# Polydispersity of Hyperbranched Polyesters Based on 2,2-Bis(hydroxymethyl)propanoic Acid: SEC/MALDI−TOF MS and $^{13}$C NMR/Kinetic-Recursive Probability Analysis

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*Received July 22, 2008; Revised Manuscript Received September 19, 2008*

ABSTRACT: The absolute average molar masses and polydispersity index of a series of polyesters based on 2,2-bis(hydroxymethyl)propanoic acid (BMPA, $AB_2$-type monomer), 2,2-bis(hydroxymethyl)-1,3-propanediol (PE, $B_4$-type monomer), and 1,1,1-tris(hydroxymethyl)propane (TMP, $B_3$-type monomer) were determined by SEC/MALDI−TOF off-line coupling. The $\bar{M}_w/\bar{M}_n$ values, in the 1.8−3.1 range, were surprisingly very close to those found by SEC using the conventional linear polystyrene calibration method, but dramatically lower than those calculated from conversion and composition of initial monomer mixture assuming equal reactivity of functional groups. The mol ratios of the various monomer units in final polyesters were determined by $^{13}$C NMR. The kinetic-recursive probability approach assuming first-shell substitution effects was then applied to calculate the branching factors and the average molar masses of these polyesters from their final composition. The AB- and B-branching factors were significantly lower than expected for random polymerizations, reflecting the existence of both negative A−B and B−B substitution effects, i.e. lower reaction rate of a given A or B group after reaction of the other groups present on the same monomer unit. The calculated values of $\bar{M}_w$ and $\bar{M}_w/\bar{M}_n$ were reasonably close to the experimental ones for all hyperbranched polyesters. Intramolecular esterifications and intermolecular etherifications side reactions were taken into account in the calculations with some simplifying assumptions and found to marginally broaden MW distributions.

## Introduction

The main structural feature of dendrimers is their perfectly defined topology, which can generally be described as several branches (dendrons) consisting only of dendritic (branch points) and terminal units, linked to a central core unit. The resulting molecular architecture is globular, highly symmetrical, with a considerable number of end-groups on the outer shell. This particular architecture leads to materials with unusual solubility, viscosity, reactivity or complexing properties.[1] Hyperbranched polymers, in contrast, are "imperfect" polymers, generally obtained via a simple one-pot one-step polycondensation of $AB_x$ monomers ($x \geq 2$). They present an irregular architecture, with many unreacted B-groups along the chains. In order to obtain properties resembling those of dendrimers, high content of dendritic units (high degree of branching) and narrow molar mass distributions are obviously desirable.

The molar mass distributions of polymers are generally measured by size exclusion chromatography (SEC) calibrated with linear polymer standards of similar chemical structure. When applied to hyperbranched polymers, this method leads to strongly over- or underestimated molar masses, due to the quite different hydrodynamic behavior of linear and hyperbranched polymers. For instance, Lederer et al.[2] recently investigated the SEC of polyetheramide dendrimers in different column systems and solvents. They compared the resulting dendrimer calibration curves with conventional linear polystyrene (PS) and polyvinylpyridine (PVP) calibrations. The results depended on the nature of solvent, DMAc or DMAc + water, where linear polymers could adopt more or less compact conformations. In all cases linear polymer calibration overestimated polyetheramide dendrimer molar masses. The same phenomenon was observed on fractionated hyperbranched polyurea-urethanes.[3] Lim et al.[4] evaluated the molar masses of hyperbranched polyaminoesters by SEC in THF using linear PS and polyamidoamine (PAMAM) dendrimer standards. In their case, the molar masses determined via linear PS calibration were ca. 2.5 times lower than those found with PAMAM dendrimer calibration.

Triple detection SEC, with in-line concentration detector, viscosity detector and MALLS (multi angle laser light scattering) molar mass-sensitive detector does not require polymer standard calibration and, therefore, seems interesting for studying hyperbranched polymer solution behavior and molar mass distributions. Fractionated hyperbranched polyesters,[5] branched PMMA[6] and hyperbranched polystyrene[7] were investigated by this technique. It should, however, be underlined that reliable results can be obtained only for samples without significant amount of low molar mass species due to the low sensitivity of MALLS detectors in this region.

MALDI−TOF (matrix-assisted laser desorption/ionization time-of-flight) mass spectrometry gives absolute determinations of molar mass, independent of polymer structure. MALDI−TOF MS was used for measuring the molar masses of dendrimers[8,9] and hyperbranched polymers.[10,11] However, since low molecular mass species are more easily desorbed than high molecular mass ones, MALDI−TOF MS cannot be applied to the determination of the average molar masses of polymers with $D_M = \bar{M}_w/\bar{M}_n > 1.1$.[12,13] In such cases, the dispersed polymers should be fractionated into several fractions of narrow molar mass distribution ($D_M < 1.05$), which are then analyzed by MALDI−TOF MS and used to calibrate the SEC curves against absolute molar masses (self-calibration). This method was applied to the characterization of linear polymers, such as poly(dimethylsiloxane), polyesters and copolyesters.[12,14,15]

In this study, we were interested in the SEC characterization of hyperbranched polyesters obtained by polycondensation of 2,2-bis(hydroxymethyl)propanoic acid (BMPA), $AB_2$-type monomer, and 1,1,1-tris(hydroxymethyl)propane (TMP) or bis(hydroxymethyl)-1,3-propanediol (pentaerythritol, PE) as $B_3$- and

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10.1021/ma801655x CCC: $40.75 
Published on Web 11/07/2008

$B_4$-type core molecules, respectively. Several SEC studies of poly-BMPA polyesters have already been reported. Malmström et al.[16] carried out a SEC study (THF, linear polystyrene calibration) on poly-BMPA/TMP polyesters of various pseudo-generations. They reported $\bar{M}_n$ lower than expected from theory and remarkably low dispersities ($D_M = \bar{M}_w/\bar{M}_n = 1.4-1.9$). As found in THF or DMF-LiBr on a series of fractionated commercial Boltorn BMPA polyesters using universal SEC calibration, the Mark−Houwink coefficients of these polyesters are low (0.26−0.27), as expected for highly branched polymers.[17] Similar results were found on silylated samples, showing the absence of interactions involving OH end-groups in these operating conditions.[17] On the other hand, asymmetric peaks were obtained in a SEC-MALLS-RI study of a series of Boltorn polyesters in DMAc-LiBr and THF/MeOH.[18−20] A thermal treatment of bulk samples at 140 °C for 20 min appeared necessary to allow solubilization without aggregation. This was assigned to the existence of a H-bond network in bulk samples at room temperature, which could be destroyed only after thermal treatment.[19] These hyperbranched polyesters exhibited lower $\bar{M}_n$ than expected from theoretical calculations based on core/monomer ratio and a relatively narrow molar mass distribution ($D_M = 2.0-2.7$).[18−20]

In all studies of hyperbranched condensation polymers, experimental dispersities could not be compared to theoretical ones, due to the lack of available relationships for calculating the $\bar{M}_w$ of $AB_f+B_g$ polymers from composition and conversion. In recent articles, we extended the "in-out" recursive probability approach of Macosko and Miller[21,22] to the step-growth polymerization of monomers bearing both A and B groups and established analytical expressions of $\bar{M}_w$ and dispersity for complex hyperbranched polymers.[23,24] The cases of equal reactivity of reactive groups[23] and of the existence of first shell substitution effects[24] were examined, leading to the introduction of three parameters, namely the "branching factors", which extend the concept of degree of branching (DB) to any type of monomer mixtures and can be used to calculate theoretical $\bar{M}_w$ and dispersity from NMR or kinetic data. This work is devoted:

(i) to the experimental determination of absolute molar masses of BMPA hyperbranched polyesters synthesized with or without PE or TMP core molecules, in stoichiometric ratios leading to polyesters of pseudogeneration 2 to 6 (in order to avoid the experimental errors that may be introduced for these relatively low molar mass polymers by the low sensitivity of light scattering and viscosimetric detectors in the low molar mass region, we used off-line SEC/MALDI−TOF MS determinations, and the results are compared to those obtained by conventional linear polystyrene calibration);

(ii) to the comparison of these absolute molar masses to theoretical ones calculated from the recursive probability relationships and structural information obtained by $^{13}C$ NMR analysis, both in the case of equal reactivity of functional groups and in the case of the existence of substitution effects.

## Experimental Section

**Materials.** 2,2-bis(hydroxymethyl)propanoic acid (BMPA, > 99%) was purchased from Acros, and recrystallized thrice in ethanol. *p*-Toluenesulfonic acid (PTSA, >99%), 2,2-bis(hydroxymethyl)-1,3-propanediol (PE, >99%), 1,1,1-tris(hydroxymethyl)propane (TMP, >98%) were purchased from Aldrich and used as received.

**2,2-Bis(hydroxymethyl)-1,3-propanediol (PE)−Trimethylacetyl Chloride Reaction Products.** A 8.85 g (73.4 mmol, 10-fold excess) or 3.54 g (stoichiometric amount, 29.4 mmol) sample of trimethylacetyl chloride was introduced dropwise into a solution of 1 g PE (7.34 mmol) in 25 mL of pyridine at 0 °C. The solutions were left at room temperature for 2 h then heated 1 h to 50 °C. The solutions were filtered and pyridine distilled under reduced pressure. The residues were analyzed without further purification in order to identify the $^{13}C$ NMR resonances of central quaternary carbons of esterified PE (C1−C4). $^{13}C$ NMR (75 MHz, DMSO-$d_6$, ref DMSO-$d_6$ = 39.43 ppm): 45.0 (C1), 43.9 (C2), 42.5 (C3), and 41.5 ppm (C4).

**Synthesis of HBPs.** Hyperbranched polyester without core molecule (P∞) was obtained by the bulk polycondensation of BMPA (7 g, 52.2 mmol) in the presence of PTSA as catalyst (35 mg, 0.5 wt-%) in a 50 mL-reactor equipped with a mechanical stirrer, nitrogen inlet and outlet, a sidearm and a condenser. The medium was heated to 140 °C for 24 h under nitrogen atmosphere, while esterification water was distilled off. Hyperbranched polyester P2-PE (pseudogeneration 2, PE/BMPA mol ratio = 1/12) was obtained by reacting BMPA (7 g, 52.2 mmol) and PE (0.59 g, 4.35 mmol) in the same conditions. Hyperbranched polyesters P3-PE to P6-PE (pseudogeneration 3 to 6, PE/BMPA mol ratio = 1/28, 1/60, 1/124 and 1/252, respectively) and P2-TMP to P6-TMP (pseudogeneration 2 to 6, TMP/BMPA mol ratio = 1/9, 1/21, 1/45, 1/93 and 1/189, respectively) were obtained using the same procedure. All polymers were analyzed after reaction without further purification. The actual core/monomer and various monomer unit mol ratios were determined from $^{13}C$ NMR spectra.

**Size Exclusion Chromatography (SEC).** The SEC chromatograms were obtained with a Viscotek 302 TDA equipment with a refractive index detector (RI), a differential viscosity detector (IV) and a light scattering detector (LS). It was equipped with three 5 $\mu$m PLgel columns (100 Å and two mixed-bed). The measurements were performed at 40 °C and THF was used as eluent (flow rate = 1 mL/min, injection volume of 53.6 $\mu$L of 10 mg/mL solution). SEC treatment was realized on Viscotek-TriSEC 2000 software. Polystyrene standards were used for the calibrations.

**SEC/MALDI−TOF MS Off-Line Coupling.** The SEC measurements were performed at room temperature on a Waters equipment containing a 410 refractive index detector, a 515 HPLC pump and three 7 $\mu$m Ultrastyragel columns ($10^4$, $10^3$, and 500 Å). THF was used as the mobile phase (flow rate of 5 mL/min and injection volumes of 200 $\mu$L of 10 mg/mL solutions). HBP fractionations were performed on a fraction collector, positioned at the outlet of the SEC columns. 60 fractions were collected for each analyzed polymer (time delay for one fraction = 15 s). After solvent evaporation under vacuum, the absolute molar masses of selected fractions were determined by MALDI−TOF mass spectrometry on a PerSeptive Biosystems Voyager Elite time-of-flight mass spectrometer equipped with a nitrogen laser at $\lambda$ = 337 nm. Spectra were recorded in reflector or linear delayed extraction mode at an acceleration voltage of 25 kV. Here, 10 $\mu$L of methanol polymer solutions (1 g/L) were mixed with 100 $\mu$L of the matrix solution (10 g/L α-cyano-4-hydroxycinnamic acid in methanol). Then a 1 $\mu$L portion of the final solution was deposited onto the stainless steel sample slide and allowed to dry at room temperature. The spectra represented averages of 256 consecutive laser shots. The fractions were afterward reinjected in the SEC apparatus as hyperbranched standards for absolute molar mass calibration.

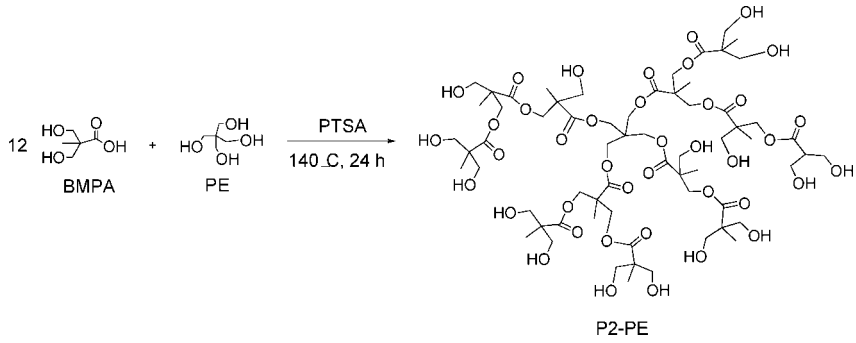
**NMR Spectroscopy.** The $^{13}C$ analyses were carried out on Bruker AC 300 or Avance 500 spectrometers. $^{13}C$ chemical shifts were referenced to DMSO-$d_6$ at 39.43 ppm. Quantitative $^{13}C$ NMR spectra were recorded using inverse gated decoupling mode with a 2 s pulse delay and the addition of chromium acetylacetonate (5 mg).

## Results and Discussion

A series of hyperbranched polyesters of pseudogeneration 2 to 6 (P2-TMP to P6-TMP and P2-PE to P6-PE) were obtained by reacting 2,2-bis(hydroxymethyl)propanoic acid (BMPA) and 1,1,1-tris(hydroxymethyl)propane (TMP) or 2,2-bis(hydroxymethyl)-1,3-propanediol (Pentaerythritol, PE). A polyester (P∞) was also prepared without core molecule. All polyesterifications were carried out in the bulk in the presence of *p*-toluenesulfonic acid (PTSA) as catalyst (Scheme 1).

The resulting polyesters were analyzed by SEC using THF as eluent, where all samples were soluble. As shown in Figure

**Scheme 1**




1, symmetrical SEC peaks were obtained and the aggregation phenomenon reported on similar commercial polymers[17,19] was not observed, presumably because freshly synthesized samples were used. Therefore, it was not necessary to apply any thermal treatment of the samples at 140 °C[19] before SEC analyses. Unfortunately, due to low sensitivity in the molar mass region of the hyperbranched polyesters, the data obtained by the light scattering detector were not exploitable for accurate molar mass determinations. Similarly, scattered viscosity data were obtained in the low molar mass region of polyester chromatograms, which could therefore not be included in calculations without committing some error, even when using extrapolation software. Nevertheless, all viscosity-molar mass curves exhibited a linear region where the Mark−Houwink coefficient $a$ could be calculated. The results reported in Table 1 show very low $a$ values (0.2 to 0.3), as expected for highly branched polymers and as reported for aliphatic[17] and aromatic polyesters.[25] As discussed above, the use of linear polystyrene standards for calibrating the SEC chromatograms of hyperbranched polymers may lead to erroneous results, and SEC/MALDI−TOF MS off-line coupling appears to be the best method to obtain reliable information on the molar masses and distributions of BMPA hyperbranched polymers.

**Characterization by SEC/MALDI- TOF MS Off-Line Coupling.** MALDI−TOF MS provides a way to determine the absolute molar mass of isomolecular polymers, but is not directly applicable to polydispersed samples such as hyperbranched polyesters. In order to establish calibration curves versus absolute molar mass for P2-TMP to P6-TMP and P2-PE to P6-PE, three of them (P4-TMP, P4-PE, P5-PE) were fractionated by SEC. Figure 2 presents the SEC chromatogram of P4-PE and the MALDI−TOF MS spectra of some nearly isomolecular polymer fractions ($D_M = \bar{M}_w/\bar{M}_n < 1.07$). A detailed discussion of the MALDI−TOF MS spectra of BMPA polymers was reported in a previous article.[26] The fraction molar masses were calculated from their MS spectra assuming that the mole ratio of each individual species is proportional to the MS detector response. This is a reasonable assumption for samples with narrow molar mass distribution. The data obtained on P4-PE are reported in Table 2 in order to illustrate the method. The fractions were then reinjected in the SEC equipment in order to determine their elution volume ($V_e$). Surprisingly, the molar mass at peak maximum ($M_{peak}$) of each fraction determined by MALDI−TOF MS is very close to the value determined by SEC using the linear polystyrene calibration method (Table 2). The logarithms of the absolute molar mass of all hyperbranched polyester fractions are aligned on a single $\log(M) = f(V_e)$ calibration line, indicating that the nature of the core molecule exerts a negligible influence on the hydrodynamic volume of

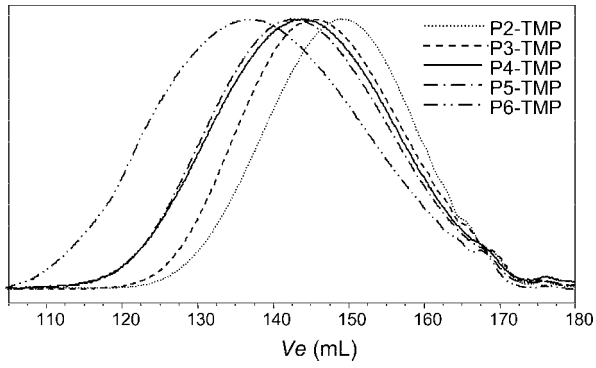



**Figure 1.** SEC chromatograms (THF) of BMPA/TMP hyperbranched polyesters P2-TMP to P6-TMP (pseudogenerations 2 to 6).

**Table 1. Mark−Houwink Coefficient $a$ of Hyperbranched Polyesters Determined by SEC (Viscosity Detector)**

| sample | $a$ |
|---|---|
| P2-TMP | 0.29 |
| P3-TMP | 0.24 |
| P4-TMP | 0.22 |
| P5-TMP | 0.22 |
| P6-TMP | 0.20 |
| P6-PE | 0.22 |

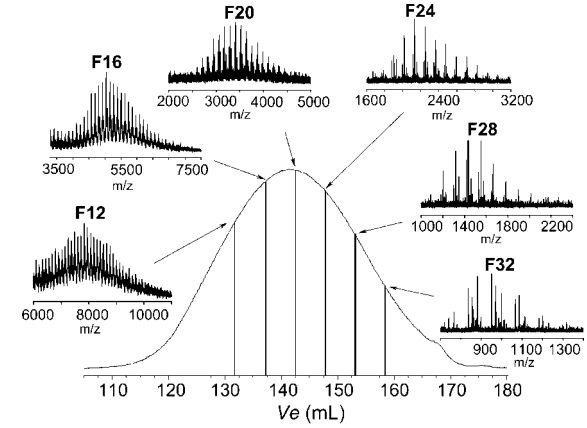



**Figure 2.** SEC chromatogram and MALDI−TOF MS spectra of some fractions of hyperbranched polyester P4-PE.

**Table 2. SEC Analysis of Hyperbranched polyester Sample P4-PE: Elution Volume ($V_e$), Molar-Mass Dispersity $D_M$ (Polydispersity Index), and $M_{peak}$ (Molar Mass at Peak Maximum) Obtained by Polystyrene Calibration and by MALDI−TOF MS**

| | | polystyrene calibration | | MALDI−TOF MS calibration | |
|---|---|---|---|---|---|
| fraction | $V_e$ (mL) | $M_{peak}$ | $D_M$ | $M_{peak}$ | $D_M$ |
| F16 | 136.8 | 5042 | 1.06 | 5345 | 1.02 |
| F20 | 141.7 | 3455 | 1.04 | 3496 | 1.02 |
| F24 | 146.8 | 2574 | 1.07 | 2312 | 1.02 |
| F28 | 151.9 | 1616 | 1.05 | 1530 | 1.02 |
| F32 | 156.8 | 1103 | 1.05 | 1005 | 1.02 |
| F36 | 161.9 | 743 | 1.04 | 704 | 1.04 |

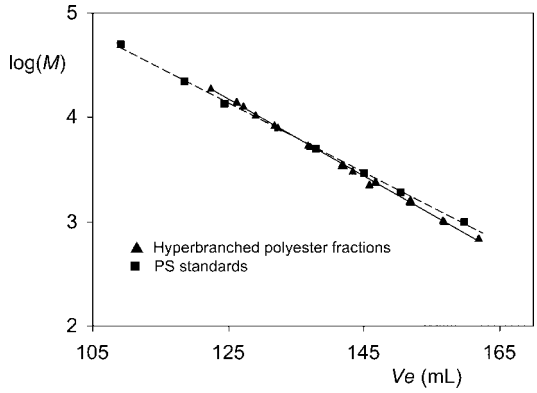



**Figure 3.** SEC calibration curves obtained with polystyrene standards (PS) and with P4-TMP, P4-PE, and P5-PE SEC/MALDI−TOF MS fractions.

**Table 3. Number- and Mass-Average Molar Masses ($\bar{M}_n$ and $\bar{M}_w$) and Molar-Mass Dispersity $D_M = \bar{M}_w/\bar{M}_n$ of BMPA Hyperbranched Polyesters with and without Core Molecule (TMP or PE) and SEC Determinations with Conventional Polystyrene Calibration and with MALDI−TOF MS Calibration**

| | | SEC polystyrene calibration | | | SEC/MALDI−TOF MS | | |
|---|---|---|---|---|---|---|---|
| sample | pseudogeneration number | $\bar{M}_n$ | $\bar{M}_w$ | $D_M$ | $\bar{M}_n$ | $\bar{M}_w$ | $D_M$ |
| P∞ | | 2330 | 6350 | 2.7 | 2170 | 6730 | 3.1 |
| P2-TMP | 2 | 1580 | 2680 | 1.7 | 1460 | 2660 | 1.8 |
| P3-TMP | 3 | 1810 | 3290 | 1.8 | 1670 | 3320 | 2.0 |
| P4-TMP | 4 | 2050 | 4290 | 2.1 | 1910 | 4420 | 2.3 |
| P5-TMP | 5 | 2120 | 4345 | 2.0 | 1960 | 4490 | 2.3 |
| P6-TMP | 6 | 2670 | 6160 | 2.3 | 2530 | 6520 | 2.6 |
| P2-PE | 2 | 1820 | 3530 | 1.9 | 1680 | 3570 | 2.1 |
| P3-PE | 3 | 1930 | 4000 | 2.1 | 1880 | 4160 | 2.2 |
| P4-PE | 4 | 2260 | 4940 | 2.2 | 2100 | 5140 | 2.4 |
| P5-PE | 5 | 3000 | 7410 | 2.5 | 2810 | 7900 | 2.8 |
| P6-PE | 6 | 2880 | 7390 | 2.6 | 2710 | 7800 | 2.9 |

BMPA hyperbranched polyesters (Figure 3). This MALDI−TOF MS calibration line is very close to the one obtained using linear polystyrene standards and, consequently, close average molar masses values are obtained by the two calibration methods for all BMPA polyester samples (Table 3). The molar masses of linear aliphatic polyesters are known to be overestimated by the conventional PS calibration method.[27,28] On the other hand, the hydrodynamic volumes of hyperbranched polymers are known to be smaller than those of linear polymers of similar molar mass, leading to molar mass underestimation. In hyperbranched aliphatic polyesters, these two effects appear to counterbalance each other, leading to correct average molar mass values. Table 3 shows that the conventional PS calibration method overestimates $\bar{M}_n$ and underestimates $\bar{M}_w$ by 5 to 8% with respect to the absolute molar mass calibration, resulting in slightly overestimated molar-mass dispersities (10−13%), i.e., on the order of magnitude of experimental error.

All of these polyesters exhibit relatively low molar masses, comparable to those reported for polyesters of similar structure.[16] As expected, the presence of increasing amounts of core molecule (generation number = 6 to 2) leads to both molar mass decrease (chain limiting effect) and dispersity decrease (distribution narrowing effect) (Table 3).

**Comparison with Theoretical Values.** Theoretical values of $M_n$ can always be calculated from conversion and stoichiometric considerations. In the case of the reaction of 1 mol $AB_f$ (monomer) and $x$ mol $B_g$ (core molecule), $\bar{M}_n$ is given by eq 1:

$$\overline{M_n} = \frac{\dfrac{M_0 + xM_C}{1+x} - M_E}{1 - \dfrac{p_A}{1+x}} + M_E \qquad (1)$$

where $P_A$ is the conversion of A-groups ($A$ = COOH), $M_0$ is the molar mass of $AB_2$ monomer, $M_C$ the molar mass of core molecule, and $M_E$ the molar mass of the byproduct, water in the present case.

Assuming equal reactivity of functional groups, Flory[29] established a relationship giving the mass-average degree of polymerization of $AB_f$ hyperbranched polymers as a function of conversion, but this relationship cannot be applied to more complex systems, such as hyperbranched polyesters synthesized in the presence of a core molecule. In a previous work, we extended the "in-out" recursive probability approach of Macosko and Miller to mixtures of monomers bearing both A- and B-type reactive groups and derived a general formula giving the mass-average molar mass ($\bar{M}_w$) of condensation polymers under the assumption of equal reactivity of functional groups.[23] We also derived a general expression of $\bar{M}_w$ under the first shell substitution effects (FSSE) assumptions, i.e. assuming that the reactivity of a given reactive group depends only on the status (reacted or nonreacted) of the other groups present on the same monomer unit.[24] In the case of the polymerization of 1 mol $AB_2$ + $x$ mol $B_g$, $\bar{M}_w$ is given by eq 2:

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

where $\overline{M_n^0} = \dfrac{M_0 + xM_C}{1+x}$ and $\overline{M_w^0} = \dfrac{M_0^2 + xM_C^2}{M_0 + xM_C}$

In this expression, the $\delta$ 's (branching factors) are average quantities that characterize the nature of polymer branching. They extend the concept of degree of branching (DB)[30−32] defined for $AB_2$-type polymerizations to any type of polymerizations, including the $AB_2$ + $B_g$ system discussed here (A = COOH; B = OH).

The AB-branching factor, $\delta_{AB}$, is the expected number of reacted B-groups present on a monomer unit chosen by picking a reacted A-group at random in the polymer (or the expected number of reacted A-groups on a monomer unit chosen by picking a reacted B-group at random). It characterizes the influence of the reaction of A-groups on the reactivity of B-groups of the same monomer unit (and vice-versa), i.e. the influence of the reaction of A-groups on the hyperbranched architecture build up through further B-group reactions.

In a similar way, the B-branching factor $\delta_B$ is the expected number of additional reacted B-groups present on a monomer unit chosen by picking a reacted B-group at random in the polymer. It characterizes the influence of the reaction of B-groups on the reactivity the other B-groups of the same monomer unit. It can be shown[24] that $\delta_B$ reduces to Frey's degree of branching[30] in the case of $AB_2$ polymerizations.

$M_b$ is the expected molar mass of a monomer unit chosen by picking a reacted B-group at random in the polymer (without taking byproduct elimination into account). $M_b$ allows to take into account differences in reactivity and molar mass between the various types of monomer units in $\bar{M}_w$ calculations.

**Equal Reactivity of Functional Groups.** In the case of equal reactivity of functional groups, $\delta_B$, $\delta_{AB}$ and $M_b$ can be calculated

**Table 4. Data Obtained from the $^{13}C$ NMR Spectra of Hyperbranched BMPA Polyesters: (i) COOH Conversion, $p_{COOH}$, and Number-Average Molar Mass, $\bar{M}_n$ calculated using Eq 1 and (ii) Mass-Average Molar Mass, $\bar{M}_w$, Molar-Mass Dispersity, $D_M = \bar{M}_w/\bar{M}_n$, and Branching Factors $\delta_B$ and $\delta_{AB}$ Calculated Using Eqs 2 and 6−8[a]**

| sample | $p_{COOH}$ | $\bar{M}_n$ | $\bar{M}_w$ | $D_M$ | $\delta_B$ | $\delta_{AB}$ |
|---|---|---|---|---|---|---|
| P∞ | 0.972 ± 0.005 | 4120 ± 150 | 6400 ± 600 | 1.55 ± 0.18 | 0.339 ± 0.006 | 0.903 ± 0.005 |
| | | | (76200 ± 4600) | (18.5 ± 0.54) | (0.486 ± 0.006) | (0.972 ± 0.005) |
| P2-TMP | 0.991 ± 0.005 | 1210 ± 50 | 2160 ± 130 | 1.78 ± 0.14 | 0.449 ± 0.013 | 0.789 ± 0.007 |
| | | | (4390 ± 230) | (3.63 ± 0.08) | (0.487 ± 0.007) | (0.864 ± 0.004) |
| P3-TMP | 0.994 ± 0.005 | 2225 ± 120 | 4050 ± 320 | 1.82 ± 0.21 | 0.441 ± 0.012 | 0.858 ± 0.006 |
| | | | (12800 ± 1150) | (5.77 ± 0.30) | (0.494 ± 0.007) | (0.926 ± 0.005) |
| P4-TMP | 0.979 ± 0.005 | 2750 ± 170 | 4940 ± 440 | 1.80 ± 0.25 | 0.395 ± 0.012 | 0.880 ± 0.005 |
| | | | (23700 ± 2830) | (8.61 ± 0.5) | (0.489 ± 0.005) | (0.947 ± 0.005) |
| P2-PE | 0.976 ± 0.005 | 1480 ± 60 | 2060 ± 130 | 1.39 ± 0.12 | 0.412 ± 0.014 | 0.787 ± 0.007 |
| | | | (5170 ± 350) | (3.49 ± 0.08) | (0.529 ± 0.005) | (0.871 ± 0.005) |
| P3-PE | 0.973 ± 0.005 | 2390 ± 140 | 3230 ± 250 | 1.35 ± 0.16 | 0.376 ± 0.013 | 0.846 ± 0.006 |
| | | | (14600 ± 1700) | (6.10 ± 0.34) | (0.506 ± 0.005) | (0.930 ± 0.005) |
| P4-PE | 0.967 ± 0.005 | 2790 ± 170 | 3750 ± 300 | 1.34 ± 0.18 | 0.350 ± 0.013 | 0.863 ± 0.006 |
| | | | (25500 ± 3800) | (9.13 ± 0.80) | (0.492 ± 0.005) | (0.949 ± 0.005) |

[a] The values in brackets were calculated assuming equal reactivity using eqs 2−5. Experimental errors were estimated from eqs 2−8 and NMR errors committed on the various monomer unit mole fractions.

from conversion $p_A$ and core/monomer stoichiometry. For 1 mol $AB_f$ and $x$ mol $B_g$: [33]

$$\delta_{AB} = p_A \frac{f}{f+gx} \tag{3}$$

$$\delta_B = p_A \frac{f(f-1)+gx(g-1)}{(f+gx)^2} \tag{4}$$

$$M_b = \frac{fM_0 + gxM_C}{f+gx} \tag{5}$$

The theoretical mass-average molar masses $\bar{M}_w$ and molar-mass dispersities $D_M = \bar{M}_w/\bar{M}_n$ calculated using eqs 2 and 3−5 with $f = 2$ and $g = 3$ and 4 are reported in Table 4 (values in brackets). These values, in the 3.5 to 18.5 range, are dramatically higher than the corresponding experimental ones, which vary between 1.8 and 3.1 (Table 3). This clearly reflects the existence of phenomena that are not taken into account in the simplifying equal reactivity assumption, such as substitution effects.

**First Shell Substitution Effects.** In this case, the branching factors $\delta_B$ and $\delta_{AB}$ and 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, etc.), which in turn can be experimentally determined by NMR or chemical analysis or can be calculated by kinetic modeling. The resulting values can be directly inserted in eq 2 to calculate the theoretical mass-average molar mass $M_w$ and dispersity $D_M$ under FSSE assumptions. For $AB_2 + B_3$ and $AB_2 + B_4$ systems, they are given by:[24]

$$\delta_{AB} = \frac{2D+L}{T+L+D} \tag{6}$$

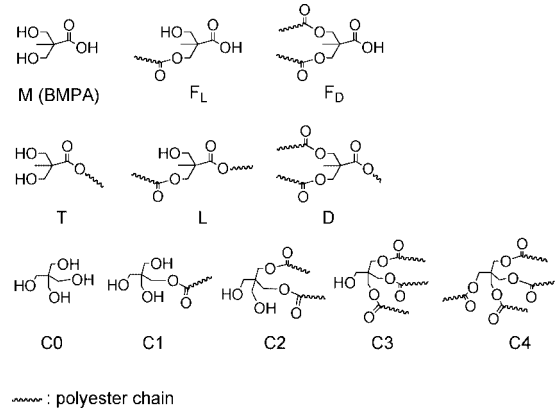
$$\delta_B = \frac{2(D+F_D)+2C_2+6C_3+12C_4}{2(D+F_D)+L+F_L+C_1+2C_2+3C_3+4C_4} \tag{7}$$

$$M_b = \frac{M_0[2(D+F_D)+L+F_L]+M_C(C_1+2C_2+3C_3+4C_4)}{2(D+F_D)+L+F_L+C_1+2C_2+3C_3+4C_4} \tag{8}$$

where $L$ and $D$ are the mole fractions of linear and dendritic units, $F_D$ and $F_L$ the mole fractions of dendritic focal and linear focal units and $C_1-C_4$ the mole fractions of core unit with 1−4 reacted groups. In eqs 6−8, the mole fractions refer to the total number of monomer units, i.e. $AB_2$-type + $B_g$-type units, including residual monomers. Mole fraction *C4* is obviously 0 for the $AB_2 + B_3$ system. The structures of the corresponding monomer units are given in Scheme 2.

The $^{13}C$ NMR spectra of BMPA-PE polyesters of various generations obtained after 24 h reaction at 140 °C are presented in Figure 4. All types of monomer units can be identified, except C4, which, according to the study of pentaerythritol−trimethylacetyl chloride reaction products, should give a signal at ca. 42 ppm. The results obtained from NMR integrations and eqs 2 and 6−8 are provided in Table 4. Several observations can be made:

**Scheme 2. Monomer Units Present in P*n*-PE Polyesters (*n* = 2−6)**




(i) $\delta_B$ is lower than the value calculated for random $AB_2 + B_g$ polymerizations, reflecting the existence of a negative substitution effect on B-groups (OH groups), i.e. the reactivity of a given B-group decreases after reaction of the other B-groups present on the same monomer unit, either BMPA-type or core-type monomer units.

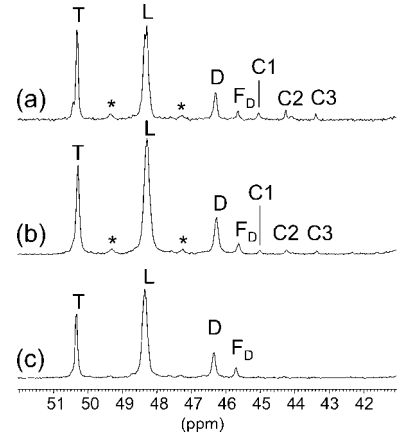
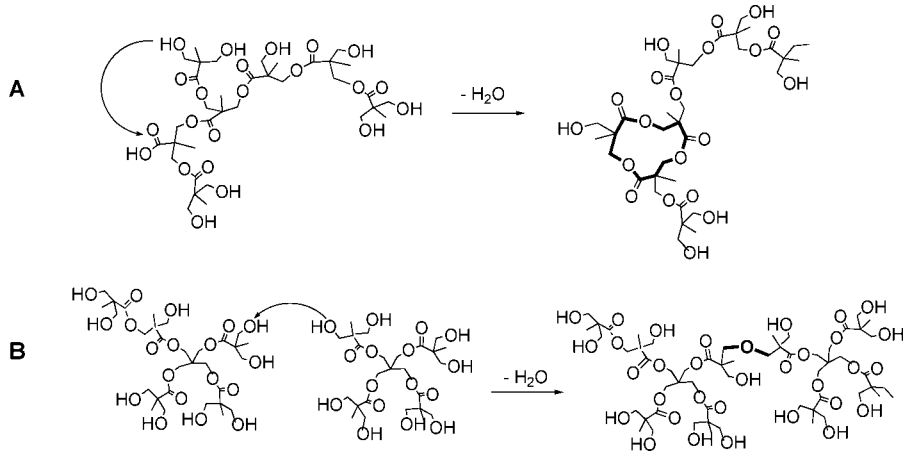



**Figure 4.** $^{13}C$ NMR spectra (75 MHz, DMSO-d6, ref DMSO-d6 = 39.43 ppm) of (a) P2-PE, (b) P3-PE, and (c) P∞. (*) Peaks corresponding to etherification reactions.[26]

**Scheme 3. (A) Cyclization in hyperbranched BMPA Polyester P∞ and (B) Intermolecular Etherification in Hyperbranched BMPA-PE Polyester**




(ii) $\delta_{AB}$ is lower than the value calculated for random $AB_2 + B_g$ polymerizations, reflecting the existence of a negative A−B substitution effect, i.e. the reactivity of a A-group (COOH) decreases after reaction of the B groups present on the same monomer unit, and vice versa. The existence of such a negative substitution effect had never been shown nor taken into account in hyperbranched polymerizations. It should be noted, however, that the existence of A−A and B−B substitution effects has already been described in some $A_2 + B_3$ hyperbranched polymerizations.[34,35]

(iii) For all polymers, $\bar{M}_w$ and $D_M = \bar{M}_w/\bar{M}_n$ are much lower than calculated for random polymerizations ($\bar{M}_n$ is obviously the same) and closer to experimental ones, indicating that these negative substitution effects account for the low dispersities of BMPA hyperbranched polymers.

The comparison of experimental and FSSE theoretical values of molar masses and dispersities (Tables 3 and 4) shows some interesting trends, which can be connected to the existence of side reactions. We previously studied the structure of similar systems by NMR and MALDI−TOF MS and found that two main side reactions take place: etherifications and intramolecular esterifications (cyclizations).[26] In the case of P∞ at 24 h reaction time, etherification reactions were negligible while ca. 35% of hyperbranched molecules underwent intramolecular esterifications, leading to molecules without COOH focal group. In the case of polymer P2-PE after 24 h reaction time, only ca. 6% of hyperbranched molecules underwent cyclizations while ca. 1.7% of oxymethylene groups were involved in - mainly - intermolecular etherifications (Scheme 3).[26] Polymers of pseudogenerations 3 and 4 were in an intermediate situation between these two extremes.

Polymer P∞ (without core molecule) is the simplest case to discuss, since only cyclization side reactions take place and no core molecule is present. This polymer exhibits an experimental $\bar{M}_n = 2170$, significantly lower than the FSSE theoretical value of 4120. At a given reaction time, the existence of intramolecular esterifications leads to a "theoretical" $\bar{M}_n$ higher than the experimental one, since a fraction of reacted carboxy groups does not actually contribute to chain growth. Experimental $\bar{M}_n$ is the ratio of polymer mass over the total number of moles of molecules, either cyclized (35%) or not cyclized (65%). Since cyclized molecules are not taken into account in the calculation of theoretical $\bar{M}_n$, a correction factor of 0.65 should be applied, leading to a "corrected" theoretical value $\bar{M}_n = 2680$, in a better agreement with the experimental one. On the other hand, $\bar{M}_w$ is an average quantity depending on monomer unit fractions and much less affected by cyclizations, which involve only ca. 1.5% of reacted COOH groups. The NMR peaks of D and L cyclized units are obviously superimposed to those of noncyclized D and L units. In order to take into account cyclizations in $M_w$ calculation, the contribution of cyclized units, behaving as end-units, were subtracted from D and L mol ratios and added to $F_D$ and $F_L$ (end-units) mol ratios. Assuming equal cyclization probability for linear and dendritic focal units, this leads to $\bar{M}_w \approx 6050$, i.e., ca. 10% and 5.5% lower than the experimental and the uncorrected theoretical values, respectively.

The experimental $\bar{M}_n$ and $\bar{M}_w$ of P2-PE and P2-TMP are greater than theoretical ones (Tables 3 and 4). In the case of P2-PE, intramolecular esterifications are much less important than for P∞, but 1.7% of OH groups are involved in intermolecular etherifications. Taking intermolecular side reactions into account in calculations would be quite complex. The trend can be estimated assuming that half of the 1.7% OH groups (B-groups) involved in etherification reactions have been transformed into A′ groups, able to react with the same amount of OH groups, i.e. assuming that 1.7/2% of initial $AB_2$ and $B_4$ were transformed into AA′B and A′$B_3$ monomers, respectively. The polymerization system becomes $AB_2 + AA'B + B_4 + A'B_3$, where A and A′ react with B only. The calculations carried out assuming equal reactivity of all functional groups[23,24] lead to $\bar{M}_n = 1650$ and $\bar{M}_w = 12950$, i.e., a small increase in $\bar{M}_n$ but a large one in $\bar{M}_w$ with respect to the values found for the equireactive $AB_2 + B_4$ system ($\bar{M}_n = 1480$ and $\bar{M}_w = 5170$, respectively). When substitution effects take place, the same trend can reasonably be expected and, therefore, intermolecular etherifications in P2-PE are likely to exert a moderate increasing effect on $\bar{M}_n$, but a larger one on $\bar{M}_w$ and dispersity $D_M$. This is experimentally observed for P2-PE and P2-TMP (Tables 3 and 4). As mentioned above, polymers of pseudogenerations 3 and 4 are in an intermediate situation between P2 and P∞.

## Conclusion

The SEC/MALDI−TOF MS calibration method was employed to obtain reliable determinations of the average molar masses of hyperbranched polyesters based on BMPA. Fractions of narrow molar mass distribution obtained by SEC fractionation of BMPA polyesters were analyzed by MALDI−TOF MS and used as narrow standards to obtain a calibration curve giving the elution volume versus absolute molar mass for these hyperbranched polymers. Surprisingly, the conventional calibration method using polystyrene standards gave very close molar mass and dispersity values. This result was unexpected for hyperbranched polymers, the molar masses of which are generally considered in the literature as underestimated by PS calibration. This result was explained by the existence of two

antagonist effects: The molar mass overestimation generally observed for linear polyesters when using PS calibration and the molar mass underestimation generally observed for highly branched polymers, due to their globular shape.

In a second part, the experimental results were compared to theoretical values calculated using the formulas of the recursive approach in the cases of equal reactivity of functional groups and of first shell substitution effects. The AB- and B-branching factors, parameters that extend the concept of degree of branching to any type of polymers, are lower than expected for random polymerizations, reflecting the existence of negative substitution effects. The $\bar{M}_n$ and $\bar{M}_w$ values calculated from NMR analysis under first shell substitution assumptions are reasonably close to experimental ones, indicating that A−B and B−B negative substitution effects are involved in the narrow molar mass distributions experimentally observed for BMPA polyesters. The existence of intramolecular esterifications, important for BMPA polyesters with low core molecule content, leads to a slight molar mass distribution broadening mainly due to $\bar{M}_n$ decrease with respect to theory. A similar effect is observed when intermolecular etherifications take place, mainly due to $\bar{M}_w$ increase with respect to theory.

It should be underlined that high extent of intramolecular esterifications would limit $\bar{M}_n$ to very low values, hindering the obtention of high molar mass polyesters. On the other hand, high extents of etherification reactions could lead to very high $\bar{M}_w$ values and even to polymer cross-linking at high conversion.

**Supporting Information Available:** Text giving the derivation of eqs 1−8. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA801655X