Kinetics of Nonideal Hyperbranched Polymerizations. 1. Numeric Modeling of the Structural Units and the Diads

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Received January 14, 2000; Revised Manuscript Received June 20, 2000

ABSTRACT: The kinetics of reactions with nonuniform reaction rate constants leading to hyperbranched polymers has been examined and discussed. A matrix notation was developed, which has then been applied to the analysis of the kinetics of AB_2, AB_3, AB_n, and ABB′ systems. All differential equations have been integrated numerically in order to obtain plots of the ratios of structural units as functions of the conversion. Three general situations for AB_2 systems and the kinetics of self-condensing vinyl polymerization as one example of an ABB′ system are discussed. It was found that the influence of the first B group on the reactivity of the second B group has the largest effect on ratio of structural units and final composition. Thus, by varying the rate constants of these reaction steps in the model the resulting degree of branching ranges between 15 and 89%. Furthermore, the diad formation of the AB_2 system is analyzed.

Introduction

Hyperbranched polymers as obtained from AB_n ($n \geq 2$) or ABB* monomers have been of interest in a large number of studies.[1] Early studies focused on synthesis and characterization of hyperbranched polymers. These studies were followed by the exploration of potential applications.[2] Although Flory[3] and Stockmeyer[4] published the first theoretical studies on the polycondensation of branched systems in the 1940s and 1950s, interest in the theory of different hyperbranched systems has risen recently as documented in publications by several groups due to the growing number of synthesized systems and their characterization. Müller et al.[5] derived the conversion dependence of the structural units for self-condensing vinyl polymerization (SCVP) and for the polycondensation of AB_2 monomers, similar to Möller et al.[6] Frey et al.[7] proposed a new definition of the degree of branching DB and discussed the polycondensation of AB_2 and AB_3 systems. Furthermore, they simulated molecular weight distribution and degree of branching for hyperbranched polymers prepared by the core-dilution/slow addition technique.[8] McCoy[9] and Hult et al.[10] reported kinetic studies on hyperbranched polymerization. Dušek et al.[11] and Fawcett et al.[12] studied the cyclization reaction of hyperbranched polymers by modeling, and Davies et al.[13] simulated the intrinsic viscosity of hyperbranched polymers.

To date, theoretical discussions about the distribution of structural units or degree of branching are mainly based on the assumption that for an AB_n system all the B functions have the same reactivity, which facilitates the calculation. When all basic reaction steps have the same rate constants, the distribution of the different structural units only reflects the probability aspect of the system. We will refer to this kinetic situation as the ideal case, whereas the nonideal case occurs when a reaction on one site influences the reactivity of the other reaction sites. Thus, hyperbranched polymers are reported with a degree of branching of 100% due to instability of the linear units[14] or the formation of favored intermediates.[15] Another nonideal case occurs when the system is not symmetric or the **B** functions are different functional groups (e.g., ABB′ instead of AB_2).

The aforementioned cases are not only of theoretical interest but also have implications in the synthesis of hyperbranched polymers. One example is the AB_2 system in which all reaction sites are located on a single benzene ring. This system does not behave like the ideal case. The monomer is 3,5-bis(trimethylsiloxy)benzoyl chloride, for which electronic effects cannot be neglected. In 1991, Fréchet et al.[16] discussed the polycondensation of 3,5-bis(trimethylsiloxy)benzoyl chloride. They reported a DB of 60%. We found a DB in the same range of 60−64% during our studies on the modification of this all-aromatic hyperbranched polymer.[17] Recent work by Frey et al.[7b,18] shows the increase of DB by an alternative synthetic method, “slow monomer addition”.

The groups of Frey and Müller have done a first approach to discussing the polymerization of AB_2 systems with nonuniform reaction rates. Frey et al.[7b] distinguished two different reaction steps of the polycondensation of an AB_2 system, the first from terminal to linear units and the second from linear to dendritic units. The ratio of the two different reaction rate constants was defined as the factor $x = k_L/k_T$,[19] which influences the DB of the final product. Müller et al.[5b] discussed the kinetics of self-condensing vinyl polymerization with nonuniform reaction rate constants $r = k_A/k_B$.[20] We will show that both studies are special cases of the complete kinetic situation.

An AB_2 monomer has three reaction sites. This leads to six different structural units and these units are connected with each other via seven reaction pathways with 12 basic reaction steps. Thus, we have to discuss 12 different rate constants. Within this paper we present a theoretical discussion of the kinetics of the nonideal polymerization of an AB_2 system. Furthermore,

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10.1021/ma000065m CCC: $19.00

we will show that our conceptualization of the kinetics can be easily generalized to describe other AB$_n$ system or a nonsymmetric ABB′ system. We do not specify the polymerization mechanism (e.g., polycondensation or self-condensing vinyl polymerization); we only discuss the rate constants for the conversion from one structural unit to the other.

Results and Discussion

We have chosen the AB$_2$ system for detailed description because this case is the most frequently occurring monomer type. In a subsequent paper we will discuss the kinetics of a nonideal AB$_2$ system: 3,5-bis(trimethylsiloxy)benzoyl chloride mentioned above.[21]

After the discussion of the AB$_2$ system we will introduce the generalization of our description by discussing AB$_3$, AB$_n$, and ABB′ systems. The self-condensing vinyl polymerization[5,22] will also be discussed as one important example for an ABB′ system.

The following terms will be used frequently and should be defined in advance: Each monomeric unit within the polymer and the monomer itself is a *structural unit*, distinguished one from the other by whether the **A** or **B** site has reacted. *Reaction pathways* give the connection between the individual structural units by reaction either at the **A** function or the **B** function. *Basic reactions* are the bimolecular reactions between two compatible structural units at particular reaction sites. Each basic reaction yields a pair of reacted structural units called a *diad*.

AB$_2$ Systems. Structural Units and Reaction Pathways. We will use a number–letter combination to specify each of the six structural units. Scheme 1 gives the notation and the different reaction pathways for each structural unit of the AB$_2$ system.

The number "**1**" indicates that the **A** function has not reacted, whereas "**2**" denotes a reacted **A** site. The letters "**t**", "**l**", and "**d**" refer to the terminal, linear, and dendritic units, depending whether zero, one, or both **B** functions have reacted, respectively.

In addition, it should be noted that capital letters **A** and **B** in the reaction schemes represent active functionalities of the five structural units **1t**, **1l**, **1d**, **2t**, and **2l**. Lower case letters **a** and **b** denote reacted functionalities. Thus, the connection between the concentrations of the **A** and **B** functionalities at time t ($[\mathbf{A}]_t$ and $[\mathbf{B}]_t$) and the concentration of the structural units is shown in the following equations.

$$[\mathbf{A}]_t = [\mathbf{1t}]_t + [\mathbf{1l}]_t + [\mathbf{1d}]_t \tag{1}$$

$$[\mathbf{A}]_0 = [\mathbf{1t}]_t + [\mathbf{1l}]_t + [\mathbf{1d}]_t + [\mathbf{2t}]_t + [\mathbf{2l}]_t + [\mathbf{2d}]_t \tag{2}$$

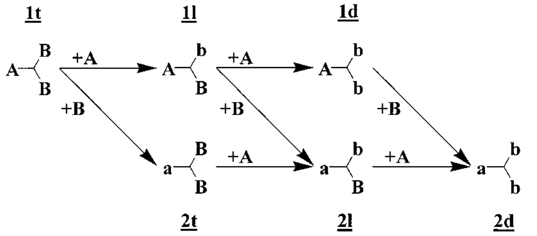
$$[\mathbf{B}]_t = [\mathbf{A}]_0 + [\mathbf{A}]_t = 2[\mathbf{1t}]_t + 2[\mathbf{1l}]_t + 2[\mathbf{1d}]_t + [\mathbf{2t}]_t + [\mathbf{2l}]_t + [\mathbf{2d}]_t = 2[\mathbf{1t}]_t + [\mathbf{1l}]_t + 2[\mathbf{2t}]_t + [\mathbf{2l}]_t \tag{3}$$

$$p_{\mathrm{A},t} = 1 - \frac{[\mathbf{A}]_t}{[\mathbf{A}]_0} = 2 - \frac{[\mathbf{B}]_t}{[\mathbf{A}]_0} \tag{4}$$

$[\mathbf{A}]_0$ = initial concentration of **A** function, $[\mathbf{A}]_t$ = concentration of **A** functions at time t, $[\mathbf{B}]_t$ = concentration of **B** functions at time t, and $p_{\mathrm{A},t}$ = conversion of **A** functions at the time t.

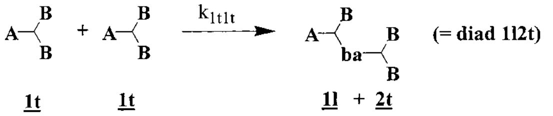
We are only interested in the ratio in the concentration of the different structural units. Therefore, we normalize the concentration of each unit by $[\mathbf{A}]_0$.

Scheme 1. Structural Units (1t, 1l, 1d, 2t, 2l and 2d) and Reaction Pathways for an AB$_2$ System[a]



[a] Capital letters A and B indicate unreacted functions; small letters a and b indicate reacted functions.

Scheme 2. The 12 Basic Reactions and the 12 Diads for an AB$_2$ System (Compare with Scheme 1 for the Notation of the Structural Units)



$$\mathbf{1t} + \mathbf{1t} \xrightarrow{k_{1t1t}} \mathbf{1l} + \mathbf{2t} \qquad (= \text{diad } \mathbf{1l2t})$$

$$\mathbf{1t} + \mathbf{1l} \xrightarrow{k_{1t1l}} \mathbf{1l} + \mathbf{2l} \qquad (= \text{diad } \mathbf{1l2l})$$

$$\mathbf{1t} + \mathbf{1d} \xrightarrow{k_{1t1d}} \mathbf{1l} + \mathbf{2d} \qquad (= \text{diad } \mathbf{1l2d})$$

$$\mathbf{1l} + \mathbf{1t} \xrightarrow{k_{1l1t}} \mathbf{1d} + \mathbf{2t} \qquad (= \text{diad } \mathbf{1d2t})$$

$$\mathbf{1l} + \mathbf{1l} \xrightarrow{k_{1l1l}} \mathbf{1d} + \mathbf{2l} \qquad (= \text{diad } \mathbf{1d2l})$$

$$\mathbf{1l} + \mathbf{1d} \xrightarrow{k_{1l1d}} \mathbf{1d} + \mathbf{2d} \qquad (= \text{diad } \mathbf{1d2d})$$

$$\mathbf{2t} + \mathbf{1t} \xrightarrow{k_{2t1t}} \mathbf{2l} + \mathbf{2t} \qquad (= \text{diad } \mathbf{2l2t})$$

$$\mathbf{2t} + \mathbf{1l} \xrightarrow{k_{2t1l}} \mathbf{2l} + \mathbf{2l} \qquad (= \text{diad } \mathbf{2l2l})$$

$$\mathbf{2t} + \mathbf{1d} \xrightarrow{k_{2t1d}} \mathbf{2l} + \mathbf{2d} \qquad (= \text{diad } \mathbf{2l2d})$$

$$\mathbf{2l} + \mathbf{1t} \xrightarrow{k_{2l1t}} \mathbf{2d} + \mathbf{2t} \qquad (= \text{diad } \mathbf{2d2t})$$

$$\mathbf{2l} + \mathbf{1l} \xrightarrow{k_{2l1l}} \mathbf{2d} + \mathbf{2l} \qquad (= \text{diad } \mathbf{2d2l})$$

$$\mathbf{2l} + \mathbf{1d} \xrightarrow{k_{2l1d}} \mathbf{2d} + \mathbf{2d} \qquad (= \text{diad } \mathbf{2d2d})$$

Since one **A** reacts with one **B** for each basic reaction step, the differential change of the **A** and **B** functions has to be equal:

$$d[\mathbf{A}] = d[\mathbf{B}] \tag{5}$$

The 12 Basic Reactions. The seven reaction pathways give the conversion from one structural unit to another due to the reaction of either **A** or **B**. As shown above, [**A**] and [**B**] are the sums of the concentrations of different structural units and therefore they cannot be treated as independent functions of time. From Scheme 1 we see that there are three structural units containing an active **A** function (**1t**, **1l**, **1d**) and four structural units containing at least one active **B** function (**1t**, **1l**, **2t**, **2l**).

This means that each pathway by which a structural unit reacts at its **B** function with an **A** function (reaction to the right within one row) consists of three basic reactions. This is because a conversion **B** → **b** is always accompanied by a conversion **A**→**a**, and there are three such possible conversions: **1t** → **2t**, **1l** → **2l**, and **1d** →

2d. Since there are four conversions **B** → **b** (i.e., **1t** → **1l**, **1l** → **1d**, **2t** → **2l**, and **2l** → **2d**), we have a total of 12 basic reactions.

By the same logic, each of the three **A** → **a** conversion pathways is governed by four basic reactions.

Scheme 2 shows a representative basic reaction and the notation of the 12 basic reactions, each of which subsequently yield two new structural units or one diad, respectively.

Equations 6−11 give the resulting differential equations for the changes in concentration of the six different structural units. The symbol $k_{\beta\alpha}$ denotes the reaction constant for which the structural unit β is reacting on its **B** site and the structural unit α is reacting on its **A** site. It is important to note that the units **1t** and **1l** can react on both sides (**A** and **B**). We distinguish between these two possibilities; each site generates its own set of basic reactions (therefore, $k_{1t1l} \neq k_{1l1t}$).

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{1t}] = -4k_{1t1t}[\mathbf{1t}][\mathbf{1t}] - 2k_{1t1l}[\mathbf{1t}][\mathbf{1l}] - 2k_{1t1d}[\mathbf{1t}] \times [\mathbf{1d}] - k_{1l1t}[\mathbf{1l}][\mathbf{1t}] - 2k_{2t1t}[\mathbf{2t}][\mathbf{1t}] - k_{2l1t}[\mathbf{2l}][\mathbf{1t}] \quad (6)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{1l}] = +2k_{1t1t}[\mathbf{1t}][\mathbf{1t}] + 2k_{1t1d}[\mathbf{1t}][\mathbf{1d}] - k_{1l1t}[\mathbf{1l}] \times [\mathbf{1t}] - 2k_{1l1l}[\mathbf{1l}][\mathbf{1l}] - k_{1l1d}[\mathbf{1l}][\mathbf{1d}] - 2k_{2t1l}[\mathbf{2t}][\mathbf{1l}] - k_{2l1l}[\mathbf{2l}][\mathbf{1l}] \quad (7)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{1d}] = -2k_{1t1d}[\mathbf{1t}][\mathbf{1d}] + k_{1l1t}[\mathbf{1l}][\mathbf{1t}] + k_{1l1l}[\mathbf{1l}] \times [\mathbf{1l}] - 2k_{2t1d}[\mathbf{2t}][\mathbf{1d}] - k_{2l1d}[\mathbf{2l}][\mathbf{1d}] \quad (8)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{2t}] = +2k_{1t1t}[\mathbf{1t}][\mathbf{1t}] + k_{1l1t}[\mathbf{1l}][\mathbf{1t}] - 2k_{2t1l}[\mathbf{2t}] \times [\mathbf{1l}] - 2k_{2t1d}[\mathbf{2t}][\mathbf{1d}] + k_{2l1t}[\mathbf{2l}][\mathbf{1t}] \quad (9)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{2l}] = +2k_{1t1l}[\mathbf{1t}][\mathbf{1l}] + k_{1l1l}[\mathbf{1l}][\mathbf{1l}] + 2k_{2t1t}[\mathbf{2t}] \times [\mathbf{1t}] + 4k_{2t1l}[\mathbf{2t}][\mathbf{1l}] + 2k_{2t1d}[\mathbf{2t}][\mathbf{1d}] - k_{2l1t}[\mathbf{2l}][\mathbf{1t}] - k_{2l1t}[\mathbf{2l}][\mathbf{1t}] - k_{2l1d}[\mathbf{2l}][\mathbf{1d}] \quad (10)$$

$$\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{2d}] = +2k_{1t1d}[\mathbf{1t}][\mathbf{1d}] + k_{1l1d}[\mathbf{1l}][\mathbf{1d}] + 2k_{2t1d}[\mathbf{2t}][\mathbf{1d}] + k_{2l1t}[\mathbf{2l}][\mathbf{1t}] + k_{2l1l}[\mathbf{2l}][\mathbf{1l}] + 2k_{2l1d}[\mathbf{2l}][\mathbf{1d}] \quad (11)$$

These equations must be solved in order to calculate the concentrations of the six structural units as a function of the conversion for a given set of the 12 k values. It seems quite obvious that this problem must be solved numerically; we will present the numerical evaluation of the concentrations of the six structural units as a function of the conversion for specific sets of k values in the following sections.

We changed the notation of this system of differential equations to matrix notation in order to analyze it systematically. This facilitates the numerical calculation and it allows easily a general treatment of this kind of problem. Furthermore, the different kinetic situations are better described in matrix notation and a fit of experimental data to a set of k values is easier.

Derivation of the Kinetics of the System through Matrix Notation and Numerical Evaluation of the Kinetics. A general approach to this problem is the development of a 6 × 6 matrix, which contains the reaction rate constant for every reaction. The rows contain the structural units reacting on the **A** site of a particular structural unit, and the columns give the structural units reacting on the **B** site of a particular structural unit.

$$\mathbf{K}^* = \begin{bmatrix} k_{1t1t} & k_{1l1t} & k_{1d1t} & k_{2t1t} & k_{2l1t} & k_{2d1t} \\ k_{1t1l} & k_{1l1l} & k_{1d1l} & k_{2t1l} & k_{2l1l} & k_{2d1l} \\ k_{1t1d} & k_{1l1d} & k_{1d1d} & k_{2t1d} & k_{2l1d} & k_{2d1d} \\ k_{1t2t} & k_{1l2t} & k_{1d2t} & k_{2t2t} & k_{2l2t} & k_{2d2t} \\ k_{1t2l} & k_{1l2l} & k_{1d2l} & k_{2t2l} & k_{2l2l} & k_{2d2l} \\ k_{1t2d} & k_{1l2d} & k_{1d2d} & k_{2t2d} & k_{2l2d} & k_{2d2d} \end{bmatrix} \quad (12)$$

To get the individual elements of the differential equations as bimolecular reactions, we would need to multiply the elements of the matrix **K*** with the corresponding elements of the matrix $\mathbf{r}^{*\mathrm{T}}\mathbf{r}^*$ (the vector $\boldsymbol{r}^*$ contains the concentrations of the six structural elements).

$$\boldsymbol{r}^* = [[\mathbf{1t}]\ [\mathbf{1l}]\ [\mathbf{1d}]\ [\mathbf{2t}]\ [\mathbf{2l}]\ [\mathbf{2d}]] \quad (13)$$

However, 24 of these 36 matrix elements are determined to equal zero, because the corresponding reactions are not possible: **1d** and **2d** cannot react on the **B** site and **2t**, **2l**, and **2d** cannot react on the **A** site.

$$\Rightarrow \mathbf{K}^* = \begin{bmatrix} k_{1t1t} & k_{1l1t} & 0 & k_{2t1t} & k_{2l1t} & 0 \\ k_{1t1l} & k_{1l1l} & 0 & k_{2t1l} & k_{2l1l} & 0 \\ k_{1t1d} & k_{1l1d} & 0 & k_{2t1d} & k_{2l1d} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \quad (14)$$

As mentioned before there are three structural units with active **A** functions and four structural units with active **B** functions. Thus, the system collapses to a 3 × 4 k value matrix **K**. The three rows represent the three "**B**-reaction-pathways" (Scheme 1, going from the upper row to the lower row) and the four columns represent the four "**A**-reaction-pathways" (Scheme 1, to the right within one row). In addition, we need to introduce two vectors representing the concentrations of the structural units with active **A**- (r^{A}) and active **B** functions (r^{B}), respectively:

$$\mathbf{K} = \begin{bmatrix} k_{1t1t} & k_{1l1t} & k_{2t1t} & k_{2l1t} \\ k_{1t1l} & k_{1l1l} & k_{2t1l} & k_{2l1l} \\ k_{1t1d} & k_{1l1d} & k_{2t1d} & k_{2l1d} \end{bmatrix} \quad (15)$$

$$\boldsymbol{r}^{\mathrm{A}} = [[\mathbf{1t}]\ [\mathbf{1l}]\ [\mathbf{1d}]], \quad \boldsymbol{r}^{\mathrm{B}} = [[\mathbf{1t}]\ [\mathbf{1l}]\ [\mathbf{2t}]\ [\mathbf{2l}]] \quad (16)$$

The different probabilities of the basic reactions also have to be considered: For the reaction on the **B** site **1t** and **2t** have a doubled probability due to the fact that two active **B** functionalities are available. This leads to the probability-vector $\boldsymbol{p}^{\mathrm{B}}$:

$$\boldsymbol{p}^{\mathrm{B}} = [2\ 1\ 2\ 1] \quad (17)$$

In a general case, this would also be a matrix expressing the probability for each matrix element of the **K*** matrix.

These expressions can be combined to the reaction-rate-matrix $\mathbf{R}^{\mathrm{r}}$ with

$$\mathrm{R}^{\mathrm{r}}_{ij} = \mathrm{r}_i^{\mathrm{A}} \cdot \mathrm{r}_j^{\mathrm{B}} \cdot k_{\mathrm{ij}} \cdot \mathrm{p}_j^{\mathrm{B}} \quad (18)$$

Table 1. Changes of the Structural Units along One Row or Column of the K Matrix (Eq 15), Respectively

1t1t	1l1t	2t1t	2l1t	⇒	1t → 2t
1t1l	1l1l	2t1l	2l1l	⇒	1l → 2l
1t1d	1l1d	2t1d	2l1d	⇒	1d → 2d
⇓	⇓	⇓	⇓		
1t → 1l	1l → 1d	2t → 2l	2l → 2d		

[a] The first number-letter-combination gives the structural unit reacting on the B site; the second combination denotes the unit reacting on the A site. The transitions along one row or column are indicated on the right side and in the bottom line, respectively.

$\mathbf{R}^r$ gives the product of the two concentrations of the bimolecular reaction multiplied with the reaction rate constant and the probability of this reaction for each of the 12 basic reactions. Each column and each row of $\mathbf{R}^r$ represents one of the reaction pathways (Table 1).

This is just another expression for the reaction Scheme 2. Summation over either the rows or columns of $\mathbf{R}^r$ gives the vectors $\boldsymbol{a}$ and $\boldsymbol{b}$ for the differential concentration changes along the single reaction pathway.

$$a_i = \sum_{j=1}^{4} \mathrm{R}^{\mathrm{r}}_{ij} = \sum_{j=1}^{4} \mathrm{r}^{\mathrm{A}}_i \cdot \mathrm{r}^{\mathrm{B}}_j \cdot k_{ij} \cdot \mathrm{p}^{\mathrm{B}}_j \qquad (19)$$

Now we create two matrices $\mathbf{N}^A$ and $\mathbf{N}^B$, which

$$b_j = \sum_{i=1}^{3} \mathrm{R}^{\mathrm{r}}_{ij} = \sum_{i=1}^{3} \mathrm{r}^{\mathrm{A}}_i \cdot \mathrm{r}^{\mathrm{B}}_j \cdot k_{ij} \cdot \mathrm{p}^{\mathrm{B}}_j \qquad (20)$$

express the changes on each reaction pathway. The six rows in $\mathbf{N}^A$ and $\mathbf{N}^B$ give the changes in the concentration for each of the six structural units. Each column refers to one element of the vector a or b, respectively.

$$\mathbf{N}^{\mathrm{A}} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \mathbf{N}^{\mathrm{B}} = \begin{bmatrix} -1 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 1 \end{bmatrix} \qquad (21)$$

Summing the products of the matrices $\mathbf{N}^A$ and $\mathbf{N}^B$ with the vectors $\boldsymbol{a}$ and $\boldsymbol{b}$, respectively, yield the same differential equations as shown above (eqs 6−11)

$$\dot{\boldsymbol{c}} = \mathbf{N}^{\mathrm{A}} \cdot \boldsymbol{a} + \mathbf{N}^{\mathrm{B}} \cdot \boldsymbol{b} \; \left(\dot{c}_j = \sum_{\mathrm{i}=1}^{3} a_i \cdot \mathrm{N}^{\mathrm{A}}_{ji} + \sum_{i=1}^{4} b_i \cdot \mathrm{N}^{\mathrm{B}}_{ji}\right) \qquad (22)$$

where $\dot{\boldsymbol{c}}$ is the vector for the differential changes of each of the six structural units:

$$\dot{\boldsymbol{c}} = \left[\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{1t}]\;\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{1l}]\;\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{1d}]\;\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{2t}]\;\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{2l}]\;\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{2d}]\right] \qquad (23)$$

Once $\mathbf{K}$, r^A, r^B, p^B, $\mathbf{N}^A$, and $\mathbf{N}^B$ are identified, we can write down the whole system of differential equations in four lines in matrix notation (eqs 18, 19, 20, and 22). This detailed description of the matrix notation is given to simplify the understanding of the AB_3 and ABB′ system, which will be discussed below.

This system of differential equations cannot be solved analytically. Therefore, we performed a numerical evaluation. The simplest method is the classical Euler method.[23] This leads to the transition from the differential (e.g., dt) to the increment (e.g., Δt) in a linear extrapolation. We also performed the Runge−Kutta method[23] (2nd and 4th order), which includes derivatives into the calculation. Both methods led to the same results. All generated graphs in this paper are based on the Euler Method.

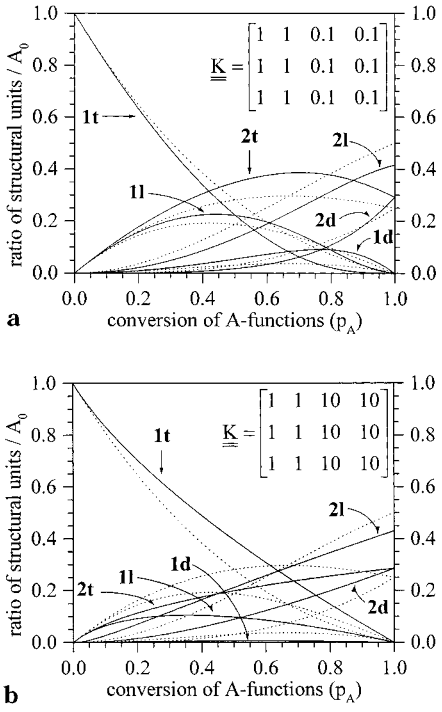


Figure 1. Simulation of conversion dependence of the structural units **1t**, **1l**, **1d**, **2t**, **2l**, and **2d**: (a) situation 1a; (b) situation 1b. The curves for the ideal kinetics are given as dotted lines.

To compare the different kinetic situations, a plot of the concentration versus the conversion of **A** functions (p_A) has been performed following eqs 1−4. These results will be shown in the following section.

Discussion of the Three Major Kinetic Situations as Functions of the Conversion. We are only interested in the relation between the different rate constants and their influence during the reaction as well as in the final product. Therefore, one rate constant can be set to 1 and the others will be varied. For the discussion of this system of an AB_2 monomer in a polymerization reaction with nonuniform reaction rate constants, we have identified three possible “general” kinetic situations, which are reasonable from the point of the chemical reactivity. The general expression and one example of each situation are shown below. Figures 1a−3b show the conversion dependence of the structural units. The matrix of the 12 reaction rate constants is denoted in each figure. The dotted lines give the conversion dependence of the structural units for the ideal situation (all $k = 1$):

1. The reacted **a** function decreases/increases the reactivity of the **B** functionalities (comparing columns 1 and 2 with 3 and 4, Table 1):

$$\{\mathbf{1t} \rightarrow \mathbf{1l}\} = \{\mathbf{1l} \rightarrow \mathbf{1d}\} > \{\mathbf{2t} \rightarrow \mathbf{2l}\} = \{\mathbf{2l} \rightarrow \mathbf{2d}\} \quad \text{(decrease)}$$

$$\{\mathbf{1t} \rightarrow \mathbf{1l}\} = \{\mathbf{1l} \rightarrow \mathbf{1d}\} < \{\mathbf{2t} \rightarrow \mathbf{2l}\} = \{\mathbf{2l} \rightarrow \mathbf{2d}\} \quad \text{(increase)}$$

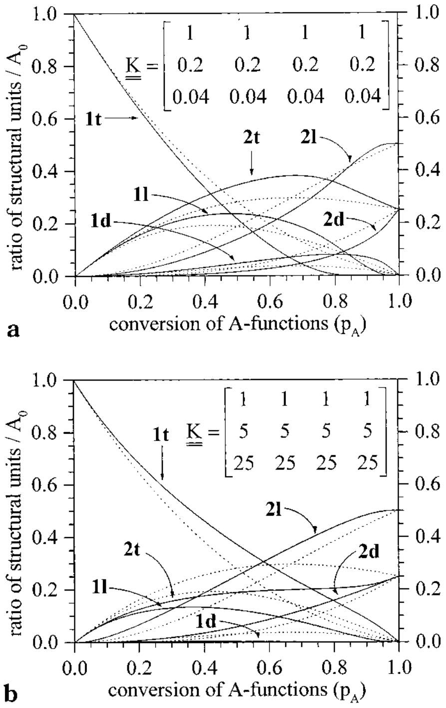


Figure 2. Simulation of conversion dependence of the structural units **1t**, **1l**, **1d**, **2t**, **2l**, and **2d**: (a) situation 2a; (b) situation 2b. The curves for the ideal kinetics are given as dotted lines.

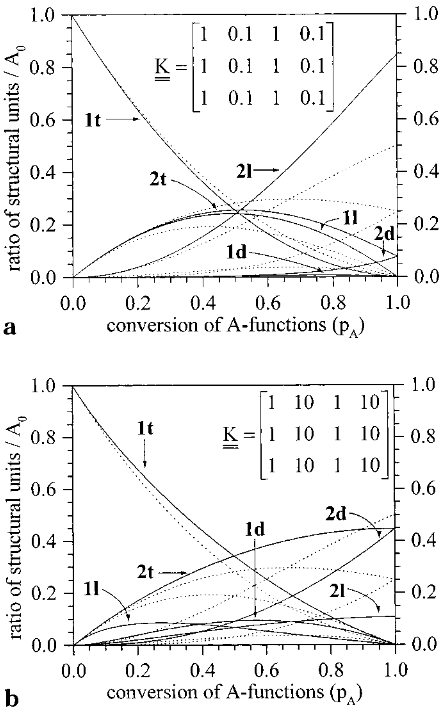


Figure 3. Simulation of conversion dependence of the structural units **1t**, **1l**, **1d**, **2t**, **2l**, and **2d**: (a) situation 3a; (b) situation 3b. The curves for the ideal kinetics are given as dotted lines.

2. The reacted **b** function decreases/increases the reactivity of the **A** function (comparing rows 1, 2, and 3, Table 1):

$$\{\mathbf{1t} \rightarrow \mathbf{2t}\} > \{\mathbf{1l} \rightarrow \mathbf{2l}\} > \{\mathbf{1d} \rightarrow \mathbf{2d}\} \text{ (decrease)}$$

$$\{\mathbf{1t} \rightarrow \mathbf{2t}\} < \{\mathbf{1l} \rightarrow \mathbf{2l}\} < \{\mathbf{1d} \rightarrow \mathbf{2d}\} \text{ (increase)}$$

3. The reacted **b** function of a linear unit decreases/increases the reactivity of the second **B** function (comparing columns 1 and 3 with columns 2 and 4, Table 1):

$$\{\mathbf{1t} \rightarrow \mathbf{1l}\} = \{\mathbf{2t} \rightarrow \mathbf{2l}\} > \{\mathbf{1l} \rightarrow \mathbf{1d}\} = \{\mathbf{2l} \rightarrow \mathbf{2d}\} \text{ (decrease)}$$

$$\{\mathbf{1t} \rightarrow \mathbf{1l}\} = \{\mathbf{2t} \rightarrow \mathbf{2l}\} < \{\mathbf{1l} \rightarrow \mathbf{1d}\} = \{\mathbf{2l} \rightarrow \mathbf{2d}\} \text{ (increase)}$$

Analyzing these three situations we can conclude that Frey's factor $x = k_L/k_T$[8] is addressed by our kinetic situation 3.

In all three of these cases, we do not consider the origin of the difference of the k values, and we neglect long-range effects of the penultimate units.

We have a two-dimensional reaction scheme with bimolecular reactions. Therefore, every step in Scheme 1 within one row from left to right is connected with one step from the upper row to the lower. The consequence of this observation is that one cannot influence one particular reaction pathway without influencing the other pathways. This renders the full kinetic system quite robust, and even a 10-fold increase in a reaction rate constant causes only moderate changes in the curve shape and the final composition. In particular, the situations 1a and 1b do not influence the curves largely. Both situations increase the ratio of dendritic units in the final composition, but 1a increases the number of dendritic units to a higher value than 1b.

Situations 2a and 2b also change the curves only moderately. Furthermore, it should be noted that the final composition of the structural units approaches the ideal situation (**2t**:**2l**:**2d** = 25:50:25). Any combination of k values with equal values within a single row changes the shape of the curve but does not alter the final composition. This observation can be explained as follows: each of the four columns in the **K** matrix represents a single pathway where a **B** function will be altered. The reaction on the **B** site actually influences the composition of the final product, but the reaction on the **A** site represents the progress of the reaction. Furthermore, if we compare the sums **1t** + **2t**, **1l** + **2l**, and **1d**+ **2d** of situation 2 with the ideal situation, they are always exactly the same curves. So, the kinetic situation 2 only alters the distribution between **1x** and **2x** units.

Situations 3a and 3b have larger effects on curve shape and final composition. In particular, at high conversion the deviation from the ideal case is significant. To influence the branching of a hyperbranched polymer one must design the monomer in such a way that the active B function of the terminal unit influences the reactivity of the other B function (besides new techniques such as slow monomer addition).[8,18]

This discussion is summarized in Table 2, which compares the final compositions of the different nonideal situations with the ideal kinetics. We distinguished always cases a and b with different rate constants for selected reaction pathways.

Situations 1a and 1b in Table 1 represent the case where the reaction steps starting from **2t** and **2l** exhibit a lower (k = 0.1) or higher (k = 10) rate constant compared to the ideal situation (k = 1). This leads in both cases to a slight increase in the DB. Situation 2

Table 2. Final Composition of the Structural Units and Final Degree of Branching (DB) at $p_A = 1$ for the Different Kinetic Situations of an AB_2 System

no.	**K**[a]	**2t**	**2l**	**2d**	DB (%)[a]
ideal situation	$\begin{bmatrix}1 & 1 & 1 & 1\\ 1 & 1 & 1 & 1\\ 1 & 1 & 1 & 1\end{bmatrix}$	0.250	0.500	0.250	50.0
1a	$\begin{bmatrix}1 & 1 & 0.1 & 0.1\\ 1 & 1 & 0.1 & 0.1\\ 1 & 1 & 0.1 & 0.1\end{bmatrix}$	0.292	0.416	0.292	58.4
1b	$\begin{bmatrix}1 & 1 & 10 & 10\\ 1 & 1 & 10 & 10\\ 1 & 1 & 10 & 10\end{bmatrix}$	0.285	0.430	0.285	57.0
2a	$\begin{bmatrix}1 & 1 & 1 & 1\\ 0.2 & 0.2 & 0.2 & 0.2\\ 0.04 & 0.04 & 0.04 & 0.04\end{bmatrix}$	0.250	0.500	0.250	50.0
2b	$\begin{bmatrix}1 & 1 & 1 & 1\\ 5 & 5 & 5 & 5\\ 25 & 25 & 25 & 25\end{bmatrix}$	0.250	0.500	0.250	50.0
3a	$\begin{bmatrix}1 & 0.1 & 1 & 0.1\\ 1 & 0.1 & 1 & 0.1\\ 1 & 0.1 & 1 & 0.1\end{bmatrix}$	0.078	0.844	0.078	15.6
3b	$\begin{bmatrix}1 & 10 & 1 & 10\\ 1 & 10 & 1 & 10\\ 1 & 10 & 1 & 10\end{bmatrix}$	0.447	0.106	0.447	89.4

[a] **K** = matrix of the reaction rate constants. DB = (2 × **2d**)/(2 × **2d** + **2l**)(definition of *DB* after Frey et al.,[7] at $p_A = 1$ only **2t**, **2l**, and **2d** units are present in the system).

does not change the final composition at all. In situation 3, however, the dependence of the calculated DB values on changes in the rate constants is quite dramatic. A 10-fold decrease of the specific rate constants which describe the influence of the reactivity of the primarily formed structural unit lead to a DB of only 15% compared to the ideal 50%. Similarly, a 10-fold increase in reactivity allows to reach a DB of almost 90%. Reported experimental values for DB range between about 20 to 80% with the largest deviations found for SCVP[22b] or in ABB* systems, e.g., for hyperbranched polyethers from 3-ethyl-3-hydroxymethyloxetane.[24] In extreme situations even a DB of 100% was reported.[14,15] Therefore, the rate constants ratios applied in these model calculations seem reasonable.

Discussion of the 12 Diads. With the expression of the 12 basic reactions, we already have a matrix that contains the rate of the formation of the 12 diads. (For the notation of the diads compare Scheme 2.) But since every reaction of two structural units not only forms one new diad, but also alters up to three adjacent diads, the calculation based on differential equations must consider the reactions of all the triads, which dramatically increases the number of basic reaction steps. With the above-mentioned assumption that we do not have any kinetic effects due to the penultimate group, we calculated the diads via a probabilistic approach based on the results of the calculation of the six structural units. This has been performed already for the ideal case, and it was shown that the different diads could be identified and quantified by NMR spectroscopy.[25] Knowledge of the diad distribution and about changes compared to the results based on a probabilistic approach would give further information about the microstructure and relative reactivity. The calculation simply takes the product of the two structural units multiplied with a normalization factor n. Equation 24 gives the calculation of the elements of the matrix **D**, which represents the ratio of diads

$$D_{ij} = n\cdot \mathrm{r}_i^{\mathrm{A}}\cdot \mathrm{r}_j^{\mathrm{B}}\cdot p_j \qquad (24)$$

with

$$n = \left(\sum_{i=1}^{3} \mathrm{r}_i^{\mathrm{A}}\right)^{-1} = \left(\sum_{j=1}^{4} \mathrm{r}_j^{\mathrm{B}}\cdot p_j\right)^{-1} \qquad (25)$$

Parts a and b of Figure 4 show the ratio of diads as a function of conversion for the ideal case, and parts c and d of Figure 4 are plots for the nonideal situation 3b.

Again, the kinetic situation 3 shows the largest influence on the distribution of the diads. As expected from the final distribution of structural units, situation 3b yields a large decrease of the **2l** diads and an increase in the **2d** diads. Table 3 summarizes the final compositions for the different diads with the respect of the different kinetic situations and compares it with the ideal kinetics.

Because of the fact that [**2t**] is at $p_A = 1$ always equal to [**2d**] also the diads exhibit a pattern for any set of k values at $p_A = 1$:

$$[\mathbf{2l2t}] = [\mathbf{2l2d}] = [\mathbf{2d2l}]/2 \quad (\text{at } p_A = 1) \qquad (26)$$

$$[\mathbf{2d2t}] = [\mathbf{2d2d}] \quad (\text{at } p_A = 1) \qquad (27)$$

AB_3 Systems. The considerations above can be extended to an AB_3 system by defining again the different structural units and the reaction pathways.

The Eight Structural Units and the 10 Reaction Pathways. Again a number-letter-combination indi-

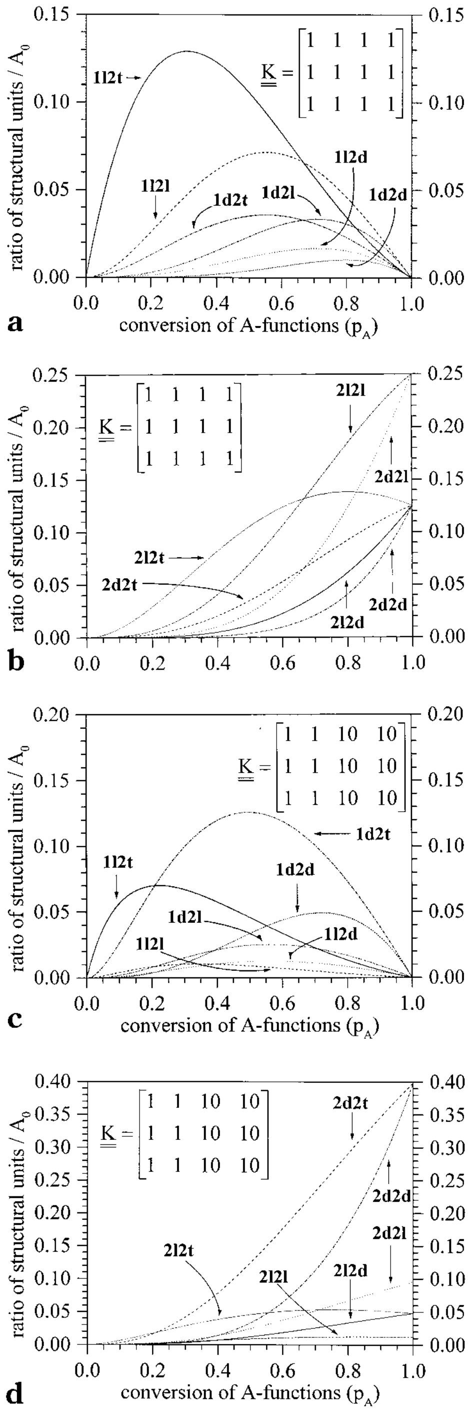


Figure 4. Simulation of conversion dependence of the diads: (a) ideal situation for diads **1l2t**, **1l2l**, **1l2d**, **1d2t**, **1d2l**, **1d2d**; (b) ideal situation for diads **2l2t**, **2l2l**, **2l2d**, **2d2t**, **2d2l**, **2l2d**; (c) situation 3b for diads **1l2t**, **1l2l**, **1l2d**, **1d2t**, **1d2l**, **1d2d**; (d) situation 3b for diads **2l2t**, **2l2l**, **2l2d**, **2d2t**, **2l2l**, **2l2d**.

cates the different structural units. We have three **B** functions, which subsequently react. The structural units are **t**erminal (**t**), **l**inear (**l**), **s**emidendritic (**s**) or **d**endritic (**d**) units depending whether zero, one, two, or all three **B** functions have reacted. And again the number **1** indicates units in which the **A** function has not reacted and **2** indicates units with reacted **A** functions. Scheme 3 gives the notation of the eight structural units and the 10 reaction pathways.

The 24 Basic Reactions. There are six structural units with at least one active **B** function and four units with an active **A** function (compare Scheme 3). This gives $4 \times 6 = 24$ basic reactions with 24 different reaction rate constants $k_{\beta\alpha}$; these can be expressed in a 4×6 matrix (indices: l = linear, t = terminal, s = semidendritic, and d = dendritic).

Derivation of the Kinetics of the System through Matrix Notation. The *k* value matrix **K**, the concentration vectors for **A** and **B** reagents $\boldsymbol{r}^{\mathrm{A}}$ and $\boldsymbol{r}^{\mathrm{B}}$, and the probability vector $\boldsymbol{p}^{\mathrm{B}}$ are shown in eqs 28–30:

$$\mathbf{K} = \begin{bmatrix} k_{1t1t} & k_{1l1t} & k_{1s1t} & k_{2t1t} & k_{2l1t} & k_{2s1t} \\ k_{1t1l} & k_{1l1l} & k_{1s1l} & k_{2t1l} & k_{2l1l} & k_{2s1l} \\ k_{1t1s} & k_{1l1s} & k_{1s1s} & k_{2t1s} & k_{2l1s} & k_{2s1s} \\ k_{1t1d} & k_{1l1d} & k_{1s1d} & k_{2t1d} & k_{2l1d} & k_{2s1d} \end{bmatrix} \tag{28}$$

$$\boldsymbol{r}^{\mathrm{A}} = [[\mathbf{1t}]\ [\mathbf{1l}]\ [\mathbf{1s}]\ [\mathbf{1d}]],\quad \boldsymbol{r}^{\mathrm{B}} = [[\mathbf{1t}]\ [\mathbf{1l}]\ [\mathbf{1s}]\ [\mathbf{2t}]\ [\mathbf{2l}]\ [\mathbf{2s}]] \tag{29}$$

$$\boldsymbol{p}^{\mathrm{B}} = [3\ 2\ 1\ 3\ 2\ 1] \tag{30}$$

With this information one can write the reaction-rate-matrix $\mathbf{R}^{\mathrm{r}}$ and the differential concentrations changes along one pathway (*a* and *b*) as follows:

$$\mathrm{R}^{\mathrm{r}}_{ij} = \mathrm{r}^{\mathrm{A}}_{i}\cdot\mathrm{r}^{\mathrm{B}}_{j}\cdot\mathrm{K}_{ij}\cdot\mathrm{p}^{\mathrm{B}}_{j} \tag{31}$$

$$a_i = \sum_{j=1}^{6}\mathrm{R}^{\mathrm{r}}_{ij} \tag{32}$$

$$b_j = \sum_{i=1}^{4}\mathrm{R}^{\mathrm{r}}_{ij} \tag{33}$$

The matrices $\mathbf{N}^{\mathrm{A}}$ and $\mathbf{N}^{\mathrm{B}}$ for the changes on the different reaction pathways are given in eq 34.

$$\mathbf{N}^{\mathrm{A}} = \begin{bmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix},\quad \mathbf{N}^{\mathrm{B}} = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{34}$$

Combining eqs 32–34 results in the set of differential equations for the differential changes in the conversion of each structural unit (written in matrix notation):

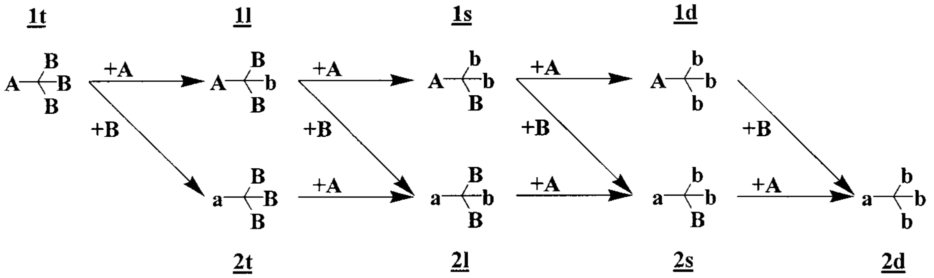
$$\dot{\boldsymbol{c}} = \mathbf{N}^{\mathrm{A}}\cdot a + \mathbf{N}^{\mathrm{B}}\cdot b \tag{35}$$

As mentioned above, when the structural units, the reaction pathways and the basic structural units are known, the derivation of the set of differential equations can be easily performed and this can be extended to any AB_n system. To analyze the AB_n systems systematically,

Table 3. Final Composition of the Diads at $p_A = 1$ for the Different Kinetic Situations of an AB_2 System

no.	K	2l2t	2l2l	2l2d	2d2t	2d2l	2d2d
ideal situation	$\begin{bmatrix}1&1&1&1\\1&1&1&1\\1&1&1&1\end{bmatrix}$	0.125	0.250	0.125	0.125	0.250	0.125
1a	$\begin{bmatrix}1&1&0.1&0.1\\1&1&0.1&0.1\\1&1&0.1&0.1\end{bmatrix}$	0.121	0.174	0.121	0.170	0.244	0.170
1b	$\begin{bmatrix}1&1&10&10\\1&1&10&10\\1&1&10&10\end{bmatrix}$	0.123	0.185	0.123	0.162	0.245	0.162
2a	$\begin{bmatrix}1&1&1&1\\0.2&0.2&0.2&0.2\\0.04&0.04&0.04&0.04\end{bmatrix}$	0.125	0.250	0.125	0.125	0.250	0.125
2b	$\begin{bmatrix}1&1&1&1\\5&5&5&5\\25&25&25&25\end{bmatrix}$	0.125	0.250	0.125	0.125	0.250	0.125
3a	$\begin{bmatrix}1&0.1&1&0.1\\1&0.1&1&0.1\\1&0.1&1&0.1\end{bmatrix}$	0.065	0.715	0.065	0.012	0.131	0.012
3b	$\begin{bmatrix}1&10&1&10\\1&10&1&10\\1&10&1&10\end{bmatrix}$	0.047	0.012	0.047	0.399	0.096	0.399

Scheme 3. Structural Units (1t, 1l, 1s, 1d, 2t, 2l, 2s, and 2d) and Reaction Pathways for an AB_3 System[a]



[a] Capital letters A and B indicate unreacted functions;, small letters a and b indicate reacted functions.

Table 4. Number of Reaction Sites, Structural Units, Reaction Pathways and Basic Reactions for an AB_n System

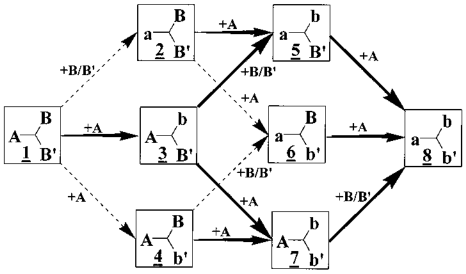
n		reaction sites	structural units	reaction pathways	basic reactions
1	AB	$1 + 1 = 2$	$2 \times 2 = 4$	$2 + 2 = 4$	$2 \times 2 = 4$
2	AB_2	$1 + 2 = 3$	$2 \times 3 = 6$	$3 + 4 = 7$	$3 \times 4 = 12$
3	AB_3	$1 + 3 = 4$	$2 \times 4 = 8$	$4 + 6 = 10$	$4 \times 6 = 24$
...					
n	AB_n	$1 + n$	$2 \times (1 + n)$	$(1 + n) + 2n$	$(1 + n) \times 2n$

Table 4 shows the number of structural units, reaction pathways, and basic reactions as a general expression.

ABB′ Systems. Reaction Pathways. The AB_n systems can be classified as two-dimensional situations, where only two different reactive groups exist (**A** and **B**). The n**B** functions are indistinguishable. In ABB′ systems there are three different species and therefore the monomer can react on three different paths (or “dimensions”). Scheme 4 illustrates the different structural units and their possible reaction pathways.

There are eight different structural units, which are connected via 12 different pathways. We have chosen a cube as a graphical representation; here, every corner represents a structural unit and every edge a reaction pathway.

Scheme 4. Eight Structural Units (1, 2, 3, 4, 5, 6, 7 and 8) and 12 Reaction Pathways for an ABB′ System[a]



[a] Capital letters A, B, and B′ indicate unreacted functions; small letters a, b, and b′ indicate reacted functions.

Basic Reactions. Under the assumption that **A** can only react with **B** or **B′** we find four units with active **A** functions, four units with active **B** functions, and four units with active **B′** functions. This leads to two 4 × 4 matrices (**A** reacts with **B** and **A** reacts with **B′**) or one 4 × 8 matrix for the expression of the 32 basic reactions (Table 5).

Derivation of the Kinetics of the System through Matrix Notation. The k value matrix **K** and the concentration vectors for **A** and **B** reagents $\boldsymbol{r}^{A}$ and $\boldsymbol{r}^{B,B'}$

are shown in eqs 36 and 37; all elements of the probability-vector $\boldsymbol{p}^{\mathrm{B}}$ are equal to 1, because the two **B** functions are now distinguishable.

$$\mathbf{K} = \begin{bmatrix} k_{11} & k_{21} & k_{41} & k_{61} & k_{1'1} & k_{2'1} & k_{3'1} & k_{5'1} \\ k_{13} & k_{23} & k_{43} & k_{63} & k_{1'3} & k_{2'3} & k_{3'3} & k_{5'3} \\ k_{14} & k_{24} & k_{44} & k_{64} & k_{1'4} & k_{2'4} & k_{3'4} & k_{5'4} \\ k_{17} & k_{27} & k_{47} & k_{67} & k_{1'7} & k_{2'7} & k_{3'7} & k_{5'7} \end{bmatrix} \qquad (36)$$

$$\boldsymbol{r}^{\mathrm{A}} = [[1]\ [3]\ [4]\ [7]],$$
$$\boldsymbol{r}^{\mathrm{B,B'}} = [[1]\ [2]\ [4]\ [6]\ [1]\ [2]\ [3]\ [5]] \qquad (37)$$

Now we can write the reaction-rate matrix $\mathbf{R}^{\mathrm{r}}$ and the differential concentrations changes for the units reacting on the **A** site and the **B**/**B′** site, respectively, (*a* and *b*) as follows:

$$\mathrm{R}^{\mathrm{r}}_{ij} = \mathrm{r}^{\mathrm{A}}_{i}\cdot\mathrm{r}^{\mathrm{B,B'}}_{j}\cdot\mathrm{K}_{ij} \qquad (38)$$

$$a_i = \sum_{j=1}^{8} \mathrm{R}^{\mathrm{r}}_{ij} \qquad (39)$$

The matrices $\mathbf{N}^{\mathrm{A}}$ and $\mathbf{N}^{\mathrm{B,B'}}$ for the changes on the

$$b_j = \sum_{i=1}^{4} \mathrm{R}^{\mathrm{r}}_{ij} \qquad (40)$$

different reaction pathways are given in eq 41.

$$\mathbf{N}^{\mathrm{A}} = \begin{bmatrix} -1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & 1 \end{bmatrix},$$

$$\mathbf{N}^{\mathrm{B,B'}} = \begin{bmatrix} -1 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & -1 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{bmatrix} \qquad (41)$$

Combining eqs 39−41 results in the set of differential equations for the differential changes in the conversion of each structural unit (written in matrix notation):

$$\dot{\boldsymbol{c}} = \mathbf{N}^{\mathrm{A}}\cdot a + \mathbf{N}^{\mathrm{B,B'}}\cdot b \qquad (42)$$

with

$$\dot{\boldsymbol{c}} = \left[\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{1}]\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{2}]\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{3}]\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{4}]\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{5}]\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{6}]\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{7}]\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{8}]\right] \qquad (43)$$

Self-Condensing Vinyl Polymerization as a Special Example for an ABB′ System. The self-condensing vinyl polymerization (SCVP) is another important technique for the preparation of hyperbranched polymers from a single monomer in a one-pot-synthesis. A large number of publications have dealt with the synthesis of hyperbranched polymers via SCVP to date.[22] In the kinetic analysis, we consider the SCVP as a special case of an ABB′ system, because one of the **B**/**B′** functions will be generated through the reaction of the **A** function with either **B** or **B′**. Scheme 5 illustrates the situation with *p*-(chloromethyl)styrene[22d] as one example for a SCVP to point out the notation. It should be noted that for SCVP the structural units **1** and **4** do not contain the **B** function, therefore they are written in brackets.

In this case **B** will be generated when the **A** function has reacted. This restriction to the kinetics simplifies the description of the system to six structural units (**1**, **2**, **4**, **5**, **6**, **8**), seven reaction pathways and 10 basic reactions:

$$\mathbf{K} = \begin{bmatrix} 0 & k_{21} & 0 & k_{61} & k_{1'1} & k_{2'1} & 0 & k_{5'1} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & k_{24} & 0 & k_{64} & k_{1'4} & k_{2'4} & 0 & k_{5'4} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad (44)$$

$$\boldsymbol{r}^{\mathrm{A}} = [[\mathbf{1}]\ 0\ [\mathbf{4}]\ 0],\quad \boldsymbol{r}^{\mathrm{B,B'}} = [0\ [\mathbf{2}]\ 0\ [\mathbf{6}]\ [\mathbf{1}]\ [\mathbf{2}]\ 0\ [\mathbf{5}]] \qquad (45)$$

$$\mathbf{N}^{\mathrm{A}} = \begin{bmatrix} -1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix},$$

$$\mathbf{N}^{\mathrm{B,B'}} = \begin{bmatrix} 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & -1 \\ 0 & 0 & 0 & -1 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 1 \end{bmatrix} \qquad (46)$$

$$\dot{\boldsymbol{c}} = \mathbf{N}^{\mathrm{A}}\cdot a + \mathbf{N}^{\mathrm{B,B'}}\cdot b \qquad (47)$$

with

$$\dot{\boldsymbol{c}} = \left[\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{1}]\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{2}]\ 0\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{4}]\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{5}]\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{6}]\ 0\ \frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{8}]\right] \qquad (48)$$

Müller et al.[5] derived also the kinetics for SCVP with nonuniform reaction rate constants. They introduced a factor $r = k_{\mathrm{A}}/k_{\mathrm{B}}$[20] which gives the ratio of their two different reactions. In our notation system the corresponding *k* value matrix would be

$$\mathbf{K} = \begin{bmatrix} 0 & k_{\mathrm{A}} & 0 & k_{\mathrm{A}} & k_{\mathrm{B}} & k_{\mathrm{B}} & 0 & k_{\mathrm{B}} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & k_{\mathrm{A}} & 0 & k_{\mathrm{A}} & k_{\mathrm{B}} & k_{\mathrm{B}} & 0 & k_{\mathrm{B}} \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \qquad (49)$$

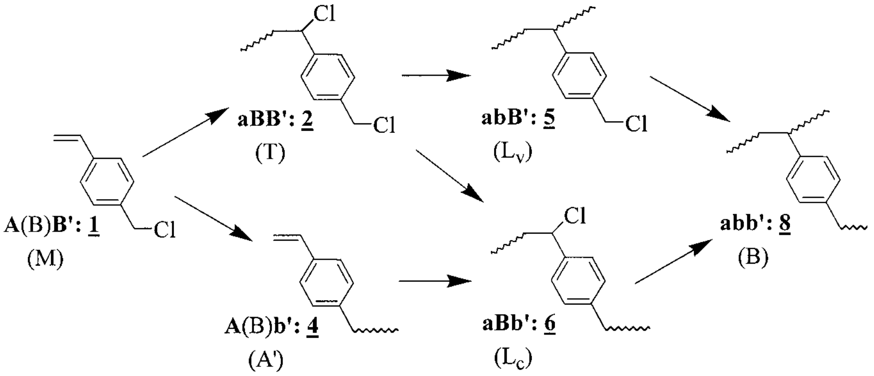
Thus, this situation distinguishes whether the A function reacts with either B or B′. Implementing these numerical models our results agreed very well with those published by Müller.[5]

Table 5. Changes of the Structural Units for an ABB′ System (Compare with Eq 36)

	A*B*B′ = 1	**a*B*B′** = 2	**A*B*b′** = 4	**A*B*b′** = 6	**AB*B*′** = 1	**aB*B*′** = 2	**Ab*B*′** = 3	*abB′* = 5
***A*BB′** = 1	k_{11} $1 + 1 \rightarrow 3 + 2$	k_{21} $2 + 1 \rightarrow 5 + 2$	k_{41} $4 + 1 \rightarrow 7 + 2$	k_{61} $6 + 1 \rightarrow 8 + 2$	$k_{1'1}$ $1 + 1 \rightarrow 4 + 2$	$k_{2'1}$ $2 + 1 \rightarrow 6 + 2$	$k_{3'1}$ $3 + 1 \rightarrow 7 + 2$	$k_{5'1}$ $5 + 1 \rightarrow 8 + 2$
***A*bB′** = 3	k_{13} $1 + 3 \rightarrow 3 + 5$	k_{23} $2 + 3 \rightarrow 5 + 5$	k_{43} $4 + 3 \rightarrow 7 + 5$	k_{63} $6 + 3 \rightarrow 8 + 5$	$k_{1'3}$ $1 + 3 \rightarrow 4 + 5$	$k_{2'3}$ $2 + 3 \rightarrow 6 + 5$	$k_{3'3}$ $3 + 3 \rightarrow 7 + 5$	$k_{5'3}$ $5 + 3 \rightarrow 8 + 5$
***A*Bb′** = 4	k_{14} $1 + 4 \rightarrow 3 + 6$	k_{24} $2 + 4 \rightarrow 5 + 6$	k_{44} $4 + 4 \rightarrow 7 + 6$	k_{64} $6 + 4 \rightarrow 8 + 6$	$k_{1'4}$ $1 + 4 \rightarrow 4 + 6$	$k_{2'4}$ $2 + 4 \rightarrow 6 + 6$	$k_{3'4}$ $3 + 4 \rightarrow 7 +6$	$k_{5'4}$ $5 + 4 \rightarrow 8 + 6$
***A*bb′** = 7	k_{17} $1 + 7 \rightarrow 3 + 8$	k_{27} $2 + 7 \rightarrow 5 + 8$	k_{47} $4 + 7 \rightarrow 7 + 8$	k_{67} $6 + 7 \rightarrow 8 + 8$	$k_{1'7}$ $1 + 7 \rightarrow 4 + 8$	$k_{2'7}$ $2 + 7 \rightarrow 6 + 8$	$k_{3'7}$ $3 + 7 \rightarrow 7 + 8$	$k_{5'7}$ $5 + 7 \rightarrow 8 + 8$

[a] The subscript letters always denote the groups which are reacting.

Scheme 5. Structural Units and Reaction Pathways of the Polymerization of *p*-(Chloromethyl)styrene as an Example for an ABB′ System[a]



[a] The notation in parentheses refers to that of Yan et al.:[5b] M = monomer; T = terminal unit; A′ = focal units; L$_v$ = linear units (vinyl type); L$_c$ = linear units (polycondensate type); B = branch points.

A second general kinetic situation is the acceleration or deceleration through the active vinyl−(**A**) function. This can be expressed in equal *k* values within one row and different *k* values between the two rows.

Conclusions

The evaluation and generalization of the kinetics of reactions with nonuniform reaction rate constants leading to hyperbranched polymers have been shown. The matrix notation facilitates the notation of the differential equation as well as simplifies the computation of the concentration of the structural units as a function of time. Our method allows us to study the effect on the kinetics, whenever a single basic reaction is accelerated or decelerated, but we focused our work on three general kinetic situations, which are reasonable from a chemical viewpoint.

We studied the AB$_2$ system extensively, because this is the most frequently occurring system of a hyperbranched polycondensation and the theoretical results can be verified by sufficient experimental data.[21,25] However, this notation of the kinetics of hyperbranched polymerization can be easily extended to similar systems such as the AB$_3$ or ABB′ types, as has also been discussed in the example of the self-condensing vinyl polymerization. One important feature of the SCVP compared to the hyperbranched polymerization is the fact that the second **B** function will be generated when the **A** function has reacted. This changes the kinetics considerably.

The analysis of AB$_2$ systems with nonuniform reaction rate constants yields a large effect on the distribution of structural units as a function of the conversion, when the reacted **B** function of a linear unit increases or decreases the reactivity of the second **B** function. In this case the degree of branching at $p_A = 1$, which is calculated from the distribution of the structural units, can deviate strongly from the ideal value of 0.5. For example a 10-fold higher or lower reactivity of the reactions **1t** → **1l** and **2t** → **2l** compared to **1l** → **1d** and **2l** → **2d** changes the DB to 0.15 and 0.89, respectively. The other general kinetic situations have minor effects.

The stochastic calculation of the diad formations has been performed via a probabilistic approach based on the numerical evaluation of the structural units. This means we do not consider any further kinetic effects due to clustering. Again the accelerating or decelerating effect of the active **B** function on the second **B** function exhibits the largest effect on the kinetics of the diad formation.

We adopted this general method for the presentation of kinetics of multistep reactions to represent the kinetic situation of a hyperbranched system, but we would like to point out that this method is not limited to hyperbranched polymerization. Any chemical reaction with different intermediates and branched reaction pathways can be described in a similar manner.

Appendix

Symbols

$[\mathbf{A}]_0$: initial concentration of **A** functions

$[\mathbf{A}]_t$: concentration of **A** functions at the time *t*

$\boldsymbol{a}$: vector of the differential concentrations changes along one pathway

$[\mathbf{B}]_t$: concentration of **B** functions at the time *t*

$\boldsymbol{b}$: vector of the differential concentrations changes along one pathway

$\dot{\boldsymbol{c}}$: vector of the differential changes of the structural units

D: matrix of the ratio of diads

K: matrix of reaction rate constants $k_{\beta\alpha}$

$k_{\beta\alpha}$: reaction rate constant for which the structural unit β is reacting on its **B** site and the structural unit α is reacting on its **A** site

$\mathbf{N}^{A}$: matrix of the changes in concentration of the structural units on the **A**-reaction pathway

$\mathbf{N}^{B}$: matrix of the changes in concentration of the structural units on the **B**-reaction pathway

n: normalization factor

$p_{A,t}$: conversion of **A** functions at time t

$\boldsymbol{p}^{B}$: probability vector

$\mathbf{R}^{r}$: reaction-rate matrix

$\boldsymbol{r}^{A}$: vector of the concentration of the structural units with active **A** functions

$\boldsymbol{r}^{B}$: vector of the concentration of the structural units with active **B** functions

Acknowledgment. The authors thank Dr. P. Friedel, Prof. A. Müller, and Dr. H. Frey for helpful discussion.

Supporting Information Available: Text detailing the kinetic situations and figures showing the plots of the different kinetic situations for AB_2 system and for SCVP. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Kim, Y. K. *J. Polym. Sci.: Part A Polym Chem.* **1998**, *36*, 1685. (b) Voit, B. I. *J. Polym. Sci.: Part A Polym Chem.* **2000**, *38*, in press. (c) Voit, B. I.; Turner, S. R. In *Polymeric Materials Encyclopedia*; Salamone, J., Ed.; CRC Press Inc.: Boca Raton, FL, 1996; Vol. 5 H–L, p 3177. (d) Hult, A.; Malmström, E. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1997**, *C37*, 555. (e) Frey, H.; Lach, C.; Lorenz, K. *Adv. Mater.* **1998**, *10*, 279. (f) Fréchet, J. M. J.; Hawker, C. J. Synthesis and Properties of Dendrimers and Hyperbranched Polymers. In *Comprehensive Polymer Science*; Aggarwal, S. L., Russo, S., Eds.; Elsevier Science Ltd.: Oxford, England, 1996; 2nd Supplement, p 71 ff.. (g) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendritic Molecules—Concept, Syntheses, Perspectives*; VCH: Weinheim, Germany, 1996 and references in these reviews.

(2) (a) Voit, B. I. *Acta Polym.* **1993**, *46*, 87–99. (b) Hult, A.; Johansson, M.; Malmström, E. *Adv. Polym. Sci.* **1999**, *143*, 1–34.

(3) (a) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718. (b) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1952.

(4) Stockmeyer, W. H. *J. Chem. Phys.* **1943**, *11*, 45–55.

(5) (a) Müller, A. H. E.; Yan, D.; Wulkow, M. *Macromolecules* **1997**, *30*, 7015–7023. (b) Yan, D.; Müller, A. H. E.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 7024–7033, 7034–7041, and 7042–7049. (c) Radke, W.; Litvinenko, G.; Müller, A. H. E. *Macromolecules* **1998**, *31*, 239–248.

(6) Beginn, U.; Drohman, C.; Möller, M. *Macromolecules* **1997**, *30*, 4112–4116.

(7) (a) Hölter, D.; Burgath, A.; Frey, H. *Acta Polym.* **1997**, *48*, 30–35. (b) Hölter, D.; Frey, H. *Acta Polym.* **1997**, *48*, 298–309.

(8) Hanselmann, R.; Hölter, D.; Frey, H. *Macromolecules* **1998**, *31*, 3790–3801.

(9) McCoy, B. J. *J. Colloid Interface Sci.* **1999**, *216*, 235–241.

(10) Malmström, E.; Hult, A. *Macromolecules* **1996**, *29*, 1222–1228.

(11) Dušek, K.; Šomvársky, J.; Smrcková, M.; Simonsick, W. J.; Wilczek, L. *Polym. Bull.* **1999**, *42*, 489–496.

(12) (a) Cameron, C.; Fawcett, A. H.; Hetherington, C. R.; Mee, R. A. W.; McBride, F. V. *Chem. Commun.* **1997**, 1801–1802; (b) Cameron, C.; Fawcett, A. H.; Hetherington, C. R.; Mee, R. A. W.; McBride, F. V. *J. Chem. Phys.* **1998**, *108*, 8235–8251.

(13) Widman, A. H.; Davies, G. R. *Comput. Theor. Polym. Sci.* **1998**, *8*, 191–199.

(14) Zech, C.; Maier, G.; Voit, B.; Komber, H. *Macromol. Chem. Phys.* **1998**, *199*, 2655–2664.

(15) Hobson, L. J.; Feast, W. J. *Chem. Commun.* **1997**, 2067–2068.

(16) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583–4588.

(17) Schmaljohann, D.; Häussler, L.; Pötschke, P.; Voit, B. I.; Loontjens, J. A. *Macromol. Chem. Phys.* **2000**, *201*, 49–57.

(18) (a) Burgath, A.; Möck, A.; Hanselmann, R.; Frey, H. *Polym. Mater. Sci. Eng.* **1999**, *80*, 126–127. (b) Möck, A.; Burgath, A.; Hanselmann, R.; Frey, H. *Polym. Mater. Sci. Eng.* **1999**, *80*, 173–174.

(19) k_L = rate constant for the reaction from **L**inear to dendritic unit, k_T = rate constant for the reaction from **T**erminal to linear unit.

(20) k_A = rate constant for the reaction of a vinyl group with a chloromethine group; k_B = rate constant for the reaction of a vinyl group with a chloromethylene group.

(21) Schmaljohann, D.; Komber, H.; Barratt, J. G.; Appelhans, D.; Voit, B. I. Manuscript in preparation.

(22) (a) Fréchet, J. M. J.; Henmi, H.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B. *Science* **1995**, *269*, 1080–1083. (b) Weimer, M. W.; Fréchet, J. M. J.; Gitsov, I. *J. Polym. Sci.: Part A: Polym. Chem.* **1998**, *36*, 955–970. (c) Matyjaszewski, K.; Gaynor, S. G.; Kulfan, A.; Podwika, M. *Macromolecules* **1997**, *30*, 5192–5194. (d) S. G. Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079–1081. (e) Hawker, C. J.; Fréchet, J. M. J.; Grubbs, R. B.; Dao, J. *J. Am. Chem. Soc.* **1995**, *117*, 10763–10764.

(23) (a) Press: W. H.; et al. *Numerical Recipes in C*; Cambridge University Press: New York; 1996. (b) Thomas, G. B.; Finney, R. L. In *Calculus and Analytic Geometry*, 7th ed.; Addison-Wesley Publishing Co.: Reading MA, 1990; pp 1129–1134.

(24) Magnusson, H.; Malmstroem, E.; Hult, A. *Macromol. Rapid Commun.* **1999**, *20*, 453–457.

(25) Schmaljohann, D.; Komber, H.; Voit, B. I. *Acta Polym.* **1999**, *50*, 196–204.

MA000065M