Degree of branching in hyperbranched polymers

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Topological considerations concerning the ratio of linear, imperfectly branched, dendritic and terminal units in hyperbranched polymers based on AB_2, AB_3 and AB_m ($m \geq 2$) type monomers are summarized. The reaction of AB_2 monomers with a core molecule of the structure B_f is also treated. For larger hyperbranched polymers based on AB_2 monomers the fraction of terminal units has to be equal to the number of dendritic units. A general expression for the degree of branching (DB) is derived for AB_2 systems, which is based on the number of dendritic and linear units. The expression is valid for low molecular weight as well as high molecular weight hyperbranched polymers in contrast to the commonly used expression based on dendritic, linear and terminal units. DB may not exceed 0.5 in hyperbranched polymers based on AB_2 systems (0.44 in AB_3 systems). Furthermore, a general expression for DB in hyperbranched polymers based on AB_m monomers is derived. Consequences for signal ratios in NMR-spectra of hyperbranched polymers are discussed. The expressions presented allow verification of NMR-integration ratios obtained experimentally on the basis of model compounds.

1. Introduction

Although the term "hyperbranched polymers" was coined only recently [1], this class of polymers has been known for a long time [2] and Flory already developed the fundamental concepts for highly branched macromolecules based on AB_m monomers [3]. Flory predicted that AB_m type momers containing one reactive group of one type and m reactive groups of another type ($m \geq 2$) would polymerize to highly branched three-dimensional structures without crosslinks. Burchard calculated the mean square radius of gyration as well as the scattering behavior for hyperbranched polymers on the basis of the cascade theory [4, 5]. Currently, there is intense research interest in synthetic routes to dendritic [6] and hyperbranched polymer topologies [7, 8], e. g., hyperbranched polyesters [9–15], polyethers [16–18], poly(ether ketones) [19], polyphenylenes [20], polyurethanes [21, 22], polysilanes [23] and polycarbosiloxanes [24, 25] have been prepared. An alternative route to hyperbranched polymers has been developed recently by various authors [26, 27], who described a "self-condensing" type of polymerization.

Present investigations aim at hyperbranched polymers with low polydispersity and high degree of branching (DB), i. e., hyperbranched structures that resemble perfect dendrimers. The DB is commonly 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. As first shown by Hawker [28] and described similarly, using different terminology, by Kim [29], the degree of branching is commonly calculated according to the following equation:

$$DB = \frac{D + T}{D + L + T} \tag{1}$$

where D, T and L are the fractions of dendritic, terminal or linearly incorporated monomers in the resulting hyperbranched polymers obtained from integration of the respective signals in NMR-spectra. The values commonly reported for DB are in the range of 0.4 to 0.8. Equation (1) has been used by several researchers to determine the degree of branching

[9–16, 18, 20, 28, 29]. In addition to NMR, degradative methods have also been used to determine DB [30].

It is obvious that Eq. (1) is only valid for hyperbranched polymers based on AB_2 monomers and cannot be employed for $m > 2$. In this paper, we will present some general considerations concerning the ratio of perfectly and imperfectly branched units in hyperbranched polymers for AB_2, AB_3 and AB_m based systems. In addition, we derive a general expression for DB for AB_m ($m \geq 2$) type monomers. We are aiming at rules that simplify determination of DB for hyperbranched polymers from NMR signal intensities and also allow the validity of signal assignments made on the basis of low molecular weight model compounds to be tested. The considerations are independent of the actual chemistry employed.

2. Theory and discussion

2.1. AB_2 systems

In AB_2 systems, which represent the most common type of hyperbranched polymers at present, 3 different modes of incorporation of the monomer units are possible: *t*erminal, *d*endritic and *l*inear, as indicated in Fig. 1 by t, d and l for a hyperbranched structure and a perfect dendrimer structure, respectively. DP_{mol}, the overall number of incorporated monomer units in *one* hyperbranched molecule is the sum of terminal, linear and dendritic units, designated t, l and d, respectively,

$$DP_{mol} = d + l + t \tag{2}$$

It is obvious that any terminal unit may become a linear unit by addition of an AB_2 monomer. This, in turn, may become a dendritic unit by attachment of another AB_2 monomer. Clearly, for every new dendritic unit formed from a linear unit, a new end group is formed. Thus, the number of terminal units t and the number of perfect dendritic units d in this hyperbranched polymer must be related. Since the polymerization starts with a terminal unit for an AB_2-based hyperbranched molecule, one obtains

$$t = d + 1 \tag{3}$$

This has been mentioned before [9]. At this point it should be noted that the formation of loops by reaction of

a)

t
l
d

b)
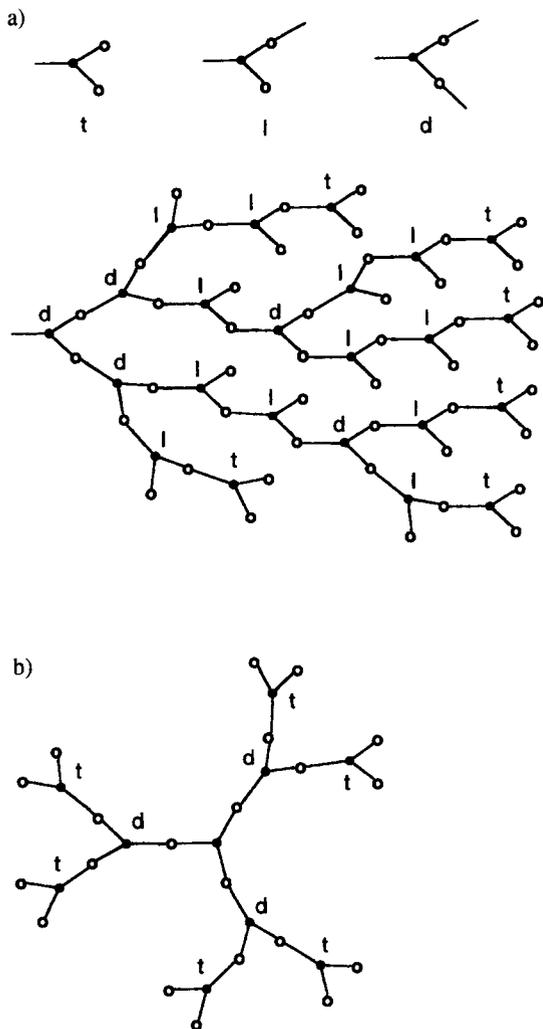
Fig. 1. Schematic representation of terminal, linear, and dendritic building units of AB_2-type hyperbranched polymer. (a) Hyperbranched structure with assignment of the building units, (b) perfect dendritic structure with assignment.

the A group of the first monomer with a B group of the same molecule is neglected in the ensuing discussion. However, the formation of loops will hardly affect the following considerations. Obviously, in larger hyperbranched molecules (i. e., at higher conversions in the course of the reaction) t and d become practically identical in one molecule. The terminal group formed as the result of the transformation of a linear to a dendritic unit may be separated from the respective dendritic unit by an arbitrary number of linear units. Therefore, the number of linear units l is independent of t or d and constitutes the key factor that determines the degree of branching of the hyperbranched structure. The relation between d and t is illustrated in Fig. 1 a, where a hyperbranched polymer with 23 monomer units is shown. In this case, 6 terminal, 5 dendritic, and 12 linear units are present, in agreement with Eq. (3).

All considerations summarized so far have treated only one hyperbranched molecule. If N hyperbranched molecules are considered, one obtains from Eq. (3)

$$\sum_{i=1}^{N} t_i = \sum_{i=1}^{N} (d_i + 1) \qquad (4)$$

If

$$\sum_{i=1}^{N} t_i = T; \qquad \sum_{i=1}^{N} d_i = D; \qquad \sum_{i=1}^{N} l_i = L$$

one obtains

$$T = D + N \qquad (5)$$

How can an expression for DB be systematically derived for N molecules? The degree of branching of a hyperbranched molecule may be expressed in terms of the number of actual growth directions compared to the maximum number of possible growth directions. A branching parameter R may be defined that describes the number of deviations from the linear direction; thus R is 0 for a linear polymer, 1 for one branch, 2 for two branches and so forth, as shown in Fig. 2:

$$DB = \frac{R}{R_{max}} \qquad (6)$$

$R =$ 0   1   2   3
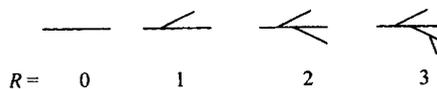
Fig. 2. Different growth directions and the branching factor R.

For an AB_2 system, every dendritic unit will inevitably introduce one new branch (i. e., one deviation from a linear structure); therefore Eq. (6) becomes

$$DB = \frac{D}{D_{max}} \qquad (7)$$

Thus, DB is the actual number of dendritic units divided by the maximum possible number of dendritic units. As two linear units can be transformed into one dendritic and one terminal unit (an analogous consideration was already mentioned in [29]), we obtain

$$D_{max} = D + \frac{1}{2} L \qquad (8)$$

Thus (with Eq. (7))

$$DB = \frac{D}{D + \frac{1}{2} L} = \frac{2D}{2D + L} \qquad (9)$$

Equation (9) is a universally applicable expression for DB in small as well as large hyperbranched (macro)molecules. According to Eq. (9), the ratio of dendritic and linear units in a hyperbranched polymer can be written as a function of DB, resulting in Eq. (9'):

$$\frac{D}{L} = \frac{DB}{2(1-DB)} \qquad (9')$$

The meaning of Eq. (9') is visualized in Fig. 3, showing D/L as a function of DB.

In order to compare our result to the commonly used Eq. (1), Eq. (9) has to be slightly modified, using Eq. (5). One obtains

$$DB = \frac{2T - 2N}{2T + L - 2N} = \frac{D + T - N}{D + T + L - N} \qquad (10)$$
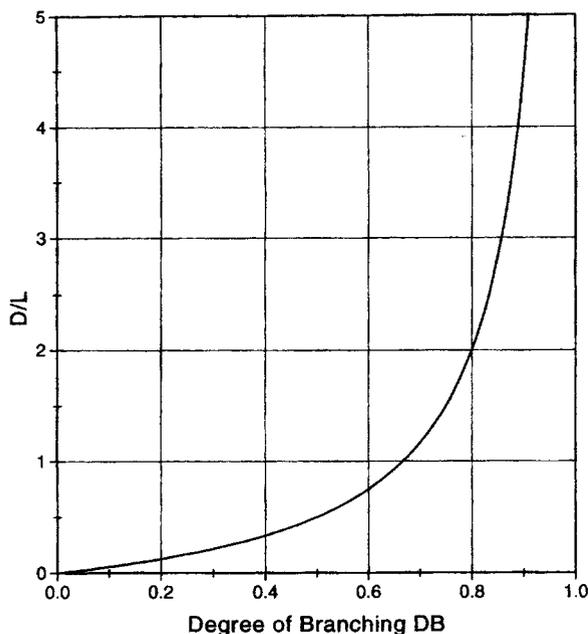
Fig. 3. Ratio of dendritic to linear units D/L in a hyperbranched polymer vs. DB.

If we compare this result to the common Eq. (1),

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

we find that Eq. (10), which was derived on the basis of a simple comparison of the number of growth directions present with the number of growth directions possible, differs from Eq. (1) in that Eq. (1) actually gives the ratio

$$DB' = \frac{R+N}{R_{max}+N} \qquad (11)$$

Clearly, the difference between Eq. (1) and our result for DB is due to the fact that in the commonly used expression (1) already the linear direction is counted as a branching direction, which leads to an overestimation of DB for small or little-branched molecules (i.e., in low generations). For small hyperbranched molecules, Eq. (9) yields more reasonable values for DB than Eq. (1). Furthermore, Eq. (9) does not require determination of T. However, if one considers large hyperbranched molecules, where $D, T \gg N$, Eqs. (9) and (11) give the same result. In this common case the following equations can be employed:

$$DB = \frac{2D}{2D+L} \approx \frac{D+T}{D+T+L} \approx \frac{2T}{2T+L} \qquad (12)$$

Thus, for large hyperbranched structures the number of molecules considered does not influence DB strongly and knowledge of the number (i. e., the NMR-signal intensity) of dendritic or terminal units with respect to linear units is sufficient for the determination of DB.

At this point, is worth mentioning that a high degree of branching does not imply a spherical or globular shape of the hyperbranched polymers. Although a perfectly centro-symmetrical dendrimer will always lead to a DB of 1, the reverse is not true. As pointed out by Kim before [29], a variety of isomers with DB = 1 and nonspherical structures is possible.

As a consequence from the relationships derived, some other interesting conclusions can be drawn. For instance, the number average degree of polymerization $\overline{DP}_n$ can be calculated from T, D, and L:

$$\overline{DP}_n = \frac{T+D+L}{N} = \frac{T+D+L}{T-D} \qquad (13)$$

Equation (13) will be useful for small hyperbranched structures; however, for large hyperbranched molecules the increasing probability of loop formation will render Eq. (5) and thereby Eq. (13) invalid. That means values may be too large in this case, but not smaller than the actual one. Furthermore, the usefulness of Eq. (13) also depends on the resolution of the NMR-spectra, since the difference between T and D can become very small in comparison with the numerator.

It is important to note that Eq. (13) can also be derived from the Carothers equation in the expression used by Flory for AB_m-type systems long ago (Eq. (14)) [3].

$$\overline{DP}_n = \frac{1}{1-p_A} = \frac{1}{1-p_B \cdot m} \qquad (14)$$

For an AB_2-system we can express the conversion of B-groups (p_B) by

$$p_B = \frac{D + \frac{1}{2}L}{T+D+L} \qquad (15)$$

We get Eq. (13) by plugging Eq. (15) into Eq. (14). In this context it is important to realize that for hyperbranched polymers – as generally in polycondensation reactions – very high conversions are necessary for reasonable degrees of polymerization.

Rearranging Eq. (5) yields

$$\frac{T}{D} = 1 + \frac{N}{D} = 1 + \frac{1}{z} \text{ and } \frac{T}{D} = 1 + \frac{2}{DB \cdot (\overline{DP}_n - 1)} \qquad (16)$$

In this expression z is

$$z = \frac{D}{N} = \frac{D}{T-D} = \frac{DB \cdot (\overline{DP}_n - 1)}{2} \qquad (17)$$

z describes the average number of branching points per hyperbranched molecule. Expressions (16) and (17) are valid if no loops occur. For $D \gg N$, z becomes large and the ratio T/D approaches unity. This occurs even more rapidly if loops are present.

So far, we have not considered the statistics of the polymerization. An intriguing question is which maximum value for DB will be obtained in a completely random hyperbranching polymerization of an AB_2-type monomer. In order to consider this, we will assume complete conversion (i. e., reaction of all A groups), equal reactivity of all A groups and equal reactivity of all B groups present, regardless of their terminal or linear nature. It is obvious that for the hyperbranched macromolecules formed a distribution of different DBs will be obtained, even for molecules consisting of the same number of monomer units. A statistical treatment of the distribution of DB is not given in this paper, but – based on simple considerations – a mean value for DB is derived.

The most probable final situation after reaction of all monomer molecules will be characterized by an equal number of unreacted B groups at linear units and terminal

monomer units. In this case the ratio of terminal units to linear units $T:L$ must be $1:2$, because terminal units contain twice as many B groups as linear units. A large hyperbranched structure must contain the same number of terminal and dendritic units. We obtain

$$\frac{T}{L} = \frac{D}{L} = \frac{1}{2}; \qquad DB = \frac{1}{2}$$

The most probable value for DB ($\overline{DB}$) in such a system will be 0.5 according to Eq. (9)! This conclusion is also obtained from other considerations: Only half of the B groups can react due to the AB_2 monomer stoichiometry ($p_B = 0.5$). Thus, terminal and dendritic units have a probability of $(0.5^2) = 0.\underline{25}$; linear units have a probability of $2 \times 0.5^2 = 0.5$. Thus $\overline{DB}$ is 0.5. Experimentally obtained values for DB will be somewhat lower, because complete conversion of all A groups will not be reached. Furthermore, linear units formed during the growth process are likely to be less accessible than terminal units. This would lead to a higher fraction of linear units than expected statistically.

How can DB > 0.5 be realized? Finding the same number of terminal (T) and linear (L) monomer units in a hyperbranched polymer would result in a value of 2/3 (0.$\bar{6}$) for DB (Eq. (1) and (9)). However, this situation would require twice as many unreacted *terminal* B groups as *linear* B groups. This is possible if reaction of a linear unit with an A functionality to a terminal unit is more probable than attachment of A to a terminal unit. Large differences between reactivity of linear and terminal units in favor of linear units will lead to hyperbranched structures with DB values close to 1, but not necessarily spherical structures. If one aims at a centrosymmetrical dendrimer structure, a stepwise algorithm using protected B functionalities is unavoidable [6].

In summary, the maximum value obtainable for DB in a statistical process (given the conditions summarized above) will be 0.5.

2.1.1. AB_2 systems with core B_f

In recent publications various authors have used a core B_f in combination with the AB_2 monomer, which apparently results in higher values for DB [12–15, 31]. Introduction of a core with a core functionality f will inevitably lead to f new end groups for the hyperbranched polymer. However, the core may not react fully. In this case, the hyperbranched polymer will possess T end groups,

$$T = D + \bar{f} \cdot C + (N - C) = D + (\bar{f} - 1) \cdot C + N \qquad (18)$$

where C is the number of core molecules, $\bar{f}$ represents the average number of reacted B-groups out of f groups at the core molecule, and $(N - C)$ represents the hyperbranched molecules formed without core, concurrently to the condensation with core. One may define $\bar{f}'$ as the average number of branches that actually grow at the core:

$$\bar{f}' = \frac{C \cdot \bar{f} + (N - C)}{N} = \frac{(\bar{f} - 1)C}{N} + 1 \qquad (19)$$

thus

$$T = D + \bar{f}' \cdot N \qquad (20)$$

Clearly, in an ideal case (when the core fully reacts), $\bar{f}' = \bar{f} = f$. However, if $D \gg N$, also in this type of hyperbranched polymer, the number of terminal and dendritic units has to be equal ($T = D$).

We obtain for DB (the core itself is not considered as a branching point, because the core influences DB only at the beginning of the reaction)

$$DB = \frac{2D}{2D + L} \qquad (9)$$

Also in this case, DB will be at maximum 0.5 for larger hyperbranched molecules. The same considerations as mentioned for AB_2 systems are valid in this case, including the ratio of D to L.

2.2. AB_3 systems

Figure 4 illustrates the possible modes of incorporation into the hyperbranched structure for AB_3-type units. In this case, four different configurations are possible: terminal (t), linear (l), semidendritic (sd), and perfect dendritic (d)
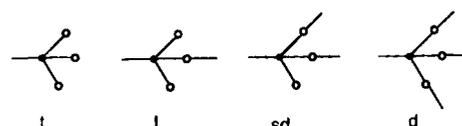
Fig. 4. Schematic representation of terminal, linear, semidendritic, and dendritic units in AB_3-type hyperbranched polymer.

(Fig. 4). Neglecting loop formation, in analogy to Eq. (3) the number of terminal units in this case is

$$t = 2d + sd + 1 \qquad (21)$$

and for N molecules

$$T = 2D + sD + N \qquad (22)$$

According to the definition of the DB (Eq. (6)) we can now derive an expression for DB in AB_3-type hyperbranched polymers. Each dendritic group results in two new growth directions, each semidendritic group in one new growth direction. Since three linear units can be transformed into one dendritic unit and three semidendritic units can be transformed into two dendritic units, we obtain for R/R_{max}

$$DB = \frac{2D + sD}{2D + 2\left(\frac{1}{3}L\right) + 2\left(\frac{2}{3}sD\right)}$$

$$= \frac{2D + sD}{\frac{2}{3}(3D + 2sD + L)} \qquad (23)$$

Similar to the case of AB_2 systems, even if one of the three parameters D, sD, or T is not known or cannot be determined, it is still possible to calculate the degree of branching DB based on the remaining two parameters for large hyperbranched polymers.

Which value is expected for DB on the basis of a random process, based on equal reactivities of all A groups and all

B groups, respectively, as well as complete conversion? Only 1/3 of all B-groups can react in this case ($p = 1/3$). Based on similar arguments as in the case of the AB_2 system, it can easily be shown that the ratio $T:L:sD:D$ is $8:12:6:1$. Thus, only a small fraction of fully reacted dendritic groups is present (1/27). Clearly, the ratios calculated on the basis of purely statistical considerations satisfy Eq. (22). The ratios of monomer units present result in $\overline{DB} = 0.44$. Again, the values obtained from experiments will be lower due to the same considerations as summarized in the case of AB_2. Interestingly, almost equal intensity can be expected for the signals of terminal and semidendritic units in NMR spectra.

2.3. AB_m $(m \geq 2)$

In the case of AB_m-type systems, a number of imperfectly branched modes of monomer incorporation can be imagined, leading to $m - 1$ possible imperfect configurations of the building unit in the hyperbranched polymer. Using this, one can derive general relationships. In the following equations y_0 to y_m represent the different units with increasing degree of perfection, e. g., for AB_3: $t = y_0, l = y_1, sd = y_2$ and $d = y_3$.

For one hyperbranched molecule:

$$y_0 = \sum_{r=2}^{m} (r-1)\, y_r + 1 \tag{24}$$

and – in analogy to the expressions discussed above for N molecules

$$\sum_{i=1}^{N} y_{0i} = \sum_{i=1}^{N} \left(\sum_{r=2}^{m} (r-1)\, y_{ri} + 1 \right) \tag{25}$$

and thus

$$Y_0 = \sum_{r=2}^{m} (r-1)\, Y_r + N \tag{26}$$

From this, DB can be calculated to be

$$DB = \frac{\sum_{r=2}^{m} (r-1)\cdot Y_r}{\left(\dfrac{m-1}{m}\right)\cdot \sum_{r=1}^{m} r\cdot Y_r} \tag{27}$$

A general expression for the most probable value of DB in the case of a random process can also be derived. Assuming complete conversion ($Y_0 = \sum_{r=2}^{m} (r-1)\cdot Y_r$) one can write:

$$\overline{DB} = \frac{Y_0}{\left(\dfrac{m-1}{m}\right)\cdot \sum_{r=0}^{m} Y_r} \tag{28}$$

The respective amounts of the different units can be expressed by the probability of the units:

$$\overline{DB} = \frac{\left(\dfrac{m-1}{m}\right)^{m}}{\left(\dfrac{m-1}{m}\right)\cdot 1} = \left(\dfrac{m-1}{m}\right)^{m-1} \tag{29}$$

It is easy to conceive that for large values of m the $\overline{DB}$ converges to 0.368 ($\lim_{m \to \infty} \overline{DB} = 1/e$). This is illustrated in Fig. 5, which shows $\overline{DB}$ versus m for $m = 2$ to 6.
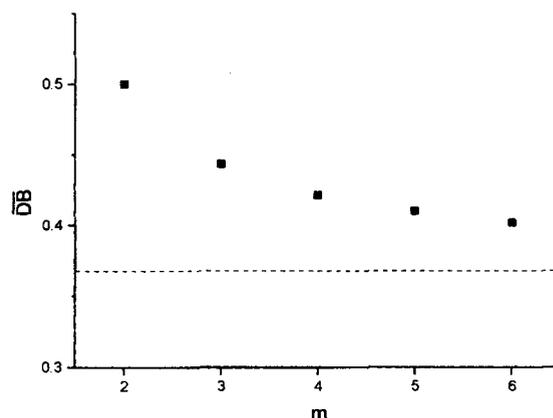
Fig. 5. The most probable degree of branching of AB_m-type polymer systems in a random process ($\overline{DB}$) vs. m.

2.4. Average number of growth directions per non-terminal monomer unit

This last section of the paper deals with an additional parameter that enables one to compare hyperbranched AB_m-type structures with different m. The degree of branching (DB) discussed so far is based on the comparison of actually existing growth directions with the maximum possible number of growth directions, keeping the number of monomer units and molecules unchanged. Thus, DB values calculated for AB_2 systems cannot be compared to those of AB_3 systems with respect to the "density of branching". A general parameter that would make such a comparison feasible should treat the *average* *number* of *branches* deviating from the linear direction per non-terminal monomer unit and is designated ANB in the following. For the definition of the ANB only the non-terminal linear units are considered, since the number of terminal units is determined by those and the number of molecules (N).

ANB should not be mistaken for the average number of growing branches per monomer unit, which for all AB_n systems approaches unity with growing conversion.

For AB_2 systems the ANB is as follows:

$$ANB = \frac{D}{D+L} \tag{30}$$

Thus, for example, the hyperbranched polymer shown in Fig. 1a possesses an ANB of 0.294, which means that only about 3 of 10 non-terminal units actually form a branching point.

For AB_3 systems we obtain

$$ANB = \frac{2D + sD}{D + sD + L} \tag{31}$$

For AB_m systems in general one obtains

$$ANB = \frac{\sum_{r=2}^{m} (r-1)\cdot Y_r}{\sum_{r=1}^{m} Y_r} \tag{32}$$

As in the case of DB, also for the ANB parameter most probable values for a random process can be determined. This results in 0.333 for AB_2 systems and 0.421 in the case of AB_3 monomers, showing that there are more deviations from the linear direction per non-linear unit when we consider AB_3-type polymers. In analogy to a general expression for $\overline{DB}$, an expression for $\overline{ANB}$ (statistically most probable value for ANB) can be derived:

$$\overline{ANB} = \frac{1}{\left(\dfrac{m}{m-1}\right)^m - 1} \tag{33}$$

$\overline{ANB}$ converges to 0.582 ($\lim_{m \to \infty} \overline{ANB} = 1/(e-1)$) for growing m. This implies that it is not possible – at least in a random process – to enhance the "density of branching" beyond a threshold value by using monomers with higher functionality.

Again, due to the above-mentioned considerations, the experimentally observed "real-world" values are likely to be smaller.

3. Conclusion

As a consequence of the expressions derived on the basis of rather simple topological arguments, a number of rules for the ratio of terminal and dendritic units in hyperbranched polymers and the related NMR signal intensities can be summarized.

(i) In NMR-spectra of high molecular weight hyperbranched polymers based on AB_2 monomer units the signal intensities of dendritic and terminal units are equal, regardless of the presence of a core. This rule can be used to test the validity of signal assignments in hyperbranched polymers based on low molecular weight model compounds.

(ii) The degree of branching (DB) in hyperbranched polymers based on AB_2-monomers calculated according to the commonly used Eq. (1) is only correct for high molecular weights. The general expression $DB = 2D/(2D + L)$ (Eq. (9)) in contrast is universally applicable for low and high molecular weight hyperbranched polymers based on AB_2 systems. In fact, Eq. (1) is a special case of the more general definition given in Eq. (9).

(iii) Knowledge of the signal intensities of dendritic and linear *or* terminal and linear units suffices to determine DB in high molecular weight AB_2-type systems. This is useful when identification of dendritic or terminal units is difficult in NMR-spectra. When assignments are based on model compounds, only two model compounds have to be prepared instead of three.

(iv) DB for AB_3 monomer systems can be calculated according to Eq. (23). Monomers of this type are known [24, 29, 32] for which Eq. (23) may be useful.

Based on the assumption of a completely random growth process, conclusions can be drawn concerning the limiting degree of branching in AB_2- and AB_3-type systems.

(v) The maximum value for DB achievable in a statistical AB_2-type polyreactions is 0.5, independent of the presence of a core molecule B_f. The maximum DB value in an AB_3 system is 0.44. Values that are obtained experimentally have to be smaller, due to incomplete conversion and sterical factors, provided the rate of monomer addition to a linear group is not orders of magnitude greater than to a terminal unit. Thus, dendrimer-like hyperbranched polymer are very unlikely to be obtained by means of an AB_n polyreaction.

On the basis of these arguments, reconsideration of DB values reported might be appropriate in some cases. It should be stressed that the degree of branching is not related to the polydispersity – although some methods may yield hyperbranched polymers with narrow polydispersity, they will not lead to high values for DB, as DB is controlled by statistics.

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