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# NMR and MALDI-TOF MS study of side reactions in hyperbranched polyesters based on 2,2-bis(hydroxymethyl)propanoic acid

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## Abstract

Hyperbranched polyesters of 2,2-bis(hydroxymethyl)propanoic acid (BMPA) with various molar ratios of tetra(hydroxymethyl)methane (PE) core molecule were characterized by NMR spectroscopy and MALDI-TOF mass spectrometry. In all polyesters, the formation of ether groups was observed. The extent of etherification increased with increasing PE content. This was assigned to a higher reactivity of PE towards etherification than BMPA. Intra- and intermolecular etherifications and intramolecular esterifications were detected by MALDI-TOF MS on the core molecule-containing polyesters, resulting in the formation of cycle-containing hyperbranched molecules. The ratio of cycle-containing molecules reached 50% at high reaction time for the polyester without core molecule, but was much lower for the polyesters containing a core molecule. As a consequence of these side reactions, the control of hyperbranched polyester molar mass by varying the core molecule (chain limiter) molar ratio is much more difficult than for linear polyesters.

*Keywords:* Hyperbranched polyesters; NMR; MALDI-TOF MS

## 1. Introduction

Hyperbranched polymers (HBPs) and dendrimers are a new class of highly branched macromolecules, extensively studied since the end of the 1980s. Dendrimers, first described by Tomalia [1], are characterized by a perfect globular shape and a monodisperse structure, but their syntheses are tedious and expensive. Hyperbranched polymers, in contrast, are obtained via a one-pot reaction, generally by polycondensation of $AB_x$-type monomers ($x \geq 2$). However, they exhibit high polydispersity and much less regular structure as compared to dendrimers. Historically, the concept of hyperbranched macromolecules was introduced by Flory [2] who predicted that the polymerization of $AB_x$ monomers would lead to a three dimensional structure without gelation, and derived a relationship between the number- and mass-average degrees of polymerization and conversion, assuming that all B-groups are equally reactive at any stage of the condensation and that no intramolecular reactions take place. The first kinetic studies of $AB_x$ polycondensations [3] were carried out under these simplifying assumptions. However, more recent papers [4,5] clearly showed that intramolecular reactions exert a strong influence on the molar mass of hyperbranched polymers. Due to the presence of a great number of unreacted B-groups in the hyperbranched architecture, intramolecular reactions are favored as compared to their linear homologs and give rise to the formation of cyclic branches. Dusek et al. [6] showed by a kinetic modelization of 2,2-bis(hydroxymethyl)propanoic acid (BMPA) polyesterification that the fraction of hyperbranched molecules containing a cyclic branch should increase with conversion and reach 100% at total conversion. Cyclization reactions may take place via direct A + B intramolecular reactions [7–9] and/or via intramolecular

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interchange reactions between unreacted B endgroups and reacted groups inside the macromolecule [10–12]. When a $B_f$ polyfunctional core molecule is copolymerized with $AB_x$ monomers, intramolecular reactions compete with the attachment to the core molecule [5,13], hindering the control of final polymer molar mass by the initial core/monomer ratio. Experimentally, cyclizations were observed by mass spectrometry in hyperbranched polyamides [11], polysiloxanes [14,15], polyetherketones [7], polyethersulfones [16], polyamidoamines [17], polyethers [8] and polyesters [6,10–13,18,19]. Several studies have shown the presence of cyclic structures in BMPA polyesters [5,6,20–22], e.g. in poly(BMPA) [6,22], in BMPA–1,1,1-tris(hydroxymethyl)propane (TMP) copolyesters [5] and in Boltorn® [20,21], a commercial BMPA polyester with an ethoxylated pentaerythritol core unit. These cyclizations were assigned to intramolecular esterifications [5,6] and/or intramolecular etherifications [20–22]. Intramolecular etherifications exert only a minor influence on polymer molar mass, but intermolecular etherifications lead to strong molar mass increase and even to polymer gelation, as observed in poly(BMPA) [22]. However, in this polyester, it is not possible to discriminate etherifications from esterifications by mass spectrometry, since both reactions lead to molecules with identical molecular mass. The same holds for BMPA–TMP polyesters, because BMPA and TMP units have exactly the same molecular mass. In order to get more information on esterification and etherification side reactions in such polyesters, we undertook a structural study of hyperbranched polyesters based on BMPA and tetra(hydroxymethyl)methane (pentaerythritol, PE) core molecule with various core/monomer ratios.

## 2. Experimental section

### 2.1. Materials

2,2-Bis(hydroxymethyl)propanoic acid (BMPA, >99%) was purchased from Acros, and recrystallized thrice in ethanol. *p*-Toluenesulfonic acid (PTSA, >99%), tetra(hydroxymethyl)methane (PE, >99%) and propane-1,3-diol (D, 98%) were purchased from Aldrich and used as received.

### 2.2. Synthesis of HBP

The hyperbranched polyester without core molecule ($P\infty$) was obtained by the bulk polycondensation of BMPA (7.00 g, 52.2 mmol) in the presence of PTSA as a catalyst (35 mg, 0.5 wt-%). The reaction was carried out in a 50 mL-reactor equipped with a mechanical stirrer, nitrogen inlet and outlet, a side arm, a condenser and a regulated heating device (oil bath). The medium was heated at 140 °C for 96 h under nitrogen atmosphere, while water resulting from esterification was distilled off. Samples were withdrawn from reaction medium at predetermined time intervals. The hyperbranched polyester of pseudo-generation 2 (P2) was obtained by mixing BMPA (7.00 g, 52.2 mmol) and PE (0.59 g, 4.35 mmol) in the presence of PTSA (38 mg, 0.5 wt-%) using the same experimental conditions as above. The polyesters from pseudo-generation 3–5 (P3–P5) were synthesized using the theoretical molar ratios presented in Table 1. All polymers were analyzed after reaction without further purification.

### 2.3. Reaction between 1,3-propanediol and polyester P5

One gram of hyperbranched polyester P5 (obtained after 24 h reaction time), 0.281 g (3.692 mmol) of propane-1,3-diol and PTSA (6.4 mg, 0.5 wt-%) were heated at 140 °C for 8 h in the equipment described above. The resulting product was analyzed without further purification.

### 2.4. NMR spectroscopy

The $^{13}C$ and $^{1}H$ NMR analyses were carried out on Bruker AC 200, AC300 and Avance 500 spectrometers. Chemical shifts were referenced to DMSO-$d_6$ at 39.43 ppm for the $^{13}C$ and at 2.5 ppm for the $^{1}H$ spectra. Quantitative $^{13}C$ NMR spectra were recorded using inverse gated decoupling mode with a 2 s pulse delay, with addition of chromium acetylacetonate (5 mg). Alkaline hydrolysis was carried out using NaOD/$D_2O$ (1 N) [22]. Sodium 3-(trimethylsilyl) propionate-2,2,3,3-$d_4$ was used as reference ($\delta(^1H) = 0$ ppm) for the $^{1}H$ NMR spectra recorded in $D_2O$.

### 2.5. Size exclusion chromatography (SEC)

The SEC equipment consisted of Rheodyne injector, a Waters 410 differential refractometer and a semi-preparative Ultrastyragel column set (19 mm × 300 mm, $500 + 10^3 + 10^4$ Å, particle size: 7 μm). THF was used as eluent (5 mL/min). Two hundred microlitres of polymer solution in THF (10 g/L) were injected and the chromatograms were recorded using a Waters Millenium software. In order to calibrate the equipment, fractions were collected every 15 s (1.25 mL) using a Waters fraction collector. The samples were evaporated, analyzed by MALDI-TOF MS to obtain their absolute molar mass and re-injected in the SEC chromatograph for calibration.

### 2.6. MALDI-TOF mass spectrometry

The MALDI-TOF MS analyses were performed on a PerSeptive Biosytems Voyager Elite time-of-flight mass spectrometer equipped with a nitrogen laser ($\lambda = 337$ nm). Spectra

Table 1
Molar ratios of tetra(hydroxymethyl)methane (PE) and 2,2-bis(hydroxymethyl)propanoic acid (BMPA) used in P2–$P\infty$ syntheses

| Polyester | Initial PE/BMPA molar ratio |
|---|---|
| P2 | 1/12 |
| P3 | 1/28 |
| P4 | 1/60 |
| P5 | 1/124 |
| $P\infty$ | 0 |

were recorded in reflector or linear delayed extraction mode at an acceleration voltage of 25 kV. Ten microlitres of methanol polymer solution (1 g/L) were mixed with 100 μL of the matrix solution (10 g/L alpha-cyano-4-hydroxycinnamic acid in methanol). One microlitre portion of the final solution was deposited onto the stainless steel sample slide and allowed to dry at room temperature. The spectra represent averages of 256 consecutive laser shots. For SEC calibration, the molar masses of fractionated samples were taken at the maximum of smoothed spectra.

## 3. Results and discussion

A series of hyperbranched polyesters of pseudo-generation 2 to 5 (P2–P5) were obtained by reacting 2,2-bis(hydroxymethyl)propanoic acid (BMPA) and tetra(hydroxymethyl)methane (pentaerythritol, PE). For comparison purposes, a polyester was also prepared without core molecule (P∞) (Table 1). All polyesterifications were carried out in the bulk under nitrogen at 140 °C, in the presence of *p*-toluene sulfonic acid (PTSA) as catalyst (Scheme 1). These polyesters were analyzed by $^{13}$C NMR and MALDI-TOF mass spectrometry in order to study cyclization and etherification side reactions.

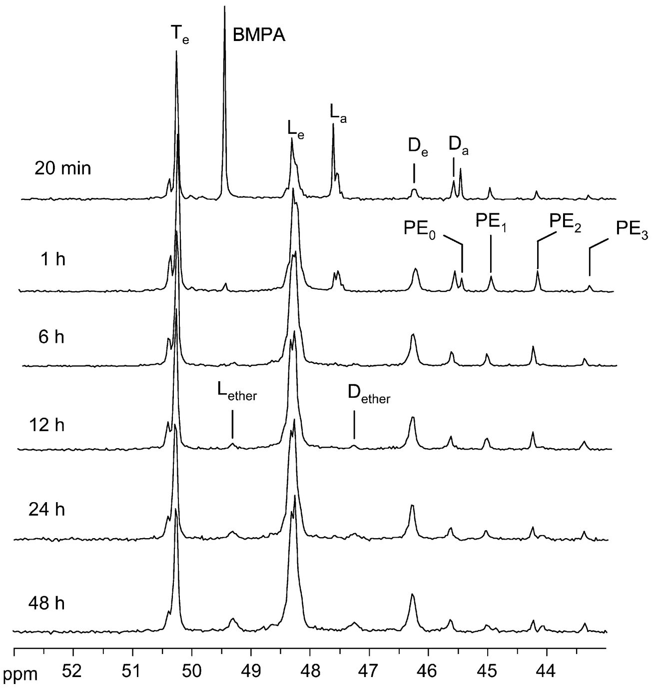
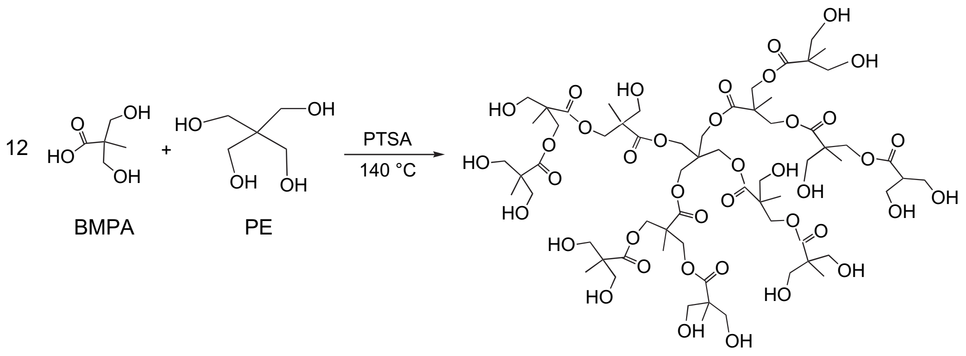


Fig. 1. Synthesis of P2: 43–53 ppm expansions of the $^{13}$C NMR spectra (50 MHz, DMSO-$d_6$) of samples withdrawn at various reaction times.

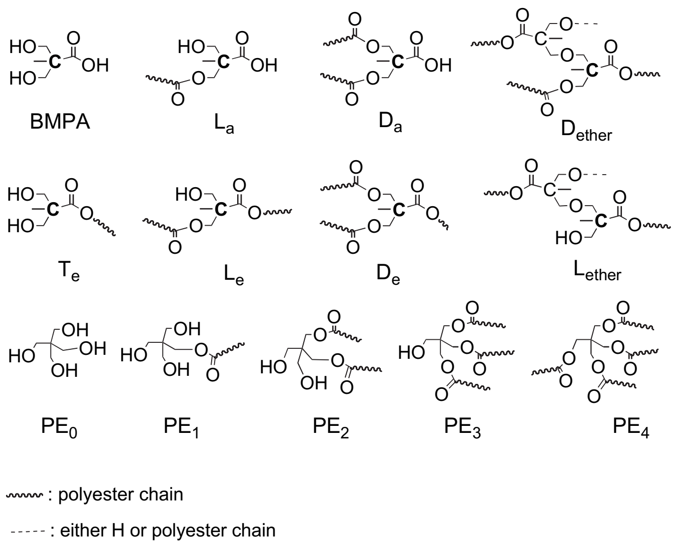
### 3.1. NMR study: etherification side reactions

Fig. 1 presents the evolution of the $^{13}$C NMR quaternary carbon signals of the various structural units formed during the synthesis of hyperbranched polyester P2 (reaction time: 20 min–48 h). The signal of the quaternary carbon of BMPA monomer at 49.6 ppm disappears after 1 h 30 min reaction. During this time, new structural units appear (Scheme 2), corresponding to terminal (T$_e$, 50.2 ppm), linear (L$_e$, 48.2 ppm) and dendritic (D$_e$, 46.2 ppm) esterified monomer units [23,24]. The resonance corresponding to linear monomer units with one –COOH group (L$_a$, 47.6 ppm) disappears with time. However, the signal of dendritic units containing a COOH group (D$_a$, 45.6 ppm) is still present after 48 h reaction, reflecting the presence of hyperbranched structures without core molecule in final polyester. This can be explained by the poor accessibility of this COOH in the bulky hyperbranched structure [20]. The signals between 43 and 45.5 ppm correspond to the quaternary carbons of unreacted pentaerythritol (PE$_0$, 45.5 ppm) and to pentaerythritol units with one (PE$_1$, 45.0 ppm), two (PE$_2$, 44.2 ppm), three (PE$_3$, 43.4 ppm) reacted OH groups. The chemical shift of the quaternary carbon of PE with four esterified OH group was estimated to be close to 42 ppm, from the spectrum of the reaction product of PE with excess trimethylacetyl chloride. This fourth esterification was not detected in the hyperbranched PE–BMPA polyesters, probably due to steric hindrance.

After 12 h reaction, new signals are observed at 49.3 and 47.3 ppm. Their intensity increases with time. These signals are characteristic of the quaternary carbons of structural units containing ether bonds [22]. Moreover, signals corresponding to –CH$_2$–O–CH$_2$– methylene carbons are observed at 73 ppm. When an ether bond is formed by the reaction of an –OH group belonging to a terminal unit, an ether-containing linear structural unit L$_{ether}$ is formed (49.3 ppm).



Scheme 1. Synthesis of a BMPA–PE hyperbranched polyester of pseudo-generation 2 (schematic representation).



Scheme 2. Structural units present in BMPA–PE hyperbranched polyesters. Esterification reaction leads to $L_a$, $L_e$, $D_e$, $D_a$ and $T_e$ structural units. $L_{ether}$ and $D_{ether}$ correspond to units formed by etherification reactions, and $PE_0$ to $PE_4$, to structural units of esterified PE core molecule.

The free −OH group of a linear $L_e$ unit can react with another −OH group, leading to the formation of ether-containing dendritic unit $D_{ether}$ (47.3 ppm). Due to the low amount of etherified hydroxyls, bis-etherified units expected close to 48 ppm [22] would be present in a much lower amount and cannot be detected in the spectrum. The same holds for etherified PE units, which are also likely to be present. These etherification reactions can be intramolecular, leading to the formation of cyclic branches inside the hyperbranched structure, or intermolecular, leading to the formation of hyperbranched macromolecules of higher molar mass, and in some conditions, to gelation. Samples withdrawn from P2 reaction medium after 3 h and 24 h reaction were hydrolyzed under alkaline conditions according to Ref. [22] and analyzed by $^1$H NMR (Fig. 2). The presence of ether groups in the sample withdrawn at 24 h is reflected by the presence of small peaks in the 3.4–3.6 ppm range ($H^c$). These resonances correspond to the $-CH_2-O-CH_2-$ methylene of the various etherified units ($L_{ether}$, $D_{ether}$) present in the hyperbranched polyester. On the other hand, when the reaction was carried out without core molecule, no ether bond was detected in 24 h reaction (Fig. 3), but the corresponding resonances appear on the samples withdrawn at 48 and 96 h.

The molar fraction of etherified methylenes, $F_{ether}$

$$F_{ether} = \frac{[-CH_2O-]_{ether}}{[-CH_2OH] + [-CH_2OOC-] + [-CH_2O-]_{ether}} \tag{1}$$

was calculated from the $^{13}$C NMR spectra according to Eqs. (2)–(4):

$$[-CH_2OH] = 2I(\text{BMPA}) + 2I(T_e) + I(L_a) + I(L_e) + I(L_{ether}) + \sum_{n=0}^{4}(4-n)I(PE_n) \tag{2}$$

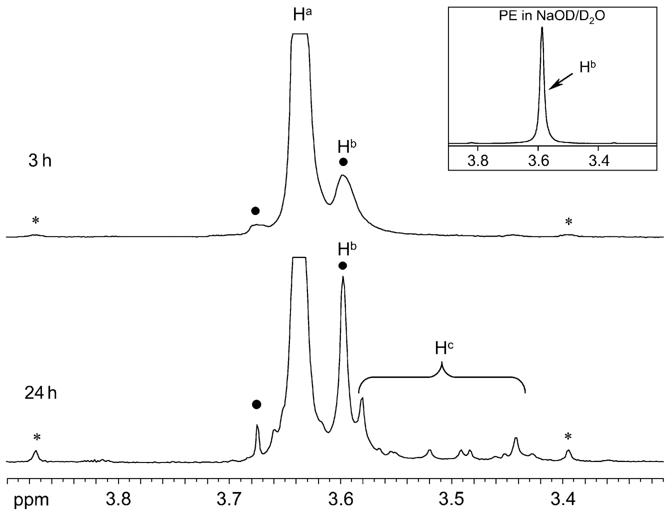


Fig. 2. NaOD/D$_2$O hydrolysis of samples withdrawn from P2 reaction medium after 3 h and 24 h reaction: $^1$H NMR spectra of the hydrolysis solutions (500 MHz, NaOD/D$_2$O). $H^a$ and $H^b$ correspond to the $-CH_2-OH$ methylenes of BMPA and PE, respectively, and $H^c$ to newly formed $-CH_2-O-CH_2-$ ether methylenes. The spectrum of PE in NaOD/D$_2$O is given in the upper insert. ●: Spinning side band; *: $^{13}$C satellite peaks.

$$[-CH_2OOC-] = I(L_a) + I(L_e) + 2I(D_a) + 2I(D_e) + I(D_{ether}) + \sum_{n=0}^{4} nI(PE_n) \tag{3}$$

$$[-CH_2O-]_{ether} = I\left(L_{ether}\right) + I\left(D_{ether}\right) \tag{4}$$

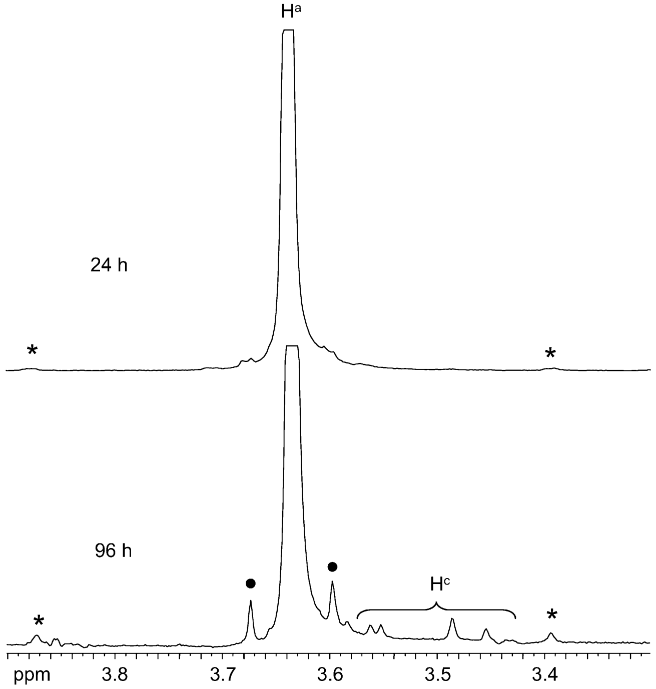


Fig. 3. NaOD/D$_2$O hydrolysis of samples withdrawn from P∞ reaction medium after 24 h and 96 h reaction: $^1$H NMR spectra of hydrolysis solutions (500 MHz, NaOD/D$_2$O); ●: spinning side band; *: $^{13}$C satellite peaks.

where $I(X)$ is the integral of the quaternary carbon resonance of unit X (see Scheme 2). Bis-etherified units, etherified focal units and etherified PE units cannot be detected in the spectra and are neglected in the calculations. Fig. 4 indicates that the rate of ether group formation increases from P∞ to P4, P3 and P2, i.e. when PE core unit concentration increases. This agrees with the results of Zagar et al. [20] on the ether content in commercial poly(BMPA) with ethoxylated pentaerythritol core (Boltorn® H20, H30 and H40). This might be due to a higher reactivity of PE with respect to BMPA towards etherification.

Gelation was observed for P2 and P3 between 60 and 72 h reaction, for P4 between 72 and 84 h reaction and for P∞ (polymer synthesized without core molecule) between 96 and 108 h reaction. This can be correlated to the decrease of the extent of intermolecular etherifications from P∞ to P2. The effect of the presence of a core molecule (decrease of gelation time) does not agree with the results of previous works on poly(BMPA) with and without various polyol core molecules [3,24].

### 3.2. MALDI-TOF mass spectrometry study

MALDI-TOF mass spectrometry is an important tool to reveal the existence of reactions like cyclizations, which cannot be observed by NMR spectroscopy. The presence of cyclic species in hyperbranched polyesters of BMPA has already been observed by ESI MS [6,20,21] and MALDI-TOF MS [5]. However, these studies were carried out either on commercial polymers (Boltorn®), leading to complex spectra [20,21], and on poly(BMPA) [5] and on poly(BMPA) with a trimethylolpropane core [6] in which esterification and etherification reactions cannot be discriminated from each other by mass spectrometry.

#### 3.2.1. Side reactions in poly(BMPA) without core molecule (P∞)

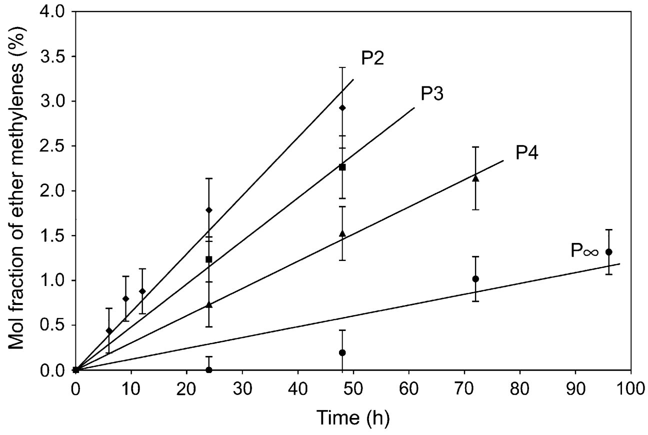


Fig. 4. Variation of ether methylene content (mol-%) with reaction time for P2–P4 and P∞.

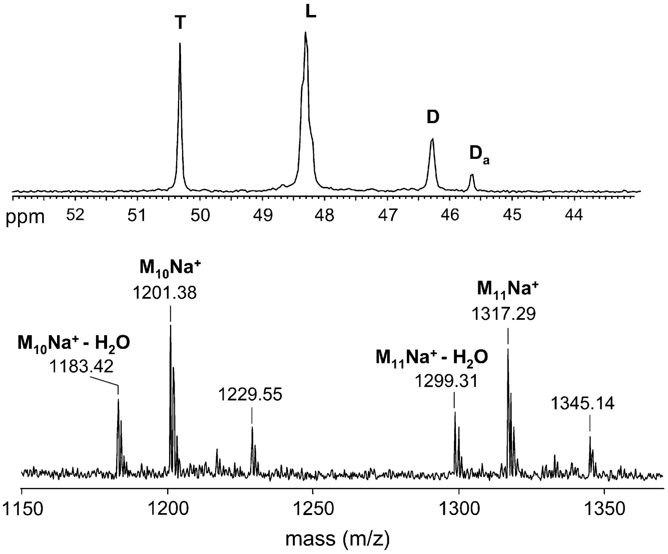


Fig. 5. $^{13}$C NMR (50 MHz, DMSO-$d_6$) (upper part) and MALDI-TOF MS (lower part) spectra of P∞ after 24 h reaction.

The MALDI-TOF mass spectrum of P∞ after 24 h reaction exhibits three series of peaks (Fig. 5). The main series ($M_xNa^+$) is relative to Na-cationized molecular ions of acyclic hyperbranched macromolecules with a focal carboxy group. These macromolecules result from either intermolecular esterifications (regular chain growth) or intermolecular etherification side reactions (Scheme 3). Their molecular mass $M_1(x)$ corresponds to the following equation:

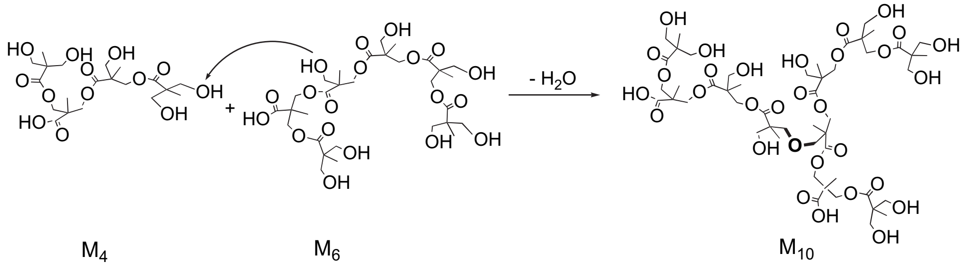
$$M_1(x) = x(M_{\mathrm{BMPA}} - M_{\mathrm{water}}) + M_{\mathrm{water}} + M_{\mathrm{Na}} \qquad (5)$$

where $x$ is the number of BMPA units in the chain and $M_{\mathrm{BMPA}}$, $M_{\mathrm{water}}$ and $M_{\mathrm{Na}}$ are the molecular mass of BMPA, water and sodium, respectively.

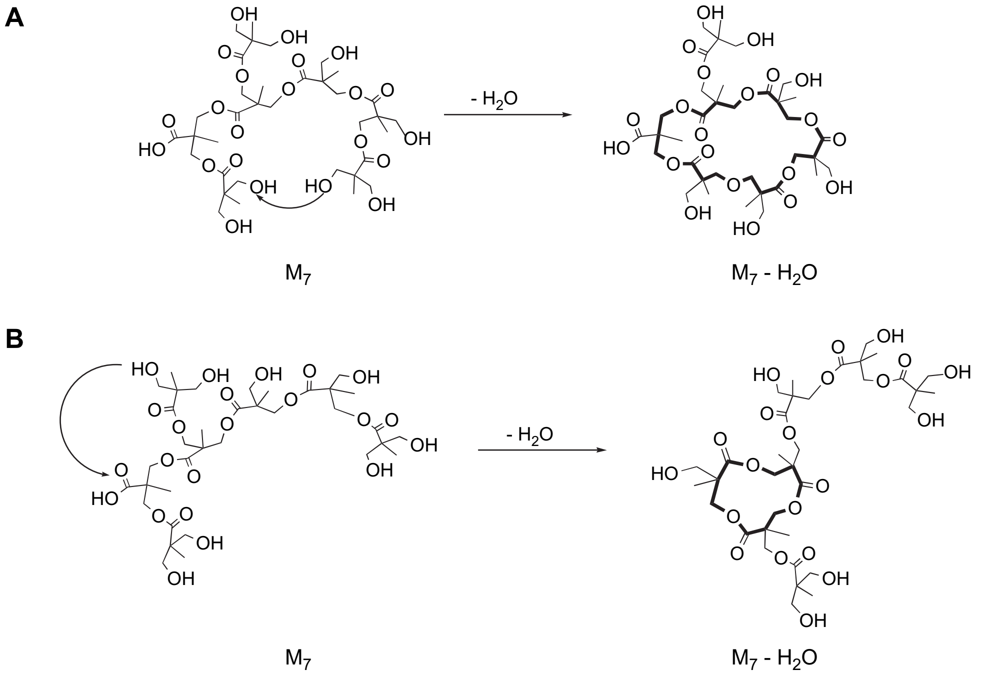
Two other series of peaks are detected at $m/z$ −18 and +28 of the main peaks. The series at $m/z$ +28 has not yet been assigned. The series at $m/z$ −18 reflects the presence of dehydrated macromolecules ($M_xNa^+ - H_2O$). The elimination of a water molecule can be due to intramolecular etherifications or esterifications (Scheme 4), which both lead to hyperbranched macromolecules containing a cyclic branch with the same molecular mass, $M_1'(x)$:

$$M_1'(x) = x(M_{\mathrm{BMPA}} - M_{\mathrm{water}}) + M_{\mathrm{Na}} \qquad (6)$$

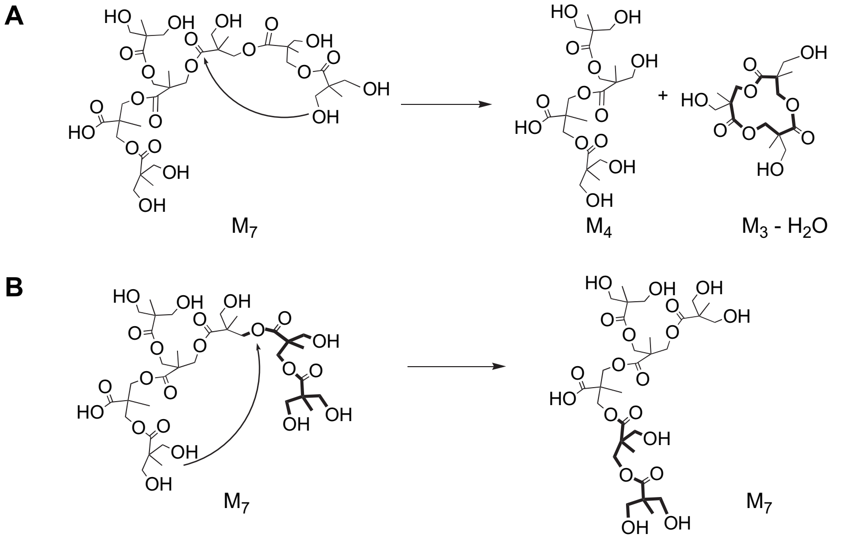
Moreover, hydroxy/ester, carboxy/ester or ester/ester intramolecular interchange reactions between groups of the same branch may also result in the formation of molecules containing a cyclic branch (Scheme 5A). It should be underlined that molecular mass is unchanged when interchange reactions take place between groups of different branches of the same macromolecule (Scheme 5B). No signal assigned to ether structures were observed in the NMR spectrum of P∞ after 24 h reaction (Fig. 5). Etherified units were detected by NMR after 48 h reaction only. Consequently, the cyclic species observed at 24 h reaction in the MALDI-TOF spectrum are mainly due to intramolecular esterification or/and intramolecular ester interchange reactions.



Scheme 3. Intermolecular etherification in P∞.



Scheme 4. Intramolecular etherification (A) and direct esterification (B) in P∞.



Scheme 5. Intramolecular hydroxy–ester interchange in P∞: (A) between groups of the same branch and (B) between groups of different branches.

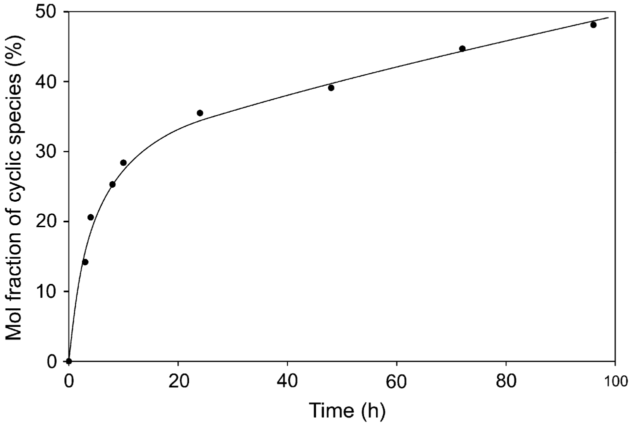


Fig. 6. Variation of the molar fraction (%) of molecules containing a cyclic branch during the synthesis of P∞ (MALDI-TOF MS determination, see text for details).

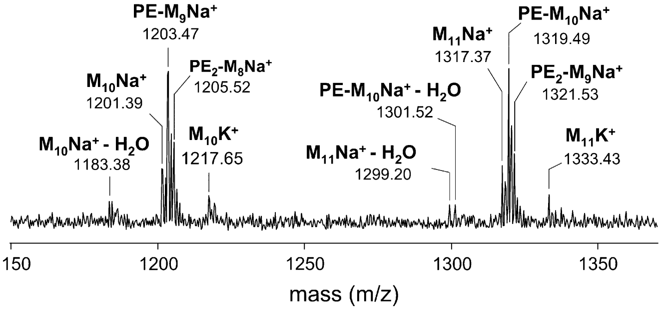


Fig. 7. MALDI-TOF MS spectrum of P2 after 24 h reaction.

MALDI-TOF MS cannot be regarded as a quantitative method since cyclic species and low molar mass species desorb and ionize more easily than linear and high molar mass ones, respectively. However, in the present case, hyperbranched molecules with or without a cyclic branch present a very close structure. Under the reasonable assumption that MALDI-TOF MS response is quantitative for such molecules in a narrow molecular mass range, it is possible to calculate the molar fraction of molecules containing a cyclic branch ($M_x - H_2O$) in polymer P∞ from the average value of:

$$F_{x\text{-cyclic}} = I_{x\text{-cyclic}} / \left(I_{x\text{-cyclic}} + I_{x\text{-acyclic}}\right) \tag{7}$$

where $I_{x\text{-cyclic}}$ and $I_{x\text{-acyclic}}$ are the integrals of the MALDI-TOF MS peaks corresponding to a cyclized and a non-cyclized $x$-mer, respectively. The molar fraction of cyclic species was taken as the average value of $F_{x\text{-cyclic}}$ for $x = 5$ to $x = 17$. Fig. 6 shows that this fraction increases with time, reaching ca 50% at 96 h reaction.

### 3.2.2. Side reactions in poly(BMPA) with core molecule

Fig. 7 presents the MALDI-TOF MS spectrum of P2 at 24 h reaction. Two main series of peaks are observed: the smaller one corresponds to molecules without PE core ($M_xNa^+$), and the bigger one to molecules containing a PE core (PE-$M_xNa^+$). The molecular mass $M_2(x)$ of the latter is given by:

$$M_2(x) = M_{PE} + x(M_{BMPA} - M_{water}) + M_{Na} \tag{8}$$

where $M_{PE}$ is the molecular mass of pentaerythritol.

For example, macromolecules containing PE (PE-$M_{10}Na^+$) are detected at $m/z$ 1319 and are clearly distinguished from those without the core molecule ($M_{11}Na^+$) at $m/z$ 1317. Weak signals at $m/z$ −18 of both series are observed at $m/z$ 1301 and 1299 and correspond to macromolecules containing a cyclic branch. Since ether groups were detected by NMR in this sample (Fig. 4), the peak at $m/z$ 1299 could be assigned (i) to intramolecular etherification or esterification on $M_{11}$ macromolecules or (ii) to intramolecular ester interchanges on PE-$M_x$-type molecules (Scheme 6). On the other hand, the peak at $m/z$ 1301 (PE-$M_{10}Na^+ - H_2O$) results exclusively from intramolecular etherification on PE-$M_{10}$ macromolecules of molecular mass $M_2'(x)$, with $x = 10$:

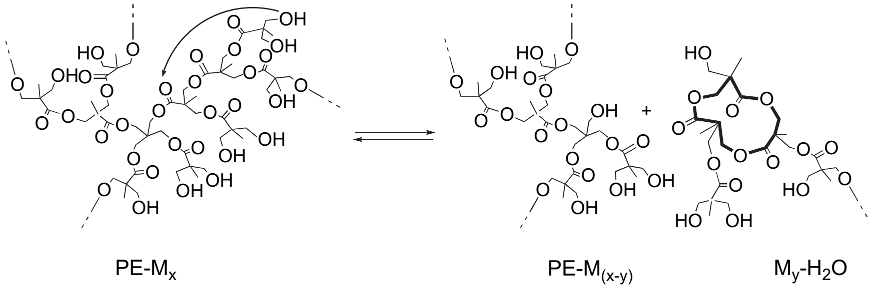
$$M_2'(x) = M_{PE} + x(M_{BMPA} - M_{water}) - M_{water} + M_{Na} \tag{9}$$

The existence of intermolecular etherification is reflected by the signal PE$_2$-$M_9Na^+$ at $m/z$ 1321, resulting from reaction between two PE-containing molecules (Scheme 7). The corresponding molecular mass is given by Eq. (10), with $x = 9$:

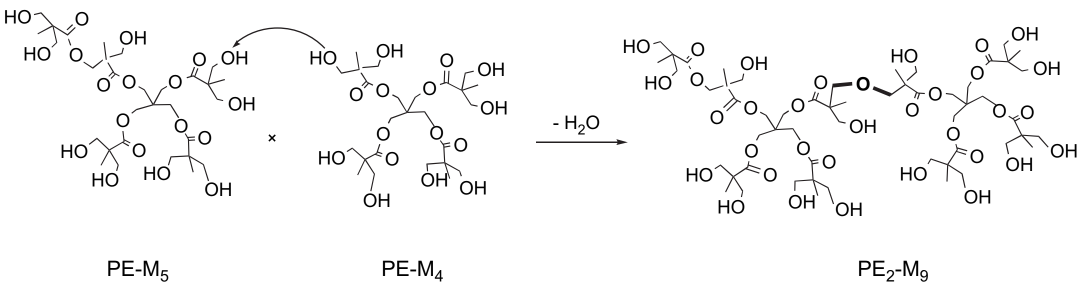
$$M_2''(x) = 2M_{PE} + x(M_{BMPA} - M_{water}) - M_{water} + M_{Na} \tag{10}$$

Intramolecular etherification, intermolecular etherification and intramolecular esterification side reactions were identified in the mass spectra of P2–P5. As discussed above, this cannot be done in the polyester without core molecule (P∞). However, all the reactions detected in P2–P5 could obviously take place in P∞ as well.

As discussed above, the content of cycle-containing molecules in P2 can be estimated from their MALDI-TOF mass



Scheme 6. Intramolecular hydroxy–ester interchange between groups of the same branch in BMPA–PE polyesters.



Scheme 7. Intermolecular etherification between two molecules containing a core unit.

spectra, by comparing peaks in a narrow molecular mass range. It is clear from Figs. 5 and 7 that the content of cycles is lower in P2 than in P∞, therefore the presence of the core molecule appears to hinder cyclizations. A similar trend was reported for 3,5-bis(hydroxyethoxy)isophthalic acid polyesters [13].

### 3.2.3. Reaction between propane-1,3-diol and hyperbranched polyester P5

In order to check whether hydroxy–ester interchange reactions could take place under the conditions used, a hyperbranched polymer of pseudo-generation 5, P5 with a PE core was reacted with propane-1,3-diol (D), in the presence of PTSA at 140 °C for 8 h. The *m/z* 1120–1210 region of the MALDI-TOF spectrum of P5 after reaction with D is given in Fig. 8. The final copolymer consists of molecules with a carboxy focal group ($M_{10}Na^+$, *m/z* 1201), of molecules with a PE core (PE-$M_9Na^+$, *m/z* 1203) and of molecules arising from intramolecular reactions ($M_{10}Na^+ - H_2O$, *m/z* 1183), already present in P5 spectrum. Besides, new peaks appear, which reflect the insertion of propane-1,3-diol in polymer chains. The signal at *m/z* 1143 is assigned to macromolecules with propane-1,3-diol core (D-$M_9$) and formed by etherification, esterification or hydroxy–ester interchange reactions involving D molecules. Cyclic species formed from D-$M_9$ are detected at *m/z* 1125 (D-$M_9Na^+ - H_2O$) and can only result from intramolecular etherifications. The presence of molecules with two core units (PE-D-$M_8Na^+$, *m/z* 1145) means that intermolecular etherifications also took place. The existence of direct esterification (COOH + OH) and/or of hydroxy–ester interchange reactions is evidenced by the resonances of esterified propanediol methylenes at 66–68 ppm in the $^{13}$C NMR spectrum of final compound (Fig. 9). Some more information about these reactions can be obtained from molar mass determinations: intramolecular etherifications and intramolecular direct esterifications leave P5 molar mass almost unchanged. On the other hand, intermolecular etherifications and intermolecular direct esterifications lead to polyesters of higher molar mass, while intramolecular ester interchange and P5–D hydroxy–ester interchanges should result in a decrease of final product molar mass. Table 2 shows that the average molar masses of P5 remain almost unchanged before and after reaction with D, while it should have increased as a consequence of the intermolecular reactions that take place in the reaction medium. This is an indirect evidence of the existence of intramolecular ester interchanges in BMPA polyesters.

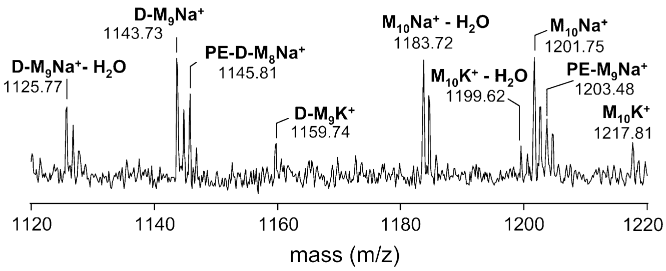


Fig. 8. MALDI-TOF MS spectra of P5 after 8 h reaction with propane-1,3-diol (D) (140 °C, 0.5% PTSA).

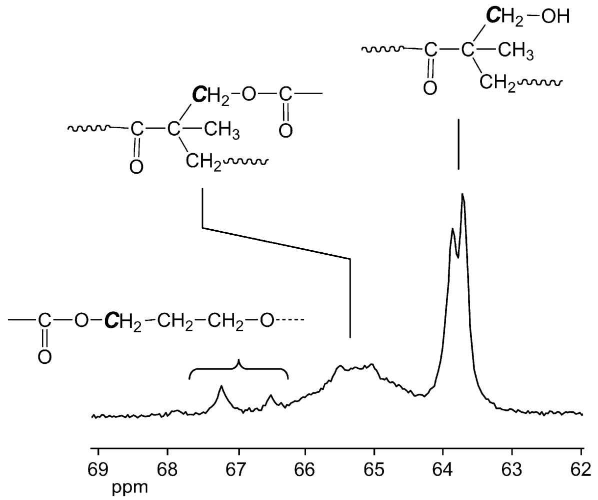


Fig. 9. $^{13}$C NMR spectrum of P5–propane-1,3-diol reaction product (140 °C, 8 h, 0.5% PTSA).

Table 2
Reaction of P5 with propane-1,3-diol (78:22 weight ratio, 140 °C, 8 h, 0.5 wt-% PTSA catalyst)

| Sample | $\overline{M}_n$ | $\overline{M}_w$ | $D_M$ | $M_{peak}$ |
|---|---|---|---|---|
| P5 | 2800 | 7260 | 2.6 | 6890 |
| P5 after reaction with D | 2500 | 8700 | 3.5 | 6800 |

SEC determination of molar masses before and after reaction (THF, SEC-MALDI-TOF MS calibration [25,26]). Number- and mass-average molar masses ($\overline{M}_n$ and $\overline{M}_w$), molar mass at the maximum of SEC peak ($M_{peak}$) and dispersity ($D_M = \overline{M}_w/\overline{M}_n$).

## 4. Conclusion

The synthesis of hyperbranched polyesters based on 2,2-bis(hydroxymethyl)propanoic acid (BMPA) with or without tetra(hydroxymethyl)methane (PE) core molecule is accompanied by many side reactions. Both inter- and intramolecular etherifications and hydroxy–ester interchange reactions were shown by NMR, MALDI-TOF MS and SEC studies in core molecule-containing polyesters. Intermolecular etherifications lead to molar mass increase and can even result in polymer gelation upon prolonged heating. Increasing PE core molecule concentration leads to higher ether content, which could tentatively be explained by a higher reactivity of PE towards etherification. On the other hand, the amount of molecules containing a cyclic branch was much lower for P2–P4, i.e. for polyesters synthesized in the presence of the largest amounts of PE core molecule. It must also be underlined that cyclizations via intramolecular hydroxy–ester interchange reactions could exert a strong influence on hyperbranched polyester molar mass, since one interchange results in the formation of two species of lower molar mass. As a consequence of all these side reactions, the control of hyperbranched polyester molar mass by the introduction of a core molecule acting as a chain limiter cannot be achieved as easily as in linear polyesters.

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