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ARTICLE

Aromatic–Aliphatic Polyesters with Tailored Degree of Branching Based on AB/AB_2 and ABB^*/AB_2 Monomers

Anna Khalyavina,[†] Falko Schallausky,[‡] Hartmut Komber,[†] Michael Al Samman,[§] Wolfgang Radke,[§] and Albena Lederer*,[†]

[†]*Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, D-01069 Dresden, Germany,* [‡]*InnoTERE GmbH, Tatzberg 47/49, D-01307 Dresden, Germany, and* [§]*Deutsches Kunststoff-Institut, Schlossgartenstr. 6, D-64289 Darmstadt, Germany*

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ABSTRACT: The synthesis and characterization of aromatic–aliphatic polyesters with tailored degree of branching (DB), i.e. hyperbranched (hb), gradually branched, and linear polymers, are described. The dilute solution properties of polymers resulting from two different synthetic approaches are compared. The ABB^*/AB_2 approach leads to homopolymers with different DB based on the same AB_2 monomer, 4,4-bis-(4′-hydroxyphenyl)pentanoic acid, employing the protection of one phenolic group (B*) in the AB_2 monomer followed by copolymerization with AB_2 monomer at different molar ratios. Because of their identical chemical origin, well-tunable DB, comparable molar masses, an absence of aggregation in common solvents, and high refractive index increments, they are suitable as model systems in branching characterization. Their solution properties are compared to those of polymers obtained by the AB/AB_2 approach. In order to study the influence of the end-groups on thermal and solution polymer properties, all terminal OH groups were modified with *tert*-butyldimethylsilyl chloride (SY-Cl). A different dependence of the thermal properties on branching was found for OH- and SY-terminated samples produced by the ABB^*/AB_2 approach. While the difference in the T_g values between linear and hb structures was found to be 16 °C for SY-terminated samples, nearly identical values were obtained for OH-terminated linear and hb polyesters due to strong effect of hydrogen bond formation.

Introduction

The importance of hb polymers in different applications is continuously increasing in the past two decades. This can be ascribed to their properties, such as globular shape and the large number of terminal groups. Consequently, a large number of hb structures was synthesized and thoroughly characterized. Several hb structures such as polyamides[1−3] and polyesters[4−6] became commercial products e.g. in the field of coatings and resin formulations.[7−10]

The large interest and the possible wide application domain motivated several researchers to study the structure–properties relationship of hb polymers and to understand them on a molecular level. In fact, conventional techniques of polymer characterization are not directly applicable to hb polymers as these methods are based on assumptions for linear polymers.[11] Moreover, hb structures have a special branching topology along with typically broadly distributed molar masses. Therefore, improved methods or even new characterization techniques are required to study their molecular parameters and to correlate them to material properties. Multidimensional separation techniques are essential for this purpose. Two-dimensional liquid chromatography (2D-LC) helps to obtain simultaneous information on molar mass and on structural characteristics, e.g., topology. Recently, several works[12−15] on the separation of star and long chain branched polymers from linear analogues were published demonstrating the high potential of 2D-LC separations. However, until now the application of 2D-LC has been only applied to structures of lower branching density. This should be ascribed essentially to the lack of model compounds of identical chemical structure and the same number of functional groups. So far, the only existing branched model polymer system satisfying these requirements is star polystyrene (PS)/linear PS, obtained by anionic polymerization.[12−14] This system was extensively studied with 2D-LC,[12,13] resulting in a separation of linear from star polymers, but star polymers cannot be directly extrapolated to hb polymers due to their densely branched structure and high functionality.

In order to obtain well-characterized, differently branched model polymers, suitable for method development in polymer chromatography, we focused on polycondensation, which already has been used in several works[16−22] for the synthesis of linear, gradually branched, and hb structures of identical chemical origin. But these investigations do not yield model polymers systems appropriate for our purposes for the following reasons: in the works of Wooley[16] and De Luca[19] the linear polymers possess low molar mass, which restrict their possible application only to the low molar mass region. Frey et al.[20] presented successfully a method for the synthesis of linear, gradually branched, and hb polymers, but these polymers aggregate strongly in routine SEC solvents, which may cause insufficient separation according to molar mass. In the work of Kricheldorf and co-workers,[21] the samples with different content of AB/AB_2 monomers were successfully synthesized and partially characterized, but without calculation of DB. In the study of Baek and Tan,[22] the differently branched para-poly(ether ketones) based on different content of AB/AB_2 monomers were practically insoluble in common solvents, making their solution characterization and DB determination not possible.

In our previous work[17] we reported on an easy synthesis of gradually branched polymers by copolycondensation of AB and

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*Corresponding author. E-mail: lederer@ipfdd.de.

AB_2 monomers with the lowest DB of this comonomer system being limited to 29%. In this article we present the more complex ABB*/AB_2 approach in order to obtain polymers with lower DB values. Finally, the dilute solution properties of both polymer systems will be compared.

Experimental Part

Materials. All reagents and solvents were purchased from Aldrich (Germany), Acros (Germany), or Fluka (Germany) and used without further purification. 4-(*N,N*-Dimethylamino)pyridinium 4-tosylate (DPTS) was synthesized and purified according to the work of Moore.[23] The synthesis of hyperbranched poly[4-bis(4,4′-hydroxyphenyl)pentanoic acid] (OH-50) is done according to Schallausky et al.[17] All glassware was dried for several hours at 80 °C.

Characterization. ^{1}H NMR and ^{13}C NMR measurements were carried out on a Bruker DRX 500 NMR spectrometer at 500.13 and 125.75 MHz, respectively. DMSO-d_6 and $CDCl_3$ were used as solvents. For internal calibration the solvent peaks were used: DMSO-d_6: $\delta(^{13}C) = 39.60$ ppm, $\delta(^{1}H) = 2.50$ ppm; $CDCl_3$: $\delta(^{13}C) = 77.00$ ppm, $\delta(^{1}H) = 7.26$ ppm. Quantitative ^{13}C NMR spectra were recorded using inverse gated decoupling and a delay time of 8 s. The absolute error of quantitative ^{13}C NMR is estimated to ±2%.

Determination of the molar masses was performed by size exclusion chromatography (SEC) equipped with HPLC pump (Knauer, Germany) and coupled to a viscosity, differential refractive index (RI) dual detector (ETA-2020, WGE Dr. Bures, Germany) and a multiangle laser light scattering detector (MALLS) DawnEOS (Wyatt Technologies, $\lambda = 632$ nm). A PLgel 5 μm Mixed C chromatography column (300 mm × 7.5 mm, Polymer Laboratories, Ltd., UK) was used with THF (Acros, Germany) as a solvent. Flow rate was 1 mL/min. All evaluations were made with the software ASTRA 4.9 (Wyatt Technology Corp.). For interpretation of SEC-MALLS measurements dn/dc values were externally determined at 25 °C using RI detector Dn 2010 (WGE Dr. Bures, Germany, $\lambda = 620$ nm). For this purpose different concentrations of the sample in THF in the range of 0.4, 0.8, 1.6, 2.0, 2.4, and 3.2 mg/mL were prepared. Refractive index increments dn/dc = 0.195 mL/g for OH-terminated samples and dn/dc = 0.155 mL/g for SY-terminated samples were determined.

MALDI-TOF-MS spectra were recorded on a Shimadzu Biotech Axima TOF^2 MALDI instrument. 1,8,9-Trihydroxyanthracene was used as a matrix. Lithium chloride was used as a salt for ionization. The irradiation source was a pulsed nitrogen laser with a wavelength of 373 nm. The length of one laser pulse was 3 ns. The measurements were carried out using the following conditions: polarity-positive, flight-path-linear, mass high (20 kV acceleration voltage), 100−150 pulses per spectrum.

TGA measurements were carried out with a TGA-Q5000 of TA Instruments in the temperature range 30−750 °C at a heating rate of 10 K/min under a nitrogen atmosphere. DSC measurements were carried out with Q1000 of TA Instruments in the temperature interval from −60 to 200 °C under a nitrogen atmosphere. The modulated DSC measurements were carried out in the same temperature range at 2 K/min with a modulated amplitude of 0.31 K and modulation period of 40 s. For the calculation of glass transition temperatures the reversing signal was used.

Synthesis. *Preparation of ABB* Monomer*. To a solution of 4,4-bis(4′-hydroxyphenyl)pentanoic acid as an AB_2 monomer (25.0 g, 83.0 mmol) in dry THF (100 mL) *tert*-butyldimethylsilyl chloride (25.0 g, 166.0 mmol) and imidazole (13.6 g, 199.2 mmol) were added. The mixture was heated at reflux for 12 h, cooled down, and evaporated to dryness. Glacial acetic acid (40 mL) was added followed by water (60 mL), and the reaction was stirred at room temperature for 2 h and then poured into water (300 mL). The organic phase was extracted with ethyl acetate (3 × 75 mL), and the combined extracts were washed with distilled water (2 × 150 mL), dried over sodium sulfate, and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:7 ethyl acetate−*n*-hexane gradually increasing to 3:7 to give monosubstituted acid as a white solid (yield 40%).

The atomic numbering is in accordance with Scheme 4 with R = TBDMS and $n = 1$.

^{1}H NMR (DMSO-d_6): δ (ppm) = 0.17 (s, 6H, H_{10}), 0.93 (s, 9H, H_{12}), 1.48 (s, 3H, H_5), 1.91 (t, 2H, H_2), 2.23 (t, 2H, H_3), 6.65 (d, 2H, $H_{8'}$), 6.72 (d, 2H, H_8), 6.93 (d, 2H, $H_{7'}$), 7.01 (d, 2H, H_7), 9.16 (s, OH), 11.96 (s, COOH). ^{13}C NMR): δ (ppm) = −4.46 (C_{10}), 17.91 (C_{11}), 25.59 (C_{12}), 27.22 (C_5), 29.99 (C_2), 36.42 (C_3), 43.99 (C_4), 114.81 (C_8), 119.09 ($C_{8'}$), 127.82 (C_7), 127.98 ($C_{7'}$), 138.97 (C_6), 142.09 ($C_{6'}$), 152.79 ($C_{9'}$), 155.16 (C_9), 174.65 (C_1).

Polymerization of ABB Monomer Resulting in SY-0*. ABB* (7.00 g, 17.5 mmol) and DPTS (3.59 g, 12.3 mmol) were dissolved in dichloromethane (60 mL) under an argon atmosphere at room temperature. After 30 min, dicyclohexylcarbodiimide (DCC) (7.22 g, 35.00 mmol) was added, and the stirring at room temperature under argon was continued from 1 to 24 h. The formed DCC−urea was filtered out and carefully washed with CH_2Cl_2. Then the solvent was reduced, and the polymer was purified by double precipitation into methanol (70%).

The atomic numbering is in accordance with Scheme 4 with R = TBDMS for a linear polymer.

^{1}H NMR ($CDCl_3$): δ (ppm) = 0.19 (s, H_{10}), 0.98 (s, H_{12}), 1.63 (s, H_5), 2.33 (t, H_2), 2.51 (t, H_3), 6.75 (d, $H_{8'}$), 6.95 (d, H_8), 7.05 (d, $H_{7'}$), 7.19 (d, H_7). ^{13}C NMR ($CDCl_3$): δ (ppm) = −4.42 (C_{10}), 18.13 (C_{11}), 25.64 (C_{12}), 27.81 (C_5), 30.46 (C_2), 36.43 (C_3), 44.95 (C_4), 119.54 ($C_{8'}$), 120.92 (C_8), 128.12 (C_7), 128.25 ($C_{7'}$), 140.50 ($C_{6'}$), 146.44 (C_6), 148.67 (C_9), 153.74 ($C_{9'}$), 172.30 (C_1).

Deprotection of SY-0 Resulting in OH-0. SY-0 (4.79 g, 12.5 mmol) was dissolved in DMF (35 mL) under an argon atmosphere, and then trifluoroacetic acid (TFA) (2.8 mL) was added drop by drop to avoid polymer precipitation; afterward, the mixture was stirred for 54 h. The deprotection conversion was controlled by ^{1}H NMR. After the reaction was complete, the solvent was reduced and the polymer was precipitated into diethyl ether, followed by reprecipitation into water. The final product was obtained as white flakes (50%).

The atomic numbering is in accordance with Scheme 4 with R = H for a linear polymer.

^{1}H NMR (DMSO-d_6): δ (ppm) = 1.51 (s, H_5), 2.29 (t, H_2), 2.41 (t, H_3), 6.69 (d, $H_{8'}$), 6.99 ($H_{7'}$ and H_8), 7.18 (d, H_7), 9.23 (OH). ^{13}C NMR (DMSO-d_6): δ (ppm) = 27.18 (C_5), 29.97 (C_2), 35.92 (C_3), 44.43 (C_4), 114.97 ($C_{8'}$), 121.21 (C_8), 127.83 and 127.98 (C_7 and $C_{7'}$), 138.11 ($C_{6'}$), 146.71 (C_6), 148.32 (C_9), 155.37 ($C_{9'}$), 171.84 (C_1).

Synthesis of OH-50. OH-terminated hb polyester OH-50 was synthesized by a procedure described in detail by Schallausky et al.[17] and will not be repeated here.

Modification of OH-50 Resulting in SY-50. OH-50 (5 g, 18.63 mmol) and imidazole (3.17 g, 46.58 mmol) were dissolved in DMF (25 mL) under an argon atmosphere at room temperature. After 30 min *tert*-butyldimethylsilyl chloride (5.69 g, 37.26 mmol) was added, and the stirring at room temperature under argon was continued for 48 h. Then, the solvent was reduced in vacuum, and the polymer was purified by double precipitation into methanol and dried under vacuum at 70 °C (55%).

The atomic numbering is in accordance with Scheme 4 with R = TBDMS for a hyperbranched polymer, and the abbreviations T, L, and D denote the terminal, linear, and dendritic units.

^{1}H NMR ($CDCl_3$): δ (ppm) = 0.19 (H_{10}), 0.97 (H_{12}), 1.60 (H_{5T}), 1.63 ($H_{5\,L}$), 1.65 (H_{5D}), 2.33 (H_2), 2.50 (H_3), 6.74 ($H_{8'}$), 6.96 (H_8), 7.05 ($H_{7'}$), 7.19 (H_7). ^{13}C NMR ($CDCl_3$): δ (ppm) = −4.42 (C_{10}), 18.12 (C_{11}), 25.64 (C_{12}), 27.81 ($C_{5\,L}$, C_{5D}), 27.89 (C_{5T}), 30.55 (C_{2D}), 30.44 ($C_{2\,L}$), 30.53 (C_{2T}), 36.31 (C_{3D}), 36.42 ($C_{3\,L}$), 36.56 (C_{3T}), 44.64 (C_{4T}), 44.95 ($C_{4\,L}$), 45.26 (C_{4D}), 119.38 ($C_{8'T}$), 119.54 ($C_{8'L}$), 120.92 ($C_{8\,L}$), 121.10 (C_{8D}), 128.17, 128.17, and 128.24 (C_7 and $C_{7'}$), 140.52 ($C_{6'L}$), 141.35 ($C_{6'T}$), 145.52

(C_{6D}), 146.42 ($C_{6\ L}$), 148.66 ($C_{9\ L}$), 148.84 (C_{9D}), 153.54 ($C_{9'T}$), 153.74 ($C_{9'L}$), 172.06 and 172.10 (C_{1D}), 172.22 and 172.27 ($C_{1\ L}$), 172.39 and 172.44 (C_{1T}).

Copolycondensation of the ABB and AB_2 Resulting into Gradually Branched Structures.* ABB* (1.5 g, 3.75 mmol), AB_2 (0.075 g, 0.249 mmol), and DPTS (0.35, 1.93 mmol) were dissolved in DMF (3 mL) under an argon atmosphere, and then DCM (24 mL) was added. After 30 min, DCC (1.12 g, 5.17 mmol) was added, and the mixture was stirred at room temperature for 48 h. The formed DCC−urea was filtered out and carefully washed with CH_2Cl_2, and then the polymer was purified by double precipitation into methanol. After drying, one part of the polymer was deprotected using the above-described TFA procedure. The second part of the polymer was modified with *tert*-butyldimethylsilyl chloride, yielding 99% modified structure.

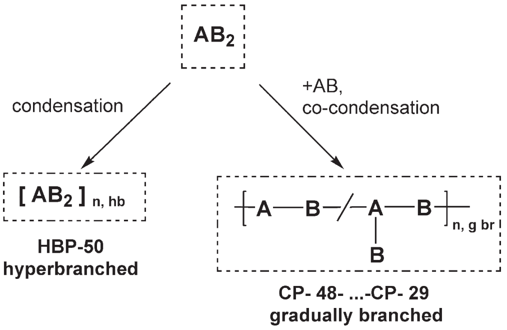
Modification of SY-0-2 with 1-Naphthyl Isocyanate for End-Group Analysis. To the mixture of SY-0-2 (0.20 g, see Table 2) in toluene (2 mL) and 1 M solution of triethylenediamine (TED) (1 mL) 1-naphthyl isocyanate (NI) (0.1 mL) was added drop by drop. The mixture was heated for 60 min at 95 °C, and then diethylamine (0.1 mL) was added to the hot solution. The reaction mixture was cooled down, the solvent was reduced by evaporation, and the polymer was precipitated in methanol.

Results and Discussion

In our previous work[17] we reported on an easy strategy for synthesis of aromatic−aliphatic hb polyesters with well-defined DB based on a copolycondensation of 4,4-bis(4-hydroxyphenyl)pentanoic acid as AB_2 monomer and 3-(4-hydroxyphenyl)-propionic acid as AB monomer. These polyesters possess several advantages in solution: high d*n*/d*c* values in THF at room temperature and absence of aggregation in common solvents, which is rather untypical for highly functional OH-terminated polymers. On the basis of this, we concluded that these polymers are well suited for method development on branched polymers separation by 2D-LC.

For systematical study of the influence of branching topology on thermal and solution properties of hb aliphatic−aromatic polyesters, the variation of branching density was adjusted by copolymerization of AB with AB_2 monomer in different molar ratios. This method, the so-called AB/AB_2 approach, is shown in Scheme 1. It was found that degrees of branching as well as thermal properties of the obtained polyesters are strongly dependent on the AB/AB_2 monomer ratio. The experimental data on weight-average molar masses, DB's, KMHS exponents, thermal properties, and number of OH groups per polymer unit are summarized in Table 1.

Scheme 1. Illustration of the AB/AB_2 Approach



In this work we introduce the solution properties of these polymer systems. Furthermore, a comparison of properties of the AB/AB_2 systems to homopolymers based only on AB_2 monomer (ABB*/AB_2 approach, see below) will be carried out.

The common parameter for the estimation of the shape of a polymer in solution is the Kuhn−Mark−Houwink−Sakurada (KMHS) exponent, α:

$$[\eta] = KM^{\alpha} \tag{1}$$

This value lies in the range between 0 for hard spheres and 0.6−0.9 for linear polymer coils in a thermodynamically good solvent.[25] In our work the KMHS exponents for copolymers with different DB are obtained by SEC-RI in combination with online viscosity detector and MALLS detector and are listed in Table 1. The sample HBP-50 has the KMHS exponent value of 0.38, which is typical for hb polymers in a thermodynamically good solvent.[26]

We expected that the introduction of the bifunctional AB monomer into the polymer structure will cause two different effects. The first effect is the increase of the molar mass of the statistical segment, which theoretically has no influence on the conformation of the polymer. This is valid as long as the spacers between the branching points are relatively short. When the spacer length becomes larger, a second effect of transformation into linear-like structure occurs, which leads to more linear-like structures and higher KMHS values, respectively.[20]

Experimentally, no clear tendency in the KMHS values was found. Scattering of the KMHS exponent values within a range of 0.32−0.43 with increasing AB fraction was observed (Table 1 and Figure 6). We conclude that the different functionality of the AB monomer is causing this behavior. Its introduction into the polymer structure dramatically changes the number of OH end groups per monomer unit: from unity in the hb sample HBP-50 to 0.39 for CP-37. This leads to deviations in the polarity of the macromolecules with different DB and different restriction of

Table 2. Molar Masses Obtained for [ABB*] Polymerization in Solution

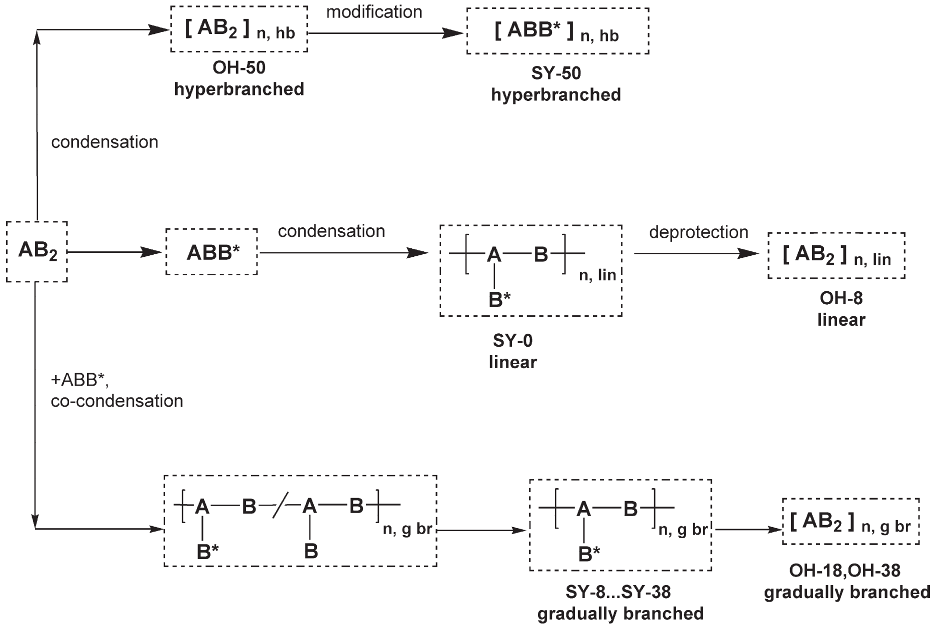
sample	DPTS, equiv	DCC, equiv	reaction time, h	$M_{\mathrm{w,SEC\text{-}MALLS}}$, g/mol	M_w/M_n
SY-0-1	0.1	1.4	1	26 500	2.3
SY-0-2	0.7	2	1	64 000	2.5
SY-0-3	0.7	2	24	111 200	2.5

Table 1. Experimental Data on Weight-Average Molar Masses, DB's, KMHS Exponents, Thermal Properties, and Number of OH Groups per Polymer Unit as a Function of the X_{AB} Fraction, Where $X_{AB} = AB/(AB_2 + AB)$[24]

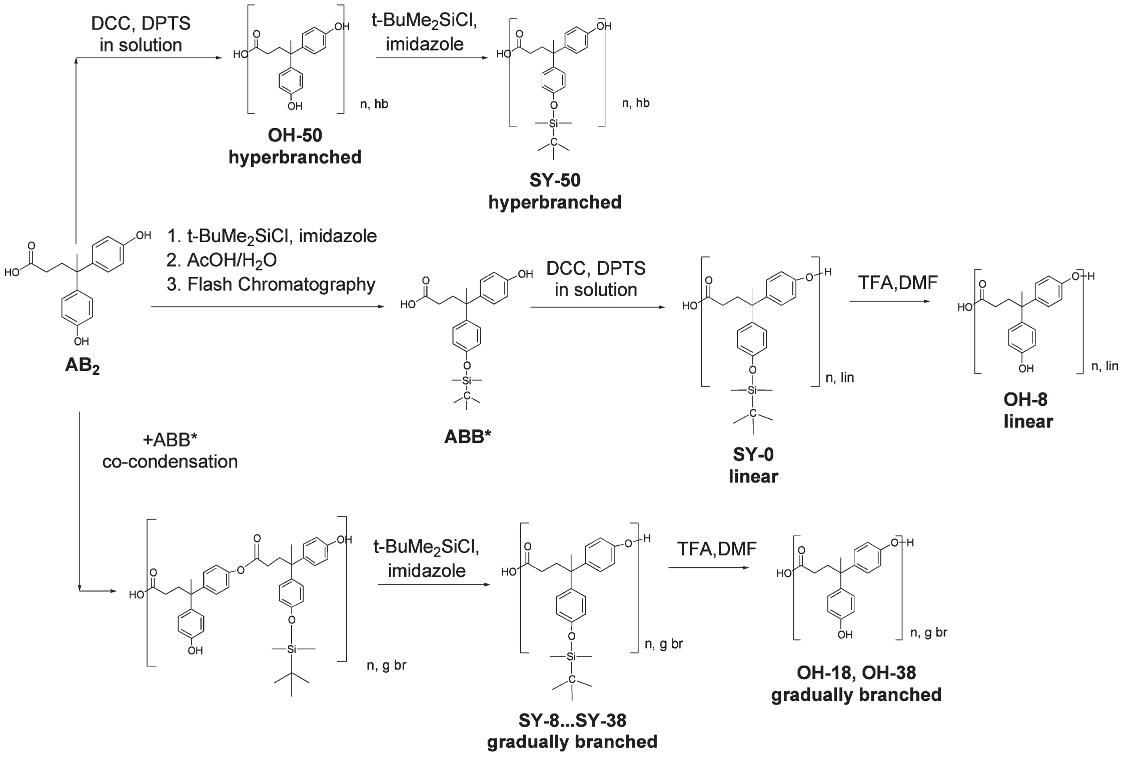
sample	M_w,[a] g/mol	PD[a]	X_{AB}	DB[a]	α[b]	T_g,[a] °C	av no. of OH groups/monomer unit[a]
CP-29[c]	43 000[d]	3.8	0.786	29	–[e]	82	–
CP-37[c]	72 000[f]	1.8	0.675	37	0.32	94	0.32
CP-44[c]	35 000[f]	1.5	0.515	44	0.40	111	0.52
CP-48[c]	36 000[f]	1.3	0.333	48	0.43	126	0.68
HBP-50[g]	38 000[f]	1.4	0	50	0.38	151	1.00

[a] Values according to the work of Schallausky et al.[17] [b] KMHS exponents, determined via SEC-MALLS-Visco with THF as a solvent. [c] Copolymer sample. [d] Molar mass determined via SEC-RI, DMAc/LiCl/H_2O as solvent. [e] Sample is not soluble in THF. [f] Molar mass determined via SEC-MALLS with THF as solvent. [g] Hyperbranched homopolymer.

Scheme 2. Schematic Representation of the ABB*/AB$_2$ Approach



Scheme 3. Chemical Reactions in the ABB*/AB$_2$ Approach

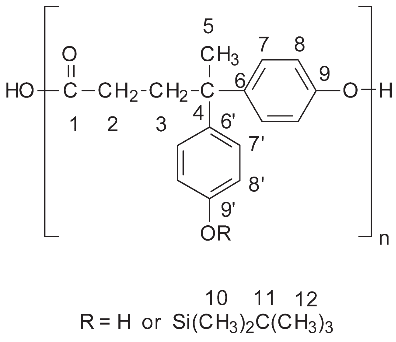


hydrogen bonds formation, which has very strong effect as it was found by the decrease of T_g with the DB (Table 1).[17]

From these results we can conclude that the dilute solution properties of the polyesters based on the AB/AB$_2$ approach depend on branching only to a minor extent, whereas other factors like polarity as well as segmental mobility play a more important role. Therefore, gradually branched polymers based on the AB/AB$_2$ approach cannot be used as model polymers for accurate separation by degree of branching. Hence, the more challenging synthetic approach ABB*/AB$_2$ for preparation of homopolymers with identical chemical nature was studied.

ABB*/AB$_2$ Approach. This approach utilizes the copolymerization of the AB$_2$ with an ABB* monomer, whereas the ABB* monomer is obtained by protection of one of the phenolic groups of the AB$_2$ monomer prior to polymerization (B*). Therefore, only one B and the A functionalities are reactive. As mentioned above, the ABB*/AB$_2$ methodology takes into account the influence of the second B function in the AB$_2$ monomer, which enables to exclude changes in the chemical structure and in the flexibility of the polymer at different DB. Moreover, we can keep the number of functional groups per monomer unit constant for both the hb and

Scheme 4. Numbering of Atoms Positions for the Assignment of NMR Signals



the linear polymer. The removal of the protective group enables us to obtain end products with two types of functionalities: with polar OH groups and with nonpolar *tert*-butyldimethylsilyl (SY) groups.

SY Protected Linear Polyester. According to Scheme 2, the synthesis of the linear model polymer consists of three steps: the first step is the protection of one B function in the AB$_2$ monomer to ABB* monomer. The second step is the polymerization in solution, giving linear polymer [ABB*]$_n$. The third step is the removal of the protective group, resulting in the linear [AB$_2$]$_n$ polymer with one phenolic group per monomer unit. The choice of the protective group is essential, since it should possess the following properties: (i) the removal of the protective group should be selective and quantitative; (ii) the protective group should be stable under the acidic polymerization conditions, caused by p-TSA.

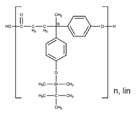
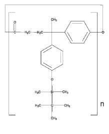
Generally, there are several protective groups which might satisfy these criteria. Our choice was made on the basis of the work of Wooley et al.,[16] where a linear polymer was obtained from 3,5-dihydroxybenzoic acid. After several experiments they found that the application of *tert*-butyldimethylsilyl (SY) protective group leads to the desired linear polymer.[16] In our work we followed the general synthetic strategy using the *tert*-butyldimethylsilyl protective group with the intention to obtain a linear polymer with high molar mass (up to 100 000 g/mol). This prerequisite was crucial in order to obtain linear polymer with a reasonable molar mass after deprotection, comparable to our branched samples. The synthetic strategy for the synthesis of the linear polymer is depicted in Scheme 3.

First, the ABB* monomer was prepared according to the work of Wooley[16] by silylation of the AB$_2$ monomer, which was obtained in 40% yield after flash chromatography. The polycondensation of ABB* with DPTS/DCC[23] gives a linear polymer SY-0 at 70% yield. It should be mentioned that in the present work the given yields are obtained after extensive purification procedure. The elaborative purification is required for subsequent use of the polymers as models in the 2D-LC analysis.

The polymerization of ABB* led to different molar masses with variation of DPTS, DCC content, and reaction time (Table 2). Lower molar mass (M_w = 26 500 g/mol) was obtained at lower amounts of DPTS and DCC. Increased amounts of DPTS and DCC to 0.7 and 2.0 equiv, respectively, resulted in M_w = 64 000 g/mol. Longer reaction time led to the highest molar mass M_w = 111 200 g/mol. The linearity of samples was confirmed by ^{13}C NMR spectroscopy (Table 4).

The chromatograms of these linear samples showed similar profile as shown in Figure 1 for SY-0-2: a main peak and a small shoulder at lower molar masses. In order to obtain more information about the origin of the shoulder in SY-0-2, MALDI-TOF-MS measurement was performed (see Figure 2). This analytical technique is suitable for distinguishing of cyclized structures. The molar mass distribution obtained by MALDI-TOF-MS shown in Figure 2 recovers evidently the molar mass range from approximately 1000 to 6000 g/mol corresponding to the shoulder of the SEC chromatogram (Figure 1). The MALDI-TOF mass spectrum in Figure 2 allows for detailed structural assignments of the peaks series for the sample SY-0-2 (Table 3).

Table 3. Structural Assignments of the Peaks Series Observed in the MALDI-TOF Mass Spectrum of the SY-0-2

Compound	Structure	Mass, m/z
1 (linear structure)		(382.5) n+18+Li$^+$: 1555 (4), 1937 (5), 2320 (6), 2703 (7), 3085 (8), 3467 (9), 3850 (10), 4233 (11), 4615 (12)
2 (cyclized structure)		(382.5)n+Li$^+$: 1537 (4), 1920 (5), 2302 (6), 2685 (7), 3068 (8), 3450 (9), 3833 (10), 4215 (11), 4598 (12)

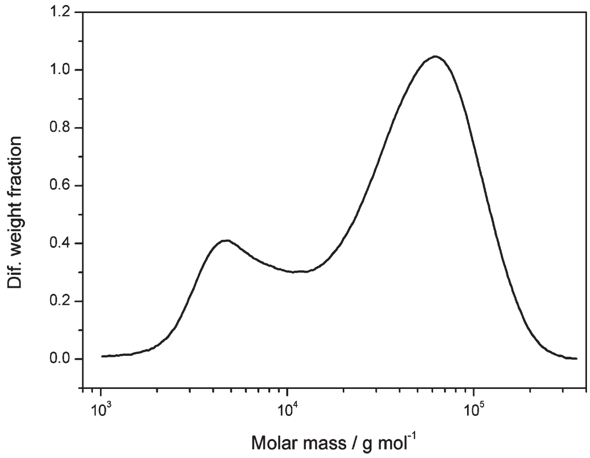


Figure 1. Differential weight distribution of the molar mass of the linear polyester SY-0-2 obtained by SEC-MALLS-RI.

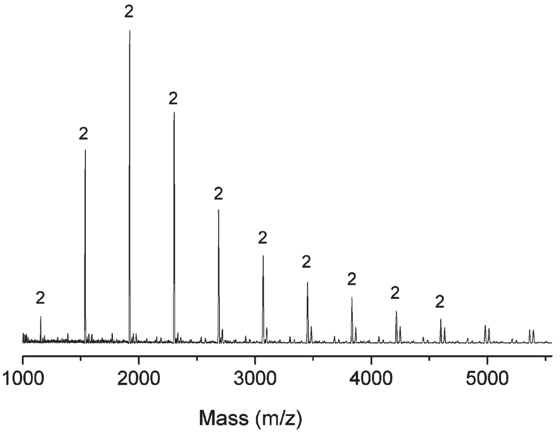


Figure 2. MALDI-TOF mass spectrum of the sample SY-0-2.

Analyzing the MALDI-TOF spectrum, we can clearly state that in the molar mass region up to 5500 g/mol primarily signals of cyclized structures are present. These structures cannot take part in the polycondensation process. Information about higher molar masses is not accessible by MALDI-TOF. Besides this technique, other conventional techniques, i.e. spectroscopic methods and potentiometric titration, can be applied to detect the presence of cycles. These techniques imply that in the cyclized structures end groups are absent in contrast to the linear polymer. However, the above-mentioned methods are limited to low molar masses due to strongly decreasing amount of end-groups relative to the polymer backbone at high molar masses. Since conventional analytical methods are not applicable for the determination of OH end-groups in our linear samples, we chose another qualitative detection of the OH end-groups. In order to enhance the sensitivity, we introduced UV-labels at the functional end-groups of the polymer. This method allows for detection of the distribution of the end-groups across the chromatogram. The original methodology was shown by Wintersteiger et al.[27] and worked very well for OH groups indication by liquid chromatography.

For our purposes, derivatization of the polymer SY-0-2 using naphthyl isocyanate (NI) as a chromophore was performed with consequent SEC-UV measurement of the modified polymer at 300 nm, where mostly NI absorbs. The comparison of the SEC measurements with UV detection at 300 nm of original and NI-modified SY-0-2 is shown in Figure 3. The relative intensity of the UV-signal decreases at higher elution volumes (lower molar masses) after modification. If all polymer chains would carry OH groups capable of labeling, the intensity due to the UV-label should increase in the lower molar mass region as well. However, opposite behavior was observed, which shows that cyclization takes place only in the lower molar mass region, while in the high molar mass region the bifunctional linear chains dominate.

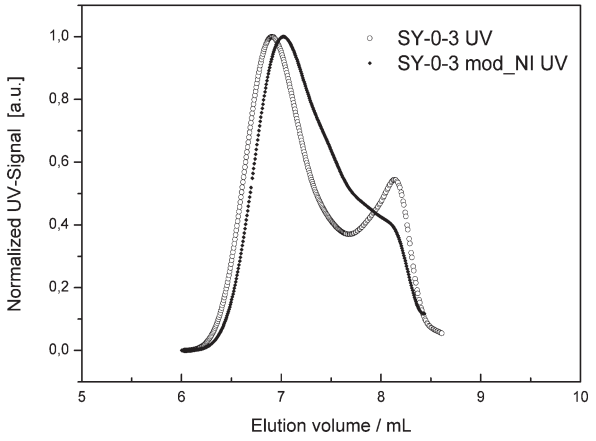


Figure 3. Normalized UV chromatograms of the original SY-0-2 and SY-0-2 modified with NI at 300 nm, where mostly NI absorbs.

OH-Terminated Linear Polyester. The third step of the synthetic strategy was the deprotection of the TBDMS group leading to OH-terminated linear polymer. Attempting deprotection by adding 1 N HCl[16] was not successful due to precipitation of the polymer. Therefore, we performed the removal of TBDMS group by tetrabutylammonium fluoride (TBAF),[28] leading to 100% cleavage of TBDMS groups as confirmed by ^{1}H NMR. However, precipitations in water and in acidified water did not lead to the removal of quaternary ammonium salt, which was found by ^{1}H NMR. Therefore, another route using potassium fluoride (KF)[29] was explored. The use of small excess of KF with catalytic amount of crown ether (18-crown-6) as a phase transfer agent led to complete cleavage of the TBDMS groups. As undesired side reaction of this deprotection, transesterification occurred, resulting in some branching, where the value of DB cannot be controlled or influenced. The only successful method found is based on the use of trifluoroacetic acid (TFA).[30] Nearly quantitative cleavage of more than 97% of TBDMS groups was reached using 3 equiv of trifluoroacetic acid in DMF as proved by ^{1}H NMR. The use of THF as reaction solvent was found to cause longer deprotection time compared to that of DMF. Since the TFA deprotection method involves the acidic hydrolysis both, the transesterification and the ester bonds hydrolysis took place. As a result, sample OH-8 with degree of branching of 8% and molar mass of 22 000 g/mol was obtained. For samples OH-18 and OH-38 lower molar masses were determined at nearly complete deprotection (Table 4).

For our further investigations, it was of great importance to elucidate the influence of hydrogen bonding on thermal and solution behavior of the branched polymers in general and specifically on their chromatographic separation. In order to obtain analogous end-capped hb polymers, we performed additional modification of the hb sample OH-50 into SY-50.

Table 4. Characterization Data of OH-Terminated and SY-Protected Linear and Gradually Branched Polyesters Using Various Fractions X_{ABB^*} for the Co-condensation of ABB*/AB$_2$

sample	X_{ABB^*}	DB$_{theor}$,[a] %	DB$_{exp}$,[b] %	$M_{w,SEC\text{-}MALLS}$,[c] g/mol	$M_{n,SEC\text{-}MALLS}$,[c] g/mol	α	T_g, °C
				SY-Terminated Samples			
SY-0-2	1[d]	0	0	64 000	25 600	0.59	124
SY-8	0.956	8	7	41 600	17 700	0.49	114
SY-13	0.925	13	13	59 800	26 500	0.44	119
SY-18	0.889	17	18	45 400	22 800	0.43	118
SY-22	0.856	21	22	60 300	22 300	0.41	119
SY-38	0.658	38	37	47 000	23 700	0.43	113
SY-50	0[e]	50	50	41 900	22 000	0.35	108
				OH-Terminated Samples			
OH-8	1	0	8	26 800	13 200	0.58	155
OH-18	0.889	17	18	10 800	4 800	0.43	140
OH-38	0.658	38	37	21 000	8 900	0.42	137
OH-50	0[e]	50	50	33 900	16 800	0.36	152

[a] DB$_{theor}$ – DB, calculated according to eq 3. [b] DB$_{exp}$ – DB determined by ^{13}C NMR. [c] Determined by SEC-MALLS in THF. [d] Linear homopolymer. [e] Hyperbranched homopolymer.

SY-Protected hb Polyester. The synthesis of OH-50 was performed according to the work of Schallausky et al.[18] Its modification with *tert*-butyldimethylsilyl chloride and imidazole in DMF for 48 h gave the silylated sample SY-50 in 55% yield. One could expect that a part of the end-groups are located in the inner part of hb macromolecule and, therefore, are hardly accessible for the modification agent. However, modification of 99% of the hydroxyl groups was confirmed by ^{13}C NMR. Therefore, the increase of the molar mass of the SY-50 is solely attributed to the addition of one TBDMS group per monomer unit. The molar mass values for both OH-50 and SY-50 are listed in Table 4.

The number-average molar masses detected by SEC-MALLS should be interpreted carefully since lower molar masses could remain undetected by the light scattering detector. Nevertheless, the high refractive index increment values (d*n*/d*c*) of 0.195 mL/g for OH-terminated and 0.155 mL/g for SY-terminated samples in THF at room temperature enable good detection even in the oligomer molar mass region. For this reason, we can observe good overlapping of the RI and LS signals leading to a reliable calculation of the molar mass values in the high as well as in the low molar mass regions.

Gradually Branched Polyesters. The synthesis of gradually branched polymers employs the copolymerization of the ABB* and AB_2 monomers in different ratios as it is shown in the Scheme 2. These ratios can be calculated according to eq 2, derived by Frey et al.,[31] where the theoretical degree of branching is a function of a given molar fraction of the linear comonomer at full conversion and at equal reactivity of the comonomers:

$$X_{\mathrm{ABB*}} = \frac{\mathrm{ABB*}}{\mathrm{AB_2} + \mathrm{ABB*}} \tag{2}$$

$$\mathrm{DB_{theor}} = 2\frac{1 - X_{\mathrm{ABB*}}}{(2 - X_{\mathrm{ABB*}})^2} \tag{3}$$

Equation 3 enables one to control the DB of the branched copolymers in the range of 0−50% using the known linear comonomer molar fraction $X_{\mathrm{ABB*}}$. The theoretically expected DB and the used linear comonomer molar fractions $X_{\mathrm{ABB*}}$ are listed in Table 4. As a result, the synthesized gradually branched SY-terminated polyesters reflected very good correlation between theoretically expected and experimentally found DB (eq 4) and, additionally, comparable molar masses. In contrast to that, the obtained OH-terminated samples possess different molar masses due to the applied deprotection procedure.

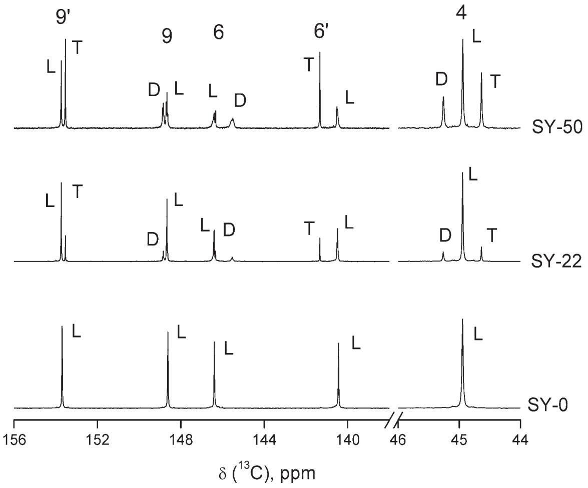


Figure 4. ^{13}C NMR spectra (regions) of the silylated polymers SY-0, SY-22, and SY-50 (solvent: $CDCl_3$).

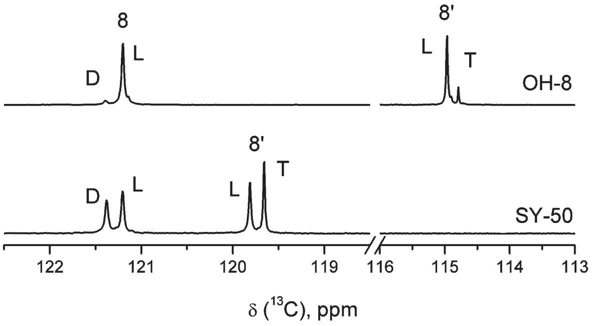


Figure 5. ^{13}C NMR spectra (region of $C_8/C_{8'}$ signals) of OH-38 (top) and SY-50 (bottom) (solvent: top, DMSO; bottom, $CDCl_3$).

NMR Structural Characterization. Previous investigations on hyperbranched polymers obtained from 4,4-bis(4′-hydroxyphenyl)pentanoic acid by melt[29] and solution[17,32] polycondensation showed that at high conversion the DB value approaches 50% corresponding to statistical type of branching.[33] On the basis of a detailed ^{1}H and ^{13}C NMR signal assignment,[29] it was found that several ^{13}C NMR signals, e.g., those of C_4, $C_6/C_{6'}$, and $C_9/C_{9'}$ (Scheme 4), show a signal splitting caused by the three different subunits, and thus, their intensities from quantitative ^{13}C NMR spectra can be used to calculate DB. The silylation of the phenolic groups of L and T units results in characteristic ^{1}H and ^{13}C chemical shift effects (Experimental Part), but the signal splitting due to the subunit remains. This is illustrated in Figure 4, which depicts regions from the ^{13}C NMR spectra of the linear sample SY-0 containing only L units and of two branched samples with different DB. The lowered content of T and D units of the gradually branched sample SY-22 compared to the hyperbranched sample SY-50 is obvious. The experimental degree of branching (DB_{exp}) was determined according to Frey[33] (eq 4) based on the intensities of C_4, $C_6/C_{6'}$, and $C_9/C_{9'}$ signals characteristic for terminal, linear, and dendritic units (Figure 4). The mean value is given in Table 4 and compared to the theoretical value calculated from the AB_2/ABB* feed ratio according to eqs 2 and 3.

$$\mathrm{DB_{Frey}} = \frac{2D}{2D + L} \tag{4}$$

As mentioned above, high purity and high degree of modification/deprotection of the polymers are requested for their application in 2D-chromatography. By both ^{1}H and ^{13}C NMR the successful purification from DCC−urea as well as high degree of modification/deprotection of all samples was confirmed. The completeness of deprotection can easily be followed by disappearance of the H_{10} and H_{12} signals in the ^{1}H NMR spectrum, whereas the proof of complete protection of the phenolic groups requires ^{13}C NMR. Protection is accompanied by insolubility in DMSO-d_6, and thus, $CDCl_3$ was used as solvent. Residual phenolic protons which can be well detected for samples soluble in DMSO-d_6 result in broad signals in $CDCl_3$ which are not appropriated for quantification. However, the signals of $C_{8'}$ in phenolic units at about 115 ppm which are shifted to about 119.5 ppm after silylation (Figures 5) are well distinguishable even in traces by their signals in a ^{1}H−^{13}C correlated spectrum.

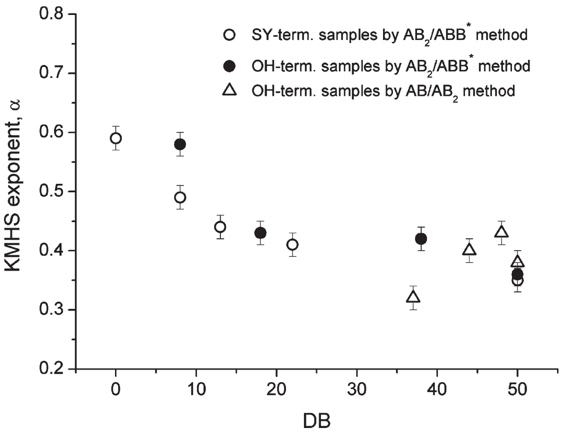


Figure 6. KMHS exponent dependence on the DB in series of branched aromatic–aliphatic polyesters.

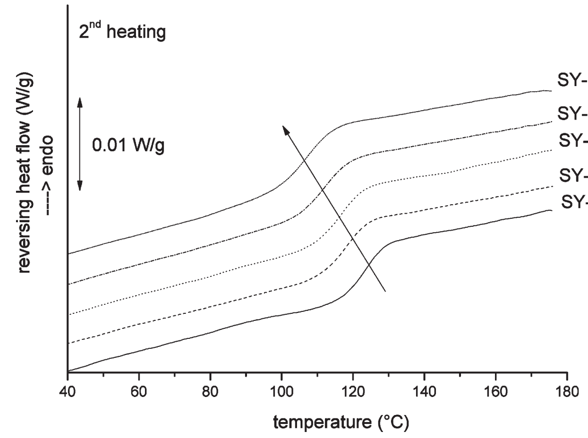


Figure 7. T_g dependence on the degree of branching for SY-terminated polyesters. SY-8 was not taken into account due to deviating M_n (see Table 4).

Dilute Solution Properties. The intrinsic viscosity of the prepared OH- and SY-terminated polyesters was measured by SEC-MALLS coupled to viscosity detector, similarly as for the series of the copolymers resulting from the AB/AB$_2$ approach discussed above. The KMHS exponents α are listed in Table 4. Figure 6 shows the dependence of α on the DB of the differently branched homo- and copolymers. As expected, CP-50 and OH-50, which have the same chemical structure and DB but were obtained independently, showed similar KMHS exponents, reflecting α values of 0.38 and 0.36, respectively. In a series of samples prepared by the ABB*/AB$_2$ approach a clear trend was observed for the dependence of KMHS exponents on DB. The α values are decreasing with DB from 0.59 to 0.35 for the nonpolar polymers and from 0.58 to 0.36 for the OH-terminated polymers, which indicates a more compact shape of the macromolecule at higher DB. Interestingly, there is no difference between the OH- and SY-terminated hb samples having KMHS exponents of 0.36 and 0.35, respectively, whereas one could expect more dense molecular structure of the SY-terminated sample due to its quite voluminous protective groups. On the other hand, this change in polarity leads to an increased affinity to the solvent, which leads to better flushed and more open polymer coil. However, this influence seems to disappear at lower DB and the deviation of the KMHS exponents at the same DB becomes more pronounced.

The KMHS exponents of the AB/AB$_2$ (Table 1) copolymers are plotted for comparison in Figure 6. The behavior of α does not correlate with the DB as it was observed for the samples based on the ABB*/AB$_2$ approach. An introduction of the bifunctional AB monomer into the polymer structure causes an increase of the molar mass of the statistical segment on the one hand and, on the other hand, an increase of the spacer length. At the same time, an increase of the spacer length causes reduction of the number of OH groups per monomer units and of the affinity to the solvent, respectively. Additionally, the influence of these factors is difficult to clarify due to the limited range of the DB obtained by the AB/AB$_2$ approach.

In the study of the ABB*/AB$_2$ system these additional factors are eliminated, and hence, the behavior of KMHS exponents is in a good agreement with the theoretical expectations providing clear comparison of the polymers solely depending on the branching architecture and avoiding strongly overlapping side effects.

Thermal Behavior. It is well-known that branching affects the thermal behavior of polymers; e.g., it strongly impedes crystallization and reduces glass transition temperature. Our calorimetric results, listed in Table 4 and presented in Figure 7, indicate gradual decrease of T_g with the branching for SY-terminated polyesters. Because of their identical chemical structure, comparable molar masses, and absence of crystallization, the pure effect of the branching on T_g can be accurately extracted. For SY-terminated polyesters a shift of 16 °C was observed between hyperbranched and linear sample. The difference of 16 °C is much lower compared to that of the AB/AB$_2$ system (69 °C, see Table 1), where complex influence of different parameters such as hydrogen bonding, branching, and different chemistry of the bifunctional AB monomer takes place.

Different behavior was observed for OH-terminated samples. The T_g value of OH-50 with 152 °C is much higher than that of SY-50 (108 °C) as a consequence of multiple hydrogen bonds. In a similar manner, the decrease of T_g with introduction of protective group was observed in the work of Mikhaylova,[34] where the T_g values (227 °C) of OH-terminated hb aromatic polyesters drops down to 158 °C when OH end-groups were end-capped.

Comparing OH-terminated samples with different DB, no systematic variation of T_g was observed. This is due to the strongly deviating molar masses and molar mass distributions. The only meaningful comparison can be carried out between OH-8 (155 °C) and OH-50 (152 °C), which interestingly possesses similar T_g values. This observation leads to the conclusion that hydrogen bonds have stronger influence on the glass transition temperature than branching. This fact is supported by the results of Wooley et al.,[16] where similar T_g values were obtained for fully aromatic OH-terminated linear, hyperbranched, and dendritic polyesters with comparable amount of phenolic groups. On the other side, Schallausky et al.[17] observed that the branching effect could be completely overlapped by the H-bonding effect corresponding to the number of OH-end groups per monomer unit (Table 1).

Two other groups investigated the exact influence of branching on the T_g for well-defined polyesters. In the work of Ramakrishnan[35] a comparison of the thermal behavior of linear, branched, and "kinked" PET showed similar T_g values for those types of samples. The report of Finelli et al.[36] on linear and branched poly(butylenes isophtalate) confirmed a lack of effect of branching on T_g. The different behavior of these polyesters is additionally influenced by their partially crystalline nature. The crystallinity acts similar as cross-linking and raises T_g through its restrictive effect on the segmental motion of the polymer chains.[36] In contrast to these polymers, the polyesters investigated in this work are completely amorphous, which enable us to observe the pure influence of the branching topology on the glass transition.

TGA measurements on the SY-terminated samples showed a high thermal stability up to 350 °C for polymers with different degree of branching with the 10% weight loss occurring at 385 °C, with the maximum of decomposition temperature between 415 and 430 °C. OH-terminated samples except OH-50 are thermally stable up to 300 °C with the maximum of decomposition temperature around 410 °C. The lower thermal stability (up to 250 °C) of the sample OH-50 is the subject of further investigation.

Conclusions

Within this work two sets of model compounds (with polar and nonpolar end-groups) of the same chemical origin employing the ABB*/AB$_2$ approach were obtained and compared to model compounds obtained previously by AB/AB$_2$ co-condensation. Both approaches provide model polymers with tailored degree of branching. As a result of bifunctional AB monomer addition in the copolymer, the behavior of KMHS exponents is deviating from theoretical predictions due to influence of different polarity and segmental flexibility. In contrast to that, the theoretically predicted decrease of the KMHS exponents of the samples obtained by the ABB*/AB$_2$ methodology was observed. The performed modification of the OH-terminated samples with the voluminous *tert*-butyldimethylsilylgroups causes an increase in the packing density of the macromolecules, and therefore, slightly lower values of α for SY-terminated samples in comparison to OH-terminated analogues have been obtained. A different dependence of the thermal properties on branching was found for OH- and SY-terminated samples produced by the ABB*/AB$_2$ approach. While the difference in the T_g values between linear and hb structures was found to be 16 °C for SY-terminated samples, nearly identical values have been obtained for OH-terminated linear and hb polyesters due to strong effect of hydrogen bond formation. Therefore, we assume that the hydrogen bonding influences the glass transition stronger than branching.

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