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Polymer Networks from Precursors of Defined Architecture. Activation of Preexisting Branch Points

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ABSTRACT: A growing group of polyfunctional precursors of polymer networks contains more than one branch point (cross-link). The bonds they extend lead either to another branch point or to a functional group. When such precursors are cross-linked, these branch points are gradually activated to reach the status of elastically active cross-links (EAC), i.e., such cross-links from which three or more bonds extend that have infinite continuation. The contribution of EAC's to the concentration of elastically active network chains (EANC) increases gradually with conversion of functional groups and depends on precursor architecture. Cross-linking of specially assembled precursors, functional dendrimers, and hyperbranched polymers is treated theoretically using the stochastic theory of branching processes based on generation of structures from units in different reaction states. Each bond extending from a branch point is considered as to whether the issuing subtree is finite or whether an infinite continuation exists. Several examples of development of concentration of EANC's and other structural parameters of the network demonstrate the importance of the activation process. It is shown that the branch points of dendritic precursors closer to its center are activated sooner than those at the precursor periphery.

1. Introduction

At present, cross-linked systems are prepared from predesigned polymeric or oligomeric structures carrying functional groups or cross-linkable sites. They are called *precursors* of polymer networks.[1,2] Bifunctional or polyfunctional telechelic polymers with terminal groups at their extremities having none or one branch point rank among simple precursors. However, a number of precursors contain more branch points in their structure. Functional copolymers, combs, dendrimers, hyperbranched polymers, or branched A_f-B_g prereacted products can serve as examples. Also, modern synthetic methods make possible to prepare more complex structures that contain a pattern of variously organized branch points of different functionality and bearing groups of different reactivity (cf., e.g., refs 3−5).

The increase in molecular weights in the course of cross-linking reaction, critical conversion at the gel point, and sol or gel fractions are determined by precursor functionality, functionality distribution, and group reactivities but do not depend on how many branch points exist in the precursor molecule and how the branch points are topologically arranged. However, one important quantity determining the equilibrium elastic properties of networks—the concentration of elastically active network chains (EANC)—does depend on the internal structure of the precursor. For instance, a hexafunctional precursor can have a simple-star structure containing one hexafunctional branch point or four trifunctional branch points (Figure 1). At full connectivity of the network, these two hexafunctional structures contribute by $^6/_2 = 3$ and $4 \times {^3/_2} = 6$, respectively, to the number of EANC's.

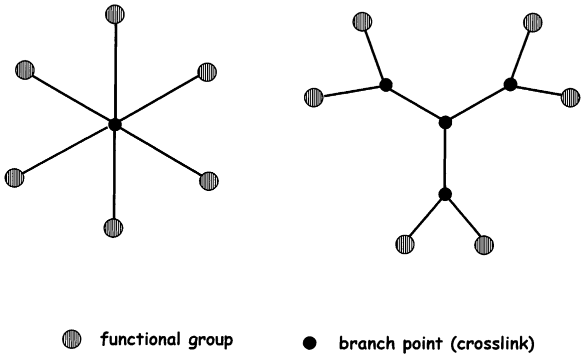

Figure 1. A hexafunctional precursor of different architecture.

Beyond the gel point, cyclic structures (circuits) exist in the gel. The number of bonds in excess to the minimum needed to connect existing nodes (branch points) into *spanning tree* is called *cycle rank*. The cycle rank,[6] ξ_e, is closely related to the number of elastically active network chains (EANC), N_e,[7]

$$\xi_e = \frac{1}{2} f_e N_e - (N_e - 1) = N_e \frac{f_e - 2}{2} \qquad (1)$$

As was pointed out in ref 7, ξ_e is to be understood as elastically effective cycle rank, since the composition of the gel is generally different from that of the sol and not all excess bonds contribute to equilibrium elasticity. Some of these bonds may close elastically inactive loops. Here, we will first disregard the possibly existing elastically inactive loops. Equation 1 is generally valid for any size of the system, but it does not specify how these circuits are topologically distributed. In the mean-field generation of infinite systems[6] as well as finite but very large systems,[8] uncorrelated circuits are formed only in the gel and not in the sol. For percolation sol−gel transition, the ring size distribution is different near

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the critical point, but farther from it, the structure and related properties are described well by the mean-field models.[9]

According to the generally used topological definition,[10] an elastically active network chain is a sequence of units between two elastically active cross-links (EAC) (branch points, junctions). An EAC is a polyfunctional unit from which at least three paths of units issue to infinity (to the surface of the sample). Thus, it is the number of EAC's and the number of infinite paths issuing from them that determine the number of EANC's, and the length (molecular weight) of EANC's is only a quantity derived from the number of EAC's. When the cross-linking proceeds before the gel point, the preexisting branch points in the precursor units do not fulfill the requirements of being EAC's, but as the connectivity increases, beyond the gel point, more and more of them reach the status of EAC. This process is coupled with other changes occurring in the system, e.g., sol-to-gel transformation and decrease in the number and size of dangling chains (cf., e.g., refs 11 and 12).

Most frequently, statistical theories are used at present: the *theory of branching processes (cascade theory)* in its random or first-shell substitution effect versions[10−19] and its combination with kinetic theory (*combined method*)[21−23] or the equivalent *recursive branching theory* of Miller and Macosko.[24−29] Within these theories, the probability that a bond has finite or infinite continuation at the given fraction of bonds formed is obtained by recursive relations where one distinguishes the bond direction looking *out* or *in* the building unit under consideration. In the theoretical treatment, mostly units with a single branch point were considered so far. Cross-linking of primary chains, in which two chain segments are cross-linked with a short bond and merge into a tetrafunctional cross-link or in which they are coupled with a bifunctional molecule, was also treated.[10,18,23,28] In a few special instances, existence of more than one branch point was considered like in the case of diamine units in cross-linking of polyepoxides[17] or polyurethanes.[16]

In this contribution, a general method is offered for treatment of activation of preexisting branch points in network precursors within the framework of the statistical theory of branching processes. To describe the development of concentration of EANC's from the gel point until the end of the cross-linking reaction is the aim of the study. In this contribution, first artificially assembled and strictly dendritic precursors are considered. Also, the strategy for description of cross-linking of hyperbranched polymer is explained as being an example of a precursor with distributions in molecular weights and in number of functional groups that result from a branching process. Cross-linking of other distribution dominated systems with several branch points, such as functional copolymers and off-stoichiometric prereacted oligomers, will be discussed in detail later. The effect of cyclization within the precursor is not considered at present, but its possible role is discussed here.

2. Activation of Branch Point

The concentration of elastically active network chains (related to the effective cycle rank) is calculated from the number of elastically active cross-links (junctions). Each bond with infinite continuation issuing from an elastically active cross-link (EAC) contributes by $^1/_2$ to the number of EANC's. Whether a bond issuing from a unit has finite or infinite continuation is determined by the so-called *extinction probability* (cf., e.g., refs 2 and 10−18). In other words, the extinction probability is a conditional probability that, given a bond exists, it has only a finite continuation looking out of the unit. This also means that the corresponding subtree looking out of the unit through the bond is finite. The extinction probability is generally a vector $\mathbf{v} = (v_{\mathrm{JM}})$, where the subscript JM refers to a bond from unit J to unit M. [If building units J and M contain various groups, e.g., a and b, respectively, among them, the bonds are identified by the corresponding path JabM (J−a → b−M). In the present analysis, we will simplify the situation by identifying the bonds by connections between units, unless stated differently.] Let us consider precursor unit A(m,n) having m branch points and n unreacted functional groups A (Figure 2a). The branch point extending f_k bonds is denoted by $X_k(f_k - n_k, n_k)$, where $k = 1, 2, ..., m$ is the serial number of the branch point and $f_k - n_k$ and n_k are the numbers of bonds extending to another branch point and to a functional group, respectively. When this precursor reacts with a cross-linker B, some of the functional groups of A react and bonds A → B are formed (Figure 2b).

Let us select the branch points $X_k(f_k - n_k, n_k)$ (Figure 2c) and a bond issuing from it denoted by $c_{kj}(s_j)$ where j is the serial number of bond $j = 1, 2, ..., f_k$; s_j is the number of functional groups on the substructure of precursor A that is seen if one looks out of the branch point $X_k(f_k)$ through the bond $c_{kj}(s_j)$. Evidently, for each of the n_k bonds, $s_j = 1$.

If the structure of the precursor is treelike, the following relation holds between the number of unreacted groups n, branch points, m, and total number of bonds issuing from branch points $\sum_{k=1}^{m} f_k$

$$n = \sum_{k=1}^{m} f_k - 2(m - 1) \tag{2}$$

The bond $c_{kj}(s_j)$ has finite continuation looking out of $X_k(f_k - n_k, n_k)$ if and only if all bonds A → B extending from reacted groups of the corresponding subtree to the component B have finite continuations. Let us denote this probability by $p_{\mathrm{fin}}(c_{kj}(s_j))$. In simple cases discussed here, when reactivities of all A groups are the same, this quantity depends only on s_j, but it is not function of serial numbers k and j

$$p_{\mathrm{fin}}(c_{kj}(s_j)) = p_{\mathrm{fin}}(s_j)$$

Then, the probability that the extending bond has infinite continuation is equal to

$$p_{\mathrm{inf}}(s_j) = 1 - p_{\mathrm{fin}}(s_j) \tag{3}$$

An extension is possible to the case where the reactivity of A groups depends on the type of the branch point it belongs to.

For calculating the contribution of the kth internal branch point of precursor A to the concentration of EANC's, one needs to calculate the distribution of states of the branch point $X_k(f_k - n_k, n_k)$ with respect to the number of bonds with infinite continuation. This can be done using the formalism of generating functions. Thus, the probability generating function, pgf, for the number of bonds with infinite continuation $T_k(Z)$ of the

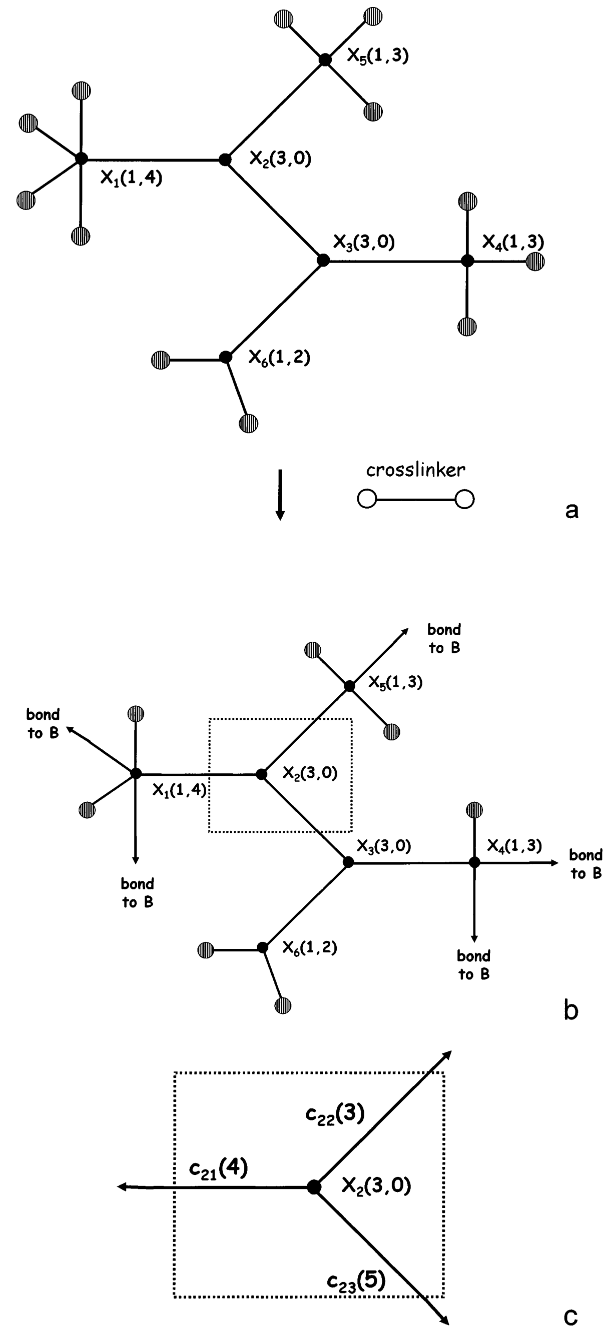

Figure 2. Designed polyfunctional precursor A(m,n) described in the text: (a) before cross-linking, (b) in the course of cross-linking, (c) cross-link X_2 examined; $X_k(f_k - n_k, n_k)$ kth branch point having $f_k - n_k$ bonds extending to other branch points and n_k links to unreacted functional group; $c_{kj}(s_j)$ denotes jth bond extending from kth branch point to a branch (subtree) with s_j functional groups.

variable Z is equal to

$$T_k(Z) = \prod_{j=1}^{f_k}(p_{\mathrm{fin}}(s_j) + p_{\mathrm{inf}}(s_j)Z) \equiv \sum_{i=0}^{f_k} t_{ki}Z^i \qquad (4)$$

In this pgf, the coefficient at Z^i, t_{ki}, is equal to the probability that the kth internal branch point can be found in a state extending i bonds with infinite continuation. Note that $T_k(Z)$ is formally equivalent to the pgf $T(z)$ used for counting bonds with infinite continuation in systems where the precursor A has only one branch point (cf., e.g., refs 2, 11, 12, and 16−18).

The contribution to the number of EANC's by the cross-link $X_k(f_k - n_k, n_k)$ of precursor A, $\Delta N_{\mathrm{Ae}(k)}$

$$\Delta N_{\mathrm{Ae}(k)} = \frac{1}{2}\sum_{i=3}^{f_k} i t_{ki} \qquad (5)$$

The sum on the right-hand side of eq 5 can be conveniently expressed by values of derivatives of the pgf $T_k(Z)$ (cf. refs 12 and 16−18)

$$\Delta N_{\mathrm{Ae}(k)} = [T'_k(1) - T'_k(0) - T''_k(0)]/2 \qquad (6)$$

where

$$T'_k(1) = \left[\frac{\partial T_k(Z)}{\partial Z}\right]_{Z=1}, \quad T'_k(0) = \left[\frac{\partial T_k(Z)}{\partial Z}\right]_{Z=0}, \quad T''_k(0) = \left[\frac{\partial^2 T_k(Z)}{\partial Z^2}\right]_{Z=0}$$

From eq 4, it can be seen that

$$T'_k(1) = p_{\mathrm{inf}}(s_1) + p_{\mathrm{inf}}(s_2) + \ldots + p_{\mathrm{inf}}(s_{f_k}) \qquad (7)$$

$$T'_k(0) = p_{\mathrm{inf}}(s_1)[p_{\mathrm{fin}}(s_2)p_{\mathrm{fin}}(s_3)\ldots) + p_{\mathrm{inf}}(s_2)[p_{\mathrm{fin}}(s_1)p_{\mathrm{fin}}(s_3)\ldots + \ldots \qquad (8)$$

$$\begin{aligned}T''_k(0) = {}& p_{\mathrm{inf}}(s_1)[p_{\mathrm{inf}}(s_2)(p_{\mathrm{fin}}(s_3)p_{\mathrm{fin}}(s_4)\ldots) + \\ & p_{\mathrm{inf}}(s_3)(p_{\mathrm{fin}}(s_1)p_{\mathrm{fin}}(s_4)\ldots) + \ldots] + \\ & p_{\mathrm{inf}}(s_2)[p_{\mathrm{inf}}(s_1)(p_{\mathrm{fin}}(s_3)p_{\mathrm{fin}}(s_4)\ldots) + \\ & p_{\mathrm{inf}}(s_3)(p_{\mathrm{fin}}(s_1)p_{\mathrm{fin}}(s_4)\ldots) + \ldots] + \ldots \qquad (9)\end{aligned}$$

Equation 9 can be further simplified because of symmetry of the expression

$$\begin{aligned}T''_k(0) = {}& 2\{p_{\mathrm{inf}}(s_1)p_{\mathrm{inf}}(s_2)[p_{\mathrm{fin}}(s_3)p_{\mathrm{fin}}(s_4)\ldots] + \\ & p_{\mathrm{inf}}(s_1)p_{\mathrm{inf}}(s_3)[p_{\mathrm{fin}}(s_2)p_{\mathrm{fin}}(s_4)\ldots] + \\ & \ldots p_{\mathrm{inf}}(s_2)p_{\mathrm{inf}}(s_3)[p_{\mathrm{fin}}(s_1)p_{\mathrm{fin}}(s_4)\ldots] + \\ & p_{\mathrm{inf}}(s_2)p_{\mathrm{inf}}(s_4)[p_{\mathrm{fin}}(s_1)p_{\mathrm{fin}}(s_3)\ldots] + \ldots + \\ & p_{\mathrm{inf}}(s_{k-1})p_{\mathrm{inf}}(s_k)[p_{\mathrm{fin}}(s_1)p_{\mathrm{fin}}(s_2)\ldots]\} \qquad (10)\end{aligned}$$

The total contribution to the number of EANC's by precursor A, N_{Ae}, is equal to the sum of contributions, $\Delta N_{\mathrm{Ae}(k)}$

$$N_{\mathrm{Ae}} = \sum_{k=1}^{m} \Delta N_{\mathrm{Ae}(k)} \qquad (11)$$

2.1. Calculation of $p_{\mathrm{fin}}(s_j)$ and $p_{\mathrm{inf}}(s_j)$. Whether the bond $c_{kj}(s_j)$ has finite or infinite continuation depends on the number of reacted groups in the corresponding subtree and on the connectivity of the system precursor A + precursor B. If the reactivity of all functional groups A is the same, the connectivity is a function of conversion of the A groups, α_A, and extinction probability, v_B. Thus, the probability that the subtree extending from the bond $c_{kj}(s_j)$ is finite is equal to

$$p_{\mathrm{fin}}(s_j) = (1 - \alpha_A + \alpha_A v_B)^{s_j} \qquad (12)$$

and

$$p_{\mathrm{inf}}(s_j) = 1 - (1 - \alpha_A + \alpha_A v_B)^{s_j} \qquad (13)$$

If groups A have different reactivities

$$p_{\mathrm{fin}}(s_j) = \prod_{i-1}^{s_j}(1 - \alpha_{\mathrm{A}i} + \alpha_{\mathrm{A}i}v_{\mathrm{B}}) \qquad (14)$$

where $\alpha_{\mathrm{A}i}$ is the conversion of groups Ai. When $\alpha_{\mathrm{A}i} = \alpha_{\mathrm{A}}$, eq 12 is recovered.

2.2. Extinction Probabilities, Sol Fraction, and Number of EANC's. Conversion of functional groups is the input information, and the extinction probabilities v_{B} and v_{A} are functions of conversions α_{A} or α_{B}. The extinction probabilities are independent of the internal structure of the precursor but are only a function of the number of functional groups A per precursor (and, possibly, their reactivities and functionality distributions). Thus, for the system of precursors A and B having A and B functional groups, respectively, the basic number-fraction probability generating function (pgf) for the number of bonds extending from component unit is equal to

$$F_{0n}(z_{\mathrm{A}},z_{\mathrm{B}}) = n_{\mathrm{A}}(1 - \alpha_{\mathrm{A}} + \alpha_{\mathrm{A}}z_{\mathrm{B}})^n + n_{\mathrm{B}}(1 - \alpha_{\mathrm{B}} + \alpha_{\mathrm{B}}z_{\mathrm{A}})^{f_{\mathrm{B}}} \qquad (15)$$

where n_{A} and n_{B} are molar fractions of precursor A and B, respectively; α_{A} and α_{B} are conversions of A and B groups; z_{B} and z_{A} are (auxiliary) variables of the pgf assigned to bonds A → B and B → A, respectively; n is the number of functional groups in precursor A(m,n) (see notation adopted above); and f_{B} is functionality of the precursor B (cross-linker).

The pgf's for the number of additional bonds issuing from precursor units A and B already bound in the structure by one of the reacted groups read respectively

$$F_{\mathrm{A}}(z_{\mathrm{B}}) = (1 - \alpha_{\mathrm{A}} + \alpha_{\mathrm{A}}z_{\mathrm{B}})^{n-1} \qquad (16)$$

$$F_{\mathrm{B}}(z_{\mathrm{A}}) = (1 - \alpha_{\mathrm{B}} + \alpha_{\mathrm{B}}z_{\mathrm{A}})^{f_{\mathrm{B}}-1} \qquad (17)$$

The gel point conversion is obtained by differentiation of eqs 16 and 17 and is given by the well-known Stockmayer equation

$$\alpha_{\mathrm{A}}\alpha_{\mathrm{B}} = [(n-1)(f_{\mathrm{B}}-1)]^{-1} \qquad (18)$$

According to the standard procedure, the extinction probabilities are derived from the pgfs $F_{\mathrm{A}}(z_{\mathrm{B}})$ and $F_{\mathrm{B}}(z_{\mathrm{A}})$-

The extinction probabilities are roots of eqs 19 and

$$v_{\mathrm{A}} = (1 - \alpha_{\mathrm{A}} + \alpha_{\mathrm{A}}v_{\mathrm{B}})^{n-1} \qquad (19)$$

$$v_{\mathrm{B}} = (1 - \alpha_{\mathrm{B}} + \alpha_{\mathrm{B}}v_{\mathrm{A}})^{f_{\mathrm{B}}-1} \qquad (20)$$

20 in the interval (1,0). The sol fraction, w_{s}, is also a function of extinction probabilities

$$w_{\mathrm{s}} = m_{\mathrm{A}}(1 - \alpha_{\mathrm{A}} + \alpha_{\mathrm{A}}v_{\mathrm{B}})^n + m_{\mathrm{B}}(1 - \alpha_{\mathrm{B}} + \alpha_{\mathrm{B}}v_{\mathrm{A}})^{f_{\mathrm{B}}} \qquad (21)$$

where m_{A} and m_{B} are mass fractions of precursors A and B.

The contribution by the precursor A, N_{Ae}, is given by eqs 5, 6, and 11. For simplicity, in this article, a simple bifunctional structure or structure with a single branch point is assumed for the cross-linker (component B), but the procedure can be used for more complex cross-linker structures. The pgf for the number of bonds with infinite continuation $T_{\mathrm{B}}(Z)$ reads

$$T_{\mathrm{B}}(Z) = [1 - \alpha_{\mathrm{B}} + \alpha_{\mathrm{B}}(v_{\mathrm{A}} + (1 - v_{\mathrm{A}})Z]^{f_{\mathrm{B}}} = \sum_{j=0}^{f_{\mathrm{B}}} t_{\mathrm{B}j}Z^j \qquad (22)$$

The contribution to the number of EANC's by component B is equal to

$$N_{\mathrm{Be}} = (1/2)\sum_{j=3}^{f_{\mathrm{B}}} jt_{\mathrm{B}j} = [T'_{\mathrm{B}}(1) - T'_{\mathrm{B}}(0) - T''_{\mathrm{B}}(0)]/2 \qquad (23)$$

and the total contribution to the number of EANC's per component unit

$$N_{\mathrm{e}} = n_{\mathrm{A}}N_{\mathrm{Ae}} + n_{\mathrm{B}}N_{\mathrm{Be}} \qquad (24)$$

3. Precursors Differing in Architecture

3.1. Specially Designed Precursors. Specially designed precursors are products of stepwise synthesis and not of a stochastic process. Their structure is uniquely described; we will use the same example as before (Figure 1). It is not the purpose of this contribution to propose a general method for description of internal structure of precursors with internal branch points; the method that is used here only serves its purpose of identification number and type of branches and their sequential order.

According to section 3.1, the designed precursor having m branch points and n terminal functional A groups which can react with B groups and form A → B bonds is coded as A(m,n); it is composed of a set of branch points $X_k(f_k - n_k, n_k)$. These branch points have $f_k - n_k$ paths leading to another branch point and n_k branches terminated by unreacted functional group. Obviously

$$\sum_k (f_k - n_k) = m; \quad \sum_k n_k = n$$

Thus, for the example of Figure 2a, one can use a code

$$A(m,n) \equiv X_1(1,4)X_2(3,0)[X_5(1,3)]X_3(3,0)[X_6(1,2)]X_4(1,3)$$

Here, $m = 6$ and $n = 12$. The italicized branch points X_5 and it X_6 in square brackets are attached to the main-chain branch points X_2 and X_4. Thus, the matrix of values of s_j in $c_{kj}(j,s_j)$, $s_j \equiv s_{kj}$, reads

$$\begin{pmatrix} s_{11} & s_{12} & s_{13} & s_{14} & s_{15} \\ s_{21} & s_{22} & s_{23} & s_{24} & s_{25} \\ s_{31} & s_{32} & s_{33} & s_{34} & s_{35} \\ s_{41} & s_{42} & s_{43} & s_{44} & s_{45} \\ s_{51} & s_{52} & s_{53} & s_{54} & s_{55} \\ s_{61} & s_{62} & s_{63} & s_{64} & s_{65} \end{pmatrix} = \begin{pmatrix} 1 & 1 & 1 & 1 & 8 \\ 4 & 3 & 5 & 0 & 0 \\ 7 & 3 & 2 & 0 & 0 \\ 1 & 1 & 1 & 9 & 0 \\ 1 & 1 & 1 & 9 & 0 \\ 1 & 1 & 10 & 0 & 0 \end{pmatrix} \qquad (25)$$

Note that the sum of each row is equal to $n = 12$. According to eq 5, the contributions $\Delta N_{\mathrm{Ae}(k)}$ ($k = 1, 2, ..., 6$) are calculated from the pgf's $T_k(Z)$ (eq 4)

$$T_1(Z) = [p_{\text{fin}}(1) + (1 - p_{\text{fin}}(1))Z]^4[p_{\text{fin}}(8) + (1 - p_{\text{fin}}(8))Z] \quad (26)$$

$$T_2(Z) = [p_{\text{fin}}(4) + (1 - p_{\text{fin}}(4))Z][p_{\text{fin}}(3) + (1 - p_{\text{fin}}(3))Z][p_{\text{fin}}(5) + (1 - p_{\text{fin}}(5))Z] \quad (27)$$

$$T_3(Z) = [p_{\text{fin}}(7) + (1 - p_{\text{fin}}(7))Z][p_{\text{fin}}(3) + (1 - p_{\text{fin}}(3))Z][p_{\text{fin}}(2) + (1 - p_{\text{fin}}(2))Z] \quad (28)$$

$$\vdots$$

$$T_6(Z) = [p_{\text{fin}}(1) + (1 - p_{\text{fin}}(1))Z]^2[p_{\text{fin}}(10) + (1 - p_{\text{fin}}(10))Z] \quad (29)$$

For equal reactivity of A groups

$$p_{\text{fin}}(s) = (1 - \alpha_A + \alpha_A v_B)^s$$

Note that $1 - p_{\text{fin}}(1) = \alpha_A(1 - v_B)$.

By differentiation of $T_k(Z)$ with respect to Z, one obtains the moments of the pgf $T_k(Z)$, $T'_k(1)$, $T'_k(0)$, and $T''_k(0)$, contributions to the number of EANC's, $\Delta N_{\text{Ae}(k)}$, and sum of them N_{Ae} (cf. eqs 5−11).

3.2. Functional Dendrimers. Ideal functional dendrimers have spherically symmetric structure: they are composed of branching units with all f functional groups reacted and terminal units which have $f - 1$ functional groups capable of reacting with the cross-linker B (Figure 3a). As a result, the status of branching units is gradually transferred into the status of elastically active ones, i.e., into such that extend ≥3 bonds with infinite continuation (Figure 3b). Because of the symmetry, one does not have to sum contributions by individual branching units but consider contributions by generations.

For calculation of the fraction of elastically active branch points, one has to consider the numbers of unreacted groups at the dendrimer periphery looking from the selected unit through the selected bond to the periphery (in the *direction "p"*) or in the direction to the dendrimer center (in the *direction "c"*) (Table 1).

The total amount of unreacted functional groups of the dendrimer is $f(f - 1)^g$. Each unit extends one bond in the direction "c" and $(f - 1)$ bonds in the direction "p" (Figure 3c). For a bond extending from unit in the 0th generation, all directions can be classified as "p", or in other words, "p" and "c" directions are equivalent.

The probability generating function $T_{g,i}(Z)$ for the number of bonds with infinite continuation extending from a unit in generation i of the dendrimer composed of g generations of units is equal to

$$T_{g,i}(Z) = [1 - t_{\uparrow}(i) + t_{\uparrow}(i)Z]^{f-1}[1 - t_{\downarrow}(i) + t_{\downarrow}(i)Z] \equiv \sum_{j=0}^{f} \tau_{i,j}Z^j \quad (30)$$

where $\tau_{i,j}$ is fraction of units in generation i having j bonds with infinite continuation. The probabilities $t_{\uparrow}(i)$ and $t_{\downarrow}(i)$ correspond to branches "p" and "c", respectively, and are equivalent to p_{inf} (eq 3). They are given by the following equations (cf. Table 1)

$$t_{\uparrow}(i) = 1 - s^{(f-1)^{g-i}} \quad (31)$$

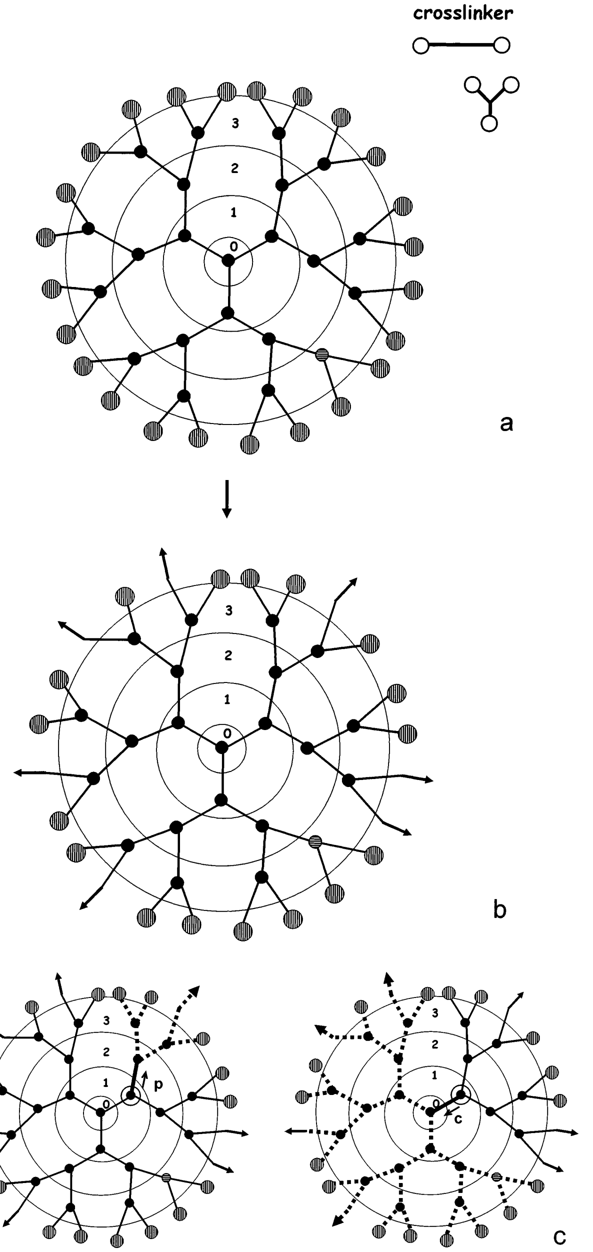

Figure 3. A functional dendrimer (a) before cross-linking, (b) in the course of cross-linking, and (c) examination of contribution of encyrcled branch point in generation $i = 1$ to the number of EANC's; directions "p" and "c" are indicated; the status of dashed subtrees (two of the three shown) decides whether the branch point is elastically active.

and

$$t_{\downarrow} = 1 - s^{[f(f-1)^g - (f-1)^{g-i+1}]} \quad (32)$$

where

$$s \equiv 1 - \alpha_A + \alpha_A v_B$$

The contribution to the number of elastically active network chains by unit in generation i is equal to

$$\Delta N_{ei} = \frac{1}{2}\sum_{j=3}^{f} j\tau_{i,j} \quad (33)$$

It can be calculated using the values of derivatives of $T_{g,i}(Z)$ (eq 30) as in the case of designed precursors (cf.

Table 1. Distribution of the Number of Units and Unreacted Functional Groups Looking through a Selected Bond to the Periphery (“p”) or Center (“c”) in a Dendrimer Composed of *g* Generations

generation i	no. of units in generation i, N_i	unreacted groups/bond direction “p”	unreacted groups/bond direction “c”
0	1	$(f-1)^g$	$(f-1)^g$
1	f	$(f-1)^{g-1}$	$f(f-1)^g-(f-1)^g$
2	$f(f-1)$	$(f-1)^{g-2}$	$f(f-1)^g-(f-1)^{g-1}$
⋮	⋮	⋮	⋮
i	$(f-1)^{g-i-1}$	$(f-1)^{g-i}$	$f(f-1)^g-(f-1)^{g-i+1}$
⋮	⋮	⋮	⋮
$g-1$	$f(f-1)^{g-2}$	$f-1$	$f(f-1)^g-(f-1)^2$
g	$f(f-1)^{g-1}$	1	$f(f-1)^g-(f-1)$

eqs 6−10)

$$\Delta N_{ei} = \frac{1}{2}[T'_{g,i}(1) - T'_{g,i}(0) - T''_{g,i}(0)] \qquad (34)$$

The contributions by individual branch points in different generations are additive, and the total contribution of the component A to the number of EANC’s is equal to

$$\Delta N_{Ae} = \sum_{i=0}^{g} N_i \Delta N_{ei} = \frac{1}{2}\sum_{i=0}^{g} N_i [T'_{g,i}(1) - T'_{g,i}(0) - T''_{g,i}(0)] \qquad (35)$$

where N_i is the number of units in generation i

$$N_i = 1 \qquad \text{if } i = 0 \qquad (36)$$

$$N_i = f(f-1)^{i-1} \qquad \text{if } i \geq 1 \qquad (37)$$

and

$$N_{sg} = \sum_{i=0}^{g} N_i = 1 + f\sum_{i=1}^{g}(f-1)^{i-1}$$

is the total number of units.

The gel point condition, extinction probabilities, sol fraction, and total number of EANC’s in the cross-linking system (components A and B) are derived from the basic pgf $F_{0n}(z_A,z_B)$

$$F_{0n}(z_A,z_B) = n_A(1 - \alpha_A + \alpha_A z_B)^{\phi_A} + n_B(1 - \alpha_B + \alpha_B) z_A)^{f_B} \qquad (38)$$

where ϕ_A is number of functional groups per dendrimer molecule; n_A and n_B are molar fractions of dendrimer molecules and cross-linker, respectively

$$\phi_A = f(f-1)^g \qquad (39)$$

The gel point conversion is given by the condition

$$\alpha_A\alpha_B = [(\phi_A - 1)(f_B - 1)]^{-1} \qquad (40)$$

and the extinction probabilities are given by

$$v_A = (1 - \alpha_A + \alpha_A v_B)^{\phi_A - 1} \qquad (41)$$

$$v_B = (1 - \alpha_B + \alpha_B v_A)^{f_B - 1} \qquad (42)$$

The molecular weight of the precursor also depends on the value of g. The degree of polymerization P_A is equal to

$$P_A = 1 + \sum_{i=1}^{g} f(f-1)^{i-1} \qquad (43)$$

and its molecular weight to

$$M_A = P_A M_{A0} \qquad (44)$$

where M_{A0} is the molecular weight of dendrimer unit. The weight fractions od A and B units are equal to

$$m_A = n_A M_A/(M_A M_B), \quad m_B = 1 - m_A$$

The sol fraction is given by the equation

$$w_s = m_A(1 - \alpha_A + \alpha_A v_B)^{\phi_A} + m_B(1 - \alpha_B + \alpha_B v_A)^{f_B} \qquad (45)$$

Since the contribution to number of EANC’s, ΔN_{Ae}, has been counted per dendrimer molecule which is component unit A, the total number of EANC’s, N_e, is given by the equation

$$N_e = n_A N_{eA} + n_B N_{eB} \qquad (46)$$

The contribution by the B component to the number of EANC’s, N_{eB}, is formally described by eqs 22−24 using the expression for extinction probabilities given in this section.

3.3. Hyperbranched Polymers. Hyperbranched polymers prepared from BA_f ($f \geq 2$) monomers contain many branch points as well as many functional groups. They resemble dendrimers but differ from them in the distributions of degrees of polymerization as well as isomeric structures ranging from dendritic to linear polymers[5,30−33] Hyperbranched polymers have already been tested as polymer network precursors;[34−36] however, no basic study of structural changes during cross-linking is available.

Simple (ideal) hyperbranched polymers are an example of system where a relatively complex distribution (Figure 4) is generated by a relatively simple stochastic process. Therefore, it would be impractical to sum contributions to the concentration of EANC’s by active branch points in different fractions. We will rather employ implicitly generated distribution and use it in the cross-linking process. The cross-linker is denoted as component C. This procedure is conceptually related to multistage cross-linking processes.[38]

We will take as an example the simplest case of condensation (reversible step addition) of monomer BA_f where the reactivity of all A groups is the same and there is no substitution effect, although extension to systems with groups of unequal reactivity and substitu-

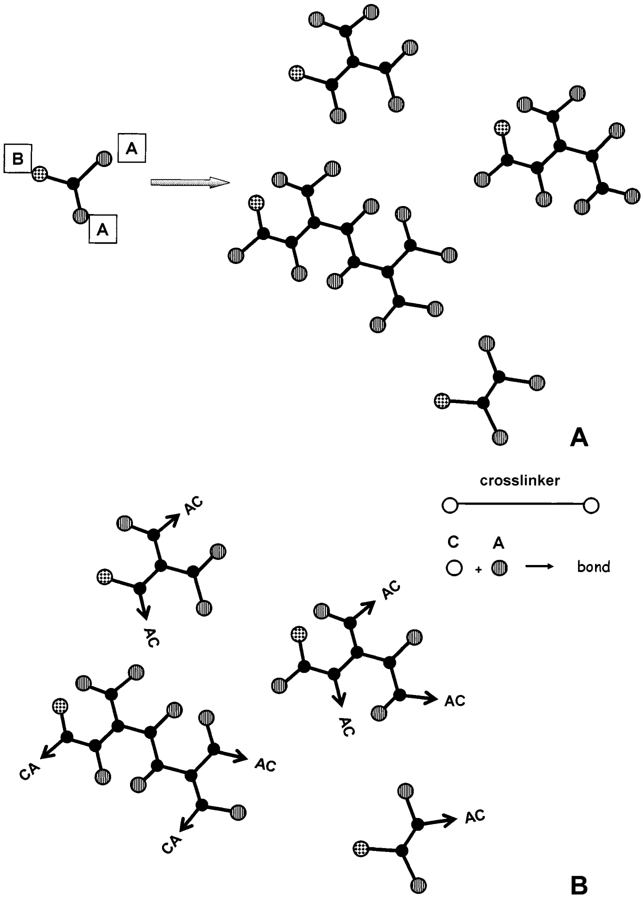

Figure 4. Distribution of molecules of a hyperbranched polymer before cross-linking (a) and units of hyperbranched polymer in the course of cross-linking (b); bonds AC and CA are indicated.

tion effect is possible. Also, possible cyclization is not considered.[39] Under these conditions, the probability generating function for the number of A → B (variable z_{AB}) and B → A (variable z_{BA}) bonds between BA_f units reads (cf. ref 2)

$$F_{0n}(z_A,z_B) = [(1-\alpha_{AB})Z_{Af} + \alpha_{AB}z_{AB}]^{f_A}[(1-\alpha_{BA})Z_{Bf} + \alpha_{BA}z_{BA}] \quad (47)$$

where α_{AB} and α_{BA} are conversions of functional groups A in reaction with groups B and groups B in reaction with groups A, respectively. Because of reaction stoichiometry

$$\alpha_{BA} = f_A\alpha_{AB}$$

Equation 47 contains variables Z_{Af} and Z_{Bf} denoting so far unreacted (free) functional groups A and B which will be later used in the cross-linking process with the cross-linker C. The pgf's for the number of additional bonds extending from units already bonded by one bond depend on whether this unit is, in the direction of looking in the unit, rooted by bond A → B (F_{AB}, B unit) or B → A (F_{BA}, A unit). This means that the unit has consumed its B group or one of its A groups, respectively.

$$F_{BA} = [(1-\alpha_{AB})Z_{Af} + \alpha_{AB}z_B]^{f_A-1}[(1-\alpha_{BA})Z_{Bf} + \alpha_{BA}z_A] \quad (48)$$

$$F_{AB} = [(1-\alpha_{AB})Z_{Af} + \alpha_{AB}z_B]^{f_A} \quad (49)$$

These equations can be used for calculation of molecular weight and free (unreacted) functionality averages of the hyperbranched polymer (cf., e.g., ref 2). For more complicated cases (unequal reactivities or substitution effect), the statistical buildup of molecules can be used with slightly more complex equations than eqs 47−49 (cf. ref 39). For kinetically controlled systems, the output of a kinetic generation[40,41] based on systems of differential equations for the generating function of degree-of-polymerization distribution can be used. This system results in a generating function for the distribution as input information in which track is kept of unreacted functional groups.

Here, we are interested in the postgel stage when this hyperbranched polymer further reacts with the cross-linker C. In this reaction, the unreacted groups A and B identified by variables Z_{Af} and Z_{Bf} take part. Let us neglect the reaction of the minority group B, either because it does not react with C, or its concentration is too small $\alpha_B \approx 1$ (usual case) that the possibly formed B−C bonds can be neglected. This bond formation is expressed by substitution of the variables

$$Z_{Af} \rightarrow (1-\alpha_{AC} + \alpha_{AC}z_{AC})$$

$$Z_{Bf} \rightarrow (1-\alpha_{BC} + \alpha_{BC}z_{BC}) \approx 1$$

for $\alpha_{BC} = 0$.

Cross-linker C is also a component of the system, so that eq 47 now reads

$$F_{0n}(z_A,z_B) = n_A[(1-\alpha_{AB})(1-\alpha_{AC} + \alpha_{AC}z_{AC}) + \alpha_{AB}z_{AB}]^{f_A}[1-\alpha_{BA} + \alpha_{BA}z_{BA}] + n_C(1-\alpha_{CA} + \alpha_{CA}z_{CA})^{f_C} \quad (50)$$

The distributions of units in different reaction states determined by pgf 47 (before cross-linking) and 50 (cross-linking system) are shown in Figure 5. Because there are four variables of the vector $\mathbf{z}$, there exist four components of the vector $\mathbf{F}$:

$$F_{BA} = [(1-\alpha_{AB})(1-\alpha_{AC} + \alpha_{AC}z_{AC}) + \alpha_{AB}z_{AB}]^{f_A-1}[1-\alpha_{BA} + \alpha_{BA}z_{BA}] \quad (51)$$

$$F_{CA} = [(1-\alpha_{AB})(1-\alpha_{AC} + \alpha_{AC}z_{AC}) + \alpha_{AB}z_{AB}]^{f_A-1}[1-\alpha_{BA} + \alpha_{BA}z_{BA}] \quad (52)$$

$$F_{AB} = [(1-\alpha_{AB})(1-\alpha_{AC} + \alpha_{AC}z_{AC}) + \alpha_{AB}z_{AB}]^{f_A} \quad (53)$$

$$F_{AC} = (1-\alpha_{CA} + \alpha_{CA}z_{CA})^{f_C} \quad (54)$$

Equations 51−54 are used for calculation of the gel point and extinction probabilities. The gel point is determined by the condition that at least one branch has infinite continuation. This is determined by the condition that the determinant D of values derivatives of pgf's $\mathbf{F}$, is equal to zero[14,16,17]

$$D = \begin{vmatrix} 1 - F_{AB}^{AB} & F_{BA}^{AB} & F_{AC}^{AB} & F_{CA}^{AB} \\ F_{AB}^{BA} & 1 - F_{BA}^{BA} & F_{AC}^{BA} & F_{CA}^{BA} \\ F_{AB}^{AC} & F_{BA}^{AC} & 1 - F_{AC}^{AC} & F_{CA}^{AC} \\ F_{AB}^{CA} & F_{BA}^{CA} & F_{AC}^{CA} & 1 - F_{CA}^{CA} \end{vmatrix} = 0$$

Thus, the gel point equation reads

$$(\alpha_{CA}\alpha_{AC})_{crit} = \frac{(1-\alpha_{BA})^2}{(f_A-1)(f_C-1)(1-\alpha_{AB})} \quad (55)$$

Conversions $\alpha_{BA} = r_A\alpha_{AB}$ determine the average degrees of polymerization of the hyperbranched polymer. The number and weight averages, P_{0n} and P_{0w}, respectively, are equal to

$$P_{0n} = \frac{1}{1-\alpha_{BA}}; \quad P_{0w} = \frac{1-\alpha_{BA}{}^2/f_A}{(1-\alpha_{BA})^2} \quad (56)$$

Equation 55 is also obtained using the Stockmayer equation

$$(\alpha_{CA}\alpha_{AC})_{crit} = \frac{1}{(\langle\Phi_{Af}\rangle_2 - 1)(f_C - 1)} \quad (57)$$

where (cf. eq 10 of ref 2 Chapter 6 after correcting the misplaced exponent in the denominator)

$$\langle\Phi_{Af}\rangle_2 = 1 + \frac{(f_A-1)(1-\alpha_{AB})}{(1-\alpha_{BA})^2} \quad (58)$$

is the second-moment-average number of A groups in the hyperbranched polymer.

From eqs 51–54 the extinction probabilities are obtained:

$$v_{BA} = [(1-\alpha_{AB})(1-\alpha_{AC}+\alpha_{AC}v_{AC}) + \alpha_{AB}v_{AB}]^{f_A-1} [1-\alpha_{BA}+\alpha_{BA}v_{BA}] \quad (59)$$

$$v_{CA} = [(1-\alpha_{AB})(1-\alpha_{AC}+\alpha_{AC}v_{AC}) + \alpha_{AB}v_{AB}]^{f_A-1} [1-\alpha_{BA}+\alpha_{BA}v_{BA}] \quad (60)$$

$$v_{AB} = [(1-\alpha_{AB})(1-\alpha_{AC}+\alpha_{AC}v_{AC}) + \alpha_{AB}v_{AB}]^{f_A} \quad (61)$$

$$v_{AC} = (1-\alpha_{CA}+\alpha_{CA}v_{CA})^{f_C} \quad (62)$$

One can note that $v_{BA} = v_{CA}$.

The weight fraction of sol is equal to

$$w_s = m_A[(1-\alpha_{AB})(1-\alpha_{AC}+\alpha_{AC}v_{AC}) + \alpha_{AB}v_{AB}]^{f_A} [1-\alpha_{BA}+\alpha_{BA}v_{BA}] + m_C(1-\alpha_{CA}+\alpha_{CA}v_{CA})^{f_C} \quad (63)$$

where m_A and m_C are weight fractions of components A and C.

The concentration of elastically active network chains, ν_e, is calculated in a similar way, as in the previous case. The pgf for the number of bonds with infinite continuation, $T(z)$, reads

$$T(z) = n_A T_A(z) + n_C T_C(z) \quad (64)$$

where

$$T_A(z) = [(1-\alpha_{AB})(1-\alpha_{AC}+\alpha_{AC}\tau_{AC}(z)) + \alpha_{AB}\tau_{AB}(z)]^{f_A}[1-\alpha_{BA}+\alpha_{BA}\tau_{BA}(z)] \quad (65)$$

and

$$T_C(z) = [1-\alpha_{CA}+\alpha_{CA}\tau_{AC}(z)]^{f_C} \quad (66)$$

where

$$\tau_{AB}(z) = v_{AB} + (1-v_{AB})z$$

$$\tau_{AC}(z) = v_{AC} + (1-v_{AC})z$$

$$\tau_{CA}(z) = v_{CA} + (1-v_{CA})z$$

The number of EANC's, N_e, can be calculated from eq 64 by the pgf moment method in analogy with eqs 6 and 22–24, i.e., $N_e = [T'(1) - T'(0) - T''(0)]/2$.

4. Discussion

Several examples have been calculated showing the development of the basic network characteristics beyond the gel point—the gel fraction and concentration of elastically active network chains (EANC)—as a function of conversion of functional groups. For comparison, instead of the number of EANC's, N_e, we have chosen the concentration of EANC's, ν_e. It is defined by the relation

$$\nu_e = \frac{N_e\rho}{M_{cn}} \quad (67)$$

The concentration ν_e (not N_e) is directly correlated with the mechanical equilibrium modulus. In eq 67, ρ is specific gravity of the polymer and M_{cn} is the number-average molecular weight of component unit. Molecular weights of the components, their molar fractions, and N_e must be related to the same reference unit. The structure of the cross-linker of functionality higher than 2 is always considered starlike; i.e., such a cross-linker has always one branch point. All systems generated here are stoichiometric with equal concentrations of the functional groups of the precursor and cross-linker. The quantity ν_{er} is equal to the reference concentration of EANC's for the case the internal structure of the precursor is ignored and all internal cross-links are considered fused into one n-functional cross-link. The

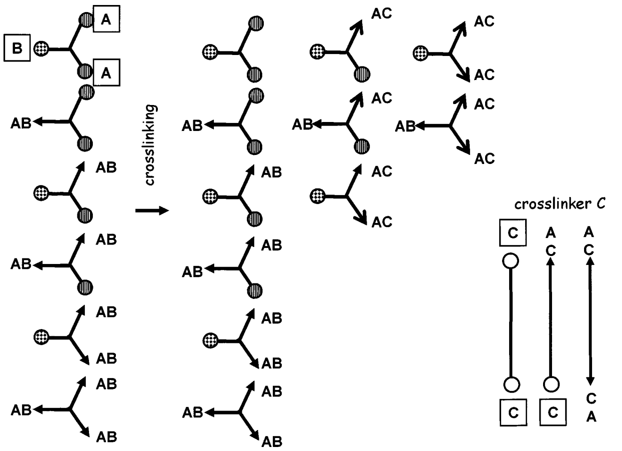

Figure 5. Distribution of building units of hyperbranched polymer shown in Figure 4 before and after cross-linking; types of bonds indicated.

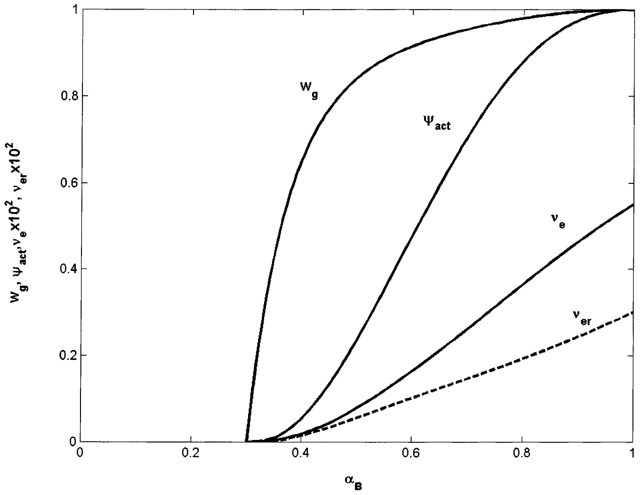

Figure 6. Designed precursor of Figure 2: Gel fraction, w_g, activation efficiency, ψ_{act}, concentration of EANC's, ν_e, and reference concentration of EANC's ν_{er} as a function of conversion of B groups; cross-linker $f_B = 2$; molecular weight of the precursor A $M_A = 600$, $M_B = 100f_B$, $n = 12$; $\rho = 1.2$ g/cm^3, stoichiometric system.

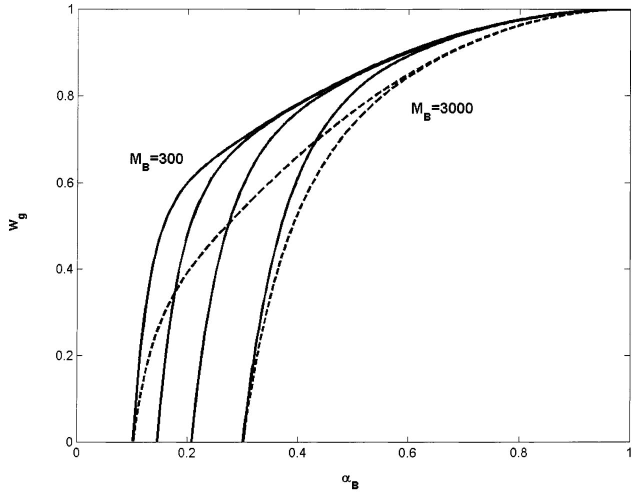

Figure 7. Dendrimers with trifunctional branch points cross-linked with a bifunctional cross-linker. Gel fraction, w_g, as a function of conversion of B groups. Size of dendrimer given by the number of generations $g = 2, 3, 4, 5$; curves from right to left. Molecular weight of dendrimer unit $M_A^0 = 100$; molecular weight of the cross-linker, M_B, indicated; $\rho = 1.2$ g/cm^3, stoichiometric system.

activation efficiency ψ_{act} is equal to the contribution to the number of EANC's by branch points of component A that have no reactive group (inner branch points), $X_k(f_k,0)$ (cf. Figure 2a) at the given conversion relative to the maximum contribution (100% conversion).

Figure 6 shows the change of network parameters for the case of cross-linking of the 12-functional designed precursor shown in Figure 2a−c and for cross-linker of functionality $f_B = 2$. The activation efficiency, ψ_{act}, shows a typical upturn beyond the gel point and tends to reach a constant value near 100% conversion. A continuous increase in ν_e in this region is due to the fact that ν_e is contributed more by outer branch points bearing originally functional groups which become activated later.

Figures 7−10 show the results of calculation for cross-linking of a dendrimer with a bifunctional cross-linker. With increasing size of the dendrimer (g varying from 2 to 5), the gel point is shifted to lower conversions; the increase of the gel fraction has a peculiar shape determined by the relatively high functionality and monodispersity of the dendrimer. Not far from the gel point along the conversion scale, almost all dendrimer molecules are bound in the gel and sol is composed almost exclusively of the cross-linker molecules (Figure 7). This explanation is corroborated by the change in the shape of gel fraction dependence when the molecular weight of the cross-linker increases from 300 to 3000. The concentration of EANC's does not depend very much on the size of the dendrimer and the number of functional groups given by the value of g (Figure 8). This conclusion depends somewhat on relative molecular weights of dendrimer and cross-linker units. By considering the dendrimer molecule as a $f(f-1)^g$-functional pointlike precursor, ν_e would drop to ν_{er}, which is about $^1/_3$ of ν_e at conversion close to 100%.

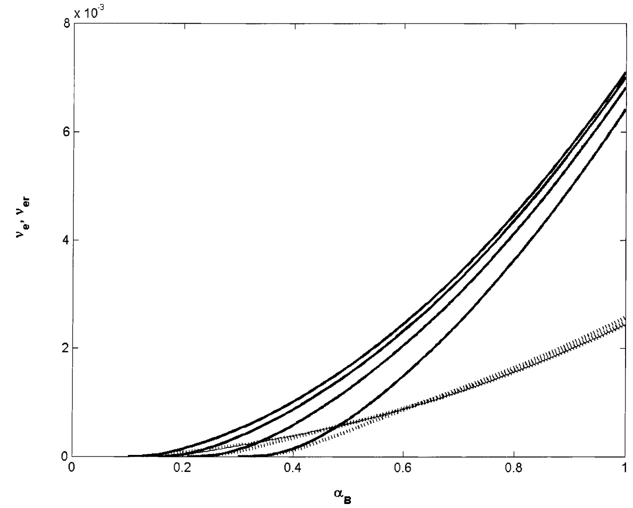

Figure 8. Dendrimers with trifunctional branch points cross-linked with a bifunctional cross-linker. Concentration of EANC's, ν_e (full lines), and reference concentration of EANC's ν_{er} (dotted lines) as a function of conversion of B groups. Sequence of curves and other parameters as for Figure 7.

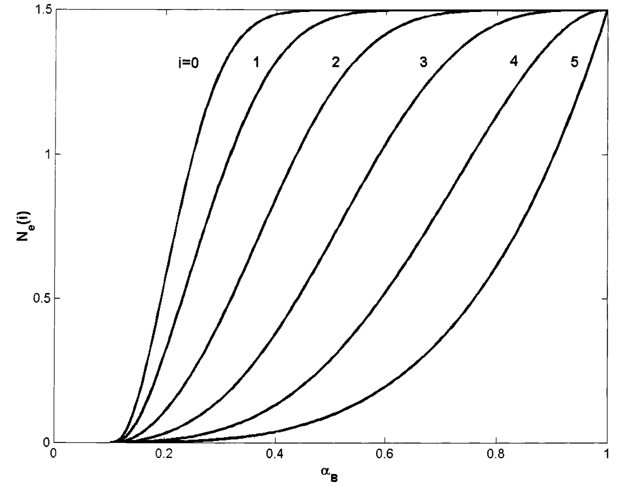

Figure 9. Dendrimers with trifunctional branch points cross-linked with a bifunctional cross-linker. Dendrimer size $g = 5$. Contribution to the number of EANC's by a unit in generation i of the dendrimer indicated. Other parameters as in Figure 7.

It is interesting to examine how elastically active cross-links develop in successive generations of the dendrimer. Figure 9 shows the increase in the number of EANC's per trifunctional unit of the dendrimer of f

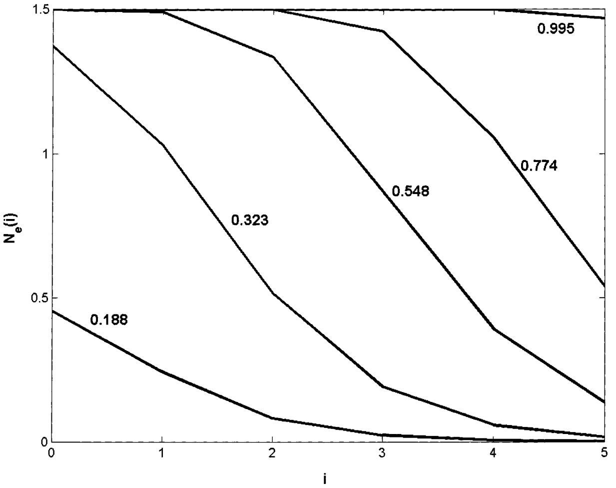

Figure 10. Dendrimers with trifunctional branch points cross-linked with a bifunctional cross-linker. Dendrimer size $g = 5$. Contribution to the number of EANC's by one trifunctional unit in different generations $i = 0-5$ at constant conversion of functional groups. Other parameters as in Figure 7.

$= 3$ and $g = 5$ located in successive generations from 0 to 5. It is seen that N_e develops the fastest in the center of the dendrimer and the slowest at its periphery. The isoconversion cross-linking density profiles (Figure 10) at conversion about 55% show that ν_e drops from the maximum value (100%, near the dendrimer center) to about 10% at the periphery. Even at conversion close to 80%, the cross-linking density in the outer shell is only about $^1/_3$ of that in the dendrimer core. This may have an important implication when precursors of the dendritic type are used. The resulting network is expected to have on nanoscale core–shell structure with diffuse transition between more cross-linked (stiffer) core and less cross-linked (softer) shell.

The dependences for cross-linking of hyperbranched polymers differ from those for dendrimers of comparable number-average functionality in several respects. Gelation occurs at lower conversion due to polydispersity of the hyperbranched polymers in the degree of polymerization and number of functional groups. The increase in w_g is smoother for the same reason (Figure 11). The increase in the concentration of EANC's with conversion has a typical shape with upturn near the critical point.

Several polymer network precursors with internal branch points are already used in applications, and the number of such architectures is growing. Three types of them were analyzed in this contribution: specially designed architectures, dendrimers, and hyperbranched polymers. This analysis should primarily highlight the phenomenon of activation of internal branch points in the precursors and show the strategies to handle this problem. The results should serve as reference basis for evaluation of experimental results. The systems treated here are based on two assumptions: (1) no ring formation and (2) equal reactivity of functional groups of the precursor. Real systems deviate more or less from these assumptions. Unequal reactivity including the substitution effect is not a real problem and makes the resulting equations somewhat more complex.

Cyclization and its modeling is a hard problem, especially beyond the gel point where many cyclic structures naturally exist. With respect to the concentration of EANC's, only such cyclic structures are not counted that do not contain any additional unit with continuation to infinity (e.g., smallest rings). Structure and elastic response of larger rings may be complex,[42] the elastic response being somewhat lower than that assuming all branch points with ≥3 continuations to infinity as elastically active.

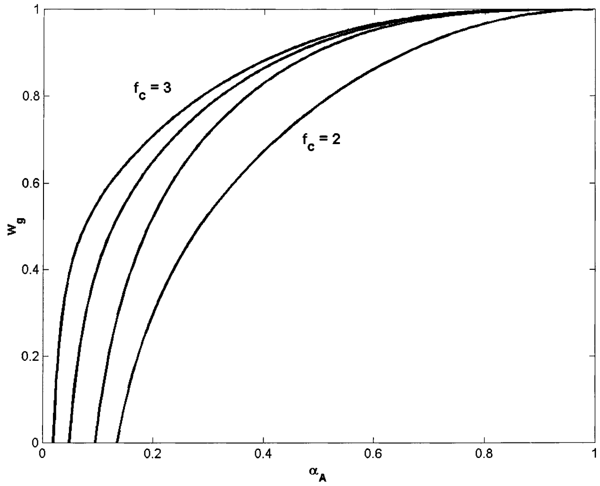

Figure 11. Hyperbranched polymer of varying degree of polymerization cross-linked with a bi- and trifunctional cross-linker of functionality f_C indicated. Gel fraction as a function of conversion of B groups. The family of curves for $f_C = 3$ corresponds to the number-average degree of polymerization of the dendrimer $P_{0n} = 10, 20, 50$ from right to left, curve for $f_C = 2$ to $P_{0n} = 10$. Molecular weight of a unit of the hyperbranched polymer $M_A = 100$ and cross-linker $M_C = 300$; $\rho = 1.2$ g/cm^3, stoichiometric system.

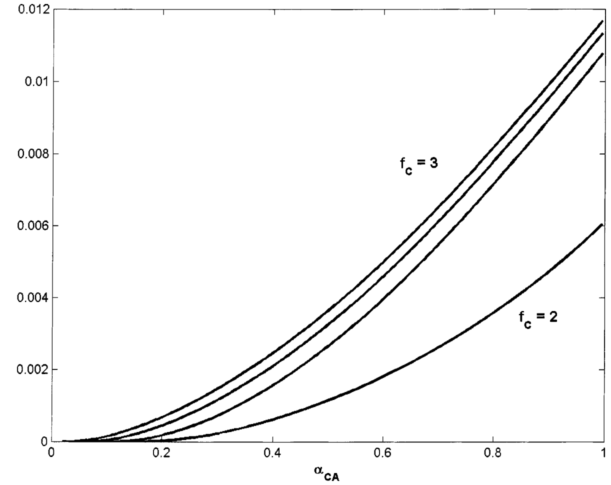

Figure 12. Hyperbranched polymer of varying degree of polymerization cross-linked with a bi- and trifunctional cross-linker of functionality f_C indicated. Concentration of EANC's as a function of conversion of B groups. Sequence of curves and the corresponding parameters the same as in Figure 11.

It is known that cyclization is stronger for systems if high functionality.[1,43] From our preliminary gel point measurements, it follows that cyclization increases with functionality of stars and is important for hyperbranched polymers. Since small rings are more frequent than the larger ones, the branch point activation process is slowed down. This results in a shift of EANC's concentration dependence to higher conversions or, at the same conversion, in a shift of ν_e to lower values. This trend has been predicted both by a mean-field spanning-tree treatment of postgel cyclization[44,45] or rate theory[1] as well as from Monte Carlo simulation in space.[46,47] The latter method was a basis of the present Accelrys Polymer module software. The shift of the gel point conversion or critical molar ratio in the case of alternating reactions seems to be a suitable factor for rescaling.

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