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Hyperbranched Polymers Prepared via the Core-Dilution/Slow Addition Technique: Computer Simulation of Molecular Weight Distribution and Degree of Branching

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ABSTRACT: A novel synthetic procedure for the preparation of hyperbranched polymers with narrow molecular weight distribution and enhanced degree of branching (DB) has been studied, using computer simulation to model the kinetics of the process. Slow addition of AB_m monomers to B_f core molecules in solution ("core-dilution/slow addition technique") can be used to prepare hyperbranched polymers in a controlled manner, provided the coupling reaction $B_f + AB_m$ to B_{f+m-1} is rapid and quantitative. The computer simulation is based on random addition of AB_m monomers to B-functionalities of the B_f core molecules for $m = 2$, 3 and f ranging from 2 to 12, excluding sterical constraints. It is shown that this synthetic strategy permits one to (i) control molecular weights, (ii) lower polydispersity, and (iii) enhance the DB of the resulting hyperbranched polymers. In the ideal case (AB_m molecules react only with core B-functionalities and not with other AB_m monomers) narrow molecular weight distributions are obtained, ranging from $M_w/M_n = 1.33$ to 1.08 for $f = 3$ and $f = 12$, respectively; i.e., polydispersities are controlled by the core functionality f. Obviously, for $m = 2$ the polydispersity for the core-dilution/slow addition process obeys the expression $M_w/M_n = 1 + 1/f$. The DB obtained from the simulation is $^2/_3$ for $m = 2$ and $^3/_5$ for $m = 3$, in excellent agreement with recent theoretical predictions, showing that DB = $m/(2m - 1)$ for slow addition of AB_m monomers (*Acta Polym*. **1997**, *48*, 298). Also, the nonideal case is considered, when AB_m monomers form new core molecules B_m in the course of the reaction due to deactivation of the reactive A-function. In this case bimodal distributions are obtained.

Introduction

Polymers with a treelike structure (cascade polymers) are eliciting rapidly increasing interest. Such macromolecules, also termed "multibranched" or "dendritic" polymers, are non-cross-linked and in contrast to linear macromolecules possess a large number of branching points and endgroups.[1−4] Cascade polymers comprise the structurally perfect (or close to perfect[2]) dendrimers as well as hyperbranched polymers.[3,4] Whereas dendrimers have to be prepared in a stepwise synthetic "algorithm", hyperbranched polymers are conveniently obtained in one synthetic step via a random one-pot polymerization of multifunctional monomers of the AB_m-type, which represents an advantage in view of potential applications. In most cases reported to date, AB_2 monomers have been used, but some AB_3 monomers are also known.[5,16] As already shown by Flory, random polymerization of such monomers leads to extremely broad molecular weight distributions.[6] Molecular weights and polydispersity of the hyperbranched polymers obtained are essentially determined by conversion as well as monomer functionality m. Syntheses for various hyperbranched polymer topologies have been developed, e.g., hyperbranched polyesters,[7−9,17,30] polyphenylenes,[10] polyethers,[11] poly(ether ketones),[12] polyurethanes,[13,14] and polycarbosiloxanes[5a,15] as well as polycarbosilanes[16] have been described. Whereas dendrimers are maximum-branched polymers constructed from fully reacted (i.e. "dendritic") and unreacted ("terminal") AB_m units, hyperbranched polymers formed by a random polycondensation-type of reaction are highly, but not perfectly branched structures. Topologically speaking, hyperbranched polymers possess at least two branching points and exactly one focal point unit clearly distinguishable from the end groups. The branching perfection of hyperbranched polymers can be characterized by the degree of branching (DB), which is 0 for a linear polymer and 1 for a perfect dendrimer per definition. The DB concept was introduced for AB_2 systems by Hawker and Fréchet.[17] Commonly, the DB is determined by NMR spectroscopy on the basis of low molecular weight model compounds, which possess structures similar to the linear, dendritic, and terminal units in the respective hyperbranched polymers. The DB is obtained by comparison of the intensity of the signals for the respective units in the hyperbranched polymers. In addition to NMR, degradative methods have also been used to determine the DB.[18] However, it should be mentioned that the definition proposed by Hawker and Fréchet[17] does not lead to DB = 0 for a strictly linear structure. Recently, we have developed a systematic definition of the DB[19] for AB_m monomers in general, based on the number of actual growth directions in comparison to the maximum number of possible growth directions for a given number of monomer units. We have been able to show that the DB in case of equal reactivity of all m B groups, i.e., in case of a random polymerization of AB_m monomers is $[(m - 1)/m]^{m-1}$ at complete conversion (e.g., DB = $^1/_2$ for $m = 2$ and $^4/_9$ for $m = 3$). This value is independent of the presence of a core molecule B_f in the reaction. In subsequent work, we have discussed three methods that permit one to enhance the DB beyond this limiting value of a random polymerization of AB_m monomers:[20] (i) activation of the second B group of the AB_2 units after reaction of the first B group; (ii) polymerization of prefabricated perfect AB_w dendrons;[21] (iii) the slow addition procedure.

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A major drawback for the systematic investigation of structure–property relationships of hyperbranched polymers at present is the lack of control over molecular weight (degree of polymerization, DP_n), polydispersity (PD), and the DB. For instance, it would be desirable to control the molecular weight, keeping the polydispersity low and the DB constant or varying the DB, while keeping molecular weights constant.

The slow addition method has already been considered in recent theoretical work by our group.[20] Continuing our efforts in this area, in the current work we analyze a novel synthetic technique for hyperbranched polymers with narrow polydispersity, designated the core-dilution/slow addition method, which is based on the following prerequisites in the AB_2 case: (i) To a given concentration of core molecules B_f are added the AB_2 monomers slowly in high dilution. Thus, in the reaction mixture the concentration of B groups belonging to AB_2 monomers is always by orders of magnitude smaller than the concentration of B_f molecules (or B_n macromolecules in the course of the reaction, respectively). Furthermore, (ii) the coupling reaction between B_f and AB_2 leading to B_{f+1} ($=B_n$) is rapid and quantitative. Conditions i and ii lead to preferential growth of a given number of B_n macromolecules, reaction between two AB_2 monomers being highly unlikely. Also, in contrast to the random polycondensation of AB_2 monomers, coupling reactions between growing hyperbranched polymer molecules cannot occur.

In the current paper, we summarize the results of extensive computer simulation studies on this synthetic strategy, focusing on the effects of a variation of the basic parameters core functionality f, monomer functionality m, and monomer/core ratio $n(AB_m)/n(B_f) = X$ on molecular weights, molecular weight distributions, and the DB of the resulting polymers. It should be emphasized that the simulation is based on a random polymerization process, neglecting excluded volume effects as well as differences in the reactivity of the B-functionalities. We will show that this core-dilution/slow addition procedure results in considerable narrowing of the molecular weight distribution as well as enhanced values of the DB, in agreement with recent theoretical predictions.[20] In addition, we also consider the nonideal case, when a fraction of the AB_m monomers is deactivated in the course of the reaction to form B_m-core molecules.

Simulation Method and Program Algorithm

The simulation algorithm is based on the following prerequisites: A given number $n(B_f)$ of core molecules B_f ($50 < n(B_f) < 100$) with a defined number of functional groups f is selected. A predetermined number $n(AB_m)$ of AB_m monomers (the results for $m = 2$ and 3 are summarized in the current paper) is then added to the core molecules one after another. In the program, $n(B_f)$ and $n(AB_m)$ are only limited by the time required for the calculations. In dependence on computer performance, simulation of one specific polymer system, e.g., 50 B_3 cores and 5000 AB_2 monomers, required between 20 and 35 h, when this procedure was carried out 5000 times (i.e., the number of iterations was set to 5000).

The added monomer can be linked to every B function of every core molecule with the same probability. The address of the B-functionality, at which the added AB_2 monomer unit reacts is generated by a random function. Each added AB_m monomer raises the total number of available functionalities of the cores by $m - 1$; e.g., in the case of AB_2 the number is increased by 1. This procedure is repeated for every newly added monomer. The system-supplied function of DELPHI (Random) and as control the well-documented functions Ran1 and Ran3[22] were used as random number generators. No significant deviations were obtained in dependence of the used random function. Therefore the quickest function Random was used for most of the calculations. The start parameters, which can be varied in the simulation program for every run are as follows: (i) the number of cores $n(B_f)$; (ii) the functionality of the cores f; (iii) the number of monomers $n(AB_m)$; (iv) monomer functionality m; (v) the monomer mass; (vi) the number of iterations.

If the simulation is carried out in the described manner, it describes an ideal experiment, where all added monomers react with the growing molecules B_n only. This means that the total number of macromolecules remains constant; i.e., $X + 1 = DP_n$ (average number of monomers per core + core molecule).

The modified algorithm for the nonideal case described in the second part of this paper includes the possibility that the reactive function A of an added monomer AB_m is deactivated. In this case, this monomer cannot react with the available core B functionalities but represents a new B_m core which may start growing itself. To take this into account, a probability factor is introduced that determines which fraction of the AB_m monomers is deactivated and forms new B_m core molecules. The deactivation probability of an AB_m-monomer is referred to as probability of deactivation $P(da)$. Thus, in this simulation mode, which includes the possibility of deactivation of the A groups, a fraction of $P(da)$ of the AB_m monomers is deactivated randomly upon addition to the reaction mixture, representing new B_m cores in the further course of the reaction.

The following parameters are calculated for the ideal case (no deactivation, $P(da) = 0$) as well as the nonideal case ($P(da) > 0$), based on the given parameter set f, m, $n(B_n)$, and $n(AB_m)$: After addition of all monomers, the simulation program calculates (a) the molecular weight averages M_w and M_n; (b) the polydispersity $PD = M_w/M_n$; (c) the molecular weight distribution which is plotted in various forms (e.g. linear or logarithmic) according to the settings chosen by the operator; (d) the DB according to the definition of Hawker and Fréchet[17] (DB′) and the recent general definition of our group;[19] (e) the molecular weight dependence of the DB; (f) the DB average for the whole distribution; (g) the core distance distributions of the dendritic, linear, and terminal units; and (h) the core distance distribution of the monomer units, which in some cases yields information on the segment density distribution of the polymer.

Results and Discussion

A. AB_2 Monomers. We will consider an ideal system without deactivation first, where a definite number $n(AB_2)$ of AB_2 monomers is slowly added to $n(B_f)$ core molecules with functionality f. For all ensuing calculations the mass of the monomer unit as well as the mass of the core molecule is arbitrarily set to 1; thus, the molecular weight M_n of the hyperbranched polymer is equal to the degree of polymerization (DP_n). The calculated DP_n includes the core molecule; thus, a molecule consisting of, e.g., one B_3 core and two AB_2 monomers possesses a DP_n of 3 and therefore a molecular weight of 3.

In the ideal case, excluding formation of new cores during addition of the AB_2 monomers, the number of core molecules $n(B_f)$ is equal to the number of macromolecules formed eventually. Obviously, if $n(B_f)$ is 1, one hyperbranched polymer molecule is formed; therefore, the polydispersity is 1. With increasing value $n(B_f)$, the polydispersity increases and reaches a limiting value dependent on the chosen parameters above a core number of 30. This is clearly shown in Figure 1a for a B_3 core. In the range of $n(B_f) = 35–50$, a similar result was obtained for different X values (X range: 20–120). The standard deviation σ for the polydispersity was

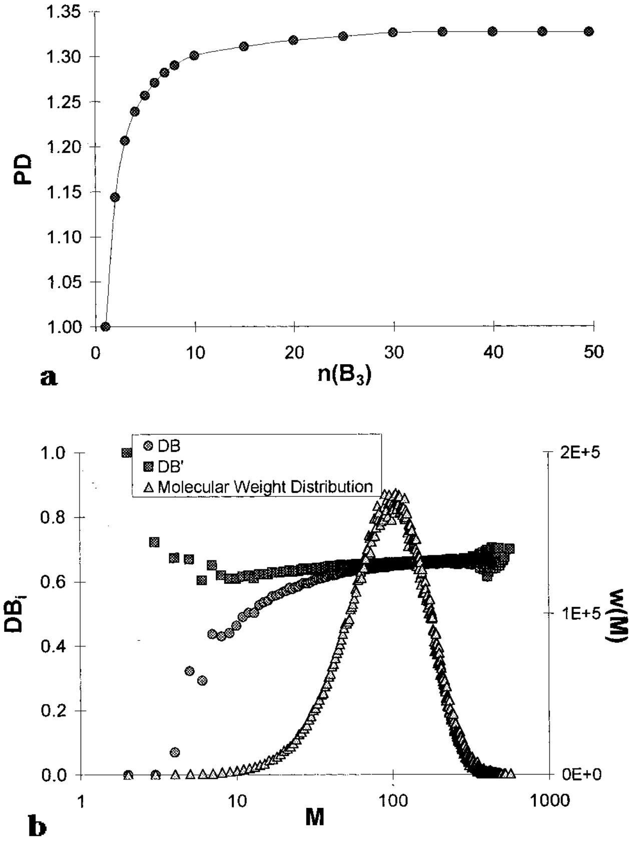

Figure 1. (a) Polydispersity PD vs number of core molecules B_f (in this case B_3), showing that above 30 core molecules the PD approaches a limiting value. Similar observations were made for higher values of *f*. (b) Typical molecular weight distribution as obtained in the computer-simulated core-dilution/slow addition procedure and corresponding DB_i' as well as DB_i values. DB_i is the DB of the respective monodisperse slices of the molecular weight distribution.

smaller than 0.003 in all cases. On the basis of this observation, for all simulation experiments $n(B_f) > 40$ was chosen in order to obtain statistically significant results.

Figure 1b demonstrates the result of one typical simulation run for a specific parameter set. In this case 5000 AB_2 monomers ($n(AB_2) = 5000$) were added to 50 B_3 cores ($n(B_f) = 50$; $X = 100$). Figure 1b shows the resulting molecular weight distribution of the system after addition of all AB_2 monomers. In this simulation, a polydispersity of 1.328 was obtained. A typical general feature of the molecular weight distributions obtained from the simulation of the core-dilution/slow addition process is the slight asymmetry of the molecular weight distribution, which exhibits a “tailing” to lower molecular weights.

The simulation program also permits to calculate the degree of branching (DB) of the hyperbranched polymers formed on the basis of the terminal (T), linear (L), and dendritic (D) units present. The DB′ according to the definition of Hawker and Fréchet[17] (DB′) is given by

$$\mathrm{DB}' = \frac{\mathrm{D} + \mathrm{T}}{\mathrm{D} + \mathrm{L} + \mathrm{T}} \tag{1}$$

We have recently shown, that a more general definition for the DB in AB_2 systems is given by[19]

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

DB′ and DB are properties of the whole molecular weight distribution of a hyperbranched polymer. Therefore, in the following, we designate the degree of branching of a monodisperse slice of the molecular weight distribution with DB_i. Figure 1b illustrates the dependence of DB according to both definitions (DB and DB′) on the molecular weights of the hyperbranched polymers formed, represented by DB_i. As is clearly seen in Figure 1b, DB′ and DB differ considerably at low molecular weights. The DB according to our recent definition assumes a value of 0 for low molecular weights and then slowly increases with increasing molecular weight, until it finally reaches its limiting value at DP_ns above 50. The DB′ possesses a value of 1 at low molecular weights and decreases with increasing molecular weight, reaching a minimum value at a DP_n of approximately 10. Subsequently, the DB′ increases slightly and also approaches the same plateau value as DB at higher molecular weights. This dependence of the DB′ and DB on molecular weight confirms recent conclusions by our group[19,20] as well as Möller et al.[23] that DB′ according to expression 1 leads to an overestimation of the branching perfection at low molecular weights, which is the most likely explanation for DB values exceeding the limiting value of 0.5 for a random AB_2 polymerization in the current literature. In recent work we have shown that for slow AB_m monomer addition (“sequential addition, abbreviated sa”) enhanced DB values are obtained,[20] described by expression 3. The DB′ values obtained from the simulation (Figure 1b) at high molecular weights are slightly higher (about 0.665) than that of DB (about 0.660); however, both values for the DB obtained from the simulation are in excellent agreement with our theoretical predictions[20] of DB = ²/₃ for $m = 2$, evidencing that the DB can be enhanced from 0.5 to 0.66 via the slow monomer addition procedure.[33] It should be mentioned, however, that close inspection of the numeric values of the DBs reveals that both degrees of branching do not reach their limiting value for the given DP_n; even at DP_ns above 200, the values increase slightly with the DP_n. The large scattering of the DB values at very high DP_ns seen in Figure 1b is due to statistical limitations, because very large macromolecules are rarely produced. For instance, a polymer molecule with DP_n of 494 was only produced once within 5000 iteration steps, while a macromolecule with a DP_n of 90 was produced 1579 times, leading to a statistically significant average DB value. Thus, 5000 iterations are insufficient to obtain a reliable value above a DP_n of 300, if $X < 100$.

$$\mathrm{DB}_{\mathrm{sa}} = \frac{m}{2m - 1} \tag{3}$$

On the basis of these results, in the following we will calculate the degree of branching using our recent definition (eq 2), i.e., DB. If the definition according to eq 1 is employed, DB′ will be used to specify this.

(i) Dependence of the Polydispersity and the DB on $n(AB_m)/n(B_f) = X$. Considering an ideal case (i.e. excluding deactivation; $P(da) = 0$), the ratio $X + 1$ (adding the core molecule) is equal to the number average degree of polymerization DP_n and M_n, if the weight of a monomer unit is set to 1. The following results describe the dependence of the molecular weight distribution after complete monomer addition on the DP_n. As expected, the molecular weight distributions shift to higher molecular weights with increasing ratio

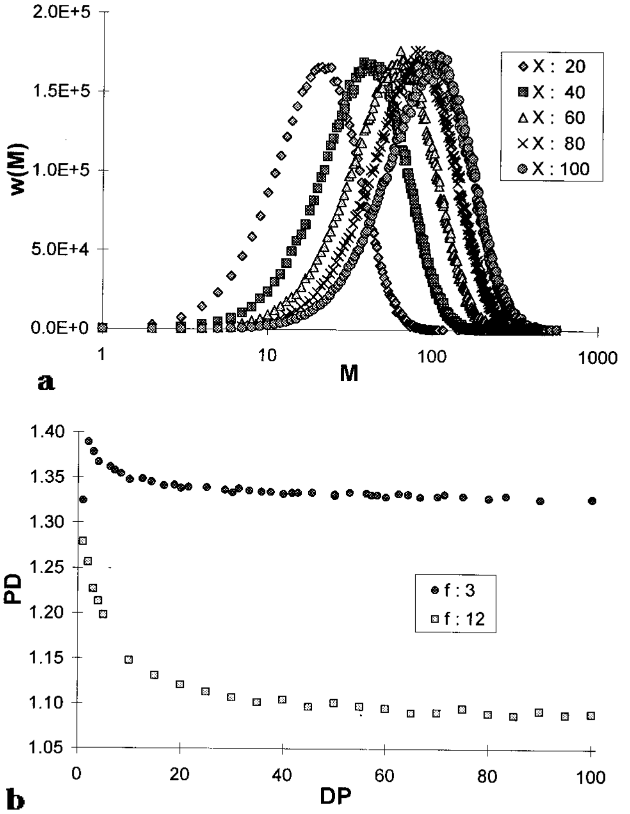

Figure 2. (a) Molecular weight distributions for various ratios $X = n(AB_2)/n(B_3)$. (b) Polydispersity vs DP_n for the AB_2 system with B_3 and B_{12} core molecules, respectively, as obtained from the simulation.

$n(AB_m)/n(B_f) = X$. This is illustrated in Figure 2a, which shows five superimposed molecular weight distributions with different ratios X. As is clearly seen, a slow addition procedure in this ideal case permits one to control the molecular weights of the resulting hyperbranched polymers. Furthermore, the typical asymmetry of the molecular weight distribution discussed before is observed for all ratios X.

Figure 2b shows the dependence of the polydispersity $PD = M_w/M_n$ on the DP_n for two different core functionalities $f = 3$ and $f = 12$. For $DP_n = 1$, obviously the polydispersity is 1 (not shown in Figure 2b). Thus, at low values of DP_n the polydispersity must increase with increasing degree of polymerization. In the figure this is only illustrated for the core functionality $f = 3$, where the polydispersity for $DP_n = 2$ is significantly lower than for $DP_n = 3$. At a DP_n of 3, the polydispersity reaches a maximum and then decreases to a limiting value. In principle the behavior for a core functionality of 12 is similar; however, since DP_n values below 2 were not considered in the figure, the increase in the polydispersity at low DP_n is not depicted. The threshold value of the polydispersity for $f = 12$ is approximately 1.08 and therefore considerably lower than that for $f = 3$, in which case a limiting value of 1.33 is obtained. The correlation between f and the polydispersity will be discussed in detail below in section ii. Table 1 summarizes the polydispersities obtained for different ratios X for $f = 3$ and $f = 12$ ($P(da) = 0$, columns 1 and 4).

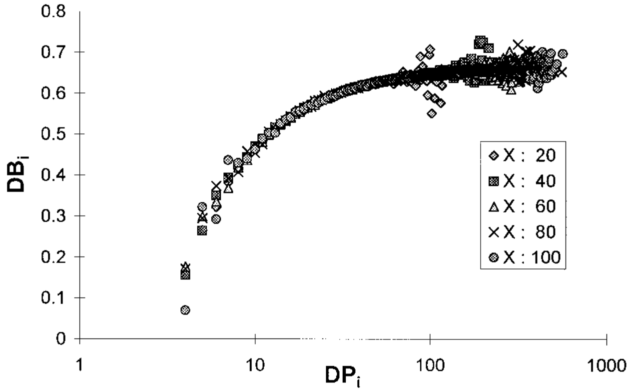

Figure 3. DB_i for various ratios $X = n(AB_2)/n(B_3)$ vs DP_n.

Figure 3 illustrates the molecular weight dependence of the DB for hyperbranched polymers for $f = 3$ and varying ratios X. It should be mentioned that the DBs shown are not the DBs of the whole distributions but are the values (DB_i) of each monodisperse slice within the corresponding molecular weight distribution. As already mentioned shortly, the DB increases with increasing molecular weight and eventually reaches a value of 0.66 at high molecular weights, which is in excellent agreement with theory.[20] Apart from the different molecular weight ranges of the hyperbranched polymers due to different average DP_ns, it is obvious that variation of the ratio X does not affect the DB_i.

In Table 1 (lines 1 and 4) the corresponding DBs are listed, which are averages over all DB_i values within one distribution. Due to the large number of high molecular weight polymers formed with high DB_i values, the DB average values increase slightly as X increases.

(ii) Dependence of Polydispersity and DB on Core Functionality *f*. It is an intriguing question, in which way an increase of the core functionality f will affect the polydispersity as well as the DB of the hyperbranched polymers formed. As is clearly seen in

Table 1. Polydispersities of Hyperbranched Polymers Prepared via the Core-Dilution/Slow Addition Procedure, in dependence on the Core Functinoality *f* and the Ratio $X = n(AB_2)/n(B_3)$[a]

	$f = 3$			$f = 12$		
X	$P(da) = 0.0\%$	$P(da) = 1.0\%$	$P(da) = 2.0\%$	$P(da) = 0.0\%$	$P(da) = 1.0\%$	$P(da) = 2.0\%$
10	1.348	1.413	1.489	1.148	1.223	1.301
20	1.338	1.503	1.681	1.121	1.300	1.444
30	1.334	1.608	1.860	1.107	1.367	1.615
40	1.332	1.727	2.040	1.105	1.458	1.800
50	1.330	1.827	2.230	1.101	1.555	1.980
60	1.329	1.957	2.441	1.095	1.644	2.123
70	1.330	2.059	2.665	1.091	1.738	2.303
80	1.328	2.187	2.843	1.089	1.825	2.475
90	1.326	2.275	3.019	1.093	1.934	2.633
100	1.328	2.375	3.146	1.090	2.022	2.803

[a] The probability of deactivation $P(da)$ is varied between 0 and 2% (given in %).

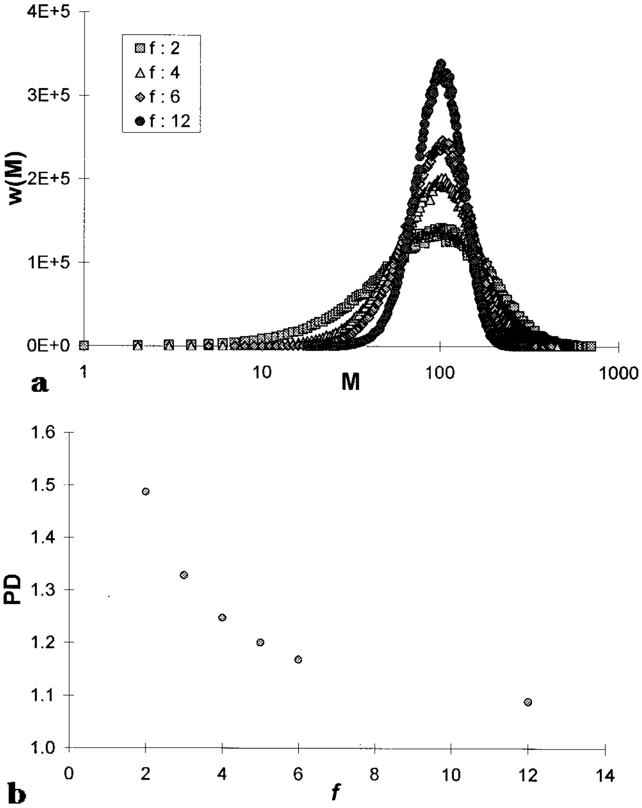

Figure 4. (a) Molecular weight distributions of AB_2-system with B_f core for $f = 2-12$. (b) Polydispersity of AB_2-system vs core functionality f, demonstrating that increasing core functionality leads to decreasing polydispersity.

Figure 2b, enhancement of f leads to a decrease of the polydispersity. Figure 4a. shows the effect of an increase of the core functionality f on the molecular weight distribution (calculated on the basis of 5000 runs, core number = 50, $X = 100$). With increasing f, the molecular weight distributions show considerable narrowing, while the maxima of the distributions remain at the same DP_n. Consequently, the polydispersity decreases as f increases. Polydispersity values below 1.1 can be reached with a core functionality of 12. It should be noted at this point that the values of the polydispersity obtained from the simulation (summarized in Table 3) obviously can be described by the expression

$$PD = 1 + 1/f \tag{4}$$

Interestingly, expression 4 was derived by Schulz[24] long ago for the formation of star polymers obtained via a random one-pot copolymerization of B_f core molecules with AB monomers. Figure 4a,b demonstrate the decrease of the polydispersity with increasing f. Thus, it can be concluded that the core-dilution/slow addition procedure permits one to control the polydispersity via the functionality f of the core molecule B_f.[33]

As the polydispersity can be lowered by enhancing the core functionality f, it is an important question whether the DB will also be affected. When the core functionality f is varied from 3 to 12, the DB has been calculated to be in dependence on the molecular weight. The simulations show that the DBs (Table 3) decrease slightly with increasing core functionality. Furthermore they increase with increasing DP_n, always reaching a limiting value close to $^2/_3$ for high DP_ns above 200. Figure 5a reveals that for $f = 3$ the limiting value for the DB is reached approximately at DP_ns above 80, whereas in the case of $f = 12$ this value is only reached at considerably higher molecular weights. The higher the core functionality, the higher is the DP_n, at which the threshold value for the DB is reached. It should be kept in mind that the DB, however, per definition does not include the core molecule, as it is difficult to verify the number of actually reacted core functionalities. Nevertheless, we have shown in a recent theoretical paper that the core has no significant effect on DB at higher molecular weights.[19] The slower increase of the DB for increasing core functionality f can be explained by the fact that per definition the DB is calculated for every branch extending from the core of the hyperbranched molecule. Thus, the limiting value for the DB in case of the core-dilution/slow addition strategy is only reached at higher molecular weights with increasing core functionality f, since the DP of the branches for a certain X decreases with increasing f. This is demonstrated in Figure 5b, where the degrees of branching (DB_i values) are plotted vs the DP_n.

The same plot (Figure 6) for the degrees of branching according to DB′ (eq 1) shows, however, only slight but also noticeable differences in the dependence on the core

Table 2. Numerical DB Values of Hyperbranched Polymers in Dependence on the Probability of Deactivation $P(da)$ (Given in %), Core Functionality f, and $X = n(AB_2)/n(B_3)$

	$X = 10$	$X = 20$	$X = 30$	$X = 40$	$X = 50$	$X = 60$	$X = 70$	$X = 80$	$X = 90$	$X = 100$
					$f = 3$; $P(da) = 0.0\%$					
DB′	0.625	0.634	0.642	0.647	0.650	0.652	0.654	0.655	0.656	0.658
DB	0.512	0.579	0.606	0.620	0.629	0.635	0.639	0.643	0.645	0.647
					$f = 3$; $P(da) = 1.0\%$					
DB′	0.623	0.635	0.643	0.647	0.649	0.651	0.654	0.654	0.655	0.656
DB	0.504	0.575	0.603	0.617	0.624	0.629	0.636	0.637	0.640	0.642
					$f = 3$; $P(da) = 2.0\%$					
DB′	0.624	0.634	0.641	0.647	0.648	0.650	0.652	0.653	0.655	0.656
DB	0.499	0.570	0.596	0.612	0.619	0.624	0.630	0.633	0.636	0.638
					$f = 12$; $P(da) = 0.0\%$					
DB′	0.682	0.637	0.625	0.626	0.628	0.630	0.632	0.634	0.637	0.639
DB	0.301	0.420	0.475	0.514	0.539	0.556	0.569	0.579	0.588	0.595
					$f = 12$; $P(da) = 1.0\%$					
DB′	0.687	0.636	0.627	0.625	0.628	0.630	0.633	0.634	0.637	0.639
DB	0.296	0.410	0.471	0.508	0.533	0.551	0.566	0.575	0.584	0.591
					$f = 12$; $P(da) = 2.0\%$					
DB′	0.688	0.637	0.628	0.626	0.629	0.629	0.631	0.634	0.637	0.638
DB	0.292	0.405	0.466	0.503	0.529	0.545	0.558	0.570	0.579	0.586

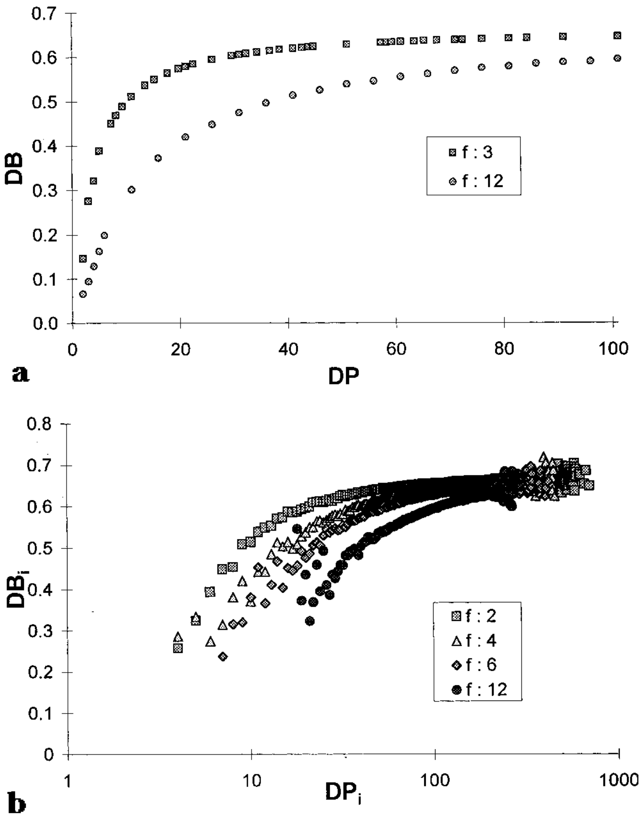

Figure 5. (a) Degree of branching DB vs DP_n for core functionality $f = 3$ and f = 12. (b) DB_i plotted vs DP_i for core functionality $f = 2-12$.

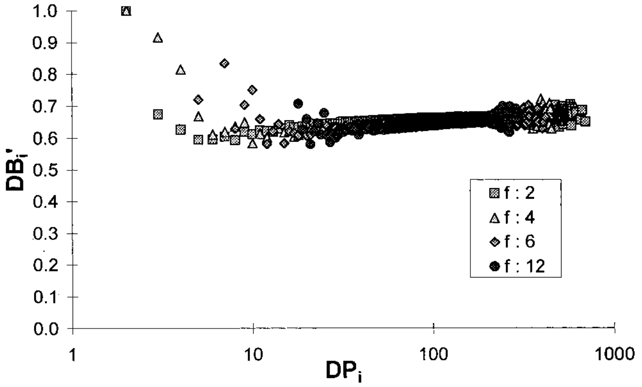

Figure 6. DB'_i plotted vs DP_i showing the development of DB′ with molecular weight for different core functionality *f*.

Table 3. Polydispersity and DB′ as well as DB in Dependence on the Core Functionality *f* ($X = 100$)

f	PD	DB′	DB
2	1.487	0.660	0.654
3	1.328	0.658	0.647
4	1.248	0.655	0.641
5	1.201	0.652	0.635
6	1.169	0.650	0.629
12	1.090	0.639	0.595

functionality. It is obvious that values considerably larger than the limiting value of $^2/_3$ are observed at low molecular weights.

(iii) Core-distance Distribution of Linear, Terminal, and Dendritic Units. It is long known from calculations for the Bethe lattice,[25,26] which is the simplest case of a perfectly branched AB_2 system with B_3 core, that at higher generations of branching the space required by the branching units on the surface of

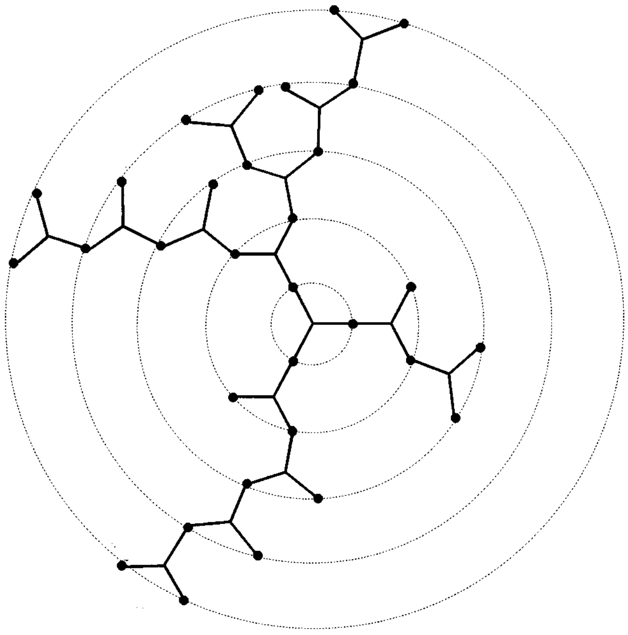

Figure 7. Schematic representation of a hyperbranched macromolecule with B_f core, based on AB_2 units, showing the "pseudo"-generations ($X = 14$, B_3 core molecule, DP = 15).

the structure exceeds the space actually available. This is also true for any kind of dendrimer like perfect structure with AB_m monomer units, where the number of units on the surface increases exponentially with m^g (g = generation), while the available surface only increases with R^2 (R = radius of spherical structure). As a result, in higher dendrimer generations the molecules approach the behavior of hard spheres, where the interior is increasingly shielded by a shell of densely crowded units on the surface. A density gradient from the molecular core to the endgroups is typical for the structurally perfect dendrimers. This leads to unusual physical properties of dendrimers, such as a decrease of the intrinsic viscosity $[\eta]$ in higher generations, when the molecules approach hard-sphere-like behavior.[27] Hyperbranched polymers are sometimes supposed to be globular macromolecules with structures similar to dendrimers. It is an intriguing question whether the hyperbranched polymers prepared via the core-dilution/slow addition procedure will show dendrimer like viscosity behavior. Furthermore, as already mentioned, our simulation neglects spatial constraints, such as sterical crowding or backfolding of polymer segments. This may affect the probability of reaction of functional groups, especially inside the molecule. It might be argued that shielding of functional groups from further reactions is proportional to the segment density within and especially at the surface of the hyperbranched macromolecule, which should result in a decrease of the DB above certain molecular weights.

To judge to which extent the molecular architecture is affected by sterical crowding in the slow addition process, information on the segment density (i.e. monomer unit density) in the macromolecule as well as on the molecular surface is required. A typical structure of a hyperbranched polymer molecule consisting of 14 monomer units is displayed schematically in Figure 7. The circles define the "pseudo"-generation number, which is the distance of a selected monomer unit from the core, expressed in monomer unit distances. This means a monomer unit in the "fourth generation" is

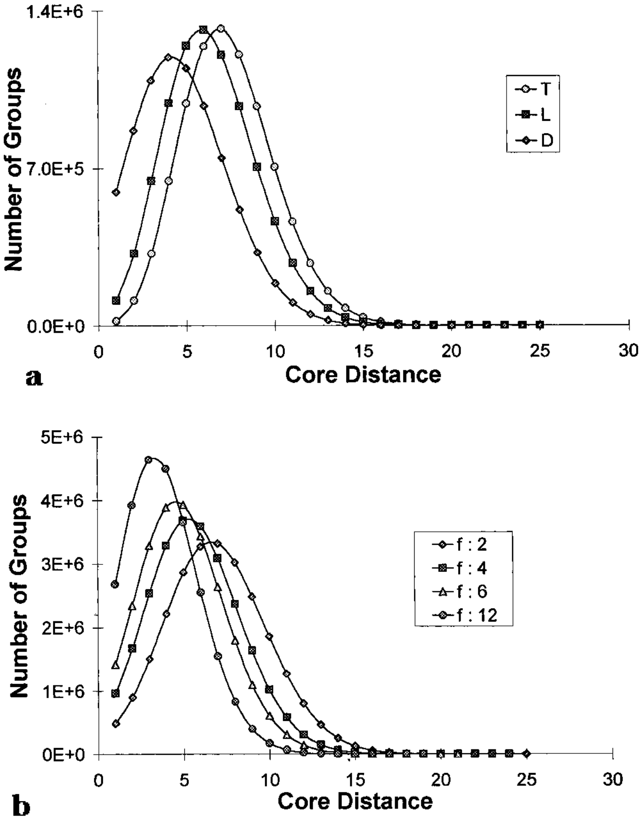

Figure 8. (a) Core-distance distribution of terminal (T), linear (L), and dendritic (D) groups in a hyperbranched polymer prepared via the core-dilution strategy. (b) Core-distance distribution of AB_2 units in hyperbranched macromolecules prepared by the core-dilution/slow addition procedure for different core functionalities $f = 2$ to $f = 12$.

linked to the core via three monomer units situated between core and the selected unit.

First insight into the structure of the simulated macromolecules is revealed by the core distance distributions of the linear (L), dendritic (D), and terminal (T) groups. This is exemplified for one system in Figure 8a ($X = 100$; $DP_n = 101$; $f = 3$). As expected, on average dendritic groups are closer to the core than linear groups, whereas terminal groups are located mostly at the periphery of the macromolecules. In comparison to the maximum distances (25 for *T*-units), the maxima of the three distributions (7 for T units) are situated relatively close to the core. This is quite different when compared with the behavior of perfect dendrimers, where the terminal groups, which represent about half of all units, are located at the surface, i.e., at the maximum distance. This result is a first indication that hyperbranched polymers are by no means as dense as dendritic structures, and the abovementioned steric restrictions are unlikely to play an important role.

Further information can be extracted from these calculations. If at each distance from the core the fractions of terminal, linear, and dendritic groups are summed up, a core distance distribution of all monomer units is obtained, which may help one to answer the question of sterical crowding due to a possible, in a generation-dependent manner, increasing segment density of the macromolecules.

Four core distance distributions with core functionalities *f* of 2, 4, 6, and 12, respectively, are superimposed in Figure 8b. Two important results are obtained: (i) the maximum of the distribution shifts toward smaller core distances, when the core functionality increases, and (ii) the maximum distance from the core decreases with increasing core functionality *f*. Neglecting possible size differences of the cores, these distributions are proportional to segment density distributions. In this case, our results indicate that the segment density of the hyperbranched polymer molecules increases with increasing *f*.

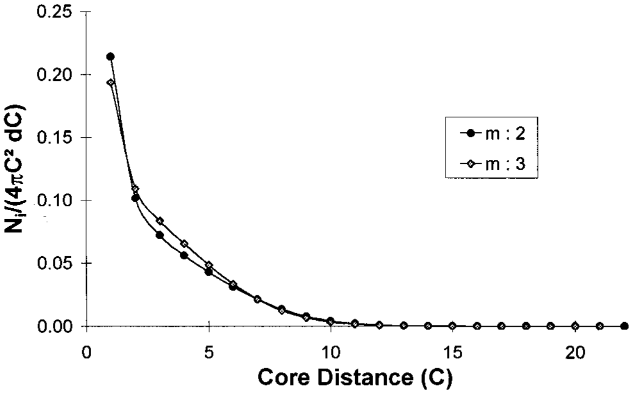

Figure 9. Number of units in the respective "pseudo"-generation divided by the available space in the respective pseudo-generation plotted vs the core distance *C*. Clearly, the segment density of the hyperbranched polymers decreases on going outwards from the core; N_i = number of monomer units per pseudogeneration.

If the number of monomers in each pseudogeneration is divided by the surface area available in the respective shell (assuming spherical geometry of the molecules), a one-dimensional density distribution of the monomer units within the molecule is obtained. This distribution (Figure 9) gives the average monomer unit density in dependence of the core distance along a one-dimensional axis. As the chosen distance unit is the distance between two adjacent generations, the maximum possible density value at a definite distance is 1. Figure 9 illustrates the density distributions for the cases of AB_2 and AB_3 monomers coupled to a B_3 core. The DP_n in this case was 101.

Figure 9 shows that the simulated hyperbranched polymer molecule is by no means a spherelike structure with a hard, i.e., sterically crowded shell. The maximum segment density is located directly at the core, i.e., not at the surface of the macromolecules. With increasing distance the monomer unit density decreases. Despite the slight differences in the behavior of the two different types of monomers ($m = 2$, 3) the general behavior is similar. Compared to the maximum possible segment density mentioned above, the absolute values are considerably lower, especially on the surface of the macromolecules. On the basis of our simulation, we conclude that the structural picture of a spherical structure with sterically crowded surface—like in the case of dendrimers—is not correct for these hyperbranched polymers.

On the basis our simulation data, we can also give an estimate of the fraction of the space in the respective pseudogenerations that is actually occupied by monomer units. If it is assumed that the volume of one monomer unit is $^4/_3\pi r^3$, where *r* is half of the distance between two adjacent generations, this allows one to estimate the space actually occupied by the monomer units in one pseudogeneration. It should be mentioned that this most probably overestimates the space actually required for a monomer unit. However, based on this prerequi-

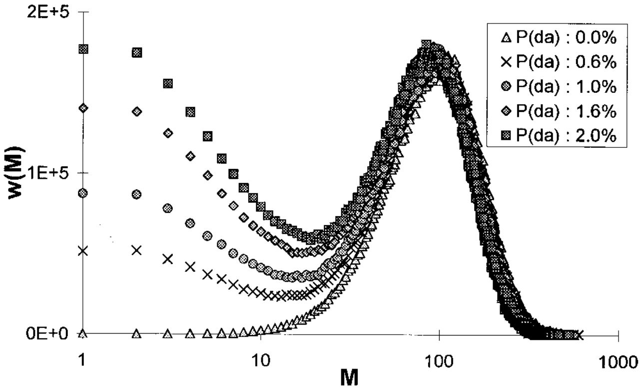

Figure 10. Molecular weight distribution of hyperbranched polymers, based on different deactivation probabilities $P(da) = 0{-}2.0\%$. A bimodal distribution is obtained.

site we find that only 3% of the available space is occupied in the fourth pseudogeneration and only 0.23% in pseudogeneration 10.

At this point, it should be emphasized that these conclusions from the simulation of the hyperbranched polymers obtained via the core-dilution/slow addition procedure can be extended to common hyperbranched polymers prepared in a random one-pot AB_2-polycondensation. In this case, a lower value for DB is obtained (0.5), and thus the macromolecules must possess a considerably less dense structure than hyperbranched polymers prepared via core-dilution/slow addition. Sterical overcrowding of the hyperbranched macromolecules in higher generations, which has been mentioned as a potentially important factor,[23] is therefore clearly not to be expected.

(iv) Simulation Results Including Deactivation of the Monomer A Group. For the core dilution/slow addition procedure highly reactive monomers are required in order to maintain rapid coupling and quantitative reaction. In most cases, the A group represents the highly reactive functionality, while the B groups are often less reactive functionalities. Examples of a reactive A group in combination with suitable, less activated B groups are numerous, e.g., the preparation of hyperbranched polyurethanes based on bishydroxyazides[28] as well as polyesters based on silylated 3,5-bisacetoxybenzoic acid.[29] Clearly, the most important side reaction when using such monomers for the core-dilution/slow addition procedure is deactivation of the A group of the newly added AB_2 monomer, preventing reaction of these monomers with the core. However, the remaining two B functions can still react with A functionalities of other monomers. Consequently, a deactivated AB_2 monomer behaves like a new B_2 core. If new core molecules are formed in the course of the reaction, the number of macromolecules $n(B_n)$ is no longer constant, but increases with increasing amount of monomer. In this case $X + 1$ is no longer equal to the degree of polymerization.

The probability for the occurrence of monomer deactivation is described by the parameter $P(da)$, which determines the fraction of added monomers that is deactivated. The effect of increasing $P(da)$ on the molecular weight distribution is demonstrated in Figure 10. (in the figure, $P(da)$ is given in %). Consideration of the deactivation leads to a separate second low molecular weight mode in the molecular weight distribution. The mass fraction of this second mode increases with increasing values of $P(da)$, leading to a bimodal distribution. Remarkably, the high molecular weight mode remains almost constant. There is only a slight shift toward lower molecular weights. As a consequence of the low molecular weight mode there is a significant decrease in the number average molecular weight M_n, whereas the weight average molecular weight M_w decreases only slightly. Therefore the polydispersities increase with increasing $P(da)$, which is documented in Table 1 for $P(da) = 1\%$ and 2%, respectively (rows 2, 3, 5, and 6).

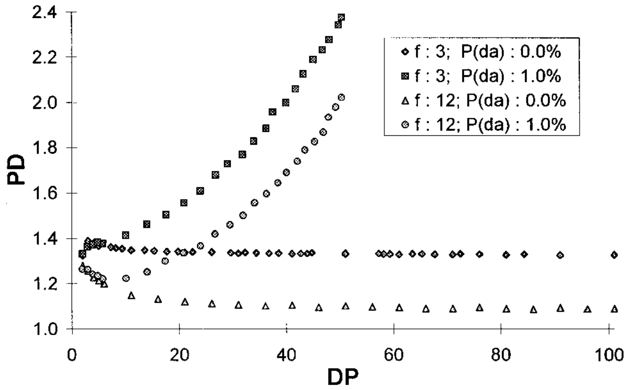

Figure 11. Polydispersity vs DP for $f = 3$ and $f = 12$; $P(da)$ is 0% and 1%, respectively.

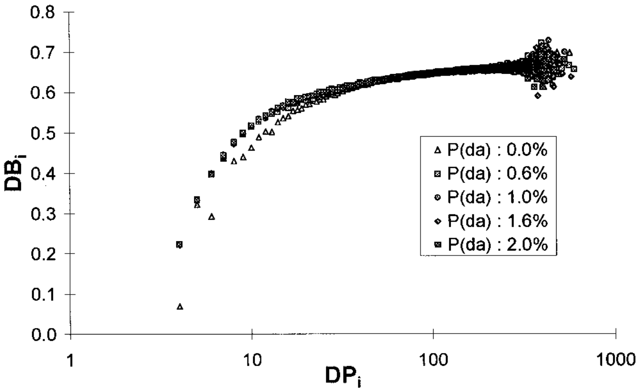

Figure 12. Degree of branching including deactivation ($P(da) = 0\%$ to 2%) vs DP. Clearly, deactivation up to 2% has little influence on the DB.

Furthermore, in contrast to the results obtained in sections i–iii, neglecting deactivation, the polydispersity increases at higher values of X. This is seen in Figure 11, where the polydispersities with ($P(da) = 0.01$, i.e., 1%) and without deactivation ($P(da) = 0$) are compared. The low molecular weight mode also induces a slight decrease of the DB average values (Table 2). This is caused by the higher amount of small macromolecules formed. As seen in Figure 12 the DB of small macromolecules is significantly lower than that of larger polymers. Therefore, if the amount of low molecular weight polymer increases, the DB decreases. It is further shown that at low DP_ns there are slight differences between the relationships for different probabilities of deactivation. This is explained by the change of the average core functionality. Initially, a definite number of B_3 cores are given. During the addition process, monomers are deactivated, and thus B_2 cores are formed. The DB, however, depends on the core functionality (section ii). Thus, we conclude that regardless of the strong impact of deactivation on molecular weight distribution and polydispersities, there are only small changes in the average degrees of branching.

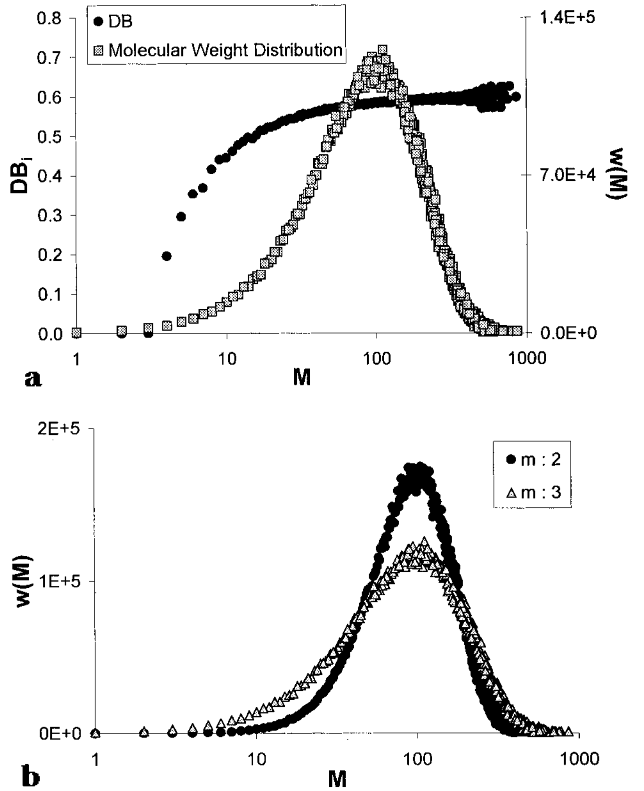

Figure 13. (a) AB_3 system: typical molecular weight distribution obtained from the computer simulation with respective DB. (b) Comparison of molecular weight distribution of AB_2 ($m = 2$) and AB_3 systems ($m = 3$).

This means that even at higher $P(da)$ high branching densities can be obtained.

B. AB_3 Monomer System. In the case of the AB_2 system three different kinds of units, i.e., terminal (T), linear (L) and dendritic (D) have to be considered. In the case of AB_3 monomers a fourth, semidendritic unit (sD) must be considered that has reacted only twice. As a result the calculation of the degree of branching differs from the AB_2 system, although defined analogously. The DB of an AB_3 system is calculated using eq 5,[19] which

$$\mathrm{DB} = \frac{2\mathrm{D} + \mathrm{sD}}{\frac{2}{3}(3\mathrm{D} + 2\mathrm{sD} + \mathrm{L})} \tag{5}$$

has been employed to determine the DB of hyperbranched carbosilane macromonomers recently, evidencing the random character of the hydrosilation type polymerization employed.[16] Theoretical calculations[20] have shown that the limiting value of the DB for a slow addition process is 0.6 in an AB_3 system. Our simulation reveals that the average DB of an AB_3 system indeed approaches this threshold value. The slightly lower value obtained for the DB at higher molecular weights is due to the lower DB of the low molecular weight fraction of the molecular weight distribution. Figure 13a shows the molecular weight distribution of an AB_3 system, where X is 100, $P(da)$ is 0, and the core functionality f is 3. The qualitative behavior is similar to that observed for the AB_2 system. The DB is close to zero for oligomers and increases with increasing molecular weight, reaching its limiting value of 0.6 at high molecular weights, which is somewhat lower than in the AB_2 system. This result is in excellent agreement with theory. As predicted theoretically, the lower DB value for AB_3 systems is due to the fact that the total number of possible branching directions in the macromolecules for a certain number of monomers increases more strongly with the monomer functionality m than the number of actually existing branches.

Table 4. AB_3 System: Polydispersities and DB in Dependence on $P(da)$ as well as $X = n(AB_2)/n(B_3)$, with Fraction $P(da)$ Given in %

X	PD $P(da) = 0.0\%$	DB $P(da) = 0.0\%$	PD $P(da) = 1.0\%$	DB $P(da) = 1.0\%$
10	1.612	0.496	1.689	0.492
20	1.638	0.538	1.811	0.537
30	1.649	0.557	1.977	0.551
40	1.647	0.564	2.137	0.561
50	1.643	0.571	2.250	0.568
60	1.649	0.576	2.409	0.572
70	1.645	0.580	2.553	0.575
80	1.645	0.582	2.700	0.578
90	1.644	0.583	2.833	0.580
100	1.644	0.585	2.980	0.582

Table 5. AB_3 System: Polydispersity and DB in Dependence on the Core Functionality f and the Probability of Deactivation P(da) ($X = n(AB_2)/n(B_3) = 100$)

f	PD $P(da) = 0.0\%$	DB $P(da) = 0.0\%$	PD $P(da) = 1.0\%$	DB $P(da) = 1.0\%$
2	1.941	0.590	3.513	0.586
3	1.644	0.585	2.980	0.582
4	1.487	0.580	2.675	0.577
5	1.387	0.576	2.555	0.572
6	1.327	0.571	2.467	0.567
12	1.170	0.548	2.195	0.545

How does the polydispersity in AB_3 systems compare to AB_2 systems? As shown in Figure 13b, where the molecular weight distributions of both an AB_2 and an AB_3 system are superimposed, the polydispersity increases, when the monomer functionality is raised from $m = 2$ to $m = 3$. Except for the monomer functionality, the applied set of parameters is identical in both cases and similar to the set of Figure 13a mentioned above. Clearly, the AB_3 distribution is broader than the AB_2 distribution, and consequently the polydispersity is higher. The numerical values of the DBs and the respective polydispersities based on $f = 2-12$ and P(da) = 0 and 1%, respectively are listed in Tables 4 and 5. Although the absolute values of the polydispersity and the DB differ between AB_2 and AB_3 systems, the qualitative behavior is similar, if system parameters such as core functionality f or the deactivation probability $P(da)$ are varied. The polydispersity decreases, when the ratio $n(AB_m)/n(B_f) = X$ increases and approaches a threshold value at higher DP_ns.

In analogy to eq 4 in the case of AB_2 monomers, the dependence of the polydispersities for AB_3 systems on f (Table 5) obviously can be described reasonably well by the expression

$$\mathrm{PD} = 1 + 2/f \tag{6}$$

Similar to the AB_2 case, the average values of DB increase and approach the limiting DB close to 0.6 at higher ratios X (i.e., at higher DP_ns). Furthermore, higher core functionalities induce lower polydispersities and DBs. In addition, the polydispersity increases with increasing $P(da)$, whereas the DB remains almost unchanged.

Another point of interest is the behavior of the core distance distributions of the four different units T, L,

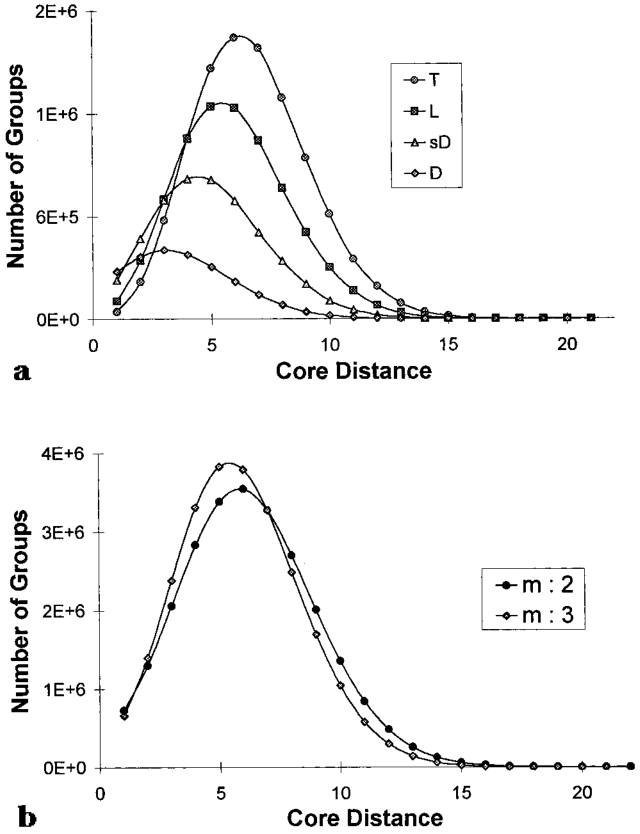

Figure 14. (a) Core-distance distribution of terminal (T), linear (L), semidendritic (sD), and dendritic (D) units obtained from the simulation of an AB_3 system. (b) Comparison of core-distance distribution of the building units for AB_2 ($m = 2$) and AB_3 systems ($m = 3$).

sD, and D, plotted in Figure 14a. As expected and in analogy to the AB_2 system (Figure 8a), the average distance of dendritic units is closest to the core. Semidendritic units are on average closer to the core than linear units, whereas the average distance of terminal groups again is larger than for linear groups. The total number of the respective units, which is equal to the sum of all points of the core distance distribution, increases in the direction D < sD < L < T with a ratio close to 1:2:3:4. This differs from the result obtained for the AB_2 polymers, where the abundances of the different units and thus the integrals over the core distance distributions (Figure 8a) did not differ significantly. Both results are in agreement with our recent theoretical work.[20]

On the basis of the assumption that AB_2 and AB_3 monomer units do not differ significantly in size, the core distance distribution of the monomer units can be used to extract information on the segment density distribution. This is illustrated in Figure 14b, in which the core distance distributions of both systems (AB_2 and AB_3) are superimposed. In both cases the number average degree of polymerization is 101 and $P(da)$ is set to zero. The diagram reveals that although the degree of branching of the AB_3-type polymer is lower, the segment density is somewhat higher in comparison to the AB_2 system (see also Figure 9). This is in agreement with expectation, as we have shown previously that in addition to the DB another parameter can be defined, designated ANB (*a*verage *n*umber of *b*ranches deviating from the linear direction per nonterminal monomer unit) which makes a comparison between AB_m systems with different m feasible.[19] For the slow addition case, the ANB_{sa} is described by expression 7. It is important

$$ANB_{sa} = \frac{m-1}{m} \tag{7}$$

to mention at this point that with increasing m the DB *decreases*, however the ANB *increases*, which is also evident from eqs 3 and 6. This means that with increasing m, in comparison to the respective perfect dendrimer the structures become less perfect, yet the segment density increases.

The distribution of the monomer units in the AB_3 system is shifted to somewhat lower core distances (Figure 14b) in comparison to the AB_2 system. For the AB_3 system the maximum of the core distance distribution as well as the maximum distance is one monomer unit closer to the core in comparison to the AB_2 system.

Conclusions

Our simulation shows that in case of an ideal core-dilution/slow addition polymerization, excluding deactivation, the molecular weights of the resulting hyperbranched polymers can be controlled by the ratio $n(AB_m)/n(B_f) = X$. The functionality f of the core molecule B_f permits one to control the polydispersity, which in the AB_2 case obeys the expression $PD = 1 + 1/f$ and in the AB_3 case can be described by $PD = 1 + 2/f$. On the basis of these results, we suggest that for general m the dependence of the polydispersity on the core functionality f for high molecular weights in a core-dilution/slow addition procedure may be described by eq 8. The hypothetical eq 8 describes the polydispersities obtained for the special cases $m = 2$ and $m = 3$ correctly. However, it is easy to conceive that also for the case of $m = 1$ (slow addition of AB monomers to a B_f-core molecule) eq 8 leads to the correct value, since in the ideal case a star polymer with PD = 1 is obtained by this procedure, which is comparable to a living core-first strategy for the preparation of star polymers.

$$PD = 1 + \frac{m-1}{f} \tag{8}$$

In addition to the interesting results concerning the polydispersity of hyperbranched polymers prepared via a core-dilution/slow addition strategy, we have been able to confirm our recent theoretical results, based on topological and statistical considerations, showing that the core-dilution/slow addition procedure leads to higher degrees of branching than the random one-pot polymerization. In the ideal case, at higher DP_ns a value of $DB = {}^2/_3$ is obtained for an AB_2-monomer-based hyperbranched polymer.

The conclusions concerning the DB hold true, even if the reactive A function of the monomers is deactivated to a certain extent by side reactions and new B_2 (or in the general case B_m) core molecules are formed in the course of the reaction. In this case, deactivation does not lead to broader monomodal molecular weight distributions but to bimodal distributions with a second molecular weight mode at low molecular weights, which, however, remains separated from the high molecular weight mode. The polydispersity increases considerably. The effect of deactivation on the average DB is small, resulting in a slight decrease. Thus, despite deactivation high degrees of branching can be obtained. Separation of low and high molecular weight modes might be possible by common fractionation procedures, such as careful precipitation or ultrafiltration. If the low molecular weight mode is removed successfully, a relatively narrow molecular weight distribution with a degree of branching close to $^2/_3$ is obtained for AB_2 systems.

In the current synthetic literature on hyperbranched polymers, no systematic studies on slow addition of AB_m monomers, based on the objectives described in this paper, have been reported to date. Some authors have speculated on the enhancement of the DB by a stepwise addition of discrete amounts of AB_2 monomers to a B_f core.[30] However, on the basis of our theoretical study as well as the simulation reported here, we find no theoretical support for an increase of the DB in this case. From a theoretical point of view, this type of monomer addition is classified as a repeated one-pot procedure due to the large increments added and not a slow addition process. Thus, the maximum value for the DB obtainable in this case is 0.5. In fact, the initially reported high DBs (0.8) have been corrected to values ≤ 0.5 in the meantime.[31] On the other hand, Fréchet et al. reported on a slow addition procedure for the synthesis of hyperbranched polyethers some years ago.[11] In this case, no core molecule B_f was used. On the basis of our recent theoretical study as well as the simulation reported here, one would expect no effect on the polydispersity, but the DB of the macromolecules prepared should be enhanced. However, the authors did not report DB values that would allow us to judge whether the synthesis used satisfies the criteria for a dilution/slow addition procedure.

Narrow polydispersities and control of molecular weights by the amount of added monomer have been reported recently in elegant work by Moore et al., who used a solid support to attach a B_2-core molecule (a 3,5-diiodophenyl unit).[32] Dropwise addition of a suitable AB_2 monomer (3,5-diiodophenylacetylene) was used to prepare hyperbranched poly(phenylacetylene)s. Narrow polydispersities ($M_w/M_n = 1.3$) were obtained after cleavage of the hyperbranched polymer from the support; however, when the same synthesis was carried out without solid support in solution, a bimodal elution profile characterized by a relatively narrow peak at very high molecular weight, as well as a tailing to low molecular weights, was obtained. This result appears to be in excellent agreement with our simulation (Figure 10), as the attachment to the solid support allows one to separate the core-controlled polymerization from the polymerization influenced by the deactivation side reaction discussed. Thus, polymerization on the support should represent the ideal case of a core-dilution/slow addition procedure discussed in sections i–iii of this paper, whereas polymerization in solution leads to a bimodal distribution due to a finite deactivation probability.

Moore et al. explained the narrow polydispersities obtained tentatively by spatial limitations due to the support. Although this might play an additional role, by comparison with our simulation data, it appears highly plausible that the narrow polydispersities obtained by Moore and co-workers are a consequence of the special kinetic features of the slow addition process. Additional support for this picture might be obtained by analysis of the DB, which should be significantly enhanced but was not reported.

As demonstrated recently,[33] some of the results of the simulation presented here, particularly for the ideal case (i.e., excluding deactivation) can also be derived analytically.[33] However, the advantage of the simulation lies in the fact that additional information can be gained that has not been obtained previously by analytical techniques. For instance, the dependence of the DB on the DP for each slice of a molecular weight distribution can be determined or the effect of deactivation can be evaluated. Furthermore, AB_3 systems have only been considered with respect to the DB[19,20] and not with respect to molecular weight distribution yet.

Summarizing the results of this simulation study, it appears possible to prepare hyperbranched macromolecules with enhanced DB and low polydispersity using the core-dilution/slow addition strategy. In fact, in the ideal case this strategy represents a living process with steadily increasing number of potentially active end groups. This is important in two respects: On one hand, control of the abovementioned molecular parameters is a crucial prerequisite for the systematic investigation of structure–property relationships of hyperbranched polymers. On the other hand, hyperbranched polymers, prepared in a controlled manner, might well become strong competitors for dendrimers with respect to applications that require narrow polydispersity and high functionality, but no hard sphere behavior.

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Supporting Information Available: Figures demonstrating convergence of the simulation algorithm, showing the polydispersity PD as a function of $(1/n)(B_f)$ (2 pages). Ordering and Internet access information is given on any current masthead page.

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(33) After submission of this manuscript, Müller et al. published calculations concerning the slow addition of AB_2 monomers to B_f core-molecules in a similar manner as described in our work (Müller, A. H. E.; et al. *Macromolecules* **1998**, *31*, 239). The results of Müller et al. are in excellent agreement with our simulation study for the special case of AB_2 monomers, confirming the dependence of the polydispersity on f ($PD = 1 + 1/f$) as well as $DB = {}^2/_3$ for this case.

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