Synthesis of Hyperbranched Aromatic Homo- and Copolyesters via the Slow Monomer Addition Method

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ABSTRACT: Random bulk polycondensation and the slow monomer addition (SMA) strategy have been employed for the preparation of hyperbranched aromatic homo- and copolyesters, based on 3,5-bis-(trimethylsiloxy)benzoyl chloride (AB_2 monomer) and 3-(trimethylsiloxy)benzoyl chloride (AB comonomer). Whereas random copolycondensation in bulk yielded limited molecular weights ($M_n = 2900-8400$; SEC-LALLS in DMF/GHC), considerably higher molecular weights and low polydispersities were obtained under slow monomer addition conditions (M_n = 83 000−278 000; PD = 1.09−1.49). Copolymerization of the AB_2 and AB monomers resulted in polymers with controlled degrees of branching (DB) in the range 0−0.5. In the random copolycondensation the theoretical DB values could be confirmed by detailed analysis of the ^{13}C NMR data, demonstrating equal reactivity of the comonomers. Using the slow monomer addition strategy (SMA), the DB was significantly enhanced above the value of 0.5 for bulk AB_2 polycondensation to 0.61−0.66, in agreement with theoretical predictions (DB = 0.66), and also high molecular weight polymers were obtained. Also, for all copolymerizations enhanced DBs were obtained. A strictly linear dependence of the intrinsic viscosity $[\eta]$ on molecular weight was observed for all copolymers, measured by online SEC viscosimetry. The Mark−Houwink exponents α_{MH} clearly decreased with the DB and were in the range 0.18−0.55.

Introduction

Cascade branched polymers, i.e., dendrimers and hyperbranched polymers, represent a new, rapidly developing facet of polymer chemistry. Dendrimers are synthesized by multistep reaction procedures, whereas hyperbranched polymers are prepared by polycodensation of multifunctional AB_m monomers ($m \geq 2$) in one step. As already shown by Flory almost 50 years ago, molecular weights and polydispersities of hyperbranched polymers are determined by conversion due to the step growth kinetics of the polymerization.[1] Reasonable molecular weights can only be achieved at high conversion, which inevitably leads to extremely broad molecular weight distributions. Cyclization of the growing macromolecules by *intra*molecular reaction of the focal unit—intentionally neglected by Flory in his seminal theoretical treatment—lowers the polydispersity somewhat; however, this reaction severely limits molecular weights and therefore complicates the synthesis.[2,3]

Intense theoretical efforts are being made at present to develop control strategies for the key parameters of hyperbranched polymers: degree of branching (DB), molecular weight, and polydispersity. The DB describes the branching perfection of a hyperbranched polymer in comparison to the respective perfectly branched dendrimer structure.[4] For linear polymers, DB is zero, whereas for dendrimers the DB is 1. We have developed a general definition of the DB, which is based on the comparison of the actual number of growth directions to the number of possible growth directions in the macromolecules.[5] In subsequent theoretical work we analyzed the random one-pot copolymerization of AB_2 monomers with AB monomers, using probability considerations and neglecting possible steric and excluded-volume effects.[6] Along these lines, we have been able to derive an expression for the expected DB in a random AB/AB_2 copolymerization, which depends on the ratio r of AB and AB_2 monomers ($r = AB/AB_2$) employed. The considerations are based on the same reactivity of A and B groups at both AB and AB_2 comonomers. In this case, eq 1 was obtained which describes the expected DB for a given molar fraction of linear comonomer $x_{AB} = [AB/([AB] + [AB_2])$

$$DB_{AB/AB_2} = 2\,\frac{1 - x_{AB}}{(2 - x_{AB})^2} \tag{1}$$

Thus

$$x_{AB} = 2 + \frac{\sqrt{1 - 2DB} - 1}{DB} \tag{2}$$

Equation 2 enables one to control the DB of hyperbranched copolymers for the copolycondensation of AB and AB_2-type monomers in the range 0−0.5 via the linear comonomer fraction x_{AB}, provided both comonomers possess the same reactivity. In further theoretical and simulation work it has been demonstrated that the slow addition of highly reactive AB_m monomers to B_f functional core molecules should enable one to control molecular weights and reduce the polydispersity of hyperbranched polymers considerably.[7] In an ideal slow monomer addition process a given number of core molecules B_f grows in an active chain growth like mechanism by addition of AB_m monomers, in contrast to the random AB_m-type batch polycondensation. In an ideal slow monomer addition procedure, polydispersities are controlled by the core functionality f, and the DB should be enhanced to a maximum value of 0.66 from the value 0.5 in a random polycondensation process. In elegant work, Bharati and Moore achieved the synthesis of hyperbranched poly(phenylacetylene)s under slow

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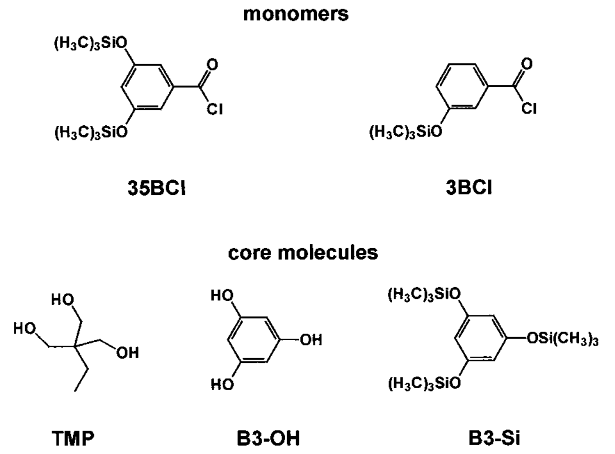

Figure 1. Monomers and core molecules used in this study: AB_2 monomer 35BCl, AB comonomer 3BCl, and B3-core molecules TMP, B3-OH, and B3-Si.

monomer addition conditions by attaching a B_2-core molecule to a solid support via a cleavable linker.[8] The synthesis of well-defined polyglycerols with controlled molecular weight via this procedure from glycidol as a latent AB_2 monomer represents a recent successful example of a slow addition procedure.[9] In this paper we present our results on the synthesis of hyperbranched aromatic homo- and copolyesters via the SMA method, using highly activated trimethylsiloxybenzoic acid chlorides and different core molecules (Figure 1). We systematically vary the amount of the linear comonomer fraction. The DB and molecular weights were determined by means of NMR spectroscopy and a combination of size exclusion chromatography with light scattering (SEC-LALLS), respectively. In addition, the dependence of the intrinsic viscosity $[\eta]$ on molecular weights as well as the DB has been investigated for all copolyesters.

Experimental Section

Materials. Since moisture causes deactivation of the monomers, all syntheses and polymerizations were carried out under an argon atmosphere. Solvents used for the synthesis of monomers and polymers were dried and distilled over powdered calcium hydride (DMF) or sodium wire (benzene and diglyme). 2-Ethyl-2-hydroxymethyl-1,3-propanediol (TMP) was recrystallized from a mixture of acetone and diethyl ether[10] and dried under high vacuum before use. Other starting materials and reagents were used as received.

Monomer Synthesis. Monomer synthesis as well as the preparation of the silylated core molecule 1,3,5-tris(trimethylsiloxy)benzene were carried out according to the procedure reported for 3,5-bis(trimethylsiloxy)benzoyl chloride by Wooley et al.[11] Monomers and the core compounds were distilled several times and obtained in high purity. For respective abbreviations used cf. Figure 1.

35BCl: H NMR ($CDCl_3$): δ [ppm] = 0.27 (s, 18 H, Ar−O−Si−(CH_3)$_3$), 6.63 (t, 1 H, *para*), 7.20 (d, 2 H, *ortho*). ^{13}C NMR ($CDCl_3$): δ [ppm] = 0.12 (6 C, Ar−O−Si−(CH_3)$_3$), 116.23 (1 C, *para*), 119.11 (2 C, *ortho*), 134.85 (1 C, *C−C═O)*, 156.44 (2 C, *meta*), 167.91 (1 C, *C*═O).

3BCl: H NMR ($CDCl_3$): δ [ppm] = 0.28 (s, 9 H, Ar−O−Si−(CH_3)$_3$), 7.14 (d, 1 H, *para*), 7.35 (t, 1 H, *meta*), 7.54 (s, 1 H, *ortho*), 7.69 (d, 1 H, *ortho*). ^{13}C NMR ($CDCl_3$): δ [ppm] = 0.12 (3 C, Ar−O−Si−(CH_3)$_3$), 122.42 (1 C, *ortho*), 124.60 (1 C, *para*), 127.23 (1 C, *ortho*), 129.94 (1 C, *meta*), 134.51 (1 C, C−C═O), 155.66 (1 C, *C*−O), 168.11 (1 C, *C*═O).

B3−Si: ^{1}H NMR ($CDCl_3$): δ [ppm] = 0.24 (s, 9 H, Ar−O−Si−(CH_3)$_3$), 6.00 (s, 3 H, Ar−H). ^{13}C NMR ($CDCl_3$): δ [ppm] = 0.12 (3 C, Ar−O−Si−(CH_3)$_3$), 106.04 (3 C, (H_3C)$_3$Si−O−C−C−C−O−Si− (CH_3)$_3$), 156.43 (3 C, (H_3C)3Si−O−C−).

Bulk Polymerization. General procedure for homo- and copolyesters: The calculated quantities of the different monomers 3BCl and 35BCl (respective ratios *r* given in Table 3) were mixed with DMF as catalyst and heated for 2 h under a weak stream of Ar to the reaction temperature of 200 °C. The solid, brown crude reaction products were dissolved in hot DMF and precipitated in deionized water. The light brown to dark reddish brown (depending on molecular weight and degree of branching) precipitate was dried under reduced pressure. Yields of all polymers were in the range of 70−85% after precipitation. The products were characterized by ^{1}H NMR, ^{13}C NMR, and SEC-LALLS-VISK (online viscosimetry). NMR data of a typical hyperbranched homopolyester (P_B50): 300 MHz ^{1}H NMR (d_6-DMSO): δ [ppm] = 6.52 (s, 1 H, *t*), 7.0−7.8 (m, 6 H, *t*, *l* and *d*), 7.9−8.2 (m, 2 H, *d*). ^{13}C NMR (d_6-DMSO): δ [ppm] = 108.07 (3 C, *t*), 114.17 (3 C, *l*), 121.52 (3 C, *d*), 130.91 (3 C; *t*, *l* and *d*), 151.82 (3 C, *t*, *l* and *d*), 158.97 (3 C, *t*, *l* and *d*), 163.79 (3 C, −*C*═O).

Polymerization Using the Slow Monomer Addition Method. General procedure for homo- and copolyesters: In analogy to the bulk polymerization, in the case of copolyesters, the monomer ratio *r* was chosen according to eq 2. The monomers were dissolved in dry diglyme, using a concentration of 1 wt %. The dilute monomer solution was now slowly added (within 80 h) by a dispensing pump to a highly concentrated solution of dry 2-ethyl-2-hydroxymethyl-1,3-propanediol (TMP, Figure 1) in dry quinoline as catalyst. The reaction temperature was held at 200 °C, and the condensation product trimethylsilyl chloride was removed in a slow stream of dry argon. After quantitative addition, the solvents were evaporated. The crude reaction products were dissolved in hot DMF and precipitated in deionized water. The purification step was carried out several times to achieve complete removal of catalyst and byproducts. Yields of all polymers were in the range of 60−75% after the repeated precipitation procedure. The products were characterized by ^{1}H NMR, ^{13}C NMR, and SEC-LALLS-VISK. NMR data of the hyperbranched copolymer P_{SMA}25 as an example for the copolymers prepared in this manner: ^{1}H NMR (d_6-DMSO): δ [ppm] = 7.09−7.8 (m, 11 H, *t*, *l*, l_t, and *d*), 7.9−8.2 (m, 2 H, *d*), 7.67 (s, 2 H, l_l), 8.05 (s, 2 H, l_l). ^{13}C NMR (d_6-DMSO): δ [ppm] = 114.67 (3 C, *l*), 116.51 (2 C, l_t), 120.85 (2 C, l_t), 121.52 (3 C, *d*), 123.52 (1 C, l_l), 127.79 (2 C, l_l), 130.40 (5 C, *t*, *l*, *d*, l_l and l_t), 150.88 (4 C, *d*, *l* and l_l), 157.92 (3 C, *t* and *l*), 163.88 (3 C, −*C*═O), 164.73 (1 C, −*C*═O).

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300 NMR spectrometer in $CDCl_3$ and DMSO-d_6 as internal standards. Determination of the DB relied on ^{13}C-INVGATE experiments with a pulse delay time of 5 s. Refractive indices were determined with a Brice-Phoenix differential refractometer, resulting in values between 0.165 and 0.175. For detection of molecular weights a combination of a Chromatix KMX-6 low-angle light scattering detector with a UV detector from Pharmacia and a combination of four polystyrene columns with different sizes was used. Intrinsic viscosities $[\eta]$ were determined on-line with a viscosity detector from Knauer. DMF with guanidine hydrochloride (GHC) was used as solvent for SEC-LALLS with on-line viscosimetry.

Results and Discussion

Monomers used for the slow addition procedure must meet strict requirements, such as (i) rapid, quantitative, and irreversible reaction between A and B groups; (ii) reaction only upon activation or addition of catalyst; and (iii) condensation byproducts must be easily removable.[7a] For instance, due to incomplete conversion, the coupling reaction between bishydroxybenzoic acid as AB_2 monomer and core molecules by thermal activation, using carbonyldiimidazole activation (CDI) permitted only limited control over molecular weight.[12] Therefore, we used the highly activated monomers 3,5-bis(trimethylsiloxy)benzoyl chloride (35BCl) and 3-(trimethylsiloxy)-

Table 1. Comparison of SEC Data of Linear Polyester P_B00 and Hyperbranched Polyester P_B50, Measured in THF as Well as DMF/GHC; Polymerization Was Carried Out in Bulk without Core Molecule (SEC-LALLS)

	P_B50 (THF)	P_B50 (DMF/GHC)	P_B00 (THF)	P_B00 (DMF/GHC)
M_w	349700	4700	14200	14300
M_n	65600	3400	6900	7000
M_w/M_n	5.33	1.38	2.06	2.04

benzoyl chloride (3BCl) as AB_2 monomers and AB comonomer, respectively, which can be expected to fulfill the requirements of a slow addition procedure. These monomers are shown in Figure 1 together with the different B_3 core molecules employed, i.e., 2-ethyl-2-hydroxymethyl-,3-propanediol (TMP), 1,3,5-trihydroxybenzene (B_3-OH), and 1,3,5-tris(trimethylsiloxy)benzene (B3-Si).

35BCl, 3BCl, and B3-Si were synthesized from 3,5-dihydroxybenzoic acid, 3-hydroxybenzoic acid, and 1,3,5-trishydroxybenzene using the synthetic procedure reported by Wooley et al.[11] 35BCl has also been used by several other groups for the synthesis of hyperbranched polymers in random polycondensation procedures.[4,13−16] B3-OH, B3-Si, and TMP were employed in order to study the effect of the reactivity of the B_3-core molecule employed on molecular weights and polydispersities. In the abbreviations used in following, the index B or SMA designates the polymerization mode (bulk polymerization vs slow monomer addition), and the number gives the targeted DB; e.g., $P_{SMA}30$ represents a hyperbranched copolyester of 3BCl and 35BCl with a targeted DB of 0.30 (30%), prepared in the slow monomer addition mode. Unless mentioned otherwise (i.e., by a prefix, such as T-), the core molecule used is B3-Si.

A. Homopolymerization. Molecular weights and molecular weight distributions of all polyesters prepared were characterized by size exclusion chromatography coupled with a light-scattering detector (SEC-LALLS). In previous works, we have shown that SEC can grossly overestimate molecular weights of hydroxyfunctional hyperbranched polymers.[9,12,20] To assess the effect of SEC conditions on molecular weights measured, a linear homopolymer of the AB monomer 3BCl prepared in bulk (P_B00) as well as a hyperbranched homopolymer of 35BCl (P_B50) has been characterized with SEC-LALLS, both in THF and in DMF/guanidinium hydrochloride (GHC). DMF/GHC is often used for the characterization of polysaccharides by SEC to avoid aggregation due to hydroxyl end groups. The results, summarized in Table 1, evidence that for the linear homopolymer no difference of the molecular weights is observed in the different solvents; however, for the hyperbranched homopolymer P_B50 molecular weights measured in THF were strongly overestimated. This trend was systematically confirmed in the whole series of copolymers listed in Tables 3 and 4: with increasing DB and number of hydroxyl end groups, molecular weights measured in THF were overestimated to an increasing extent.

Thus, standard SEC conditions (i.e., THF or other common organic solvents, PS standards) are clearly not suitable for the characterization of hyperbranched polyesters. The high polarity of the numerous end groups in combination with aggregation leads to incorrect results. SEC in THF used in previous reports on hyperbranched aromatic polyesters[4] is likely to have resulted in similarly overestimated molecular weights. On the basis of this observation, all molecular weight data of the hyperbranched copolyesters prepared in this work have been measured in DMF/GHC via SEC-LALLS.

Table 2. Experimental Data for Hyperbranched Homopolyester Samples Based on TMP, B3-OH, and B3-Si, Respectively, as Core Molecules; Preparation by Slow Monomer Addition

sample[a]	m/c[b]	DB[c]	M_w	M_n	PD
T-$P_{SMA}(1)$	110/1	0.55 ± 0.02	275 300[d]	184 600[d]	1.49[d]
T-$P_{SMA}(2)$	220/1	0.63 ± 0.02	136 200[d]	112 700[d]	1.21[d]
T-$P_{SMA}(3)$	440/1	0.64 ± 0.02	301 900[d]	277 900[d]	1.09[d]
T-$P_{SMA}(4)$	660/1	0.64 ± 0.02	273 100[d]	247 200[d]	1.11[d]
T-$P_{SMA}(5)$	880/1	0.64 ± 0.02	117 400[d]	83 900[d]	1.40[d]
B-$P_{SMA}(1)$	660/1	0.61 ± 0.02	505 100	323 900	1.42
BSi-$P_{SMA}(1)$	147/1	0.66 ± 0.02	254 200	193 900	1.31

[a] T = TMP as core molecule, B = B3-OH as core molecule, BSi = B3-Si as core molecule. [b] Monomer/core ratio. [c] Determined by eq 1 from IG ^{13}C NMR spectra. [d] Main mode of the distribution.

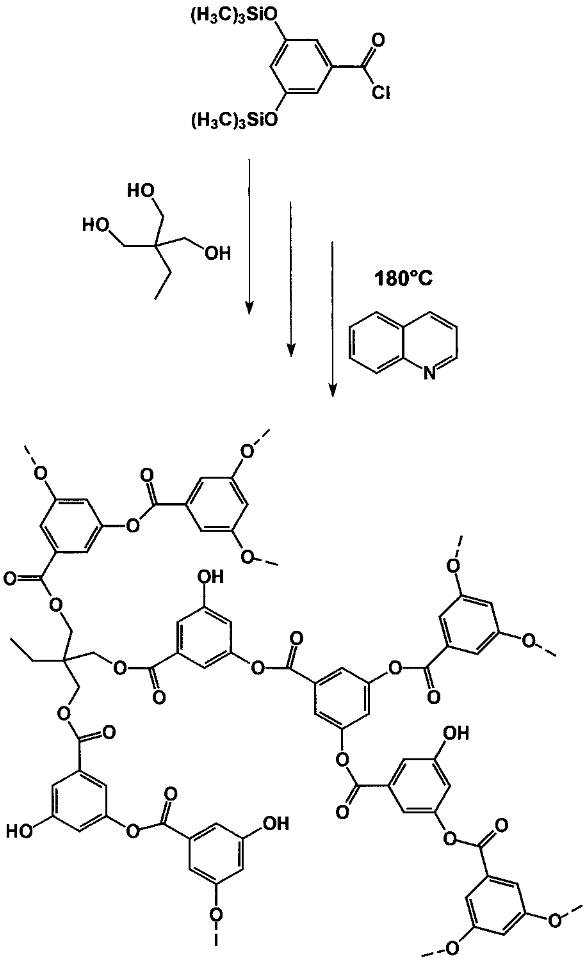

Figure 2. Synthesis of the hyperbranched aromatic homopolyesters.

Using TMP, B3-OH, and B3-Si as core molecules and 35BCl as AB_2 monomer, a series of homopolymerizations with different monomer/core ratio (cf. Table 2) have been performed in the slow monomer addition mode, as shown in Figure 2.

A typical SMA polymerization was carried out as follows: 35BCl was dissolved in dry diglyme and then slowly added to a preheated solution of TMP (or the respective core) in quinoline at 200 °C via a dispensing pump within 80 h. Quinoline served as both a catalyst and solvent for the TMP core. Several other amine-based catalysts have also been tested; however, quino-

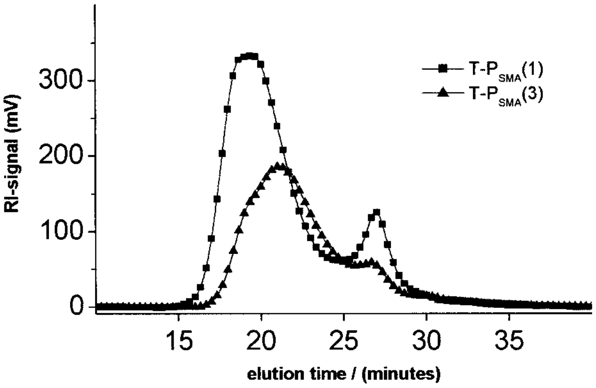

Figure 3. SEC traces of T-P_{SMA}(1) and T-P_{SMA}(3) obtained by SEC/LALLS.

line proved to be the best choice due to its high boiling point, which is important with respect to the required reaction temperature of 200 °C. Furthermore, complete dissolution of TMP in quinoline was possible in contrast to diglyme. Within several days of reaction time, the color of the reaction mixture turned to dark brown. After complete monomer addition, the polymers were precipitated several times in deionized water to achieve complete removal of catalyst and potential byproducts. The hyperbranched aromatic polyesters were obtained as light brown powders.

Characterization of the hyperbranched polyesters included determination of the DB as well as measurement of molecular weights and polydispersities. The DB was determined by ^{13}C NMR-INVGATE spectroscopy, employing the signal assignment of model compounds for the units with different branching perfection.[4] Molecular weight measurements were performed by a combination of SEC and low-angle laser light scattering (SEC/LALLS) in DMF/GHC. Figure 3 shows the SEC/LALLS diagram of the hyperbranched homopolyester samples T-PSMA(1) and T-PsMA(3) obtained by the slow monomer addition procedure. The elution curve is typical for this series of polyesters.

In contrast to hyperbranched aromatic polyesters prepared using CDI as coupling agent,[12] considerably higher molecular weights could be achieved with the highly activated silyl chloride monomers. Table 1 summarizes the results of the SEC/LALLS measurements and the values obtained for the DB.

All samples with the exception of T-P_{SMA}(5) possessed higher molecular weights than planned from the monomer/core ratio. Possibly, added monomer reacted only with a fraction of the core molecules. This is tentatively explained by partial evaporation of the catalyst in the beginning of the reaction, leading to a deactivation of a certain fraction of the core molecules. All polymer samples with TMP as core molecule exhibited bimodal distributions as shown in Figure 3. This can be explained by deactivation or cyclization of a certain monomer fraction, leading to the formation of new core molecules in the course of the slow monomer addition.[7]

However, if only the main distribution modes are considered, polydispersities are relatively low (cf. Table 2). The second distribution mode at lower molecular weights leads to an increase of the polydispersity. This side reaction is tentatively explained by deactivation of monomers by solvent impurities and remaing traces of moisture or by differences in reactivity between aliphatic core and aromatic monomer.

Table 3. Results of a Series of Copolymerizations Carried Out in Bulk, Using Various Fractions x_{AB} of the Monomer 3BCl in Combination with 35BCl

	DB_{pl}[a]	x_{AB}	DB_{ex}[b]	M_w[c]	M_n[c]	M_w/M_n[c]
P_B00	0	1[d]	0	14300	6950	2.06
P_B10	0.1	0.94	0.11 ± 0.05	11500	8400	1.37
P_B20	0.2	0.87	0.18 ± 0.05	14600	6800	2.15
P_B25	0.25	0.83	0.24 ± 0.05	11500	5800	1.98
P_B30	0.3	0.77	0.34 ± 0.05	9800	5100	1.92
P_B35	0.35	0.71	0.33 ± 0.03	9700	4900	1.98
P_B40	0.4	0.62	0.39 ± 0.03	8900	4200	2.12
P_B45	0.45	0.48	0.47 ± 0.03	9600	4600	2.09
P_B50	0.5	0[e]	0.51 ± 0.03	5900	2900	2.03

[a] Planned DB according to eq 2. [b] DB determined by IG ^{13}C NMR. [c] Determined by SEC-LALLS in DMF/GHC. [d] Linear homopolymer. [e] Hyperbranched homopolymer.

Possible differences in reactivity between aliphatic core and aromatic monomer were evaluated by using the two core molecules (B3-OH) and (B3-Si), whose chemical structure possesses similarity to the aromatic AB_2 monomer 35BCl. As discussed before, molecular weights were considerably higher than the theoretical values due to partial deactivation of the core molecules. In contrast to the samples with TMP as a core molecule, the samples B-P_{SMA}(1) and BSi-P_{SMA}(1) showed only a very small second distribution mode. This can be explained by the similar reactivity of core molecule and AB_2 monomer. The obtained polydispersities are relatively low.

According to theory,[7,17] the slow addition method should lead to an enhanced value for the DB (in the ideal case 0.66 for AB_2/B_3 systems) in comparison to a random bulk polymerization of AB_2 monomers (maximum DB value 0.5). In this work, we are able to demonstrate that this is actually observed experimentally (cf. Table 2). Clearly to be seen, the measured DB of all hyperbranched homopolymer samples prepared by slow monomer addition (0.61−0.66) is enhanced in comparison to the samples synthesized in random bulk polymerizations (cf. Table 3, sample P_B50), corresponding very well to the maximum value of 0.66 predicted by theory. In summary, the slow addition method leads to higher molecular weights and relatively low polydispersities in comparison to the random bulk polycondensation. The DB of all hyperbranched polyesters prepared by slow monomer addition was significantly enhanced.

B. Copolymerization. Surprisingly, copolymerization of branching AB_2 monomers with linear comonomers has hardly been investigated to date although this can represent an interesting approach to lower the cost of hyperbranched polymer-based materials. In AB/AB_2 copolymers five different modes of monomer incorporation are possible. IG ^{13}C NMR (inverse gated decoupling) was used to determine the degree of branching DB of the different copolymers, using previously derived expressions.[6] The signal assignments for the three incorporation modes *T*, *L*, and *D* were based on previous work by Fréchet et al.[4] The signal assignments for the two possible incorporation modes of AB units, L_l and L_t, were obtained by comparison of the ^{13}C NMR signals of the series of copolymers. The DB was determined by integration of the signals of the five different modes of incorporation of the AB_2 and AB monomer units in the copolymers (T, L, D, L_l, and L_t units), using the previously derived eq 3:

$$DB = \frac{2D}{2D + L + L_l} \tag{3}$$

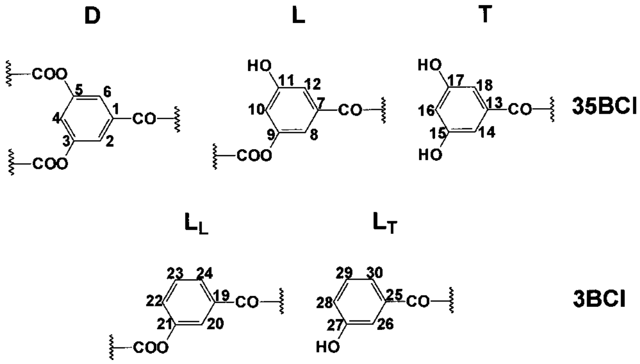

Figure 4. Numbering of the carbon atoms for the assignment of the ^{13}C NMR spectra.

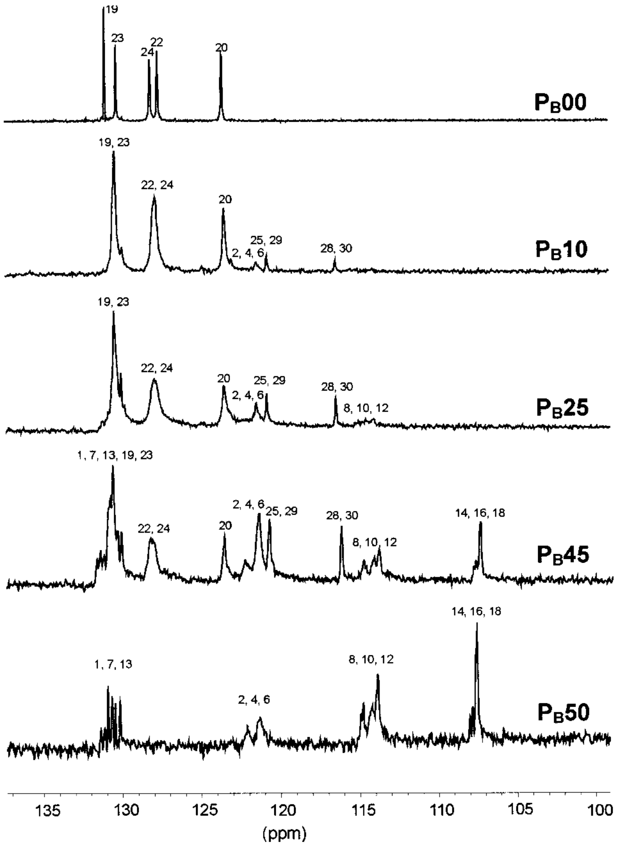

Figure 5. Inverse gated ^{13}C NMR spectra of the copolyesters prepared in bulk with detailed signal assignment.

Figure 5 shows the ^{13}C NMR-spectra of five copolyesters of different composition synthesized in bulk copolymerizations. All signals could be assigned in detail. Determination of the DB via integration of the respective signals in the IG ^{13}C NMR spectra resulted in an error of ±0.03.

In previous synthetic work Kricheldorf et al. reported on the bulk polymerization of trimethylsiloxybenzoyl chlorides.[18] In contrast to this work, we aim at the synthesis of copolymers with controlled degree of branching. The monomer ratios *r* for the desired DB (0, 0.1, 0.25, 0.45, 0.5) were chosen according to eq 2.

Table 4. Results of the Copolymerization of Various Fractions x_{AB} of 3-BCl with 35BCl via the Slow Monomer Addition Method (SMA); B3-OH Was Generally Used as Core Molecule

	DB_{Pl}^{a}	x_{AB}	DB_{ex}^{b}	M_w^{c}	M_n^{c}	M_w/M_n^{c}
$P_{SMA}0$	0	1	0	97 000	52 000	1.87
$P_{SMA}10$	0.10	0.94	0.08 ± 0.05	127 000	61 000	2.08
$P_{SMA}20$	0.20	0.88	0.22 ± 0.05	61 000	46 000	1.32
$P_{SMA}25$	0.25	0.83	0.24 ± 0.05	40 000	30 000	1.35
$P_{SMA}30$	0.30	0.79	0.28 ± 0.05	37 000	23 000	1.61
$P_{SMA}35$	0.35	0.73	0.37 ± 0.05	56 000	38 000	1.48
$P_{SMA}40$	0.40	0.67	0.41 ± 0.05	47 000	39 000	1.21
$P_{SMA}45$	0.45	0.59	0.48 ± 0.05	140 000	65 000	2.16
$P_{SMA}50$	0.50	0.50	0.52 ± 0.05	90 000	56 000	1.61
$P_{SMA}60$	0.60	0.25	0.57 ± 0.03	55 000	35 000	1.57
$P_{SMA}67$	0.67	0^{d}	0.64 ± 0.03	160 000	75 000	2.12

[a] Planned DB according to eq 4. [b] DB determined by ^{13}C NMR. [c] Determined by SEC-LALLS in DMF/GHC. [d] Hyperbranched homopolymer.

The results summarized in Table 3 demonstrate that the measured degrees of branching of the copolymers (DB_{ex}) are in good agreement with the DBs expected from theory. This is a consequence of the similar reactivity of 3BCl and 35BCl. Molecular weights of the linear homopolymer P_B00 and of the hyperbranched homopolymer P_B50 were similar to the results of the bulk polymerization reported previously. The molecular weights of all copolymers (e.g., P_B10, P_B25, and P_B45) fit in the trend of the homopolymers. In summary, it should be noted that in all bulk polymerizations M_n was always lower than 10 000 g/mol. The low polydispersity of the polymers is caused by the characterization method SEC-LALLS, by which the fraction of higher molecular weight can be underestimated and lower molecular weights are overrated for values under 10 000 g/mol.

In pronounced contrast to the random one-pot polycondensation in bulk, the synthesis and preparation of hyperbranched polymers via the slow monomer addition method are based on a pseudo-chain-growth mechanism,[19] in which a given number of B_n-core molecules grows by slow addition of highly reactive AB_2 and AB monomers. For all copolymers described in the following text, on the basis of the results of the homopolymerization detailed in the previous section of this paper, B3-OH was used as the core molecule.

According to theory,[5,6] in the ideal case the advantages of this method are (i) low polydispersity depending on the functionality of the core B_n, (ii) higher molecular weights in contrast to the one-pot synthesis in bulk or solution, (iii) control of the molecular weight by the amount of added monomer, and (iv) and enhancement of the degree of branching above the maximum of 0.5 for the bulk polymerization to a maximum value of 0.66.

In a recent paper we have derived an equation that permits to predict the DB for the slow monomer addition-based copolymerization.[20] Thus, for a targeted DB, the molar fraction of linear comonomer can be calculated (eq 4):

$$x_{AB}^{SMA} = \frac{1}{2}\frac{3DB - 2}{DB - 1} \tag{4}$$

The experimental results shown in Table 4 for the AB/AB_2 copolymers confirm the advantages of the slow monomer addition. For all hyperbranched (co)polyesters narrow monomodal molecular weight distributions were obtained. Molecular weights were considerably higher than in the bulk polymerizations. M_n was generally close to 50 000 g/mol, the molecular weight targeted on the basis of the monomer/core ratio employed for all copolymerizations. The polydispersities were in the range 1.2−2.1, being very low for hyperbranched polyesters

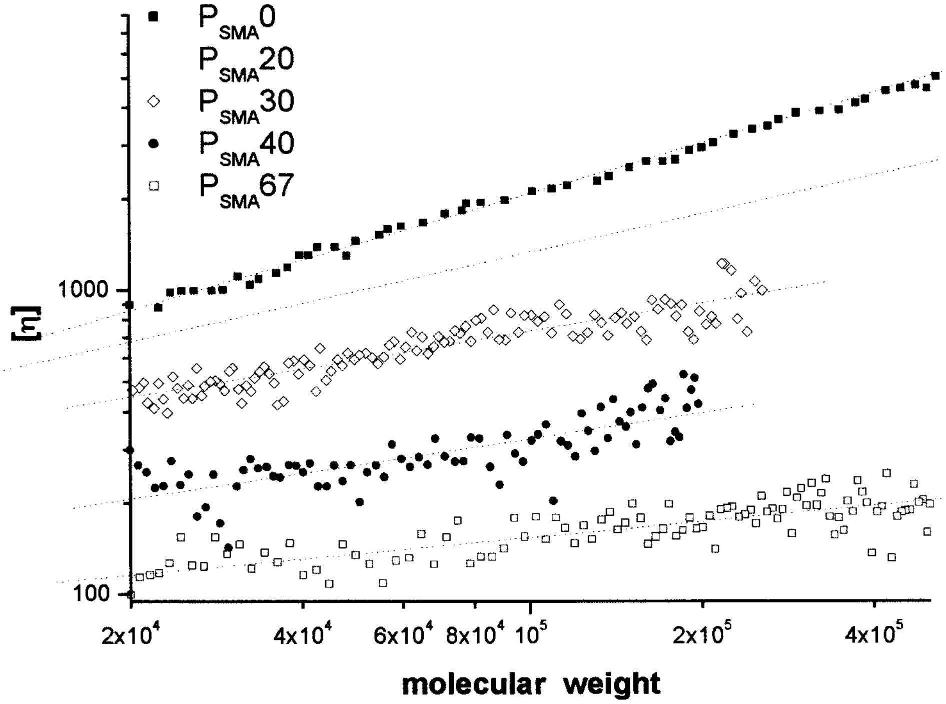

Figure 6. Mark−Houwink plot, showing the dependence of [η] on M_n for the samples $P_{SMA}0$, $P_{SMA}20$, $P_{SMA}30$, $P_{SMA}40$, and P_{SMA}-67 with respective linear fits; double-logarithmic axes.

Table 5. Mark−Houwink Constants α_{MH} and Degree of Branching DB of the Copolymers Prepared via the Slow Monomer Addition Method (SMA)

polymer	DB_{exp}	α_{MH}	polymer	DB_{exp}	α_{MH}
$P_{SMA}0$	0	0.55	$P_{SMA}40$	0.41	0.28
$P_{SMA}10$	0.08	0.47	$P_{SMA}45$	0.48	0.27
$P_{SMA}20$	0.22	0.43	$P_{SMA}50$	0.52	0.24
$P_{SMA}25$	0.24	0.32	$P_{SMA}60$	0.57	0.23
$P_{SMA}30$	0.28	0.31	$P_{SMA}67$	0.64	0.18
$P_{SMA}35$	0.37	0.3			

of such high molecular weight. As already observed in the homopolymerization case, the measured DB values were clearly enhanced in comparison to the values for the random bulk copolymerization of a given comonomer composition and were in agreement with the values calculated from eq 4. The Mark−Houwink parameter α_{MH} depends on the shape of a polymer in solution. Generally, the values of α_{MH} are in the range between 0 for hard spheres and 2 for rod-shaped structures. The intrinsic viscosity of the copolymers prepared was measured using an online viscosity detector. Using the data of the concentration-dependent SEC-UV detector and the viscosity detector, we were able to calculate a viscosity distribution. By combining this viscosity distribution with the molecular weight distribution, the Mark−Houwink relationship was obtained.

The dependence of the intrinsic viscosity on molecular weight for hyperbranched polymers has been a subject of controversial discussion in several reports.[21] We find a linear dependence in the Mark−Houwink plot for all hyperbranched homo- and copolyesters prepared. This is exemplified by Figure 6 for DB = 0, 0.20, 0.30, 0.40, and 0.67. The slope of the log [η] vs log M lines clearly depends on the copolymer composition and decreases with increasing DB, as expected from theory.

Thus, the Mark−Houwink constants α_{MH} for the hyperbranched copolyesters, listed in Table 5, are determined by the DB and are in the range 0.55−0.18 (for the highest DB, 0.64), indicating an increasingly compact structure with increasing DB (Table 5). This is illustrated in Figure 7 which shows the correlation between the DB and α_{MH}.

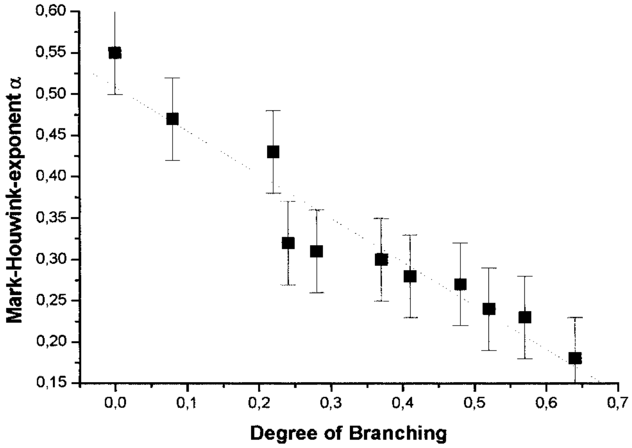

Figure 7. Dependence of the Mark−Houwink coefficient α_{MH} on the degree of branching DB in the series of hyperbranched aromatic copolyesters.

Conclusions

Hyperbranched aromatic homo- and copolyesters based on the AB_2 monomer 3,5-bis(trimethylsiloxy)-benzoyl chloride and the AB monomer 3-(trimethylsiloxy)benzoyl chloride have been prepared by random polycondensation in bulk as well as via the slow monomer addition procedure. In the latter case, the DB for the homopolymers was found to be enhanced up to 0.61−0.66, in agreement with theoretical predictions.

Hyperbranched copolymers with tailored DB could be prepared by copolymerization with the AB comonomer 3-(trimethylsiloxy)benzoyl chloride. Copolymerizations have been carried out both in bulk and in the slow monomer addition mode. In contrast to the bulk copolymerization, considerably higher molecular weights and low polydispersities as well as enhanced DB could be achieved by the slow monomer addition strategy. Viscosimetry measurements revealed a linear dependence of the intrinsic viscosity on molecular weight as well as decreasing Mark−Houwink exponents α_{MH} with increasing DB, pointing to an increasingly compact structure. A remarkably low Mark−Houwink exponent of only 0.18 was obtained for the hyperbranched homopolymer prepared under SMA conditions. Further work concerning the correlation of physical properties of the hyperbranched copolymers with the DB is in progress.[22]

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