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# Polyfunctional Cross-Linking of Existing Polymer Chains[†]

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ABSTRACT: Polyfunctional cross-linking of polydisperse copolymer primary chains is described theoretically, and dependences of structural parameters on conversion ($\alpha$) before and after the gel point are derived. In particular, concentrations and average molecular weights of the sol, the elastically active network chains and their backbone chains, and dangling chains are given as functions of $\alpha$. The theory can be used for chemical as well as physical gelation processes. A generalized theory of branching processes (TBP) is used, in which two sets of variables are introduced, for units and for links.

## 1. Introduction

Verification of theories of rubber elasticity as well as deeper understanding of relations between the structure and mechanical and other physical properties of polymer networks require knowledge of detailed network topology [sol fraction, concentration of elastically active network chains (EANC) and their topology−length and distribution of dangling chains (DC) and backbone chains (BC)]. It was found that the chain ends and trapped entanglements affect the value of equilibrium modulus,[1−3] whereas the shape of viscoelastic functions in dependence on frequency and temperature in the main transition region also depends on the length of the DCs.[4−7] The strong increase in the width of the retardation spectrum with increasing number and length of dangling chains was observed for polyurethane[5,6] as well as epoxide[7] networks. It was also established that the decisive influence on the spectrum width is exerted by the increasing molecular weight of DCs. Therefore, a theoretical description of the network formation process in terms of parameters characterizing not only the average length but also the distribution of various substructures as a function of cross-linking conversion has been introduced.[8,9] Using the theory of branching processes (TBP) such description was already used for cross-linking of polyepoxides[7] with polyamines and of polyols with polyisocyanates[5,6] (alternating stepwise polyaddition reactions).

Theoretical models for the calculation of network parameters in cross-linking of primary chains have been developed and described by many authors.[l,10−22] In most cases, only the information about the concentration of EANCs and the amount of sol fraction (polymer molecules that are not bound to the network) were obtained. The TBP was used to describe covalent cross-linking of polymer molecules[12−14] where every monomeric unit was able to take part in tetrafunctional cross-links (e.g., vulcanization of natural rubber). Later on, the probabilistic approach for multifunctional random cross-linking of polydisperse primary chains was generalized by Pearson and Graessley.[17] However, in many cases the number of potential cross-links is limited, e.g., the primary chains are composed of more than one type of structural units (e.g., isobutylene copolymerized with several per cent of isoprene to make it vulcanizable). Block copolymers with glassy or crystalline domains and ionomer networks can serve as other examples. Moreover, in many physical thermoreversible gels, the chains are connected by junction zones of high and, in general, unknown functionalities (PVC gels in plasticizers, aqueous gelatin, agarose, carrageenan, and PVA gels[22,23]). These systems consist of chains which are not covalently but ‘physically’ cross-linked, the cross-links themselves being of low energy and/or of finite lifetime, but the cooperativity makes them relatively strong. As was mentioned recently,[24−26] some common features of gelation of covalently and noncovalently cross-linked gels exist and a model of physical gelation requires that the molecular weight distribution of primary chains be known together with the number of sites per chain and the length of junction zones with their distribution along the chain. Recently, Tanaka and Stockmayer described thermoreversible gelation of primary chains with junctions of variable multiplicity.[27] Although several theoretical models for special cases of network formation from polymer chains exist, to our knowledge, no unified description of chemical and physical gelation with detailed development of structure topology of multifunctional polydisperse homopolymer or copolymer primary chains was suggested in the literature.

The theoretical model presented in this paper can be used for chemical as well as physical gelation, for homopolymer or copolymer primary chains, possibly with more than one type of link (distinguished, for example, according to the type of structural unit issuing a link), with nonrandom distribution of the numbers and types of links per primary chain, and with polydisperse multifunctional cross-links. This description is based on a generalization of the TBP,[28,29] where separate sets of variables for structural units and links are introduced in generating functions (this approach has already been used for description of network formation by stepwise polyaddition reaction[6,30−32]). It uses the improved generation of structures from units which enables one to take into account correlations exceeding the nearest

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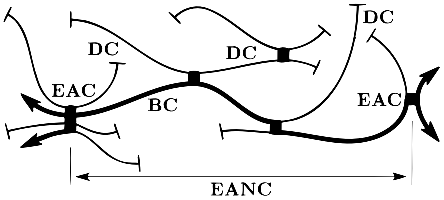

**Figure 1.** EAC (elastically active cross-link) is a junction with at least three independent paths leading to infinity, EANC (elastically active network chain) is part of a gel between two EACs composed of an elastically active backbone chain (BC) and dangling chains (DC). The primary chain may belong partly to BCs and partly to DCs. Finite branches (finite continuation) are denoted by ⊥ and infinite branches by ↓.

neighbors and guarantees possibility to obtain the *number* distribution of size and composition of sol molecules (not always possible in existing theories). The model allows one to describe, in dependence on the conversion of the cross-linking reaction, not only the amount and composition of sol and gel, but also substructures in sol and gel. Special attention is paid to the explanation of relations between the mathematical theory of branching processes and application to a network structure, which is a weak point in the literature. As an example, the system with a limited number of potential junctions along the chains is analyzed. It should be mentioned that the suggested model takes into account only random (uncorrelated) ring formation which generates cycles only in an infinite structure (gel) but not in finite substructures like EANCs, BCs, and DCs.

## 2. Basic Considerations

Typical building units used in TBP are monomeric units or their parts, but sometimes larger fragments are formed during the network formation process (e.g., chains by initiated reaction[33]), or larger pre-prepared molecules (e.g. primary chains) with a given nonrandom degree of polymerization/composition distribution enter the cross-linking reaction. Such units (chains) should be taken as building units in order to keep the precision of structure generation. In such a case, substructures of sol and gel are not composed of the whole building units but only of parts of them. Thus, the structure of such objects depends on the internal structure of the building units (e.g., in the case of primary chains, on the sequential distribution of structural (monomeric) and cross-linked units (zones) along chains), and additional specific considerations are necessary in order to characterize these objects.

The various substructures in a gel (Figure 1) can be defined as follows:

(1) An elastically active cross-link (EAC) is a junction issuing three or more bonds with infinite continuation.

(2) An elastically active network chain (EANC) is a sequence of units issuing one or two bonds with infinite continuation.

(3) An elastically active backbone chain (BC) is a sequence of units issuing two bonds with infinite continuation (an EANC without dangling chains).

(4) A dangling chain (DC) is a sequence of units issuing one bond with infinite continuation.

## 3. Specification of the Model

We will consider a network formation process in which polydisperse copolymer primary chains are cross-linked and junctions of variable functionality (multiplicity) are formed. Primary chains are composed of “repeating” or “structural” units of several types. The types of structural units can be changed when they are cross-linked or they can even be redefined (for example, in the case of a physical network with microcrystalline junctions, a sequence composed of $n$ structural units of type A bounded into a crystalline junction can be redefined as one structural unit of type $B_n$).

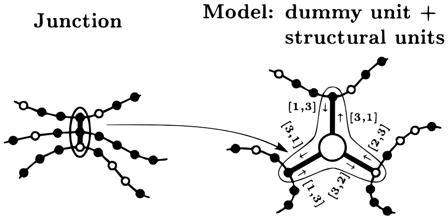

**Figure 2.** Junction is represented by an artificially introduced *dummy* unit (○) together with cross-linked structural units. In the figure, two types of structural units (● ↔ 1 and ○ ↔ 2) and dummy units (○ ↔ 3) are distinguished, and the links are characterized by pairs of types of connected units, *(i, j)*. A distinction is made between the orientations of links. Oriented links are characterized by an ordered pair of numbers [$i$, $j$], where the first number, $i$, is the type of unit itself and the second, $j$, is the type of unit linked to it. (From the viewpoint of a unit, it is a link oriented *from* unit ‘*i*’ or *issued* by this unit.)

For mathematical purposes, we represent a junction as an object composed of an artificially introduced *dummy unit* and structural units linked to it (Figure 2). This stratagem has already been used for modeling network formation by cyclotrimerization of polyacetylenes and polyisocyanates compounds.[34,35] The functionality of a dummy unit is equal to the number of connected chains, and the functionality of a junction is assumed to be twice as large. Links are characterized by pairs of numbers, ($i$, $j$), where $i$ and $j$ are usually types of linked units. Generally, $i$ and $j$ characterize the chosen neighborhood of a link (in the molecule) in the both directions. A distinction is made between the orientations of links. An *oriented* link is characterized by the *ordered* pairs of numbers, [$i$, $j$]; this sequence [$i$, $j$] means looking out from $i$ to $j$.

Building units—primary chains and dummy units—are characterized by the composition vector $\mathbf{k} = (k_1, k_2, ...)$ and the numbers and types of oriented links by vector $\boldsymbol{l} \equiv (l_{11}, l_{12}, ...)$, where $k_i$ is usually the number of $i$th type structural units in a building unit, and $l_{ij}$ is the number of oriented [$i$, $j$]-links issued by a building unit.[39]

The input information of our model is a set of molar concentrations (or molar fractions) of building units,[40] $\{c^{\text{build}}_{\mathbf{k},\boldsymbol{l}}\}$, as a function of the extent of reaction (conversion or cross-linking index). This set is composed of two subsets: the set for chains, $\{c_{\mathbf{k},\boldsymbol{l}}\}$, and the set for dummy units, $\{C_{\mathbf{k},\boldsymbol{l}}\}$ (or $\{C_{\boldsymbol{l}}\}$).[41]

An additional input information is required for gel substructures which depend also on the sequential distribution of structural units and links along the chain. In this article, the random one is assumed. (For different sequential distributions, the corresponding part of the procedure should be modified.)

We will derive structural parameters for this general model, and as an example we will give random cross-linking of polydisperse homopolymer primary chains complicated by the assumption that only a fraction $r \leq 1$ of all structural units is available as cross-linkable (active) units, and these active units are randomly distributed along chains.

The distribution of building units is bound by the balance conditions which follow from the fact that [$i$, $j$]-links and [$j$, $i$]-links are equal in number

$$B_{ij} = B_{ji} \tag{1}$$

where

$$B_{ij} \equiv \sum_{\mathbf{k},\boldsymbol{l}} l_{ij} c^{\mathrm{build}}_{\mathbf{k},\boldsymbol{l}} \tag{2}$$

is the concentration or the number per building unit of [$i$, $j$]-links (according to the meaning (normalization) of $\{c^{\mathrm{build}}_{\mathbf{k},\boldsymbol{l}}\}$).

The TBP describes the structure which is generated by the following logical construction: in every moment of the reaction, the system is split into building units and then these units are randomly reconnected with the numbers and types of links issued by them before splitting being respected. For a given [$i$, $j$]-link, one of the [$j$, $i$]-links is chosen with the same probability, and the building unit which this link belongs to is reconnected. The (conditional) probability $p^{ij}_{\mathbf{k},\boldsymbol{l}}$ that a building unit which is connected to another unit by a [$j$, $i$]-link, has composition $\mathbf{k}$ and $\boldsymbol{l}$ oriented links *not* counting the link used for connection, is therefore proportional to the number of its [$j$, $i$]-links:

$$p^{ij}_{\mathbf{k},\boldsymbol{l}} = (l_{ji} + 1)c_{\mathbf{k},\boldsymbol{l}}(l_{11},...,l_{ji}+1,...)/\mathrm{B}_{ji} \tag{3}$$

Note that the number of [$j$, $i$]-links of the considered building unit is $(l_{ji} + 1)$ because one of the [$j$, $i$]-links which is used to connect this unit is by definition not included in $l_{ji}$. Note the reverse order of subscripts $i$, $j$ in the definition of $p^{ij}_{\mathbf{k},\boldsymbol{l}}$, which is necessary for handling generating functions (see the next section).[42]

This construction removes possible correlations which arise if more complicated cross-linking mechanisms are operative, e.g., if the ability of a structural unit to be joined with a junction depends on the number of cross-linked units in the chain and on the functionality of the junction. For such systems, we should adopt a more general 'type' of link: a link is characterized by the structure of the neighborhood of the link in both directions up to a chosen distance (shell). The larger the chosen distance, the better the approximation, but then serious problems arise with obtaining the input information.

In addition, this construction generates cycles only in an infinite structure—gel—because the probability to close a ring in a given finite structure, i.e. to choose randomly a link of this structure among the infinite number of all available links, is zero. This statment is valid for finite molecules as well as for finite substructures like EANCs, BCs, and DCs.

If the set of distributions $\{p^{ij}_{\mathbf{k},\boldsymbol{l}}\}$ is known, then it is possible to calculate distributions of various fragments, branches, or molecules by using the rules for dealing with conditional probabilities. However, the equations become simpler and more elegant if the generating function formalism is used.

**3.1. Generating Functions (GF).** The degree-of-polymerization distribution of primary chains, $\{c_P\}$, and functionality distribution of dummy units, $\{C_F\}$, can be transformed into GFs $g(z)$ and $G(z)$ of these distributions, defined in a standard way:

$$g(z) \equiv \sum_{P=1}^{\infty} c_P z^P \tag{4}$$

$$G(z) \equiv \sum_{F=2}^{\infty} C_F z^F \tag{5}$$

GFs $g(z)$ and $G(z)$ depend on an auxiliary variable $z$. In definition (4), primary chains are characterized only by the number of structural units, and therefore, only one variable is used. This variable corresponds to a structural unit, but it has no physical meaning.

Similarly (eq 5), the dummy units are characterized only by the number of links, and the variable $z$ represents a link. Using GF, structural parameters can be expressed in a simple form, e.g., the average value of polymerization degree of primary chains is

$$\bar{P}^0_{\mathrm{n}} \equiv \sum_P P c_P / \sum_P c_P = g'(1)/g(1) \tag{6}$$

where $g'(arg) \equiv [\mathrm{d}g(z)/\mathrm{d}z]_{z=arg}$. Note that variable $z$ does not occur in the eq 6. At the end of calculation, it was substituted by a particular value, in this case $z = 1$. In general, auxiliary variables do not occur in formulas for quantities with physical meaning, for structural parameters.

The GFs may depend on more than one variable. Variables concerning structural objects can be divided into two categories:[28]

(1) Variables of the first category, $\mathbf{Z} \equiv (Z_1, Z_2,...)$, correspond to objects, by numbers of which various (sub)structures (building units, molecules, branches, EANCs, etc.) are characterized. Structural units play the role of such objects. They should be distinguished according to properties of our interest, usually molecular mass.

(2) Variables of the second category, $\mathbf{z} \equiv (z_{11}, z_{12}, ..., z_{21}, ...)$, correspond to oriented links and enable us to construct a GF of various objects in a way similar to construction of the objects themselves: adding a building unit to a fragment is represented by substitution of the corresponding oriented link variable. These variables do not appear in final objects like molecules, branches, EANCs, as they have no unused links for further connection. Note that these variables have usually two subscripts but they are arranged in one row or column (in arbitrary, but fixed order) to represent a vector, not a matrix.

The use of these two sets of variables enable us to define types of links independently of the definitions of types of units. Thus, the theory becomes more flexible and its logical structure is simplified.

The basic GF from which all other GFs will be derived is the $F_{\mathrm{n}}(\mathbf{Z}, \mathbf{z})$ of molar concentrations or molar fractions of building units, defined as follows:

$$\begin{aligned} F_{\mathrm{n}}(\mathbf{Z}, \mathbf{z}) &\equiv \sum_{\mathbf{k},\boldsymbol{l}} c^{\mathrm{build}}_{\mathbf{k},\boldsymbol{l}} Z_1^{k_1} Z_2^{k_2} ... z_{11}^{l_{11}} z_{12}^{l_{12}} ... z_{21}^{l_{21}} ... \\ &\equiv \sum_{\mathbf{k},\boldsymbol{l}} c_{\mathbf{k},\boldsymbol{l}} Z_1^{k_1} Z_2^{k_2} ... z_{11}^{l_{11}} z_{12}^{l_{12}} ... + \\ &\qquad \sum_{\mathbf{k},\boldsymbol{l}} C_{\mathbf{k},\boldsymbol{l}} Z_1^{k_1} Z_2^{k_2} ... z_{11}^{l_{11}} z_{12}^{l_{12}} ... \\ &\equiv F^{\mathrm{chain}}_{\mathrm{n}}(\mathbf{Z}, \mathbf{z}) + F^{\mathrm{du}}_{\mathrm{n}}(\mathbf{Z}, \mathbf{z}) \end{aligned} \tag{7}$$

The subscript 'n' indicates proportionality of coefficients to the numbers of building units (molar fractions, molar concentrations), as distinct from proportionality to the weights (weight fractions, weight concentrations) marked by 'w'. In the literature, $F_{\mathrm{n}}(\mathbf{Z}, \mathbf{z})$ is called GF for the zeroth generation, and usually several GFs are defined for individual types of units, e.g., $\mathbf{F}_0(\mathbf{z}) \equiv (F_{01}(\mathbf{z}), F_{02}(\mathbf{z}), ...)$.

In the simplest case of homopolymer primary chains, two oriented links are distinguished, from a structural unit to a dummy unit and from a dummy unit to a structural unit, say a [1, 2]-link and [2, 1]-link. Therefore, two variables, $z_{12}$ and $z_{21}$, are introduced, and arranged in the order $\mathbf{z} \equiv (z_{12}, z_{21})$.

The GF $F_{\mathrm{n}}(Z, z_{12}, z_{21})$ for cross-linking of homopolymer primary chains with a general distribution, $\{c_{P,l}\}$, of degree of polymerization, $P$, and of number of cross-linked units ([1, 2]-links), $l$, can serve as an example

$$F_{\mathrm{n}}(Z, z_{12}, z_{21}) \equiv \sum_{P,l} c_{P,l} Z^P z_{12}^l + \sum_F C_F z_{21}^F \equiv F_{\mathrm{n}}^{\mathrm{chain}}(Z, z_{12}) + F_{\mathrm{n}}^{\mathrm{du}}(z_{21}) \quad (8)$$

where $F_{\mathrm{n}}^{\mathrm{du}}(z_{21}) \equiv G(z_{21})$ (see eq 5).

In the literature, the special case of the previous one—random cross-linking—is usually considered. It is characterized by the assumption that any structural unit is cross-linked with the same probability $\alpha$. In this case

$$c_{P,l} = c_P \binom{P}{l} \alpha^l (1-\alpha)^{P-l} \quad (9)$$

$$F_{\mathrm{n}}(Z, z_{12}, z_{21}) = g(Z(1 - \alpha + \alpha z_{12})) + G(z_{21}) \quad (10)$$

where $g(z)$ and $G(z)$ are GFs of distributions $\{c_P\}$ and $\{C_F\}$, respectively (eqs 4 and 5).

We will also analyze a random cross-linking complicated by the assumption that only fraction $r \leq 1$ of structural units of each chain are "active" units available for cross-linking. The distribution $\{c_{P,l}\}$ and the GF $F_{\mathrm{n}}(Z, z_{12}, z_{21})$ have the following form

$$c_{P,l} = c_P \binom{rP}{l} (1 - \alpha_{\mathrm{act}})^{rP-l} \alpha_{\mathrm{act}}^l \quad (11)$$

$$F_{\mathrm{n}}(Z, z_{12}, z_{21}) = g(Z(1 - \alpha_{\mathrm{act}} + \alpha_{\mathrm{act}} z_{12})^r) + G(z_{21}) \quad (12)$$

where $\alpha_{\mathrm{act}}$ is the fraction of cross-linked units among active units ($\alpha_{\mathrm{act}} = \alpha/r$).

The GFs

$$\mathbf{F}(\mathbf{Z}, \mathbf{z}) \equiv (F_{11}(\mathbf{Z}, \mathbf{z}), F_{12}(\mathbf{Z}, \mathbf{z}), ..., F_{21}(\mathbf{Z}, \mathbf{z}), ...) \quad (13)$$

of distributions $\{p_{\mathbf{k},\mathbf{l}}^{ij}\}$ (eq 3) of building units linked by a $[j, i]$-link are defined in the same way as GF $F_{\mathrm{n}}(\mathbf{Z}, \mathbf{z})$, and they can be expressed in terms of derivatives of $F_{\mathrm{n}}(\mathbf{Z}, \mathbf{z})$ (eq 7):

$$F_{ij}(\mathbf{Z}, \mathbf{z}) \equiv \sum_{\mathbf{k},\mathbf{l}} p_{\mathbf{k},\mathbf{l}}^{ij} Z_1^{k_1} Z_2^{k_2} ... z_{11}^{l_{11}} z_{12}^{l_{12}} ... z_{21}^{l_{21}} ... = \frac{\partial F_{\mathrm{n}}(\mathbf{Z}, \mathbf{z})}{\partial z_{ji}} / B_{ij} \quad (14)$$

where $B_{ij}$ given by eq 2 can be expressed using GF:

$$B_{ij} = \frac{\partial F_{\mathrm{n}}(\mathbf{1}, \mathbf{1})}{\partial z_{ij}} \quad (15)$$

The construction of GFs for larger fragments, molecules, or branches is based on two simple mathematical theorems: (a) convolution of distributions and (b) combination of a random number of distributions. These theorems can be found in basic textbooks on probability theories (for example, see ref 36) as well as in specialized books on the (mathematical) theory of branching processes.[37] Hence we will only indicate these theorems, but we will pay special attention to the relation between GFs obtained by application of the theorems and the structure parameters of a network, which is a weak point in the literature.

The convolution $\{c_n\}$ of the distributions $\{a_n\}$ and $\{b_n\}$ is defined by the equation $c_n = a_0 b_n + a_1 b_{n-1} + ... + a_n b_0$ and the relation for GF $C(z) = A(z)B(z)$ is easy to recognize when the GFs are defined in a standard way: $A(z) \equiv \sum_n a_n z^n$, and similarly for $B(z)$ and $C(z)$. The relation to our problem is shown by the following example: If $\{a_n\}$ represents, for example, the probability distribution of the number of links of *one* unit, then the distribution of the total number of links of *two* units is given by the convolution of $\{a_n\}$ and $\{a_n\}$. The reason is as follows. The total number of links of two units is equal to $n$ if one of the following $(n+1)$ cases occurs: $(0, n)$, $(1, n - 1)$, ..., $(n, 0)$ where the components of the pairs are the numbers of links in the first and the second unit. Thus, the probability of this event is equal to $(a_0 a_n + ... + a_n a_0)$. This theorem can be extended for any number of distributions and also for multivariate distributions where the subscript $n$ and the variable $z$ are vectors, e.g. the GF of three building units linked by [2, 1]-links and two building units linked by [1, 2]-links is $F_{12}^3(\mathbf{Z}, \mathbf{z}) F_{21}^2(\mathbf{Z}, \mathbf{z})$. The fragments, each composed of a building unit (root) and its nearest topological neighbors (first shell, first generation), are a combination of such cases, each with fixed numbers of links of the root. Thus the GF of the molar concentrations of the fragments is equal to $\sum_{P,l} c_{P,l} Z_1^P F_{12}^l(\mathbf{Z}, \mathbf{z}) + \sum_F C_F F_{21}^F(\mathbf{Z}, \mathbf{z}) = F_{\mathrm{n}}(\mathbf{Z}, \mathbf{F}(\mathbf{Z}, \mathbf{z}))$, where the structural units of the root were taken into consideration by the factor $Z_1^P$. Hence, substitution $z_{ij} \rightarrow F_{ij}(\mathbf{Z}, \mathbf{z})$ in the GF of some fragments gives the GF of fragments larger by one shell. Similarly, if $u_{ij}(\mathbf{Z})$ is the GF of branches rooted by a $[j, i]$-link, then substitution $z_{ij} \rightarrow u_{ij}(\mathbf{Z})$ adds branches; e.g. $F_{\mathrm{n}}(\mathbf{Z}, \mathbf{u}(\mathbf{Z}))$ is the GF of the molar concentration distribution of objects, each composed of building unit and branches connected to it, i.e. of *rooted* molecules. Now we are ready to search for logical relations between such nonphysical quantities (like the distribution of rooted molecules) and many structural parameters.

**3.2 Structure Parameters of the Sol. Gel Point.** GFs of branches, $\mathbf{u}(\mathbf{Z}) \equiv (u_{11}(\mathbf{Z}), u_{12}(\mathbf{Z}),...)$, where $u_{ij}(\mathbf{Z})$ is the GF of a branch rooted by a $[j, i]$-link, can be in principle obtained by successive (cascade) substitutions $z_{ij} \rightarrow F_{ij}(\mathbf{Z}, \mathbf{z})$ in GFs $\mathbf{F}(\mathbf{Z}, \mathbf{z})$, repeated infinite number times: $\mathbf{F}(\mathbf{Z}, \mathbf{F}(\mathbf{Z}, \mathbf{F}(\mathbf{Z}, ...)))$. Actually, every branch can be seen as an object composed of the 'root' building unit of the branch and the branches linked to the root. According to the theorems, such objects have GFs $\mathbf{F}(\mathbf{Z}, \mathbf{u}(\mathbf{Z}))$; they must be equal to the GFs of the branches themselves, $\mathbf{u}(\mathbf{Z})$. Hence, functions $\mathbf{u} = \mathbf{u}(\mathbf{Z})$ are obtained by solving the set of equations

$$\mathbf{u} = \mathbf{F}(\mathbf{Z}, \mathbf{u}) \quad (16)$$

The GF of the molar concentration distribution of molecules, $N(\mathbf{Z})$, can be derived using the fact that a ring-free (tree-like) molecule composed of $n$ building units has $(n - 1)$ links between them. Since $n - (n - 1) = 1$, $N(\mathbf{Z})$ is equal to the difference between the GF of the molar concentration distribution of molecules weighted by the number of building units and that weighted by the number of links. Both of these GFs are easily accessible.

The distribution of rooted molecules has the GF $F_n(\mathbf{Z}, \mathbf{u}(\mathbf{Z}))$ (see above), since a rooted molecule can be imagined as a building unit (root) + branches. But this distribution is the desired one—the distribution of molecules weighted by the number of building units—because every molecule is chosen to be rooted as many times as the building units it contains.

Similarly, the distribution of molecules "rooted by a link"—objects each composed of two branches starting from a common link—is a distribution of molecules weighted by the numbers of links. The probability distribution that such objects start from a nonoriented $(i, j)$-link is given by a convolution with GF $u_{ij}(\mathbf{Z})\, u_{ji}(\mathbf{Z})$. The molar concentration distribution of molecules "rooted by a link" is equal to the sum of such terms weighted by the concentrations of corresponding (nonoriented) links. These concentrations are equal to $B_{ij} = B_{ji} = {}^1/_2(B_{ij} + B_{ji})$ for nonsymmetrical links $(i \neq j)$ and ${}^1/_2B_{ii}$ for symmetrical $(i, i)$-links. This results in the following expression for GF $N(\mathbf{Z})$:

$$N(\mathbf{Z}) = F_n(\mathbf{Z}, \mathbf{u}(\mathbf{Z})) - \frac{1}{2}\sum_{i,j} B_{ij} u_{ij}(\mathbf{Z}) u_{ji}(\mathbf{Z}) \qquad (17)$$

The weight concentration is defined as the product of the molar concentration and the molecular weight of the respective object. The GF of the weight concentration distribution of objects (building units, molecules, etc.) is therefore obtained by application of an operator $D_w$, defined as:

$$D_w \equiv \left(M_1 Z_1 \frac{\partial}{\partial Z_1} + M_2 Z_2 \frac{\partial}{\partial Z_2} + ...\right) \qquad (18)$$

to the GF of the molar concentration distribution of the objects. $M_1$, $M_2$, ... are molecular weights of objects to which the variables $Z_1$, $Z_2$, ... correspond (structural units of individual types). In particular, application of $D_w$ to the GF $F_n(\mathbf{Z}, \mathbf{z})$ leads to the GF of weight concentrations of building units, $F_w(\mathbf{Z}, \mathbf{z})$:

$$F_w(\mathbf{Z}, \mathbf{z}) = D_w F_n(\mathbf{Z}, \mathbf{z}) \qquad (19)$$

and application to the GF $N(\mathbf{Z})$ gives the GF of weight concentrations of sol molecules, $W(\mathbf{Z})$:

$$\begin{aligned} W(\mathbf{Z}) &= D_w N(\mathbf{Z}) \\ &= D_w F_n(\mathbf{Z}, \mathbf{u}(\mathbf{Z})) + \mathbf{d}\, F_n(\mathbf{Z}, \mathbf{u}(\mathbf{Z})) D_w \mathbf{u}(\mathbf{Z}) - \\ &\qquad \sum_{i,j} B_{ij} u_{ji}(\mathbf{Z}) D_w u_{ij}(\mathbf{Z}) \\ &= F_w(\mathbf{Z}, \mathbf{u}(\mathbf{Z})) \end{aligned} \qquad (20)$$

where the operator $\mathbf{d}$ is defined:

$$\mathbf{d} \equiv \left(\frac{\partial}{\partial z_{11}}, \frac{\partial}{\partial z_{12}}, ...\right) \qquad (21)$$

Note that $B_{ij}u_{ji}(\mathbf{Z}) = \partial F_n(\mathbf{Z}, \mathbf{u}(\mathbf{Z}))/\partial z_{ij}$ according to eqs 14 and 16. In this article, application of the operators $D_w$ and $\mathbf{d}$ does *not* mean the differentiation of a composed function (e.g., $D_w\ F_n(\mathbf{Z}, \mathbf{u}(\mathbf{Z})) \equiv D_w\ F_n(\mathbf{Z}, \mathbf{z})|_{\mathbf{z}=\mathbf{u}(\mathbf{Z})}$).

Equation 20 for the GF $W(\mathbf{Z})$ can be recognized directly: the GF of the weight concentration distribution of rooted molecules (≡building unit + branches) is according to the theorems obtained by substitution $z_{ij} \rightarrow u_{ij}(\mathbf{Z})$ in GF $F_w(\mathbf{Z}, \mathbf{z})$. But this distribution is equal to the desired one because every molecule becomes a rooted one whenever one of its building units is chosen to be a root, with a weight equal to the sum of the molecular weights of its building units, i.e., to the molecular weight of the molecule itself.

The function values of $\mathbf{u}(\mathbf{Z})$, $D_w\mathbf{u}(\mathbf{Z})$, $D_w^2\mathbf{u}(\mathbf{Z})$, ... at point $\mathbf{Z} = \mathbf{1}$ are needed for the calculation of the number-, weight-, $z$-, ... average molecular weights.

The set of equations (16) at point $\mathbf{Z} = \mathbf{1}$ for $\mathbf{v} \equiv \mathbf{u}(\mathbf{1})$

$$\mathbf{v} = \mathbf{F}(\mathbf{1}, \mathbf{v}) \qquad (22)$$

has always as a solution $\mathbf{v} = \mathbf{1}$. After the gel point, there is also another solution $\mathbf{v} \neq \mathbf{1}$, $v_{ij} \in \langle 0, 1\rangle$, which are called extinction probabilities; $v_{ij}$ is defined as conditional probability that an $[i, j]$-link has a finite continuation, i.e. that a branch rooted by a $[j, i]$-link is finite (composed of a finite number of building units).

The equation for $D_w\, \mathbf{u}(\mathbf{Z})$ can be derived even without solving eqs 16, by applying the operator $D_w$ to both sides:

$$D_w\mathbf{u} = D_w\mathbf{F} + \mathbf{dF}D_w\mathbf{u} \qquad (23)$$

This yields the following solution at point $\mathbf{Z} = \mathbf{1}$

$$D_w\mathbf{u}(\mathbf{1}) = (\operatorname{diag} \mathbf{1} - \mathbf{dF}(\mathbf{1}, \mathbf{v}))^{-1} D_w\mathbf{F}(\mathbf{1}, \mathbf{v}) \qquad (24)$$

where diag $\mathbf{1}$ is the unit matrix, and

$$\mathbf{dF} \equiv \begin{pmatrix} \partial F_{11}/\partial z_{11}, & \partial F_{11}/\partial z_{12}, & ... \\ \partial F_{12}/\partial z_{11}, & \partial F_{12}/\partial z_{12}, & ... \\ \vdots & & \end{pmatrix} \qquad (25)$$

The next application of operator $D_w$ to eqs 23 leads to equations for the second differentials of GFs $\mathbf{u}(\mathbf{Z})$:

$$D_w^2\mathbf{u} = D_w^2\mathbf{F} + 2D_w\mathbf{dF}D_w\mathbf{u} + \mathbf{ddF}D_w\mathbf{u}D_w\mathbf{u} + \mathbf{dF}D_w^2\mathbf{u} \qquad (26)$$

The third term on the right-hand side deserves an explanation: it is a vector whose $[i, j]$-th component is the expression $\sum_{kl}\sum_{mn}(\partial^2 F_{ij}/\partial z_{kl}\partial z_{mn})(D_w u_{kl})(D_w u_{mn})$. In such a way any differentials of $\mathbf{u}$ can be obtained.

The number-, weight-, $z$-, ... average molecular weights of (sol) molecules, $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_z$, ... are given by

$$\bar{M}_n = \frac{D_w N(\mathbf{1})}{N(\mathbf{1})} = \frac{F_w(\mathbf{1}, \mathbf{v})}{F_n(\mathbf{1}, \mathbf{v}) - \frac{1}{2}\sum_{ij} B_{ij} v_{ij} v_{ji}} \qquad (27)$$

$$\bar{M}_w = \frac{D_w W(\mathbf{1})}{W(\mathbf{1})} = \frac{D_w F_w(\mathbf{1}, \mathbf{v}) + \mathbf{d}F_w(\mathbf{1}, \mathbf{v}) D_w\mathbf{u}(\mathbf{1})}{F_w(\mathbf{1}, \mathbf{v})} \qquad (28)$$

$$\bar{M}_z = \frac{D_w^2(\mathbf{1})}{D_w W(\mathbf{1})} \qquad (29)$$

$$\vdots$$

When the gel point is reached, $\bar{M}_w$ (and higher moments) diverges. This happens if $D_w\mathbf{u}(\mathbf{1})$ diverges, i.e., if the matrix of the linear equation system for $D_w\mathbf{u}(\mathbf{1})$ becomes singular:

$$\det(\mathrm{diag}\,\mathbf{1} - \mathbf{dF}(\mathbf{1}, \mathbf{1})) = 0 \qquad (30)$$

Since $D_w\mathbf{u}$, $D_w^2\mathbf{u}$, $D_w^3\mathbf{u}$, ... are given by linear equation systems with the same matrix, diag $\mathbf{1} - \mathbf{dF}(\mathbf{1}, \mathbf{1})$ (only right-hand sides of the systems differ), the averages $\bar{M}_w$, $\bar{M}_z$, $\bar{M}_{z+1}$, ... diverge at the same time.

The weight fraction of sol, $w_s$, is equal to the ratio of the weight concentration of building units taking part in finite molecules (sol), $F_w(\mathbf{1}, \mathbf{v})$, and the weight concentration of all building units, $F_w(\mathbf{1}, \mathbf{1})$:

$$w_s = F_w(\mathbf{1}, \mathbf{v})/F_w(\mathbf{1}, \mathbf{1}) \qquad (31)$$

(Note that a building unit belongs to the sol if all its links have a finite continuation.)

**3.3. Structure Parameters of the Gel.** The standard description of a gel structure for the theory of branching processes cannot be used if the gel structure objects (EACs, EANCs, BCs and DCs) are not composed of building units, as is the case of cross-linking of primary chains: some parts of the primary chain may belong to DCs and other parts to BCs (see Figure 1). Thus, basic units, which the gel objects are composed of, are structural (repeat) units. The structure of gel objects depends on the sequential distribution of structural units and links along primary chains. We show calculations for randomly distributed structural units and links along primary chains. In other cases, different procedures should be used which may be more difficult but also easier.

The concentrations of EANCs or DCs are related to the distribution of junctions which are characterized by the number of issuing finite and infinite bonds. The GF $T(z_{\mathrm{fin}}, z_{\mathrm{inf}})$ of this distribution depends on two variables corresponding to the bond with finite ($z_{\mathrm{fin}}$) and infinite ($z_{\mathrm{inf}}$) continuation. Junctions are composed of randomly chosen structural units and thus GF $T(z_{\mathrm{fin}}, z_{\mathrm{inf}})$ can be expressed in terms of a GF of structural units distinguished by the numbers of intrachain bonds with finite and infinite continuation, linked by an $[j, i]$-link, $S_{ij}(z_{\mathrm{fin}}, z_{\mathrm{inf}})$:

$$\begin{aligned} T(z_{\mathrm{fin}}, z_{\mathrm{inf}}) &= \sum_{\boldsymbol{l}} C_{\boldsymbol{l}}[S_{11}(z_{\mathrm{fin}}, z_{\mathrm{inf}})]^{l_{11}}[S_{12}(z_{\mathrm{fin}}, z_{\mathrm{inf}})]^{l_{12}}\ldots \\ &= F_n^{\mathrm{du}}(\mathbf{S}(z_{\mathrm{fin}}, z_{\mathrm{inf}})) \end{aligned} \qquad (32)$$

There are six possible "states" of cross-linked structural units (Figure 3) for each type of oriented link. These states are distinguished by the numbers of bonds with finite and infinite continuation, $\beta$ and $\delta$, respectively, $0 \le \beta + \delta \le 2$. The distributions of structural unit states linked by a $[j, i]$-link, $\{c_{ij\beta\delta}^{\mathrm{st}}\}$, are given in the Appendix. Here, the distribution of states $\{c_{\beta\delta}^{\mathrm{st}}\}$ for homopolymer chains will be derived. A general distribution $\{c_{P,l}\}$ of chains with the degree of polymerization $P$, and $l$ cross-linked units ([1, 2]-links) is assumed. The GF $F_n^{\mathrm{chain}}(Z, z_{12})$ of the distribution $\{c_{P,l}\}$ is defined by eq 8.

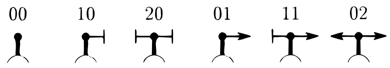

**Figure 3.** States of cross-linked structural units distinguished by the number of (chemical) bonds (existing before cross-linking in primary chains) with finite (⊥) and infinite (→) continuation. [The vertical lines represent links between structural units and dummy units (depicted by arcs) (see Figure 2)]. The first and the second subscripts are equal to the number of bonds with finite and infinite continuation, respectively. State 00 occurs when a primary chain is composed of a single structural unit (monomer). States 01 and 10 occur when the cross-linked structural unit is an end unit of a chain; the inner cross-linked structural unit of a chain is in the state 20, 11, or 02. In the literature,[17] only three states are distinguished, by the number of bonds with infinite continuation: 0 ↔ (00 + 10 + 20), 1 ↔ (01 + 11), and 2 ↔ 02, which is an appropriate simplification for long chains or within a "continuous" model of a chain.

A structural unit is in the state 00 if it is the only unit of a chain ($P = 1$) and it is cross-linked):[43]

$$c_{00}^{\mathrm{st}} = c_{P=1,l=1} = \partial^2 F_n^{\mathrm{chain}}(0, v_{12})/\partial Z \partial z_{12} \qquad (33)$$

The average number of cross-linked end units per $(P, l)$ chain is $2l/P$. The probability that the remaining $(l - 1)$ links have a finite continuation is $v_{12}^{l-1}$. Hence

$$\begin{aligned} c_{00}^{\mathrm{st}} &= 2\sum_{P\ge 2}\sum_{l\ge 1}\frac{l}{P}c_{P,l}v_{12}^{l-1} \\ &= 2\int_0^1 \frac{\partial F_n^{\mathrm{chain}}(t, v_{12})}{\partial z_{12}}\frac{\mathrm{d}t}{t} - 2\frac{\partial^2 F_n^{\mathrm{chain}}(0, v_{12})}{\partial Z \partial z_{12}} \end{aligned} \qquad (34)$$

(Note that $1/P = \int_0^1 t^P \mathrm{d}t/t$ and $l v_{12}^{l-1} = [\mathrm{d}(t^l)/\mathrm{d}t]_{t=v_{12}}$.) The number of cross-linked units not being end units per $(P,l)$ chain is $(P - 2)l/P$. Concentration $c_{20}^{\mathrm{st}}$ is given by

$$\begin{aligned} c_{20}^{\mathrm{st}} &= \sum_{P\ge 2}\sum_{l\ge 1}\left(l - 2\frac{l}{P}\right)c_{P,l}v_{12}^{l-1} \\ &= \frac{\partial F_n^{\mathrm{chain}}(1, v_{12})}{\partial z_{12}} - 2\int_0^1 \frac{\partial F_n^{\mathrm{chain}}(t, v_{12})}{\partial z_{12}}\frac{\mathrm{d}t}{t} + \\ &\qquad \frac{\partial^2 F_n^{\mathrm{chain}}(0, v_{12})}{\partial Z \partial z_{12}} \end{aligned} \qquad (35)$$

since all $(l - 1)$ remaining links must have a finite continuation. The probability that at least one of the remaining $(l - 1)$ links has an infinite continuation is $(1 - v_{12}^{l-1})$, and hence it follows that

$$\begin{aligned} c_{01}^{\mathrm{st}} &= 2\sum_{P\ge 2}\sum_{l\ge 1}\frac{1}{P}c_{P,l}(1 - v_{12}^{l-1}) \\ &= 2\int_0^1 \frac{\partial F_n^{\mathrm{chain}}(t, 1)}{\partial z_{12}}\frac{\mathrm{d}t}{t} - 2\int_0^1 \frac{\partial F_n^{\mathrm{chain}}(t, v_{12})}{\partial z_{12}}\frac{\mathrm{d}t}{t} \end{aligned} \qquad (36)$$

A unit is in the state 11 if (1) it is the first or last cross-linked unit in the chain but not an end unit of the chain (the probability $2(1 - l/P)$) and at least one of the remaining $(l - 1)$ links has an infinite continuation (the probability $1 - v_{12}^{l-1}$) or (2) it is the $i$th cross-linked unit in the chain, $i = 2, ..., l - 1$, all links in the chain in one direction from this unit having finite continuation and at least one link in the other direction having infinite continuation (the probability $v_{12}^{i-1}(1 - v_{12}^{l-i}) +$

$(1 - v_{12}^{i-1})v_{12}^{l-i})$. Hence, for concentration $c_{11}^{\mathrm{st}}$ we get

$$\begin{aligned} c_{11}^{\mathrm{st}} &= \sum_{P\geq 3}\sum_{l\geq 2} c_{P,l}\left\{\sum_{i=2}^{l-1}[v_{12}^{i-1}(1 - v_{12}^{l-1}) + (1 - v_{12}^{i-1})v_{12}^{l-i}] + 2\left(1 - \frac{l}{P}\right)(1 - v_{12}^{l-1})\right\} \\ &= 2\sum_{P\geq 1}\sum_{l\geq 0} c_{P,l}\left\{\frac{1 - v_{12}^{l}}{1 - v_{12}} - l v_{12}^{l-1} - \frac{l}{P} + \frac{l}{P}v_{12}^{l-1}\right\} \\ &= 2\frac{F_{\mathrm{n}}^{\mathrm{chain}}(1, 1) - F_{\mathrm{n}}^{\mathrm{chain}}(1, v_{12})}{1 - v_{12}} - 2\frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(1, v_{12})}{\partial z_{12}} - 2\int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(t, 1)}{\partial z_{12}}\frac{\mathrm{d}t}{t} + 2\int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(t, v_{12})}{\partial z_{12}}\frac{\mathrm{d}t}{t} \end{aligned} \quad (37)$$

The probability that the $i$th cross-linked unit in a $(P, l)$ chain, $i = 2, .., l - 1$, is between units whose links have an infinite continuation (02 unit) is $(1 - v_{12}^{i-1})(1 - v_{12}^{l-i})$. Therefore $c_{02}^{\mathrm{st}}$ can be expressed in the following form:

$$\begin{aligned} c_{02}^{\mathrm{st}} &= \sum_{P\geq 3}\sum_{l\geq 3} c_{P,l}\sum_{i=2}^{l-1}(1 - v_{12}^{i-1})(1 - v_{12}^{l-i}) \\ &= \sum_{P\geq 1}\sum_{l\geq 0} c_{P,l}\left[l(1 + v_{12}^{l-1}) - 2\,\frac{1 - v_{12}^{l}}{1 - v_{12}}\right] \\ &= \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(1, 1)}{\partial z_{12}} + \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(1, v_{12})}{\partial z_{12}} - 2\frac{F_{\mathrm{n}}^{\mathrm{chain}}(1, 1) - F_{\mathrm{n}}^{\mathrm{chain}}(1, v_{12})}{1 - v_{12}} \end{aligned} \quad (38)$$

The sum of all six concentrations is equal to the concentration of cross-linked structural units. In the general case given in the Appendix, this statement is valid for each type of oriented link, $[j, i]$, issued by structural units:

$$c_{ij00}^{\mathrm{st}} + c_{ij10}^{\mathrm{st}} + c_{ij01}^{\mathrm{st}} + c_{ij20}^{\mathrm{st}} + c_{ij11}^{\mathrm{st}} + c_{ij02}^{\mathrm{st}} = \sum_{\mathbf{k},\boldsymbol{l}} l_{ji}c_{\mathbf{k},\boldsymbol{l}} \equiv B_{ji} = B_{ij} \quad (39)$$

Finally, the GFs $S_{ij}(z_{\mathrm{fin}}, z_{\mathrm{inf}})$ of the numbers of bonds with the finite and infinite continuation of a unit linked by a $[j, i]$-link (GFs of unit states) are defined as follows:

$$S_{ij}(z_{\mathrm{fin}}, z_{\mathrm{inf}}) \equiv p_{ij00}^{\mathrm{st}} + p_{ij10}^{\mathrm{st}}z_{\mathrm{fin}} + p_{ij01}^{\mathrm{st}}z_{\mathrm{inf}} + p_{ij20}^{\mathrm{st}}z_{\mathrm{fin}}^2 + p_{ij11}^{\mathrm{st}}z_{\mathrm{fin}}z_{\mathrm{inf}} + p_{ij02}^{\mathrm{st}}z_{\mathrm{inf}}^2 \quad (40)$$

where $\{p_{ij\beta\delta}^{\mathrm{st}}\}$ are the probability distributions of unit states obtained by normalization of the concentration distributions $\{c_{ij\beta\delta}^{\mathrm{st}}\}$:

$$p_{ij\beta\delta}^{\mathrm{st}} = c_{ij\beta\delta}^{\mathrm{st}}/\sum_{\sigma,\tau} c_{ij\sigma\tau}^{\mathrm{st}} = c_{ij\beta\delta}^{\mathrm{st}}/B_{ij} \quad (41)$$

Thus, the basic GF $T(z_{\mathrm{fin}}, z_{\mathrm{inf}})$ (eq 32) for the gel structure description is known.

The GF of the molar concentration of EACs, $E(z_{\mathrm{fin}}, z_{\mathrm{inf}})$, i.e. concentration of junctions with at least three bonds going to infinity, reads:

$$E(z_{\mathrm{fin}}, z_{\mathrm{inf}}) = T(z_{\mathrm{fin}}, z_{\mathrm{inf}}) - T(z_{\mathrm{fin}}, 0) - \frac{\partial T(z_{\mathrm{fin}}, 0)}{\partial z_{\mathrm{inf}}}z_{\mathrm{inf}} - \frac{1}{2}\frac{\partial^2 T(z_{\mathrm{fin}}, 0)}{\partial {z_{\mathrm{inf}}}^2}{z_{\mathrm{inf}}}^2 \quad (42)$$

[see definitions (32) and (40)]. The effective functionality (the average number of bonds with infinite continuation) of EACs, $f_{\mathrm{e}}$, is

$$f_{\mathrm{e}} = \frac{E(1, 1)}{\partial z_{\mathrm{inf}}}/E(1, 1) \quad (43)$$

Each bond with infinite continuation issued by an EAC contributes by $^1/_2$ to the number of EANCs, and thus the molar concentration of EANCs, $\nu_{\mathrm{e}}$, is given by

$$\nu_{\mathrm{e}} = \frac{1}{2}\frac{\partial E(1, 1)}{\partial z_{\mathrm{inf}}} = \frac{1}{2}\left(\frac{\partial T(1, 1)}{\partial z_{\mathrm{inf}}} - \frac{\partial T(1, 0)}{\partial z_{\mathrm{inf}}} - \frac{\partial^2 T(1, 0)}{\partial {z_{\mathrm{inf}}}^2}\right) \quad (44)$$

if the GF $F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{Z}, \mathbf{z})$ is normalized to the total concentration of primary chains, $c^0$, ($F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1}, \mathbf{1}) = c_0$). If $F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{Z}, \mathbf{z})$ is the GF of molar *fractions* of primary chains $F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1}, \mathbf{1}) = 1$), eq 44 gives the number of EANCs per primary chain, $N_{\mathrm{e}}$:

$$N_{\mathrm{e}} = \nu_{\mathrm{e}}/c_0 \quad (45)$$

Note that for calculation of $\nu_{\mathrm{e}}$, cross-linked units are sufficiently distinguished by the number of bonds with infinite continuation only (three states). The $\nu_{\mathrm{e}}$ does not depend on sequential distribution of units and links along the chain provided only one type of the oriented link exists in chains.

DCs start on bonds with a finite continuation of a junction in BCs, i.e., on junctions with at least two bonds with infinite continuation, the GF of which, $B(z_{\mathrm{fin}}, z_{\mathrm{inf}})$, is given by

$$B(z_{\mathrm{fin}}, z_{\mathrm{inf}}) = T(z_{\mathrm{fin}}, z_{\mathrm{inf}}) - T(z_{\mathrm{fin}}, 0) - \frac{\partial T(z_{\mathrm{fin}}, 0)}{\partial z_{\mathrm{inf}}}z_{\mathrm{inf}} \quad (46)$$

Thus, the molar concentration of DCs, $\nu_{\mathrm{DC}}$, reads

$$\nu_{\mathrm{DC}} = \frac{\partial B(1, 1)}{\partial z_{\mathrm{fin}}} = \frac{\partial T(1\ , 1)}{\partial z_{\mathrm{fin}}} - \frac{\partial T(1, 0)}{\partial z_{\mathrm{fin}}} - \frac{\partial^2 T(1, 0)}{\partial z_{\mathrm{fin}}\partial z_{\mathrm{inf}}} \quad (47)$$

The concentrations of $i$th type structural units belonging to BCs, $c_{\mathrm{BC},i}$, for copolymer primary chains with a general concentration distribution of the numbers and types of units and links, $\{c_{\mathbf{k},\boldsymbol{l}}\}$, assuming the random sequential distribution of units and links along chains are given in the Appendix. Here, the $c_{\mathrm{BC}}$ for homopolymer primary chains with the concentration distribution $\{c_{P,l}\}$ will be derived.

A primary chain can partly belong to BCs and partly to DCs (see Figure 4). The part of a chain belonging to BCs is situated between two outermost cross-linked units with infinite links. Infinite links are distributed randomly along chains with a fixed number of units, $P$, and a fixed number of infinite links, $l'$. Hence, the average numbers of units between two successive

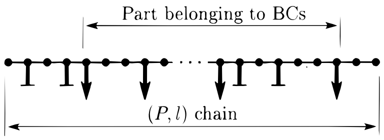

**Figure 4.** Structural units between outermost cross-linked structural units with infinite links belong to BCs.

infinite links are the same, i.e. equal to $(P-l')/(l'+1)$. The average number of units belonging to BCs per such a chain is thus $(P-l')(l'-1)/(l'+1)+l' = 2+P-2/(l'+1)-2P/(l'+1)$. The fraction of $(P, l)$ chains with $l'$ infinite links is equal to $\binom{l}{l'}(1-v_{12})^{l'}v_{12}^{l-l'}$. Hence, the concentration of units belonging to BCs, $c_{BC}$, is given by the equation

$$c_{BC} = \sum_{P\geq 2}\sum_{l\geq 1} c_{P,l}\sum_{l'=2}^{l}\left(2+P-\frac{2}{l'+1}-\frac{2P}{l'+1}\right)\binom{l}{l'}(1-v_{12})^{l'}v_{12}^{l-l'}$$

$$= 2\,F_{\mathrm{n}}^{\mathrm{chain}}(\mathrm{l},1)+\frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(1,1)}{\partial Z} - 2\int_0^1 F_{\mathrm{n}}^{\mathrm{chain}}(1, v_{12}+(1-v_{12})t)\,\mathrm{d}t - 2\int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(1, v_{12}+(1-v_{12})t)}{\partial Z}\,\mathrm{d}t + \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(1, v_{12})}{\partial Z} - (1-v_{12})\frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(1, v_{12})}{\partial z_{12}} \qquad (48)$$

where $F_{\mathrm{n}}^{\mathrm{chain}}(Z, z_{12})$ is the GF of the distribution $\{c_{P,l}\}$ (eq 8).

The weight fraction values of EANCs (gel is an assembly of EANCs), $w_g$; of BCs, $w_{BC}$; and of DCs, $w_{DC}$, in a general case of copolymerization are given by the formulas

$$w_{\mathrm{g}} = 1 - w_{\mathrm{s}} \qquad (49)$$

$$w_{BC} = \sum_i M_i c_{BC,i}/F_{\mathrm{w}}(\mathbf{1},\mathbf{1}) \qquad (50)$$

$$w_{DC} = w_{\mathrm{g}} - w_{BC} \qquad (51)$$

The number-average molecular weights of EANCs, $\bar{M}_{\mathrm{EANC,n}}$; BCs, $\bar{M}_{\mathrm{BC,n}}$; and of DCs, $\bar{M}_{\mathrm{DC,n}}$, are given by

$$\bar{M}_{\mathrm{EANC,n}} = (F_{\mathrm{w}}(\mathbf{1},\mathbf{1}) - F_{\mathrm{w}}(\mathbf{1},\mathbf{v}))/\nu_{\mathrm{e}} \qquad (52)$$

$$\bar{M}_{\mathrm{BC,n}} = \sum_i M_i c_{\mathrm{BC},i}/\nu_{\mathrm{e}} \qquad (53)$$

$$\bar{M}_{\mathrm{DC,n}} = (F_{\mathrm{w}}(\mathbf{1},\mathbf{v}) - \sum_i M_i c_{\mathrm{BC},i})/\nu_{\mathrm{DC}} \qquad (54)$$

The cycle rank $\zeta$ (the number of gel links that must be cut to get a spanning tree) is equal to the number of all links in the gel minus the number of the gel building units (with normalization, e.g., to molar concentrations):

$$\zeta = \frac{1}{2}\sum_{i,j}\left(\frac{\partial F_{\mathrm{n}}(\mathbf{1},\mathbf{1})}{\partial z_{ij}} - v_{ij}\frac{\partial F_{\mathrm{n}}(\mathbf{1},\mathbf{v})}{\partial z_{ij}}\right) - (F_{\mathrm{n}}(\mathbf{1},\mathbf{1}) - F_{\mathrm{n}}(\mathbf{1},\mathbf{v})) \qquad (55)$$

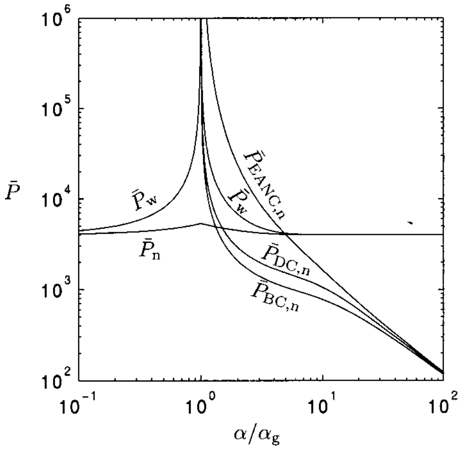

**Figure 5.** Number-average degree of polymerization of (sol) molecules, $\bar{P}_{\mathrm{n}}$; of EANCs, $\bar{P}_{\mathrm{EANC,n}}$; of BCs, $\bar{P}_{\mathrm{BC,n}}$; and of DCs, $\bar{P}_{\mathrm{DC,n}}$, and weight-average degree of polymerization of (sol) molecules, $\bar{P}_{\mathrm{w}}$, as a function of $\alpha/\alpha_{\mathrm{g}}$ for the system with uniform distribution of polymerization degrees in the primary chain and junction functionalities, $P = 4000$ and $2F = 8$.

The quantities $\zeta$, $f_{\mathrm{e}}$, and $\nu_{\mathrm{e}}$ fulfill the known relation[38]

$$\zeta = \frac{f_{\mathrm{e}}-2}{f_{\mathrm{e}}}\nu_{\mathrm{e}} \qquad (56)$$

## 4. Discussion

Usually two variables are used in literature for analysis of the effect of input parameters on the network structure formed by cross-linking of chains, namely the ratio $\alpha/a_{\mathrm{g}}$ (the reduced cross-linking conversion) or the cross-linking index $\gamma_{\mathrm{n}} = \alpha\bar{P}_{\mathrm{n}}^{0}$ (the average number of cross-links per primary chain). While the ratio $\alpha/\alpha_g$ is usually used for analysis of network structure at low cross-linking, close to the gel point in physically cross-linked systems, the index $\gamma_{\mathrm{n}}$ is used for analysis of structure in networks prepared by vulcanization of primary chains.

The gel point conversion, $\alpha_{\mathrm{g}}$, is obtained by solving eq 30. For random cross-linking of homopolymer chains complicated by the assumption that only part $r$ of all units are cross-linkable ($F_{\mathrm{n}}(\mathbf{Z},\mathbf{z})$ given by eq 12), $\alpha_{\mathrm{g}}$ can be expressed explicitly as

$$\alpha_{\mathrm{g}} = \frac{r}{r\bar{P}_{\mathrm{w}}^{0}-1}\,\frac{1}{\bar{F}_2-1} \qquad (57)$$

where $\bar{P}_{\mathrm{w}}^{0}$ is the weight-average degree of polymerization of primary chains ($\bar{P}_{\mathrm{w}}^{0} \equiv \sum_P P^2 c_P/\sum_P P c_P = g''(1)/g'(1) + 1$) and $\bar{F}_2$ is the second-moment average functionality of dummy units ($\bar{F}_2 \equiv \sum_F F^2 C_F/\sum_F F C_F = G''(1)/G'(1) + 1$). Random cross-linking (see eq 10) is the special case with $r = 1$.

The evolution of the structure as a function of the ratio $\alpha/\alpha_{\mathrm{g}}$ before and after the gel point is shown in Figure 5 for random cross-linking of homopolymer chains (see eqs 9 and 10) with $P = \bar{P}_{\mathrm{n}}^{0} = \bar{P}_{\mathrm{w}}^{0} = 4000$ and junction functionality $2F = 8$. As expected, with increasing $\alpha/\alpha_{\mathrm{g}}$, the polydispersity of the system, $\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}}$, increases before the gel point and at the gel point (eq 30), $\bar{P}_{\mathrm{w}} \to \infty$ (also $\bar{P}_{\mathrm{w}}/\bar{P}_{\mathrm{n}} \to \infty$). After the gel point, the number-average polymerization degrees of EANCs, $\bar{P}_{\mathrm{EANC,n}}$; of backbone chains (BC), $\bar{P}_{\mathrm{BC,n}}$; and of the dangling chains (DC), $\bar{P}_{\mathrm{DC,n}}$, decrease. Much higher

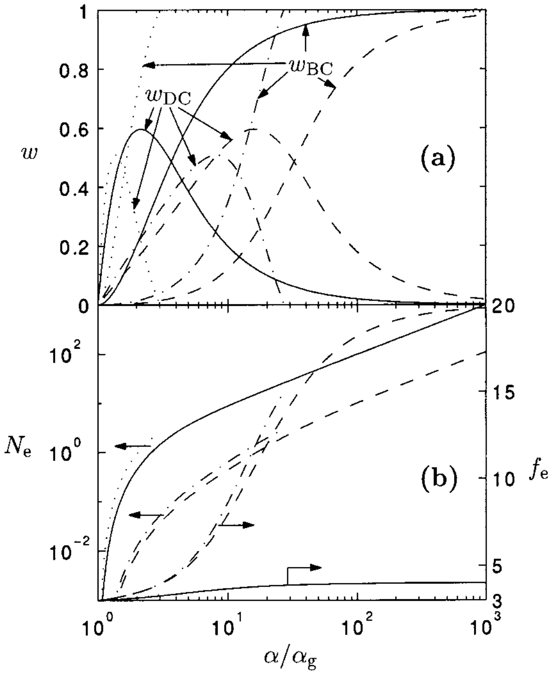

**Figure 6.** (a) Weight fractions of backbone chains, $w_{BC}$, and dangling chains, $w_{DC}$, and (b) number of EANCs per primary chain, $N_e$, and effective functionality of EACs, $f_e$, as functions of $\alpha/\alpha_g$ for systems with uniform distributions of degree of polymerization and junction functionality, varying $P$ and $F$. $P = 4\,000$, $2F = 4$, —; $P = 4000$, $2F = 20$, - - -; $P = 4$, $2F = 4$, ···; $\bar{P}_n^0 = 4$, $2F = 20$, -·-·.

$\bar{P}_{EANC,n}$ values than those of $\bar{P}_{BC,n}$ in the vicinity of the gel point reflect the fact that many dangling chains are present on a backbone chain. Upon increasing the extent of the cross-linking reaction, the number of DCs decreases and $\bar{P}_{EANC,n}$ approaches $\bar{P}_{BC,n}$.

The weight fractions of the backbone chain units, $w_{BC}$, and of the dangling chain units, $w_{DC}$, as well as the number of EANCs per primary chain, $N_e$ (eq 45), and the average effective functionality of EACs, $f_e$, (eq 43) as functions of the reduced conversion $\alpha/\alpha_g$ in the postgel region are shown in Figure 6. The curves are calculated for two values of primary chain length, $P = \bar{P}_n^0 = \bar{P}_w^0 =$ 4 and 4000, and two values of junction functionalities ($2F = 4$ and 20).

The maximum of a $w_{DC}$ versus $\alpha/\alpha_g$ plot does not depend on the junction functionality in agreement with the Pearson and Graesley[17] results. Semiempirical calculations of te Nijenhuis[21] give the same result for junction functionality $2F = 4$. For higher functionalities, smaller values of the maxima were obtained. An analysis shows that for sufficiently long chains ($P \gtrsim 30$), the maximum of a $w_{DC}$ curve does not depend on the degree of polymerization of primary chains, $P$, while for short chains, it decreases with decreasing $P$. The last statement is valid for our "discrete" model of a chain, where the whole structural unit belongs either to a backbone chain or to a dangling chain. In comparison with a simpler "continuous" model, smaller weight is ascribed to dangling chains [cf. $2(P - i)/(i + 1)$ for the discrete model and $2P/(i + 1)$ for continuous model, where $i$ is the number of cross-linked units with infinite continuation]. For the continuous model, the maximum of the $w_{DC}$ curve increases with decreasing primary chain length $P$.

This behavior can be explained as follows. The height of the maximum of a $w_{DC}$ curve depends on the average value of $1/(i + 1)$, i.e. on the width of the distribution of the numbers of links with infinite continuation, $i$, if the average number of $i$ is fixed (given by the conversion at which the maximum occurs). In our example, the distribution of the number of links (all links as well as links with infinite continuation) is binomial, which approaches the uniform distribution ($\langle i^2\rangle/\langle i\rangle \rightarrow 1$) if the number of potential links (the number of units) is sufficiently high (the order of tens should be sufficient). For shorter primary chains, the width of the binomial distribution and hence $\langle 1/(i + 1)\rangle$ as well as the maximum of the $w_{DC}$ curve increase. For the discrete model with decreasing $P$, the decrease in the weight fraction of DCs in comparison with the continuous model is more pronounced than its increase due to widening of distribution of the number of links, which results in decrease of the maximum of $w_{DC}$.

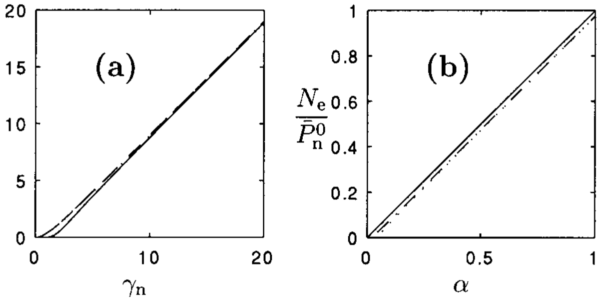

**Figure 7.** (a) Number of EANCs per primary chain, $N_e$, as a function of cross-linking index $\gamma_n = \alpha\bar{P}_n^0$, and (b) number of EANCs per structural unit, $N_e/\bar{P}_n^0$, versus $\alpha$ for systems with uniform distributions, varying $P$ and $F$. $P = 4000$, $2F = 4$, —; $P = 4000$, $2F = 20$, - - -; $P = 4$, $2F = 4$, ···; $\bar{P}_n^0 = 4$, $2F = 20$, -·-·.

The effective functionality of elastically active cross-links, $f_e$, is equal to 3 at the gel point and grows to its maximum value $2F(1 - 1/P)$ at full conversion (Figure 6b). In the case of primary chains with general distribution of polymerization degree and link number, $\{c_{P,l}\}$, the maximum $f_e$ is equal to the averaged value, $2F(1-\langle 1/l\rangle)$ (provided extinction probabilities approach zero).

In Figure 6b, the number of EANCs per primary chain, $N_e$, is plotted as a function of $\alpha/\alpha_g$. Identical results were obtained by Pearson and Graesley.[17] The results of te Nijenhuis[19] agree for long primary chains and not very high conversions provided his $\nu_e$ means 2 × cycle rank (see eq. (56), $\nu_e$, approaches $2\xi$ only for junction functionality $2F = 4$ (if $f_e \approx 4$)).

For $\alpha \gtrsim 5\alpha_g$, the $N_e$ is proportional to the extent of cross-linking reaction. If it is expressed as $\alpha/\alpha_g$, the slope of the $N_e$ curve depends on the junction functionality, which, in turn, can be determined from the known (experimentally obtained) $N_e$ vs $\alpha/\alpha_g$ dependence. The slopes of the $N_e$ vs $\gamma_n$, (Figure 7a) and the number of EANCs per structural unit, $N_e/\bar{P}_n^0$, vs $\alpha$ dependences (Figure 7b) do not depend on primary chain length and junction functionality for sufficiently long primary chains and high conversions. These dependences are linear, being nearly proportional. In the latter case, the magnitude of the shift from the proportionality increases with decreasing $\bar{P}_n^0$ and $F$.

In Figure 8, the effect of varying primary chain degree-of-polymerization distribution for $\bar{P}_n^0 = 4000$ and $2F = 4$ on network structure can be seen. Three

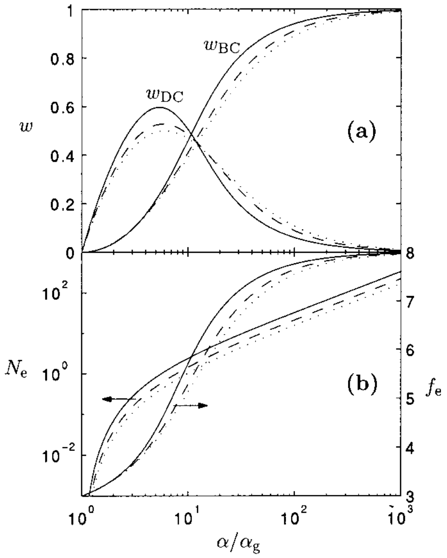

**Figure 8.** (a) $w_{\mathrm{BC}}$ and $w_{\mathrm{DC}}$ and (b) $N_e$ and $f_e$ vs $\alpha/\alpha_g$ for systems with $\bar{P}_n^0 = 4000$ and $F = \bar{F}_2 = 4$, and varying degree-of-polymerization distribution of primary chains: uniform ($\bar{P}_w^0/\bar{P}_n^0 = 1$), —; narrowed random, eq 58 ($\bar{P}_w^0/\bar{P}_n^0 = 3/2 - 1/\bar{P}_n^0 \approx 3/2$), - - -; random, eq 59 ($\bar{P}_w^0/\bar{P}_n^0 = 2 - 1/\bar{P}_n^0 \approx 2$), ···.

distributions are used: (1) uniform, (2) narrowed random

$$n_P = (1 - q)^2 q^{(P-2)}(P - 1) \qquad q = 1 - 2/\bar{P}_n^0 \qquad (58)$$

with $\bar{P}_w^0/\bar{P}_n^0 = 3/2 - 1/\bar{P}_n^0$, and (3) random (most probable)

$$n_P = (1 - q)q^{(P-1)} \qquad q = 1 - 1/\bar{P}_n^0 \qquad (59)$$

with $\bar{P}_w^0/\bar{P}_n^0 = 2 - 1/\bar{P}_n^0$. The higher the polydispersity $\bar{P}_w^0/\bar{P}_n^0$ is, the larger the fraction of short primary chains is, which leads to larger differences of structural parameters compared with those for the uniform distribution, as expected from the discussion of Figure 6.

The effect of a fraction $r$ of all structural units available for cross-linking on network formation (see eqs 11 and 12) is shown in Figure 9. As expected, the fractions of DCs and BCs of the system with $P = 4000$, $r = 0.001$ are close to those of the system with $P = 4000$, $r = 1$ (in both cases $2F = 8$) at the same value of cross-linking index $\gamma_n$. A greater value of the maximum of $w_{\mathrm{DC}}$ in the former case is in accord with the discussion of Figure 6a because (1) continuous model of a chain is approached for $P \rightarrow \infty$, $r \rightarrow 0$ and $rP =$ const and (2) the maximum number of links, $rP$, is small (equal to 4). The $w_{\mathrm{DC}}$ at full conversion is equal to $2/(4 + 1) = 0.4$ for the continuous model and 0 for the discrete model with $P = 4$, $r = 1$. Cross-linking with $P = 4000$, $r = 0.001$ and with $P = 4$ and $r = 1$ gives the same number of EANCs per primary chain, $N_e$, and average effective functionality of junctions, $f_e$, because the distribution of the number of links is the same in both the cases. For $r\bar{P}_n^0 \gtrsim 30$, the differences become negligible.

## 5. Conclusions

The presented theoretical description of network formation of existing chains is applicable to chemical as well as physical cross-linking, to copolymer polydisperse chains, and to polydisperse junction functionalities. Dependences of structural parameters on the extent of cross-linking reaction before and after the gel point are derived. In particular, the concentrations and average molecular weights of sol, EANCs, BCs, and DCs are given as functions of conversion α or of the number-average cross-linking index $\gamma_n$. The input information which must be supplied by the user is (1) the distribution of molar concentrations or molar fractions of primary chains characterized by the numbers and types of units and oriented links and (2) the distribution of molar concentrations or fractions of junctions characterized by the numbers and types of oriented links—both distributions as functions of the extent of cross-linking reaction. The types of units and links are defined by the user.

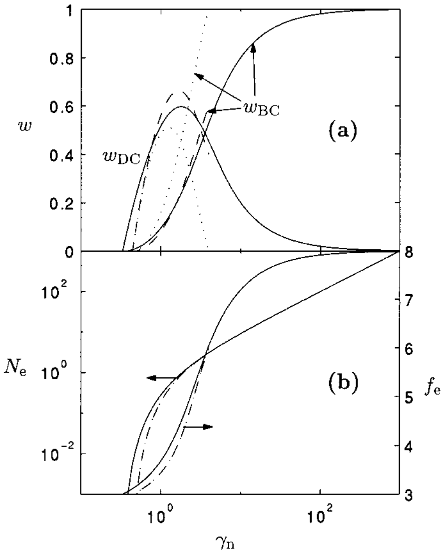

**Figure 9.** (a) $w_{\mathrm{BC}}$ and $w_{\mathrm{DC}}$ and (b) $N_e$ and $f_e$ versus $\gamma_n$ for systems with uniform distributions of $P$ and $F$, $2F = 8$, varying $P$ and the fraction of "active" (cross-linkable) units, $r$. $P = 4000$, $r = 1$, —; $P = 4000$, $r = 0.001$, - - -; $P = 4$, $r = 1$, ···.

The theory is based on the generalized theory of branching processes (TBP)[28,29] in which two sets of variables are used in generating functions, for units and for links. In this way, the logic is simplified and the theory becomes very flexible. Formulas for structural parameters are written in a general form which is independent of the specificity of a particular polymer system. Special care is given to the explanation of all logical steps, specifically to the application of the existing mathematical theory to the description of polymer network structure, which is a weak point in the literature.

The description of gel substructures required modification of the "classical" TBP because they are not composed of building units (primary chains) but parts of them (structural units) (different parts of a primary chain belong to several backbone chains and/or dangling chains). The structure of such objects also depends on the sequential distribution of structural units and links along a primary chain, which is assumed to be random. Similar procedures can be used for different sequential distributions.

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## Appendix. States of Cross-Linked Structural Units. General Case

Six states of cross-linked units are distinguished for each type of oriented links. The states are characterized by the number of (chemical) bonds (existing before cross-linking in primary chains) with finite and infinite continuation. Random distribution of structural units and links along a primary chain is assumed.

$$c_{ij00}^{\mathrm{st}} = \sum_{\substack{\mathbf{k},\boldsymbol{l}\\ k=1}} \mathbf{v}^{\boldsymbol{l}-\mathbf{1}_{ji}} c_{\mathbf{k},\boldsymbol{l}} = \sum_{m} \frac{\partial^2 F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{0},\,\mathbf{v})}{\partial Z_m \partial z_{ji}} \tag{60}$$

$$c_{ij10}^{\mathrm{st}} = 2\sum_{\substack{\mathbf{k},\boldsymbol{l}\\ k\geq 2}} \frac{l_{ji}}{k} \mathbf{v}^{\boldsymbol{l}-\mathbf{1}_{ji}} c_{\mathbf{k},\boldsymbol{l}}$$

$$= 2\int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1}t,\,\mathbf{v})}{\partial z_{ji}} \frac{\mathrm{d}t}{t} - 2\sum_{m} \frac{\partial^2 F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{0},\,\mathbf{v})}{\partial Z_m \partial z_{ji}} \tag{61}$$

$$c_{ij20}^{\mathrm{st}} = \sum_{\substack{\mathbf{k},\boldsymbol{l}\\ k\geq 2}} \left( l_{ji} - 2\frac{l_{ji}}{k} \right) \mathbf{v}^{\boldsymbol{l}-\mathbf{1}_{ji}} c_{\mathbf{k},\boldsymbol{l}} \tag{62}$$

$$= \frac{\partial^2 F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1},\,\mathbf{v})}{\partial z_{ji}} - 2\int_0^1 \frac{\partial^2 F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1}t,\,\mathbf{v})}{\partial z_{ji}} \frac{\mathrm{d}t}{t} +$$

$$\sum_{m} \frac{\partial^2 F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{0},\,\mathbf{v})}{\partial Z_m \partial z_{ji}} \tag{63}$$

$$c_{ij01}^{\mathrm{st}} = 2\sum_{\substack{\mathbf{k},\boldsymbol{l}\\ k\geq 2}} \frac{l_{ji}}{k} (1 - \mathbf{v}^{\boldsymbol{l}-\mathbf{1}_{ji}}) c_{\mathbf{k},\boldsymbol{l}}$$

$$= 2\int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1}t,\,\mathbf{1})}{\partial z_{ji}} \frac{\mathrm{d}t}{t} - 2\int_0^1 \frac{\partial^2 F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1}t,\,\mathbf{v})}{\partial Z_m\,\partial z_{ji}} \frac{\mathrm{d}t}{t} \tag{64}$$

$$c_{ij11}^{\mathrm{st}} = 2\sum_{\substack{\mathbf{k},\boldsymbol{l}\\ k\geq 3}} \left\{ \sum_{\substack{\boldsymbol{l}'=0\\ l'\geq 1}}^{\boldsymbol{l}-\boldsymbol{l}_{ji}} \binom{\boldsymbol{l}}{\boldsymbol{l}'} \mathbf{v}^{\boldsymbol{l}-\boldsymbol{l}'} (\mathbf{1} - \mathbf{v})^{\boldsymbol{l}'} \frac{1}{l'+1} (l_{ji} - l'_{ji}) + \right.$$

$$\left. \sum_{\substack{\boldsymbol{l}'=0\\ l'\geq 2}}^{\boldsymbol{l}} \binom{\boldsymbol{l}}{\boldsymbol{l}'} \mathbf{v}^{\boldsymbol{l}-\boldsymbol{l}'} (\mathbf{1} - \mathbf{v})^{\boldsymbol{l}'} \frac{l'_{ji}}{l'} - \frac{l_{ji}}{k} (\mathbf{1} - \mathbf{v}^{\boldsymbol{l}-\mathbf{1}_{ji}}) \right\} c_{\mathbf{k},\boldsymbol{l}} \tag{65}$$

$$= 2\sum_{\mathbf{k},\boldsymbol{l}} \left\{ l_{ji} \sum_{\boldsymbol{l}'=0}^{\boldsymbol{l}-\boldsymbol{l}_{ji}} \binom{\boldsymbol{l} - \mathbf{1}_{ji}}{\boldsymbol{l}'} \mathbf{v}^{\boldsymbol{l}-\mathbf{1}_{ji}-\boldsymbol{l}'} (\mathbf{1} - \mathbf{v})^{\boldsymbol{l}'} \frac{1}{l'+1} - \right.$$

$$\left. l_{ji} \mathbf{v}^{\boldsymbol{l}-\mathbf{1}_{ji}} - \frac{l_{ji}}{k} (\mathbf{1} - \mathbf{v}^{\boldsymbol{l}-\mathbf{1}_{ji}}) \right\} c_{\mathbf{k},\boldsymbol{l}} \tag{66}$$

$$= 2\int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1},\,\mathbf{v} + (\mathbf{1} - \mathbf{v})t)}{\partial z_{ji}} \mathrm{d}t - 2\frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1},\,\mathbf{v})}{\partial z_{ji}}$$

$$-2\int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1}t,\,\mathbf{1})}{\partial z_{ji}} \frac{\mathrm{d}t}{t} + 2\int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1}t,\,\mathbf{v})}{\partial z_{ji}} \frac{\mathrm{d}t}{t} \tag{67}$$

$$c_{ij02}^{\mathrm{st}} = 2\sum_{\substack{\mathbf{k},\boldsymbol{l}\\ k\geq 3}} \sum_{\substack{\boldsymbol{l}'=\mathbf{0}\\ l'\geq 2}}^{\boldsymbol{l}} \binom{\boldsymbol{l}}{\boldsymbol{l}'} \mathbf{v}^{\boldsymbol{l}-\boldsymbol{l}'} (\mathbf{1} - \mathbf{v})^{\boldsymbol{l}'} \left[ \frac{l'-1}{l'+1} (l_{ji} - l'_{ji}) + \right.$$

$$\left. \frac{l'-2}{l'} l_{ji} \right] c_{\mathbf{k},\boldsymbol{l}} \tag{68}$$

$$= \sum_{\mathbf{k},\boldsymbol{l}} \left\{ l_{ji} + l_{ji} \mathbf{v}^{\boldsymbol{l}-\mathbf{1}_{ji}} - 2l_{ji} \sum_{\boldsymbol{l}'=\mathbf{0}}^{\boldsymbol{l}-\mathbf{1}_{ji}} \binom{\boldsymbol{l} - \mathbf{1}_{ji}}{\boldsymbol{l}'} \mathbf{v}^{\boldsymbol{l}-\mathbf{1}_{ji}-\boldsymbol{l}'} (\mathbf{1} - \right.$$

$$\left. \mathbf{v})^{\boldsymbol{l}'} \frac{1}{l'+1} \right\} c_{\mathbf{k},\boldsymbol{l}} \tag{69}$$

$$= \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1},\,\mathbf{1})}{\partial z_{ji}} + \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1},\,\mathbf{v})}{\partial z_{ji}} -$$

$$2\int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1},\,\mathbf{v} + (\mathbf{1} - \mathbf{v})t)}{\partial z_{ji}} \mathrm{d}t \tag{70}$$

The concentrations of structural units of $i$th type belonging to BCs, $c_{\mathrm{BC},i}$, are given for copolymer primary chains with general concentration distribution, $\{c_{\mathbf{k},\mathbf{l}}\}$, assuming random sequential distribution of units and links along chains.

$$c_{\mathrm{BC},i} = \sum_{\mathbf{k}} \sum_{\boldsymbol{l}} c_{\mathbf{k},\boldsymbol{l}} \sum_{\substack{\boldsymbol{l}'=\mathbf{0}\\ l'\geq 2}}^{\boldsymbol{l}} \frac{k_i}{k} \left( 2 + k - \frac{2}{l'+1} - \frac{2k}{l'+1} \right) \binom{\boldsymbol{l}}{\boldsymbol{l}'} \mathbf{v}^{\boldsymbol{l}-\boldsymbol{l}'}$$

$$(\mathbf{1} - \mathbf{v})^{\boldsymbol{l}'} \tag{71}$$

$$= 2\int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1}t,\mathbf{1})}{\partial Z_i} \mathrm{d}t + \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1},\,\mathbf{1})}{\partial Z_i} -$$

$$2\int_0^1 \int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1}t_1,\,\mathbf{v} + (\mathbf{1} - \mathbf{v})t_2)}{\partial Z_i} \mathrm{d}t_1\,\mathrm{d}t_2 -$$

$$2\int_0^1 \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1},\,\mathbf{v} + (\mathbf{1} - \mathbf{v})t)}{\partial Z_i} \mathrm{d}t + \frac{\partial F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1},\,\mathbf{v})}{\partial Z_i} -$$

$$\int_0^1 (\mathbf{1} - \mathbf{v}) \frac{\partial \mathbf{d} F_{\mathrm{n}}^{\mathrm{chain}}(\mathbf{1}t,\,\mathbf{v})}{\partial Z_i} \mathrm{d}t \tag{72}$$

The following symbols were used:

$$l \equiv l_{11} + l_{12} + \ldots \tag{73}$$

$$l' \equiv l'_{11} + l'_{12} + \ldots \tag{74}$$

$$k \equiv k_1 + k_2 + \ldots \tag{75}$$

$$\mathbf{v}^{\boldsymbol{l}} \equiv v_{11}^{l11} v_{12}^{l12} \ldots \tag{76}$$

$$\binom{\boldsymbol{l}}{\boldsymbol{l}'} \equiv \binom{l_{11}}{l'_{11}} \binom{l_{12}}{l'_{12}} \ldots \tag{77}$$

$$\mathbf{1}_{ji} \equiv (0, \ldots, 0, \underbrace{1}_{\substack{[j,i]\text{th}\\ \text{componet}}}, 0, \ldots) \tag{78}$$

$$\mathbf{1}t \equiv (t,\, t,\, \ldots) \tag{79}$$

$$(\mathbf{1} - \mathbf{v})t \equiv ((1 - v_{11})t,\, (1 - v_{12})t,\, \ldots) \tag{80}$$

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(39) Note that $\boldsymbol{l}$ is a vector, not a matrix, in spite of its components having two subscripts. Components of vector $\boldsymbol{l}$ are arranged in an arbitrary but fixed order, i.e., components of any other vector related to the set of oriented links must be arranged in the same order.

(40) Instead of molar concentration, any quantity proportional to it can be used as well, e.g., molar fraction. But in such a case, "concentration of EANCs" means "number of EANCs per building unit".

(41) Note that the vector $\mathbf{k}$ in the description of dummy units, $(\mathbf{k}, \boldsymbol{l})$, usually can be ommited because normally dummy units are not composed of any physical units ($\mathbf{k} \equiv \mathbf{0}$).

(42) Connecting a unit by a $[j, i]$-link can be imagined as replacing an $[i, j]$-link of the unit which it is connecting to. Mathematically, the variable $z_{ij}$ is substituted by the generating function (GF) of a connected unit. It is possible in a vector form only if GFs have the same subscripts as the replaced variables.

(43) It is assumed that a structural unit may issue at most one link; this means that $0 \le l \le P$, i.e., $c_{P,l}, \equiv 0$ for $l >$ P. Otherwise, only the second part of eq 33 is valid. Similar note concerns all six unit states.

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