mass. A possible reason for the discrepancy in the reported results [42,56,58,60] could be the different dissolution procedures of the poly(bis-MPA). In other words, freshly prepared or stored samples, or the thermal prehistory of samples, play a significant role in the dissolution of the poly(bis-MPA) samples at the molecular level [57,42].

Solutions of Boltorn® hyperbranched polymers of different pseudo-generations (from the second to the fifth) in NMP and their blends with a high-molar-mass poly(2-hydroxyethyl methacrylate) linear polymer were studied by viscometry and rheological measurements in the dilute and semi-dilute concentration regimes [61,62–64]. Boltorn® polyesters of different pseudo-generations have low intrinsic viscosities showing only a slight increase with pseudo-generation [61,63]. In addition, the solution viscosities of the Boltorn® hyperbranched polyesters are only slightly affected by the molar mass of the different pseudo-generation hyperbranched polyesters. The hydrodynamic radius (R_h) increases with pseudo-generation according to an empirical fit [63] (Eq. (34)):

$$R_h = 0.723 \times 10^{0.142G} \tag{34}$$

where R_h is the hydrodynamic radius and G is the pseudo-generation number. The 0.142 exponent for hyperbranched polyesters is close to the values found for perfectly branched dendrimers [63].

The hydrodynamic radii of Boltorn® hyperbranched polyesters of different pseudo-generation were determined from the intrinsic viscosities using Einstein's equation for hard spheres (Eq. (35)). The hydrodynamic radius scales as $R_h \approx M^{0.39}$ [61] or $R_h \approx M^{0.4}$ [63], suggesting a less compact structure than that of the dendrimers,
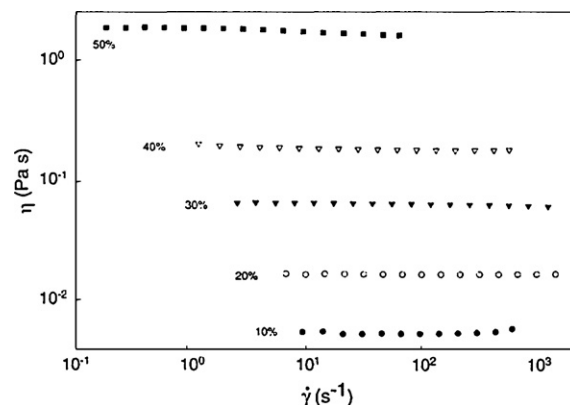
Fig. 18. Viscosity as a function of shear rate for 5th pseudo-generation Boltorn® hyperbranched polyester at different solution concentrations, which are in terms of weight percent [61]. Copyright 2000, American Chemical Society.

which exhibit a lower exponent value.

$$R_h = \left(\frac{3[\eta]M}{10\pi N_A} \right)^{1/3} \tag{35}$$

where R_h is the hydrodynamic radius, [η] is the intrinsic viscosity, M is the molar mass, and N_A is Avogadro's number.

These results are thus consistent with the low poly(bis-MPA) KMHS exponent α (between 0.2 and 0.3) determined by SEC/viscometry, which is characteristic of a compact conformation [42,58].

The solutions of Boltorn® hyperbranched polyesters exhibit Newtonian behavior, i.e., the steady shear viscosities are independent of shear rate for solution concentrations up to 50 wt%, which was ascribed to the absence of physical entanglements in hyperbranched polyesters based on bis-MPA (Fig. 18).

From the Arrhenius equation (Eq. (36)) the apparent activation energies of flow (E_η) were determined over the temperature range of 20–40 °C (Fig. 19). Boltorn® hyperbranched polyesters show comparable apparent activation energies of flow, regardless of their molar mass (E_η are 7.5,

Fig. 19. Arrhenius plot of η as a function of inverse temperature to determine the apparent activation energy of flow for the Boltorn® hyperbranched polyesters of different pseudo-generations [61]. Copyright 2000, American Chemical Society.

Fig. 20. Solution viscosities for blends of Boltorn® hyperbranched polyesters and linear poly(2-hydroxyethyl methacrylate), PHEMA. The total polymer content was kept constant at 40 wt.% [61]. Copyright 2000, American Chemical Society.

Fig. 21. Separation scheme for the THF–water separation using the hyperbranched polyester Boltorn® H3200 as an extraction solvent [65]. Copyright 2006, Elsevier B.V.

8.2, 8.1, and 8.2 kcal/mol for pseudo-generations from 2 to 5) [61].

$$\ln(\eta) = A + \frac{E_\eta}{RT} \tag{36}$$

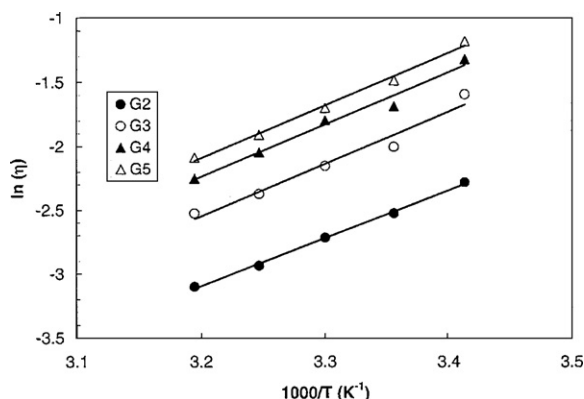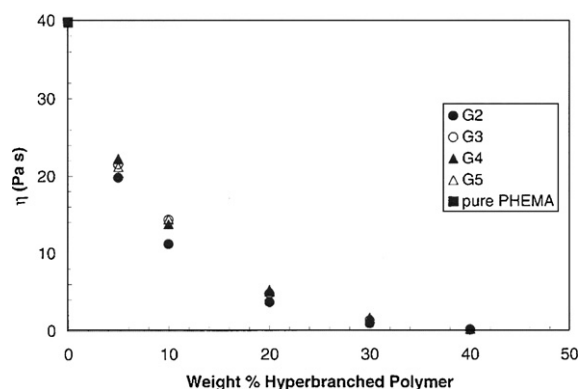where η is the viscosity, A is the pre-exponential factor, E_η is the apparent activation energy of flow, R is the gas constant, and T is the temperature.

Replacing a linear poly(2-hydroxyethyl methacrylate) polymer (PHEMA) with a hyperbranched polyester causes a large reduction in the solution blend viscosity (Fig. 20), which was attributed not only to a lower molar mass and the dense structure of the hyperbranched polymer but also to the decrease in the number of physical entanglements between the linear macromolecules [61]. The critical shear rate for the shear thinning behavior of the solution blend was greater if larger amounts of the linear polymer were replaced with the hyperbranched polymer.

The shear-thinning behavior was observed for concentrated solutions (above 50 wt.%) of self-synthesized and commercial poly(bis-MPA) in the solvent NMP [64] as well as the poly(bis-MPA) with a PP50 core molecule in the solvent DMF at higher shear rates [34], which was attributed to the strong intermolecular interactions between the polar hydroxyl groups of hyperbranched polyesters.

4.3. Phase behavior

The phase behavior of concentrated solutions of hyperbranched polymers is of great importance for their application in the field of chemical engineering, e.g., for membranes, extractive distillation, extraction, absorption, adsorption, etc.

Seiler et al. [65–71] studied the low- and high-pressure phase behavior of Boltorn® hyperbranched polyesters in ethanol and water. The investigated vapor–liquid equilibria (VLE) were studied as a function of the hyperbranched polyester molar mass, the type of end-groups, and the solvent's polarity. Special attention was devoted to the VLE of azeotropic systems, such as ethanol–water, tetrahydrofuran–water, and 2-propanol–water. The extent of the inter- and intramolecular hydrogen-bond formation
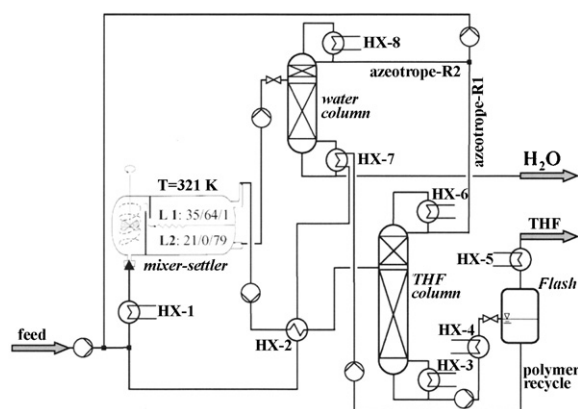
has a dominant impact on the solvent's activity and, thus, it determines the partition coefficients and the relative volatilities. For large polymer concentrations, the hyperbranched polyesters tend to form agglomerates, which limit the polymer solubility and the separation efficiency.

The hyperbranched polyester Boltorn® H3200 with partially modified hydroxyl groups with hydrophobic chains was used for a study of the liquid–liquid equilibrium (LLE) of the azeotropic tetrahydrofuran–water system, which shows a remarkably distinct solutropic phenomenon. Boltorn® H3200 exhibits great selectivity and a capacity for breaking the tetrahydrofuran–water azeotrope using single-stage extraction with distillation (Fig. 21) [65–71].

In the system of Boltorn® hyperbranched polyester, ethanol, and supercritical carbon dioxide, the position of the upper-solution-temperature (UST) curve depends on the hyperbranched polyester molar mass and the solvent polarity, but it is independent of the system pressure. However, the lower solution temperature (LST) of the respective system strongly depends on the pressure. An increase in the CO_2 concentration leads to a considerable shift of the lower-solution-temperature curve to lower system temperatures. The UST and the LST curves merge into an hourglass miscibility gap at a CO_2 concentration of 50.5 wt.% (Fig. 22) [65,66].

For the use of hyperbranched polymers as solvents in liquid–liquid extraction, or other separation processes, a knowledge of the polymer's viscosity, density, solubility parameter, activity coefficient at infinite dilution, selectivity, and capacity is fundamental. Domańska et al. [72,73] studied the density and thermodynamic properties of the Boltorn® U3000 hyperbranched polymer with long, unsaturated fatty-acid end-chains over a wide range of temperatures [72] using inverse gas chromatography [73]. The Flory–Huggins interaction parameter, the molar enthalpy of sorption, the partial molar excess enthalpy at infinite dilution of the solute and polymer, the partial molar Gibbs excess energy at infinite dilution and the solubility parameter were all determined for the dissolution of different organic solvents in the hyperbranched polymer Boltorn® U3000. The values of the mass-fraction activity coefficients and the Flory–Huggins interaction parameters
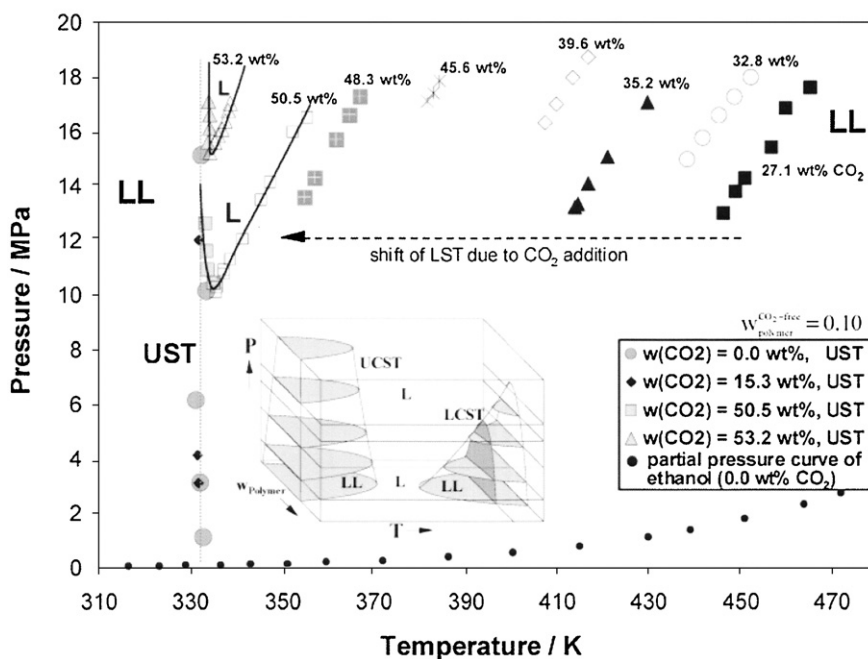
Fig. 22. High-pressure phase behavior of the system: the 2nd pseudo-generation hyperbranched polyester Boltorn® H20–ethanol–CO₂ [66]. Copyright 2003, American Chemical Society.

indicate that the best solvents for the Boltorn® U3000 hyperbranched polymer are THF, thiophene, and aromatic hydrocarbons, whereas water is the worst solvent. The investigated hyperbranched polymer exhibits high selectivity at infinite dilution in the separation processes of methanol/THF and water/THF azeotropes [73]. A similar study was performed on an amphiphilic Boltorn® W3000 hyperbranched polymer, which is partially substituted with long, unsaturated fatty-acid end-chains. The highest values of the mass-fraction activity coefficients at infinite dilution for this polymer were observed for water and aliphatic hydrocarbons from n-pentane to n-nonane [74].

5. Bulk characterization of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid

5.1. Thermal properties

The highly branched structure significantly affects the thermal properties of hyperbranched polymers, i.e., the glass-transition temperature (T_g) and the melting temperature (T_m). Hyperbranched polymers are, due to the branched structure, usually amorphous materials. Therefore, their glass transition is one of the most important thermal properties. The glass transition of hyperbranched polymers is not due to long-range segmental motions, as it is for linear polymers, but it is connected to translational motions and depends on the mobility of the backbone [75]. It is defined primarily by the chemical composition of the hyperbranched polymer, the type and the number of end-groups, the molar mass, and to some extent by the branching topology.

In the case of poly(bis-MPA) hyperbranched polyesters the molecular mobility and thus T_g is, to a large extent, controlled by the hydrogen bonding of polar hydroxyl groups. It increases with the molar mass to a limit, above which it remains nearly constant. For Boltorn® products the T_g increases from 25 °C to 40 °C for the second to fourth pseudo-generation hyperbranched polyesters (Table 1) [32,38,51]. This increase in T_g with molar mass reflects a decrease in the chain mobility as a consequence of skeleton build up.

Because of the large number of chain ends, their nature strongly affects the T_g, which is significantly reduced when poly(bis-MPA) hyperbranched polyesters possess alkyl, acetate or benzoate terminal groups instead of hydroxyl groups [51,78,83]. The significant decrease in T_g is attributed mainly to the reduced extent of the hydrogen bonding, although an increase in the chain-end free volume cannot be excluded. Hyperbranched polyesters terminated with long-enough alkyl chains not only have a lower T_g, but do have several different crystalline phases. The X-ray results suggest that hyperbranched polyesters with long terminal alkyl chains crystallize via intramolecular interactions, whereas in the case of hyperbranched polyesters with shorter alkyl chains the crystallization takes place intermolecularly by the interpenetration of end-groups from adjacent molecules [83].

The thermal properties of Boltorn® poly(bis-MPA) hyperbranched polyesters were investigated in detail using DSC. The shape of the DSC trace strongly depends on the sample's thermal prehistory, i.e., cooling rate, annealing temperature, and annealing time [49,50]. Like with amorphous polymers, an endothermic peak is superimposed on the glass transition temperature and represents an indirect
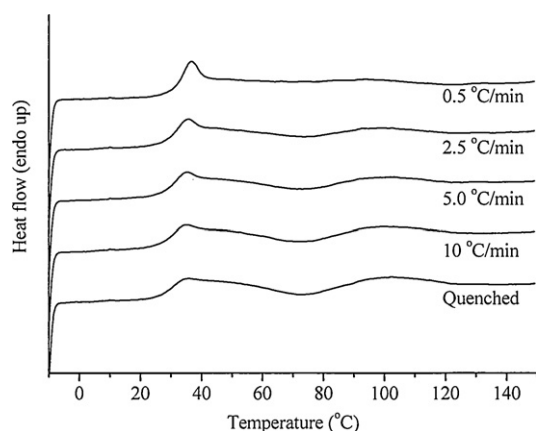
Fig. 23. DSC curves of the 4th pseudo-generation Boltorn® H40 hyperbranched polyester (heating rate 10 °C min⁻¹) after various cooling rates ($0.5 \leq q_c \leq 200$ °C min⁻¹) [49]. Copyright 2005, American Chemical Society.

measure of the relaxation of the enthalpy during the physical aging process that ensures the cohesion of the glassy state (Fig. 23). The magnitude of this peak increases with the decreasing cooling rate (Fig. 23) [49]. Above T_g, the DSC curve of the quenched samples shows a broad exothermic peak, followed by an endothermic one that extends up to a temperature of 140 °C (Fig. 23) [49].

During the first heating scan of the annealed samples there are only endothermic transitions above the T_g (Fig. 24) [32,47,49,50,57,63,77,81]. The peak position and the enthalpy change at the endothermic transition depend on the annealing temperature and time (Fig. 24). Since the end-capped hyperbranched polyesters do not show either physical aging effects or exo- or endothermic transitions, as well as taking into account the FTIR results [47], it was concluded that hydrogen bonding, especially between hydroxyl groups, is responsible for the observed thermal properties of the hyperbranched polyesters [49,50,63]. The exothermic peaks were ascribed to H-bond formation, whereas the endothermic peaks were ascribed to the cleavage of H-bonds.

The endothermic transition shifts towards a higher temperature with an increased annealing temperature and time (Fig. 24) due to the formation of a thermally more
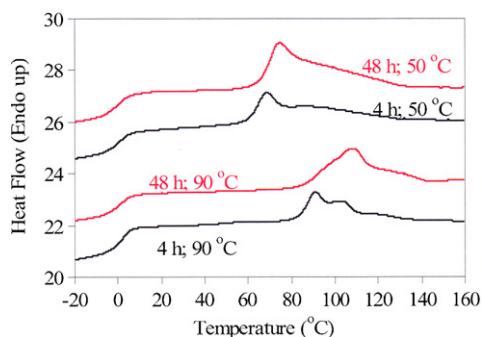

Fig. 24. The influence of the annealing time and the annealing temperature on the DSC curves for the 2nd pseudo-generation Boltorn® H20 hyperbranched polyester [50].

stable H-bond microstructure. The enthalpy (ΔH) of the endothermic transition increases with the decreasing temperature and increasing annealing time [49,50]. In the latter case the dependence of ΔH on the logarithm of time is linear and can be described by the following equation (Eq. (37)):

$$\Delta H = \Delta H_0 + k \ln(t) \tag{37}$$

where ΔH is the enthalpy of H-bond cleavage, ΔH_0 is the enthalpy of H-bond cleavage at $t = 1$ h, k is the slope of the straight line representing the rate of H-bond cleavage, and t is the annealing time.

The rearrangement of the H-bond microstructure during the annealing has a negligible effect on the T_g, but a larger one on the heat capacity (Δc_p) at the glass transition, which decreases with increasing enthalpy at the endothermic transition as a consequence of the restricted molecular mobility.

The rate of H-bond formation and the kind of H-bond microstructure formed depend not only on the annealing conditions but also on the structural and molar-mass characteristics of the hyperbranched polyesters [48–50]. At temperatures up to 80 °C the formation of H-bonds is faster (higher k values) and more extensive (higher ΔH values) for the low-molar-mass hyperbranched polyester (the second pseudo-generation Boltorn® H20) than for the higher-molar-mass hyperbranched polyester (the fourth pseudo-generation Boltorn® H40). The reason for this is the higher mobility of the lower-molar-mass molecules as well as the more easily accessible hydroxyl groups for H-bond formation, not only in the terminal but also in the linear repeat units. In other words, the low-molar-mass sample possesses an open structure, a low degree of branching, and a low actual core functionality. As a consequence, the relative fraction of OH···OH H-bonds compared to OH···O=C H-bonds is much larger in the Boltorn® H20 of the second pseudo-generation. The formation of H-bonds between the hydroxyl groups is also favored at shorter annealing times and higher temperatures, indicating that OH···OH H-bonds are thermally the most stable. At temperatures above 90 °C, the rate of H-bond formation is slower for the Boltorn® H20, since the high mobility of the molecules restricts the H-bond formation and only thermally stable H-bonds are formed.

5.2. Dielectric relaxation properties

Dielectric relaxation spectroscopy (DRS) is sensitive to the molecular fluctuations of dipoles within the polymer. The dipole fluctuations, i.e., the relaxation processes, related to the molecular mobility of the groups (subglass processes), the segments (segmental dynamics) or the whole macromolecule can be used for structural investigations.

The hydroxyl-terminated hyperbranched polyester of the fifth pseudo-generation containing a TMP core molecule was investigated by Malmström et al. [30,76,78–88]. The sample exhibits two subglass relaxation processes, γ and β (Fig. 25). The β-process ($T_\beta = 5$ °C) appears at a higher temperature than the γ-process ($T_\gamma = -64$ °C). Both relaxations are below the α-relaxation
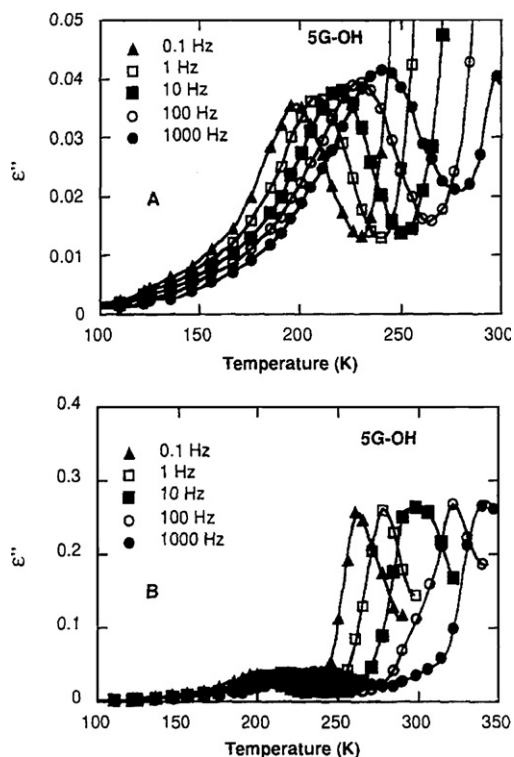
Fig. 25. Dielectric loss (ε'') for the hydroxyl-terminated 5th pseudo-generation poly(bis-MPA) hyperbranched polyester with a TMP core molecule at the frequencies shown in the graph as a function of temperature [76]. Copyright 1997, Elsevier Science Ltd.

Fig. 26. Plots of activation energy of the γ-relaxation process as a function of pseudo-generation number. The empty squares and triangles are the data obtained from the frequency and relaxation time, respectively [79]. Copyright 2001, Wiley-VCH Verlag GmbH, Weinheim.

(glass transition; $T_\alpha = 32\,^\circ$C), which was masked by the Maxwell–Wagner–Sillars polarization. The γ-relaxation was attributed to the hydroxyl-group motion, whereas the β-relaxation was attributed to the reorientation of the ester groups. The relaxation strengths of the hyperbranched polymers were lower than those of the linear polymers. These results were ascribed to the lower segmental flexibility of the backbone in a hyperbranched polymer than in a linear polymer. The temperature dependence of the relaxation rate for the γ- and β-process follows an Arrhenius relation (Eq. (38)). Both apparent activation energies are around 100 kJ/mol, which are thought to be too high for a truly localized process.

$$f_{\max} = f_0 \cdot e^{(-\Delta E/RT)} \tag{38}$$

where $f_{\max}$ is the frequency associated with the loss maximum, f_0 is a constant, T is the temperature, ΔE is the activation energy and R is the gas constant.

The molecular dynamics and conductivity of a series of hydroxyl-terminated hyperbranched polyesters (Boltorn® products) were studied with respect to the molar mass, which strongly affects the dielectric properties of the hyperbranched polyesters. The frequency and temperature dependence of the conductivity obey peculiarities found to be characteristic of semiconducting disordered materials [79]. Because of strong conductivity effects, either the α-relaxation [80], or both the α- and β-relaxations are masked [79]. The activation energy for the γ-relaxation processes is unusually high due to the hindered fluctuation
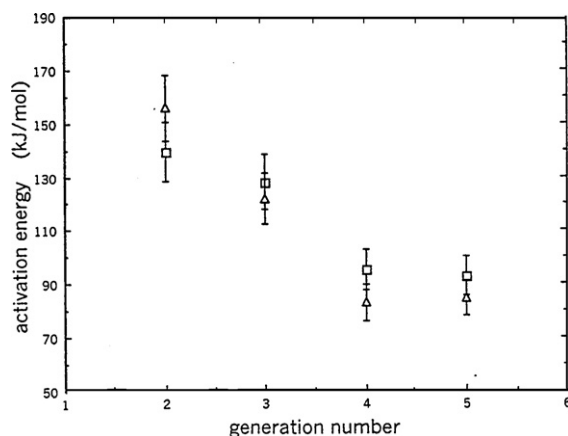
of the hydroxyl groups. The activation energy calculated by the Arrhenius relation (Eq. (38)) increases with the decreasing molar mass of the hyperbranched polyester (Fig. 26). Simon et al. [79] suggested that the motion of the hydroxyl groups is increasingly hindered when going to a lower pseudo-generation hyperbranched polyester due to the increase in the density of hydroxyl groups and the interactions between them. Turky et al. [80] ascribed the slower dynamics of the hydroxyl groups in lower pseudo-generation polyesters to stronger intramolecular, rather than intermolecular, interactions between the polyesters themselves.

This presumption was recently confirmed by a fully atomistic molecular dynamics simulation study of hyperbranched polyesters of the second and third pseudo-generation in the bulk by Tanis and Karatasos [48]. Their simulation study at the atomic level revealed that for the lower-molar-mass hyperbranched polyester a higher degree of intramolecular H-bonds are formed between the hydroxyl groups, which is consistent with more constricted or more cooperative motions, and, consequently, with a slower dynamics related to their survival or the reorientation of the resulting H-bond network. Intramolecular interactions in hyperbranched polyesters were already predicted by Hiltner et al. [51] based on the results obtained by atomic force microscopy (AFM), the theoretically calculated diameters from the known molar masses of hyperbranched polymers, the predicted spherical shape of the molecules and by X-ray diffraction. The authors assumed that the ordering of the structure of the hyperbranched polyesters that is more pronounced for lower-molar-mass samples is due to linear segments that fold back on themselves and crystallize. On the other hand, Žagar et al. [49,50] suggested, after considering the results of FTIR, NMR, DSC and X-ray diffraction, that the structure ordering in Boltorn® hyperbranched polyesters is a consequence of the formation of multiple H-bonds between long linear sequences. The low-molar-mass hyperbranched polyester (the second pseudo-generation) with a low degree of branching and core functionality facilitates the

formation of OH⋯OH H-bonds, especially at higher temperatures [49,50].

The β-relaxation process was detected in hyperbranched polyesters of a pseudo-generation higher than two [80]. In the second pseudo-generation the β-process was masked because of the strong effect of the conductivity and/or electrode polarization. The values of the activation energy for the β-relaxation process are comparable to those found for the γ-process and are also ordered in the same way. These results were again attributed to the special and complicated architecture of hyperbranched polymers.

Malmström et al. [76–78] investigated the effect of the type of terminal groups (acetate, benzoate, and propionate) on the molecular dynamics of hyperbranched polymers. In all hyperbranched polyesters with modified hydroxyl groups only two relaxation processes were observed: a low-temperature β-process appearing as a weak shoulder on the low-temperature side of the peak associated with the larger and stronger high-temperature process, α, which originates from the T_g. With increasing frequency, the temperature shift of the α peak is stronger than that for the β-process, and the two processes overlap almost completely at the lowest frequency. The temperature dependence of the α-process follows the WLF equation (Eq. (39)), as expected for the glass transition, whereas the β-process follows the Arhenious law (Eq. (38)), typical for sub-glass processes. The values of the activation energy indicate that in the benzoate-terminated hyperbranched polyester the ester groups are the most constrained groups, probably due to the segmental inflexibility of the benzoate groups.

$$f_{\max} = f_0 \cdot e^{-(A/(T-T_0))} \tag{39}$$

where $f_{\max}$ is the frequency associated with the loss maximum, f_0 and A are constants, and T and T_0 are temperatures.

5.3. Rheological and mechanical properties

When introducing a new application for any polymer, knowledge of its material and processing characteristics is required. Because of the close relationship between the rheological and processing properties, characterizing the rheological flow behavior of hyperbranched polymers is of fundamental importance. Such studies provide correlations between the bulk properties of the hyperbranched polymer and its molar mass, the nature of end-groups, and the degree of branching. Because of the highly branched structure hyperbranched polymers have low melt viscosities and, therefore, they are used in the preparation of polymer blends as flow modifiers to reduce the blend viscosity.

The rheological behavior of poly(bis-MPA) hyperbranched polyesters, especially of the commercial Boltorn® products, has been investigated by several authors [49,50,63,30,81–86]. For melts of poly(bis-MPA) some of them observed Newtonian behavior, regardless of the hyperbranched polyester molar mass, i.e., the melt viscosity is not affected by the deformation rate (shear rate or frequency) within the shear or frequency range tested [63,30,81,82]. This Newtonian behavior indicates a lack
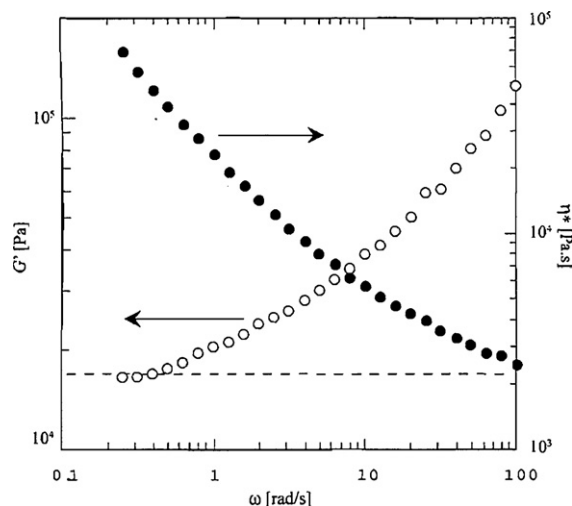
Fig. 27. Rheological behavior at 100 °C for the 5th pseudo-generation hydroxyl-terminated Boltorn® hyperbranched polyester before and after preheating. The horizontal dashed line corresponds to the viscosity observed for the fully Newtonian preheated sample [63]. Copyright 2004, Wiley Periodicals, Inc.

of entanglements between the chains, and is generally observed for linear polymers only below the critical molar mass, beyond which the viscosity significantly increases due to the onset of entanglements. The dependence of the zero shear-rate viscosity of hyperbranched polyesters on the molar mass shows a gradual decrease in the slope with the increasing molar mass. Such behavior is similar to dendrimers and was explained by the transition from the more open structure of low-molar-mass hyperbranched polyesters to the closed, globular structure of high-molar-mass samples.

The rheological behavior is significantly dependent not only on the molar mass and the structural characteristics of hyperbranched polyesters, but also on the preparation procedure used for the samples before the measurements. Månson et al. [63] observed that the rheological behavior of the fifth pseudo-generation Boltorn® polyester strongly depends on its thermal prehistory (Fig. 27). A thermally pretreated hyperbranched polyester (at 160 °C), prior to the rheological measurements, shows Newtonian behavior, whereas the original sample exhibits a viscoelastic response, which was ascribed to the H-bond microstructure developed at the storage temperatures.

On the other hand, Simon et al. [84,86] reported that melts of low-molar-mass Boltorn® hyperbranched polyesters (second and third pseudo-generation) are shear-thinning, whereas melts of higher-molar-mass Boltorn® hyperbranched polyesters (fourth and fifth pseudo-generation) are Newtonian, in both oscillatory and steady shears within the deformation rates investigated (Fig. 28).

The shear-thinning behavior of low-molar-mass hyperbranched polyesters was explained by the strong intermolecular interactions of the hydroxyl groups in the terminal units. The Cox–Merz rule (Eq. (40)) which predicts that the complex viscosity $\eta^*(\omega)$ and steady shear viscosity $\eta(\gamma)$ have the same values at the same deformation rate,
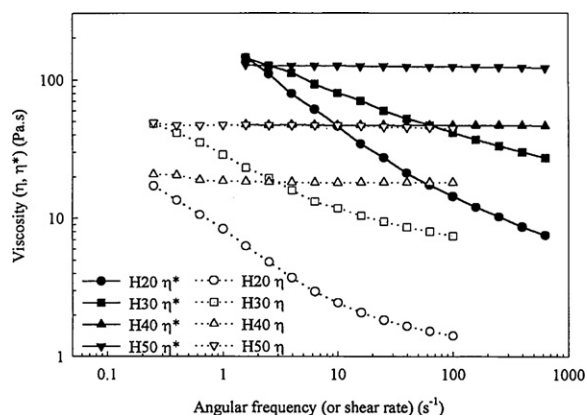
Fig. 28. Complex viscosity (η^*) (a) and steady shear viscosity (η) (b) of Boltorn® hyperbranched polyesters as a function of angular frequency and shear rate at 110 °C, respectively [84]. Copyright 2000, Elsevier Science Ltd.

does not hold for the Boltorn® hyperbranched polymers.

$$\left|\eta^*(\omega)\right| = \eta(\dot{\gamma}), \quad \text{when } \omega = \dot{\gamma} \tag{40}$$

In addition, in the dynamic strain-sweep experiments the onset of the nonlinear region occurs at much lower strains for Boltorn® hyperbranched polyesters with lower-molar-masses compared to those with higher-molar-masses. Lower-molar-mass hyperbranched polyesters relax much more slowly than higher-molar-mass hyperbranched polyesters (Fig. 29).

With increasing temperature the steady shear viscosity of Boltorn® hyperbranched polyesters decreases. From the temperature dependence of the steady shear viscosity the flow-activation energies (E_a) were determined (Fig. 30). The E_a values of the lower-molar-mass hyperbranched polyesters are higher than those of the higher-molar-mass samples due to stronger polar interactions.

Simon et al. [85] investigated the rheological properties of blends containing hyperbranched polyesters with different pseudo-generation numbers. The blends were prepared by melt blending at 110 °C and their rheological properties were compared to those of the neat hyperbranched polyesters. Newtonian behavior is the dominant flow characteristic for the blends, although hyperbranched
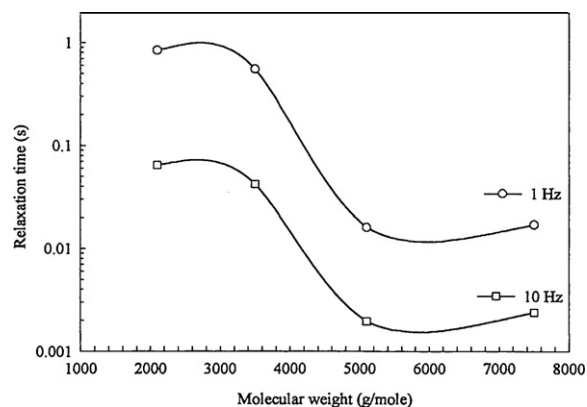
Fig. 29. Relaxation times of Boltorn® hyperbranched polymers at 1 and 10 Hz [84]. Copyright 2000, Elsevier Science Ltd.
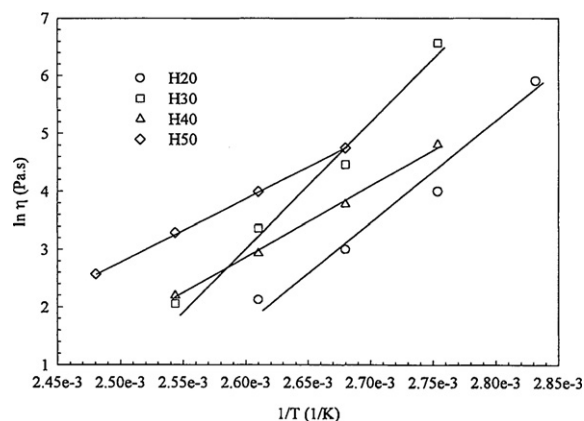
Fig. 30. Arrhenius plot of steady shear viscosity of Boltorn® hyperbranched polymers at 10 s^{-1} [84]. Copyright 2000, Elsevier Science Ltd.

polyesters of the second and third pseudo-generations exhibit shear-thinning (Fig. 31). This is an interesting property, since normally the addition of shear-thinning components to Newtonian fluids results in shear-thinning mixtures.

The changing of the rheological behavior during annealing at different temperatures was studied for low- (the second pseudo-generation) and high-molar-mass (the fourth pseudo-generation) Boltorn® hyperbranched polyesters [49,50]. After a certain induction time during annealing, both samples exhibit a pronounced increase in their viscosity (Fig. 32), which coincides with the appear-
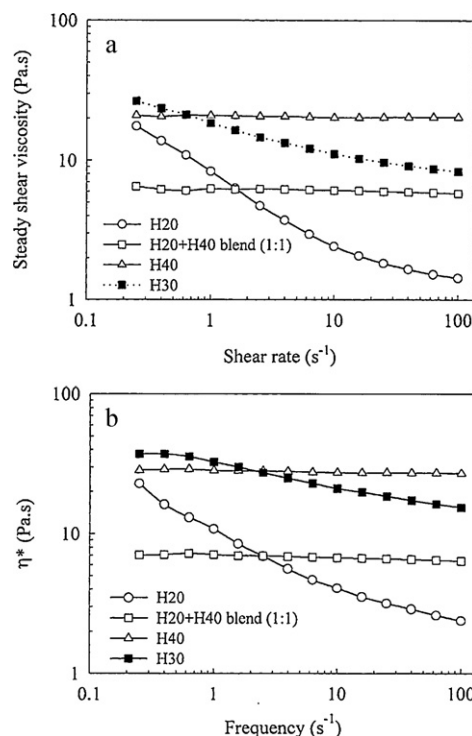
Fig. 31. Steady shear viscosity (a) and oscillatory shear viscosity (b) of Boltorn® H20, H30, H40, and H20 + H40 (1:1) blend at 110 °C [85]. Copyright 2001, Elsevier Science Ltd.
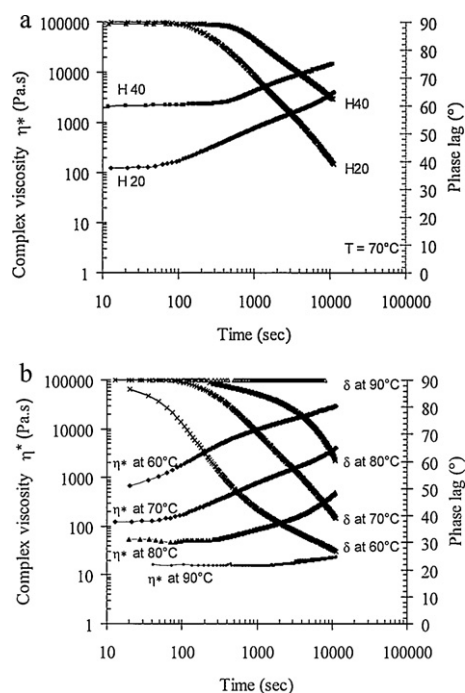
Fig. 32. Complex viscosity (η^*) and phase lag (δ) as a function of annealing time under non-destructive conditions of oscillatory tests at a frequency of 6.28 rad s^{-1} under the conditions of LVR: (a) for the 2nd and 4th pseudo-generations Boltorn H20 and H40 at 70 °C, and (b) for the 2nd pseudo-generation Boltorn® H20 hyperbranched polyester at the annealing temperatures of 60, 70, 80, and 90 °C [50]. Copyright 2007, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

ance of the elastic contribution to the viscoelastic response. Such behavior was ascribed to the beginning of the H-bond network-formation process during annealing. The induction time for the H-bond network formation is shorter for the second pseudo-generation hyperbranched polyester up to annealing temperatures of 80 °C (Fig. 32a), For both hyperbranched polyesters the induction time increases with the increasing annealing temperature (Fig. 32b). The low-molar-mass hyperbranched polyester exhibits a higher elastic contribution to its viscoelastic response than the high-molar-mass hyperbranched polyester does (Fig. 32a). These results match the enthalpy values for the endothermic transitions determined by DSC for samples with the same thermal prehistory [49,50].

As in the case of the thermal properties, dielectric relaxation properties, and solution viscosity, the melt viscosity is also strongly influenced by the chain-end composition [63,30,81,83,86]. The melt viscosity decreases with the degree of end-capping and depends on the chemical composition of the end-groups. A decrease in the viscosity is attributed to a reduction in the hydrogen bonding. The melts of the end-capped hyperbranched polymers behave as Newtonian liquids. The dynamic and steady shear measurements at the same temperature and shear rate/frequency show that the Cox-Merz equation (Eq. 40) is valid for these hyperbranched polymers.

Poly(bis-MPA) hyperbranched polyesters exhibit poor mechanical properties due to a lack of entanglements.

They are brittle polymers with limited use as thermoplastics [4,51]. The stress–strain behavior of Boltorn® products is similar to that of ductile metals. Due to the globular structure, which does not permit an extension and orientation of the molecules, hyperbranched polyesters do not strain harden. However, association through the H-bonds provides intermolecular interactions between the hyperbranched molecules.

5.4. Surface behavior

The surface properties of neat and modified Boltorn® hyperbranched polyesters were studied by water-contact-angle measurements and the micro-Wilhelmy wetting technique to determine the solid and melt surface tensions, respectively [87]. The surface tensions of the melts are extremely high for hydroxyl-terminated hyperbranched polyesters and approach that of water, indicating the preferential surface segregation of hydroxyl terminal groups. The substitution of hydroxyl groups with alkyl chains dramatically reduces the melt surface tension to the point where a large degree of substitution produces the surface tension equivalent of pure alkanes. The results for the solid surface tension, determined by water-contact-angle measurements, are similar to those for the melt-surface-tension measurements, i.e., the solid surface tension is significantly affected by the degree of alkyl substitution.

An AFM analysis of Boltorn® hyperbranched polyesters of the lower pseudo-generation deposited from dilute solutions on mica substrates show that they form, regardless of their molar mass, monolayer aggregates of spherical molecules, which are stabilized by the hydrogen bonding between the hydroxyl groups [51]. These results are surprising since most theoretical models indicate that low-molar-mass hyperbranched polyesters have an open structure with functional groups located on the periphery.

Tsukruk et al. [88,89] investigated the surface behavior of Boltorn® products on the surface of silicon oxide using the AFM method. The molecular adsorption of hyperbranched polyesters onto a surface follows a typical Langmuir adsorption isotherm. The particles coalesce into a uniform monomolecular layer; however, the surface structure depends on the hyperbranched polyester molar mass. The higher-molar-mass samples retain their spherical shape within the densely packed, adsorbed molecular layers (Fig. 33b). The average thickness of the molecular layer is close to the molecules' diameters in the compact state. On the other hand, the low-molar-mass hyperbranched polyesters go through significant conformational changes after adsorption onto a silicon surface (Fig. 33a). For the case of a low surface coverage the hyperbranched molecules are in a highly flattened shape, that is replaced by increasing surface coverage, first with patch-like structures, and then with worm-like nanoscale structures, which coalesce into a densely packed monolayer with a uniform surface morphology. Thus, the surface behavior of low-molar-mass hyperbranched polyesters varies, depending on the substrate used [51,88,89].

The surface properties of poly(bis-MPA) with modified end-groups strongly depend on the kind of end-group modification [87,89–92]. The hyperbranched polyester
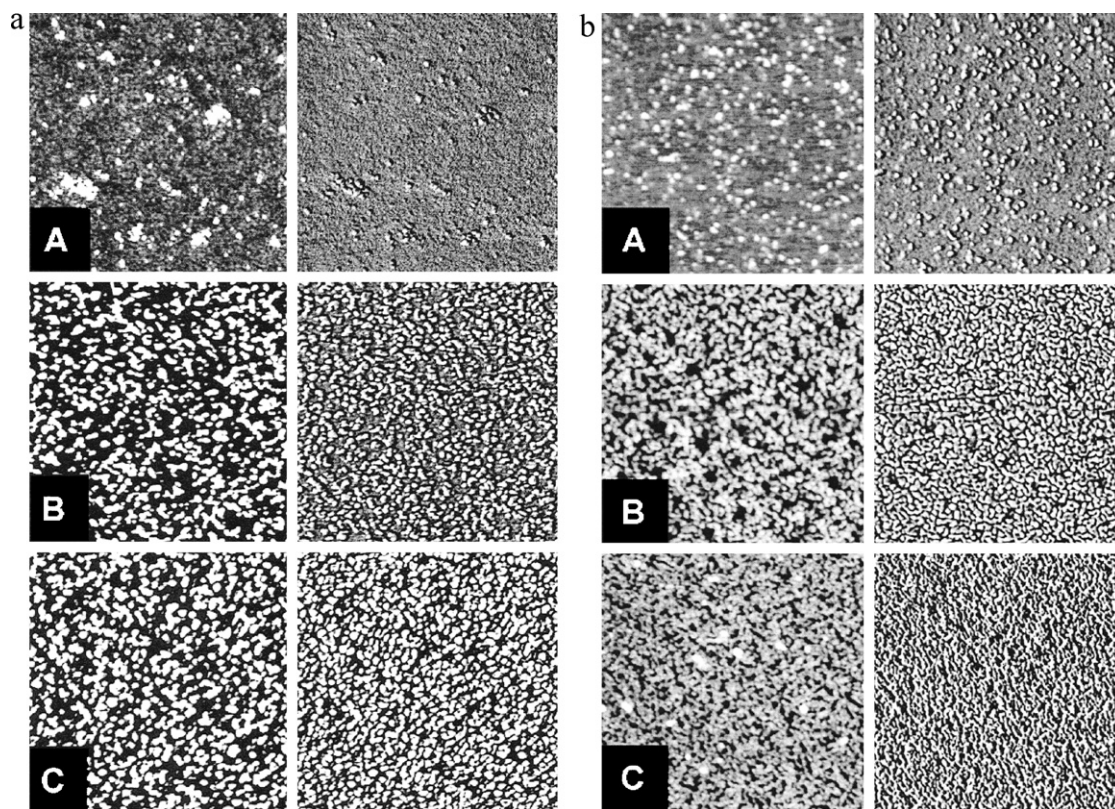
Fig. 33. AFM images of adsorbed molecules (left: topography and right: phase) obtained from different solution concentrations: 0.5 g/L (A), 1.5 g/L (B), and 5.0 g/L (C), and scan size 2 μm × 2 μm, height scale is 5 nm, phase scale is 15°: (a) for the 3rd Boltorn® pseudo-generation hyperbranched polyester and (b) for the 4th pseudo-generation Boltorn® hyperbranched polyester [89]. Copyright 2001, American Chemical Society.

with bulky and planar anthracene end-groups forms, in the course of crystallization from solution, very long and straight microfibers with a sheet-like lamellar surface (Fig. 34) [90]. The authors suggest that the directional crystallization of multiple peripheral fragments attached to irregular cores is responsible for assembling near-perfect, uniform supramolecular one-dimensional structures.

The amphiphilic hyperbranched polyesters partially modified with hydrophobic, long alkyl chains and amine (or carboxylic) groups form robust one-dimensional nanofibrillar structures on the silicon oxide surface (Fig. 35) [91–93]. The authors suggest that hyperbranched molecules adopt a highly asymmetric conformation in the nanofibril, i.e., a semi-cylindrical conformation in which the hydrophilic cores are squashed toward the solid surface, and the hydrophobic terminal chains are concentrated in the topmost layer. The critical parameter for nanofibrillar-structure formation is the presence of both long alkyl tails and amine (or carboxyl) groups that interact with the polar surface. The amino end-groups are much more effective in promoting the nanofibrillar assembly than the carboxyl end-groups.

The hyperbranched polyester was also partially modified with alkyl chains and functionalized by epoxy groups in order to graft it onto a silicon oxide surface [94]. The grafted layers were homogeneous, without any signs of microphase separation usually observed for mixed layers.

In addition to the above-mentioned techniques, time-of-flight secondary-ion mass spectrometry (ToF-SIMS) has been used for the study of neat and modified poly(bis-MPA) hyperbranched polyesters' surfaces. The fragment ions detected depend on the molar mass of the hyperbranched polyester and the kind of polyester end-groups [95,96].

5.5. Thermal and enzymatic degradation

The thermal stability of hyperbranched polyesters and their derivatives was investigated by thermogravimetric analysis (TGA) in an inert N_2 atmosphere. Poly(bis-MPA) containing a PP50 or TMP core molecule exhibits a good thermal stability. The onset of the thermal degradation is at about 250–275 °C. The thermal stability improves only slightly with an increase in the molar mass of the hyperbranched polyester [51,62,97]. However, the thermal stability improves when THECA is used as a core molecule [32]. The onset of thermal decomposition is at 275–300 °C, whereas it is independent of the monomer/core ratio [32]. A comparison of the thermal stability of hyperbranched polyesters, modified hyperbranched polyesters, and linear polyesters indicates that thermally, the most stable are the hyperbranched polyesters with the hydroxyl end-groups [97].
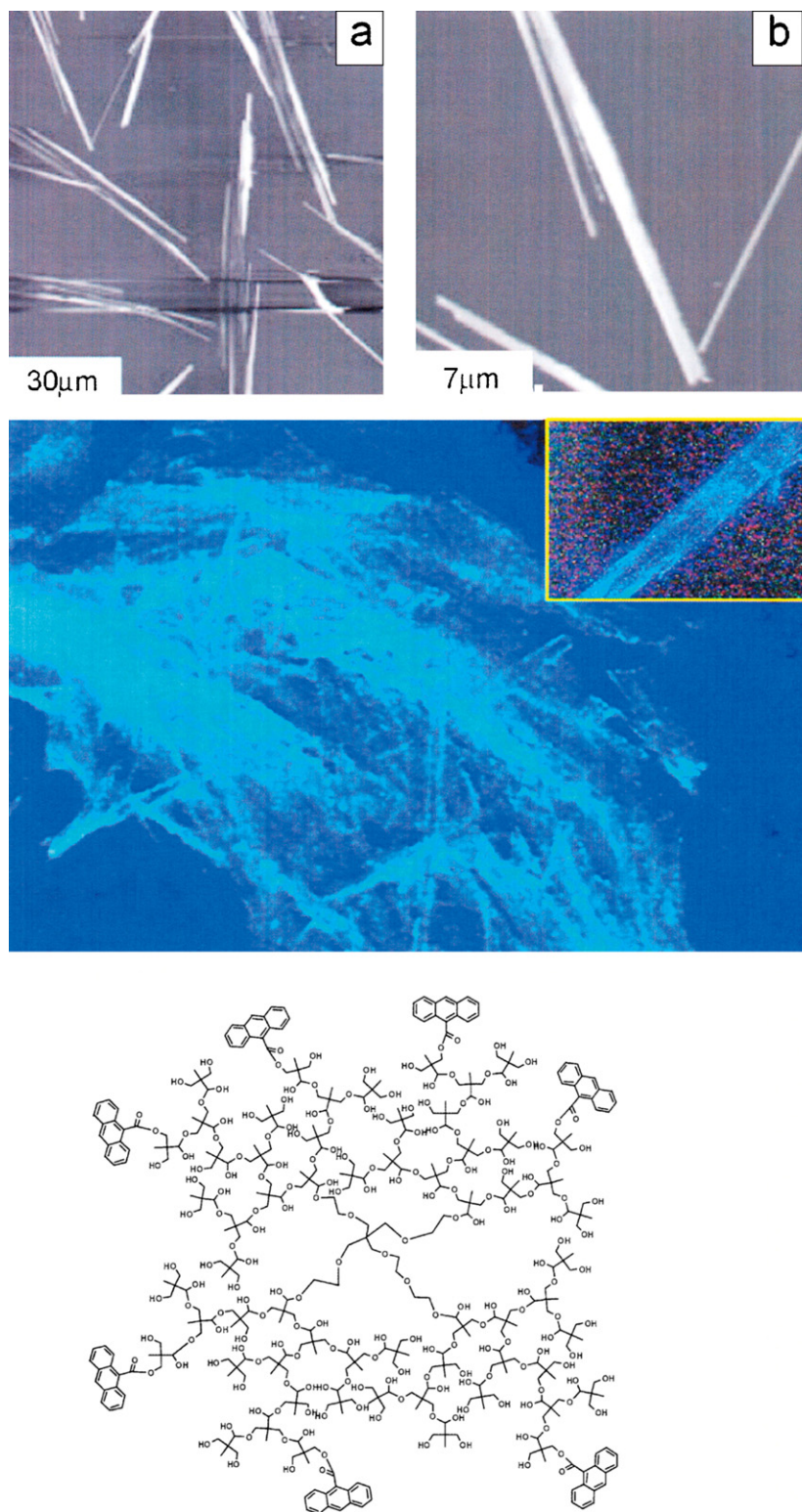
Fig. 34. Chemical structure of anthracene-functionalized hyperbranched polyester and optical images of straight polymer nanofibers and nanoribbons under normal (a and b) and UV (c) light. Inset shows an individual microfiber at higher magnification [90]. Copyright 2004, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
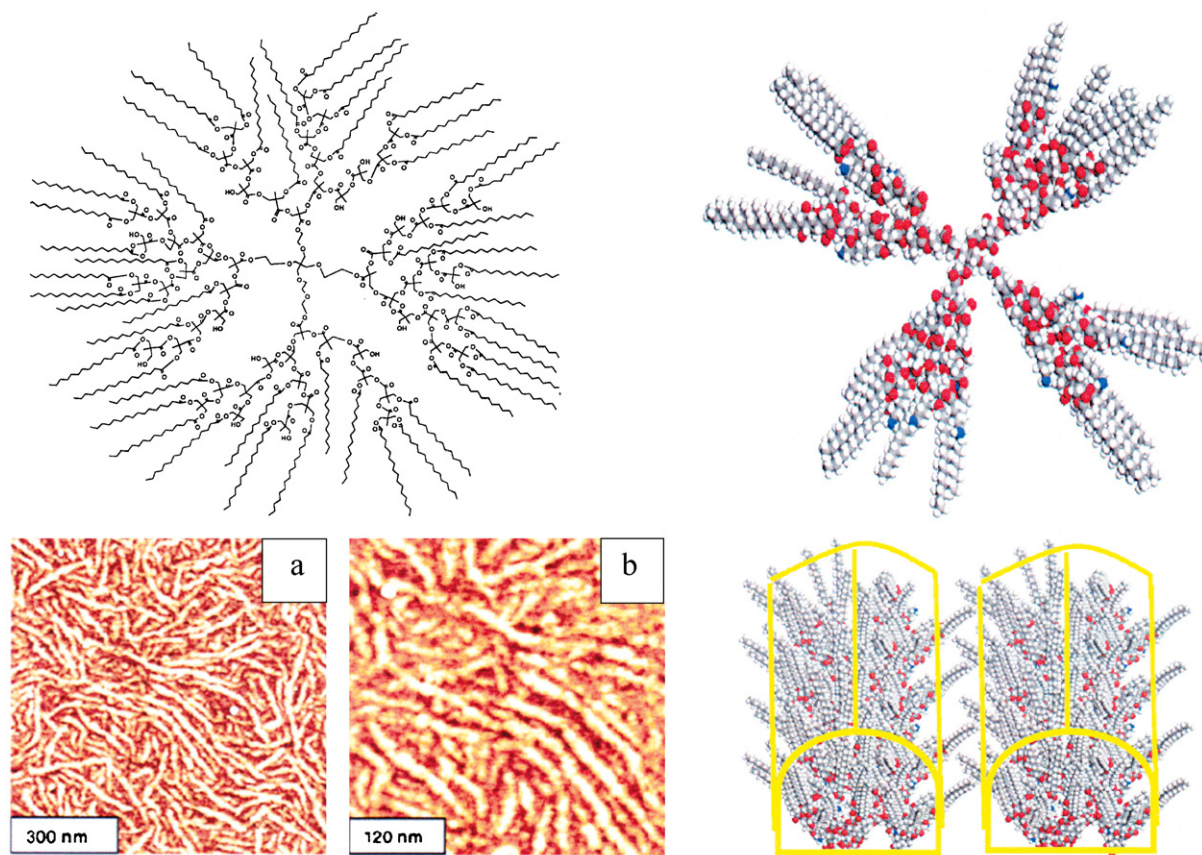
Fig. 35. Chemical formula of the amphiphilic hyperbranched polyester with modified terminal branches with the alkyl chains (left), corresponding high-resolution AFM phase images of nanofibrillar structures assembled at 20 mN/m (a and b) and suggested conformational reorganization, which leads to the formation of semi-cylindrical micelles upon compression [91]. Copyright 2004, American Chemical Society.

The enzyme-catalyzed degradation of poly(bis-MPA) hyperbranched polyesters modified with different long-chain fatty acids was performed in a phosphate buffer in the presence of various lipases [98]. The degree of degradation depends on the type and the concentration of the enzyme used, the type of the alkyl chains on the poly(bis-MPA) surface, and the temperature. Furthermore, it was determined that the hydrolysis of the core material, i.e., the hyperbranched polyester, was almost negligible.

6. Applications of hyperbranched polyesters based on 2,2-bis(methylol)propionic acid

Poly(bis-MPA) hyperbranched polyesters produced by melt polycondensation exhibit rather low molar masses and the presence of various side products, but their high functionality is still preserved. In addition to the large number of functional groups, poly(bis-MPA) hyperbranched polyesters show a low solution and melt viscosity, a globular structure that hampers chain entanglement, a negligible vapor pressure, a good thermal stability, biocompatibility, biodegradability, nontoxicity, high solubility, and storage stability. In terms of applications, it has been recognized that the modification of hydroxyl functional groups of poly(bis-MPA) hyperbranched polyesters is essential for the control of their solubility, compatibility, reactivity, thermal stability, adhesion to surfaces, self-assembly, chemical recognition, as well as the electrochemical and luminescence properties. Thus, the structural modifications provide a powerful tool for designing the properties of poly(bis-MPA) hyperbranched polyesters for various application fields, ranging from classical commodity and engineering plastics to advanced and specialty materials, which find use in nanotechnology, nanobiotechnology, nanomedicine, chemical engineering, etc.

The applications of hyperbranched polyesters are focused on the commercially available Boltorn® products. They were first considered mainly in applications fields, where the low viscosity and the high functionality are the advantages, i.e., as blend components, additives, rheology modifiers, and primarily as components for various coating resins, e.g., high solid coatings or powder coatings. In other words, hyperbranched polyesters provide a unique combination of coating properties, such as a high hardness, scratch resistance, and flexibility, whereas at the same time ensuring low viscosity and low shrinkage [99–116]. For the purpose of UV-curing, the hyperbranched polyesters were end-capped with various groups capable of undergoing photopolymerization, e.g., methacrylate, acrylate, thiol-ene, allyl ether groups, fatty acids, etc. [101–112].

Boltorn® products can act as an outstanding toughener in epoxy matrix composites, without affecting the viscosity of the uncured resins or the thermomechanical properties of the cured material [117–122].

Boltorn® hyperbranched polyesters have been widely explored as the reactive components in polyurethanes (PU). The influence of the hyperbranched polyester's incorporation into the PU structure on the properties of hyperbranched polyurethanes was investigated [123–131]. Cao and Liu reported that a hyperbranched PU copolymer with soft polyethylene glycol (PEG) segments shows good energy-storage behavior due to a reversible transition between the amorphous and crystalline PEG segments [132], whereas a hyperbranched PU composed of 4,4′-diphenylmethane diisocianate, poly(butylene adipate)glycol and poly(bis-MPA) hyperbranched polyester shows thermo-sensitive shape-memory properties [133].

Mulkern and Tan reported that Boltorn® hyperbranched polyester of the fourth pseudo-generation is an excellent processing additive for polystyrene, since it acts as a lubricant during processing, and as a self-compatibilizing toughening agent in the final formation of the blend [134]. The same hyperbranched polyester acts as a processing aid in the tubular film-blowing process of linear low-density polyethylene (LLDPE), as reported by Malmström et al. [135]. It eliminates sharkskin, without any significant influence on the other physical properties of the LLDPE films.

Recently, poly(bis-MPA) hyperbranched polyesters have also been studied for the preparation of nanocomposites [136–139]. The Boltorn® hyperbranched polyester of the second pseudo-generation was used for the functionalization of multi-walled carbon nanotubes to be applied as an electrode material for lithium batteries. The insertion/deinsertion capacity and cycle stability of lithium batteries were significantly improved in comparison to linear polymer-functionalized carbon nanotubes [136].

In the field of nanotechnology, the same Boltorn® polyester was used for the preparation of a ZnS/hyperbranched polyester nanocomposite, which exhibits a high refractive index [136]. The ZnS/hyperbranched polyester nanocomposite was prepared by dispersing ZnS nanoparticles uniformly into the acrylated Boltorn® polyester. In this system, the hyperbranched polyester plays an important role in stabilizing and dispersing the ZnS nanoparticles. These nanocomposite films are semiconducting and, thus, have various potential applications, e.g., for optical coatings, optical waveguides, displays, reflectors, etc. [137].

Månson et al. [138,139] studied the properties of polyurethane nanocomposites containing montmorillonite clay modified with hyperbranched polyesters based on bis(MPA).

The use of hyperbranched polyesters based on bis-MPA also has great potential in the field of chemical engineering, in separation processes involving solvent or metal-ion extraction and membranes [69,71,140–142].

Shi et al. [140] prepared organic–inorganic hybrid membranes based on phosphoric acid and hyperbranched polyester of the second pseudo-generation. The membranes with a high proton conductivity show potential for polymer-electrolyte-membrane fuel cells operated at temperatures above 100 °C [140]. The gas permeability of Boltorn®-modified polyimide membranes was studied by Stamatialis et al. [141].

Poly(bis-MPA) hyperbranched polyesters exhibit separation efficiencies for various metal ions [142]. The extraction efficiency depends on a medium pH, with the optimum pH range being 5.0–7.0 for Cu(II) and Pb(II), 4.5–7.0 for Fe(III), 6.0–8.0 for Co(II) and Ni(II), 6.0–7.5 for Cd(II) and 6.5–8.0 for Zn(II) ions.

Seiler et al. [69,71] investigated the separation of the azeotropic tetrahydrofuran–water system using the modified poly(bis-MPA) hyperbranched polyester Boltorn® H3200 instead of conventional distillation. The results are very promising for the use of aliphatic hyperbranched polyesters based on bis(MPA) as extraction solvents.

Chen et al. [143] employed poly(bis-MPA) hyperbranched polyesters modified with carboxylic or sulphonic acid as crystallization modifiers for calcium carbonate. The functionalized polyester exhibits remarkable polymorph selectivity and morphology control. Well-defined, core–shell-structured, vaterite spheres are obtained by the nano-aggregation of approximately 70 nm crystallites with a radial organization, which may mediate and combine the nano-aggregation and the crystal-growth formation mechanism of the vaterite polymorph.

Application fields that require polymers with a well-defined structure and molar mass have, until recently, been reserved mainly for conventional linear (co)polymers and dendrimers. However, the number of reports dealing with the application of hyperbranched polymers in these high-tech fields has recently increased significantly, especially in the areas of sensorics, nonlinear optics, molecular imprinting, catalysis, biotechnology and medicine. A review article has just been published dealing with research and development in the field of encapsulation and/or the controlled release of active substances (e.g., unstable or sensitive components, pharmaceutical substances, and inorganic nanoparticles) using various chemically versatile hyperbranched polymers [144]. The intensive research directed towards diverse applications of hyperbranched polymers based on bis-MPA has given very promising results for their use in biotechnology and medicine for the incorporation of therapeutic agents, cosmetic ingredients such as flavors, fragrances, tanning agents, amino-acid derivatives, and vitamins, as well as nucleic acids in a shell or the matrix of the hyperbranched polyester carrier [59,145–162].

Amphiphilic hyperbranched block copolymers have recently attracted considerable attention in medicine and biology as drug-delivery carriers, since a single copolymeric macromolecule forms micelle in aqueous solutions (the so-called unimolecular micelle) due to its unique chemical structure and amphiphilic nature. This is in contrast to the classical multimolecular polymeric micelles that require the aggregation of multiple amphiphilic linear copolymers to achieve the micellar behavior above the critical micelle concentration. Boltorn® hyperbranched polyesters have recently received much attention in the design of unimolecular micelles, since they are biodegradable, biocompatible, have a globular structure and a large number of functional groups. Moreover, the ability to tailor their numerous end-groups offers considerable scope for

fine-tuning their drug loading capacity and targeted drug-delivery properties. Several amphiphilic, hyperbranched block copolymers have been prepared using commercially available Boltorn® hyperbranched polyesters as the macroinitiators [59,145–154].

Månson et al. [59] prepared, from the fourth pseudo-generation Boltorn® hyperbranched polyester, an amphiphilic multi-arm star-block copolymer composed of a hyperbranched core, a hydrophobic inner shell, and a hydrophilic outer shell by the ring opening polymerization (ROP) of ε-caprolactone, followed by the atom-transfer radical polymerization (ATRP) of *tert*-butyl acrylate, which was then hydrolyzed to obtain a poly(acrylic acid) block. The thus prepared, highly functional amphiphilic core–shell structures represent unimolecular micelles and show a large capacity for the encapsulation of small, hydrophobic and volatile molecules, such as fragrances.

Kreutzer et al. [145] synthesized water-soluble unimolecular containers by the sequential ATRP of *n*-butyl methacrylate and poly(ethylene glycol) methyl ether methacrylate (PEGMA) using Boltorn® hyperbranched polyester of the fourth pseudo-generation functionalized by 2-bromoisobutyric acid as a macroinitiator. Hydrophobic guest molecules, such as benzyl acetate, geraniol, decanal, and dorisyl, were encapsulated by the hyperbranched polymeric micelles. The encapsulation was studied by means of NMR spectroscopy [146]. Benzyl acetate and geraniol were dissolved in the closely packed hydrophobic core of the carrier. The hydrophilic PEGMA shell shielded and thus facilitated the transport of the hydrophobic guest molecules into the aqueous phase. Hence, these unimolecular micelles can be employed as stable carriers for hydrophobic active substances in aqueous formulations such as creams and lotions.

The amphiphilic hyperbranched polymers composed of the fourth pseudo-generation Boltorn® hyperbranched polyester and poly(ε-caprolactone) segments as the hydrophobic part, poly(ethylene glycol) as the hydrophilic outer shell and folate moieties as the targeting groups were synthesized by Cheng et al. [147]. Folic acid was incorporated to achieve a tumor-cell targeting property. Two antineoplastic drugs, 5-fluorouracil and paclitaxel, were incapsulated into the nanoparticles. The drug-loaded nanoparticles exhibited strong inhibition on the folate-receptor positive tumor cells because the cell internalization is significantly improved through the folate-mediated targeting.

For the purpose of tumor-targeted drug delivery, Gong et al. [148,149] prepared two kinds of folate-conjugated amphiphilic hyperbranched block copolymers based on Boltorn® hyperbranched polyester of the fourth pseudo-generation as a core. The hydrophobic inner shell is composed of poly(L-lactide) [148] or poly(L-aspartate) [149], whereas in both cases a hydrophilic poly(ethylene glycol) or folate-conjugated poly(ethylene glycol) represents the outer shell. The anti-tumor drug doxorubicin was non-covalently loaded into hydrophobic poly(L-lactide) [148] or covalently by a pH-sensitive hydrazone linkage to a poly(L-aspartate) [149] inner shell. Both polymeric micelles show promising results for use in targeted cancer therapy.

Huang et al. also prepared an amphiphilic hyperbranched multiarm copolymer as a nanocarrier that is composed of the fourth pseudo-generation Boltorn® hyperbranched polyester, hydrophobic poly(L-lactide) and hydrophilic polyphosphate [150]. The copolymer self-assembles into micelles in water with an average diameter of 130 nm, thus indicating a great potential for use in drug-delivery systems.

Shi et al. [151] investigated the suitability of the amphiphilic hyperbranched polyester for the controlled delivery of a poorly water-soluble daidzein drug that is used in the treatment of cardiovascular disease. The amphiphilic hyperbranched polymer was obtained by modification of the hydroxyl groups of the second pseudo-generation Boltorn® hyperbranched polyester with succinic anhydride and then glycidyl methacrylate. The obtained amphiphilic hyperbranched polyester self-assembles in an aqueous solution to form nanoparticles with a narrow size distribution. The hydrophobic daidzein drug was encapsulated during the particle formation, which significantly improves the drug concentration in an aqueous solution and thus enhances the drug's efficacy through oral administration. The daidzein is slowly released from the nanoparticles by a process of biodegradation over a few days. This study indicates that hyperbranched polyesters can successfully molecularly encapsulate and transport the hydrophobic drug diadezin into aqueous media, which improves the bioavailability and drug efficacy.

Liu et al. [152] prepared the multi-arm star-block copolymer with the hydrophobic Boltorn® hyperbranched polyester as the core and the densely grafted poly(*N*-isopropylacrylamide) brush as the shell. This copolymer exists as unimolecular micelles in an aqueous solution. The poly(*N*-isopropylacrylamide) brush exhibits a double thermal phase-transition behavior. A two-stage thermal collapse was also observed for unimolecular micelles with the hydrophobic fourth pseudo-generation Boltorn® hyperbranched polyester as the core, swollen poly(*N*-isopropylacrylamide) as the inner shell, and swollen poly(2-dimethylamino)ethyl methacrylate as the corona [153].

The fourth pseudo-generation Boltorn® hyperbranched polyester functionalized with poly(ethylene glycole) chains also exhibits unimolecular micellar properties. By encapsulation of the anti-cancer drug paclitaxel, the drug solubility was significantly enhanced [154].

The pH-responsive polymer vesicles were generated from the solution self-assembly of the carboxylated Boltorn® hyperbranched polyesters of different pseudo-generations [155]. The self-assembly process is convenient and involves the simple addition of polymers to water at a certain pH. These polymeric vesicles are attractive for applications in drug release, template self-assembly, and functionalization since they are simple to produce with controlled sizes, and they have a biodegradable polyester backbone and abundant surface carboxyl groups. A carboxyl-terminated Boltorn® hyperbranched polyester of the fourth pseudo-generation was also used as macromolecular ligands for the anti-cancer drug cisplatin, giving a controlled drug release over 7 days [156].

The potential of the partially alkyl-modified Boltorn H3200 hyperbranched polyester for the microencapsulation of the drug acetaminophen was studied by Smirnova et al. [157]. The amount of molecularly dissolved acetaminophen in the hyperbranched polymer matrix and its release kinetics strongly depend on the encapsulation method used, e.g., the gas anti-solvent precipitation, the particles formed from the gas saturated solutions, the coacervation method or the solvent method.

The conjugates of poly(bis-MPA) hyperbranched polyester and ibuprofen are able to deliver the drug rapidly inside the cells [158].

The protein adsorption on poly(bis-MPA) hyperbranched polymer films in the aqueous buffer environment was studied by Eichhorn et al. [159]. The higher adsorption potential of hyperbranched polyesters in comparison to linear polyesters was ascribed to the large number of endgroups allowing hydrogen-bond formation, and the lower swellability of the more compact aliphatic hyperbranched polyesters.

The non-toxic and biodegradable gene carriers were also synthesized from Boltorn® hyperbranched polyesters by the modification of hydroxyl functional groups with diethylaminopropylamine to introduce tertiary amines groups into the hyperbranched structure. These non-viral gene carriers provide degradability, very low toxicity, and the ability to transfect cells. The transfection efficiency can be influenced by the degree of amine substitution [160].

By modifying Boltorn® hyperbranched polyesters of the second and third pseudo-generations with carbohydrates a multivalent scaffold was created to mediate the biological processes where carbohydrates are involved [161].

A facile template-free method for the preparation of polypeptide-based vesicles (peptosomes) was reported by Zhou and Yan [162]. The method is very simple and involves the one-step, complex self-assembly of the carboxyl-terminated hyperbranched polyester and cationic poly-L-lysine. The size of the complex peptosomes is controlled by adjusting the polymer's concentration and does not change over a broad solution pH-range. The complex peptosomes possess long-term storage stability, and almost no toxicity. Thus, they have great potential to be used as carriers in drug-delivery systems.

Hyperbranched polymers based on bis-MPA were also coated on the inner surface of fused-silica capillaries by chemical bonding [163]. The advantages of such columns in capillary electrophoresis are the suppressed electroosmotic flow, the effectively prevented absorption of basic proteins to the fused-silica capillary surface in the pH range of 4–6, the high column efficiency, and good migration-time reproducibility. Therefore, this coating method could be a powerful tool for separating biological molecules in the field of biochemistry.

7. Summary

This review covers the structural and molar-mass characterization of hyperbranched polyesters based on bis-MPA, synthesized with or without the core molecule, their solution and bulk properties as well as the fields of their application. Results published so far indicate that the content and the type of the side products (hyperbranched structures without the core molecule, cyclic structures and ether-containing structures, partially reacted functional groups of the core) present as well as the molar-mass characteristics of poly(bis-MPA) greatly depend on the presence and the type of the core molecule used, the reaction conditions (reaction temperature, reaction time, type of catalyst), the monomer/core ratio, and the degree of conversion. The solution and bulk properties of poly(bis-MPA) reflect their highly branched structure and the content of a large number of functional groups, although some differences were observed with respect to the poly(bis-MPA) molar mass. In some cases dissimilar results were related to the different sample-preparation procedure prior to the measurements, which indicates the importance of the H-bond network in poly(bis-MPA). In terms of application, a large number of modifiable functional groups are, in addition to the specific properties of poly(bis-MPA) hyperbranched polymers, the basis for the broadening of their potential usage from large-scale industrial applications to high-tech application fields.

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