(33) Jones, A. A.; Brehm, G. G.; Stockmayer, W. H. *J. Polym. Sci., Polym. Sym.* **1974**, *No. 46*, 149.
(34) Stockmayer, W. H.; Baur, M. E. *J. Am. Chem. Soc.* **1964**, *86*, 3485.
(35) Benoit, H.; Doty, P. *J. Chem. Phys.* **1953**, *57*, 958.
(36) Yamakawa, H.; Fujii, M. *Macromolecules* **1973**, *6*, 407.
(37) Schmidt, M.; Stockmayer, W. H. *Macromolecules*, in press.
(38) Koyama, R. *J. Phys. Soc. Jpn.* **1973**, *34*, 1029.
(39) Zugenmaier, P.; Gutknecht, W., to be published; see also: Sarko, A.; Zugenmaier, P. *ACS Symp. Ser.* **1980**, *No. 141*, 459–482.
(40) Yamakawa, H.; Stockmayer, W. H. *J. Chem. Phys.* **1972**, *57*, 2843.
(41) Hsu, B.; McWherter, C. A.; Brant, D.; Burchard, W. *Macromolecules* **1982**, *15*, 1350.
(42) We should mention here that in our recent measurements the same values for $\langle S^2\rangle_z$ were found with two different instruments. Probably the lower radii determined in this work result from the improvement in the clarification of the solutions compared with the technique applied 15 years ago.
(43) Schmidt, M.; Stockmayer, W. H.; Mansfield, M. *Macromolecules* **1982**, *15*, 1609.
(44) Yamakawa, H. In "Modern Theory of Polymer Solutions"; Harper and Row: New York, 1971.
(45) Pyun, C. W.; Fixman, M. *J. Chem. Phys.* **1964**, *41*, 937.
(46) Imai, S. *J. Chem. Phys.* **1969**, *50*, 2116.
(47) Yamakawa, H. *J. Chem. Phys.* **1962**, *36*, 2995.
(48) Batchelor, G. K. *J. Fluid Mech.* **1972**, *52*, 245; *1976*, *74*, 1.
(49) Felderhof, B. U. *J. Phys. A: Math. Gen.* **1978**, *11*, 929.
(50) Akcasu, A. Z.; Benmouna, M. *Macromolecules* **1978**, *11*, 1193.
(51) Schmidt, M. *Macromolecules*, paper submitted.
(52) Harris, R. A.; Hearst, J. E. *J. Chem. Phys.* **1966**, *44*, 2595.
(53) Hearst, J. E.; Beals, E.; Harris, R. A. *J. Chem. Phys.* **1968**, *48*, 537.
(54) Zimm, B. H. *J. Chem. Phys.* **1956**, *24*, 269.
(55) Scherer, P. C.; Levi, D. W.; Hawkins, M. C. *J. Polym. Sci.* **1957**, *24*, 19.
(56) Gupta, A. K.; Marchal, E.; Burchard, W.; Pfannemüller, B. *J. Am. Chem. Soc.* **1979**, *12*, 281.
(57) Rouse, P. E., Jr. *J. Chem. Phys.* **1953**, *21*, 1272.
(58) Bueche, F. *J. Chem. Phys.* **1954**, *22*, 603.
(59) Recent studies with more than two-functional primers indicate increasing difficulties for a regular enzymatic attack for steric reasons, which is observed at low primer concentration. (Ziegast, G.; Pfannemüller, B., to be published).
(60) Sharp, P.; Bloomfield, V. A. *J. Chem. Phys.* **1968**, *48*, 2149.
(61) Sharp, P.; Bloomfield, V. A. *Biopolymers* **1968**, *6*, 1201.
(62) Bloomfield, V. A.; Zimm, B. H. *J. Chem. Phys.* **1966**, *44*, 315.

Size of Network Chains[†]

Karel Dušek

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 Prague 6, Czechoslovakia. *Received July 29, 1983*

ABSTRACT: A method for calculating average degrees of polymerization and distributions of elastically active network chains (EANC), dangling chains, and EANC's with attached dangling chains is presented. The method is based on the theory of branching processes and on the Flory–Stockmayer treelike model with uncorrelated circuit closing in the gel and employs the cascade substitution and probability generating functions as a tool. The method works with the distribution of building units with respect to the number of issuing bonds having either finite or infinite continuation. The approach is developed in detail for stepwise polyaddition of f-functional components. The inadequacy in expressing the degree of polymerization of EANC's as a quantity inversely proportional to the number of EANC's for any network deviating from perfectness is stressed.

Introduction

The equilibrium elasticity of polymer networks is known to be determined by the number of elastically active network chains (EANC)[1-5] (in correlation with the effective cycle rank) and not by the degree of polymerization (size) of EANC's, provided the EANC's are sufficiently long to obey Gaussian statistics. The dangling chains are relevant only in the sense that they affect the concentration of EANC's per unit volume.

The time-dependent properties, however, are determined by the mobility of structural units of the network. They are contributed to by units in the EANC's as well as by other units present in the system—by units in the dangling chains and in the sol, if this is present. The mobility of the units in these chains is expected to depend on their average size (degree of polymerization) and possibly on the size distribution. For example, according to the Rouse theory the relaxation spectra of linear polymers depend on the weight-average degree of polymerization of the chains.[6] There exist numerous examples that the viscoelastic properties depend on the network architecture and not only on the concentration of EANC's (cf., e.g., ref 6–8). The connection between time-dependent properties of networks and dangling ends has been recently emphasized by Bibbó and Vallés.[9] However, the width of the main transition region depends on the length of EANC's in a network essentially free of dangling chains; at the same time, the width and shape of the transition region of networks with the same concentration of EANC's depend on the number of dangling chains attached to EANC's.[10] A theory relating the network architecture to its viscoelasticity is still missing, however.

In the literature, no united view has been forwarded on the size of network chains. Most often, the degree of polymerization or molecular weight between cross-links, M_c, is considered merely to be inversely proportional to the concentration of EANC's, and sometimes a correction for dangling chains[11] is applied. A rigorous method for calculating the number-average degree of polymerization has been offered by Dobson and Gordon,[12] who used the theory of branching processes employing the treelike model and cascade substitution. Recently, Bibbó and Vallés[9] have examined the size and size distribution of dangling chains formed from monomer units with equal and independent reactivities of functional groups using the conditional probability method.

The aim of the present contribution is to present a treatment for calculating the degree of polymerization averages and distributions of both EANC's and dangling chains. The theory of branching processes developed or-

---

[†] Affectionately dedicated to Professor Walter H. Stockmayer, whose integrity and dedication to polymer science has long been an inspiration to the scientific community.

0024-9297/84/2217-0716$01.50/0

iginally by Gordon[13,14] and used since in a number of network studies (cf., e.g., some recent review articles[4,5,15,16]) offers a straightforward method for solving these problems. In this contribution, we limit ourselves to the case of a single-component system with a first-shell substitution effect (i.e., the reactivity of a group in the monomer unit may depend on how many functional groups in the same unit have already reacted). The extension to copolymerization is straightforward and simple, if matrix algebra is used.

Statistical Treatment of Network Formation and Its Limitations

The postulates and limitations of the statistical theory used here deserve a comment. In this connection, it should be noted that the theory of branching processes (TBP) and the theory based on conditional probabilities developed later by Macosko and Miller[17,18] are fully equivalent since they are based on the same Flory–Stockmayer[3,19,20] treelike model allowing uncorrelated circuit closing in the gel, and they also use the same mathematical method of generating branched and cross-linked structures. Only the mathematical language is slightly different. The use of probability generating functions (pgf) in TBP makes the derivation of statistical averages, including conformational averages, highly economical and routine.

However, one has to bear in mind that using the statistical methods, one constructs the macromolecular structures from building units while respecting the rules of bond formation at any instant of reaction, irrespective of whether the reaction is equilibrium or kinetically controlled.[4] In this approach, the network formation is a Markov process, usually of the first order, and this fact may have an effect on calculated distributions and averages. For irreversible reactions, the more rigorous kinetic method[21-23]—which is based on the mass action law and in which the integrity of structures once formed remains preserved—yields in special cases of kinetic control distributions that cannot be derived from Markovian statistics (polycondensation reactions with substitution effect[21,23] or living polymerization). For multifunctional polycondensation systems with equal and independent reactivity of functional groups, the kinetic treatment was for the first time formulated by Stockmayer.[22] An analysis shows that the distributions generated by the first-order Markovian statistical methods for various linear polymerization mechanisms reduce after a proper transformation (e.g., removal of the monomer and polymer of degree of polymerization 1 from the distribution) to the most probable distribution, whereas the distributions derived from the kinetic scheme may be different. The practical implications of the essential difference between the statistical and kinetic methods are yet to be explored.

The basic assumption used in the statistical theories applied to the gel is the assumption of uncorrelated structure of the gel; it helps to retain the simplicity of the statistics also for the gel. The term uncorrelated means that the probability for a bond of a given type either to have continuation to infinity or to issue a finite subtree is assumed to depend neither on the connectivity (finite of infinite continuation) of neighboring bonds nor on the overall closed-circuit structure of the gel. The reasons why the agreement between experiments and values calculated with the statistical theory is fairly good despite this serious simplification have been discussed elsewhere.[4]

It has been the purpose of this brief discussion to draw attention to the danger that there may exist long-range effects—unaccounted for by the statistical theory—originating in chemical kinetics and/or in the long-range correlations due to closed circuits (cycles) in the gel. This means that the calculated distributions may somewhat deviate from reality. Unfortunately, the kinetic method cannot be used for treating structures in the gel, since it considers the gel to be one integral reaction species.[22]

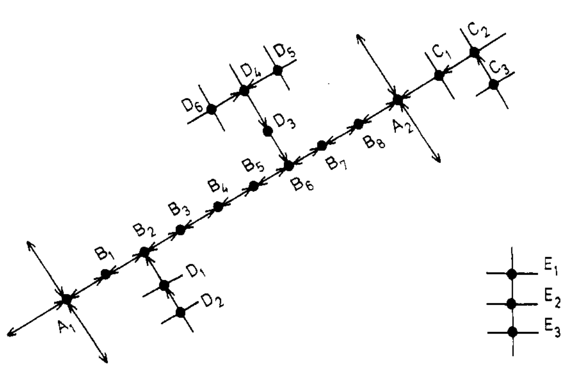

Figure 1. Schematic representation of part of a network. (For details see text.)

Using the formalism of TBP, one can characterize the composition of network chains as follows: The scheme in Figure 1 shows a part of the cross-linked system obtained from a tetrafunctional monomer in which A_1 and A_2 are active branch units (ABU) from which at least three paths issue in infinity, B_1 to B_8 are units of the backbone of an elastically active network chain (EANC) located between two ABU's, and C_1 to C_3 as well as D_1 to D_2 and D_3 to D_6 are units constituting dangling network chains attached to an ABU (C) or to a unit in an EANC. The units E_1 to E_3 constitute a molecule of the sol. The arrows denote the direction of the infinite continuation of a given bond. The different parts of a cross-linked system are thus composed of units differing in the number of issuing bonds with infinite continuation. The respective numbers are as follows: ABU (A), 3; EANC (B), 2; dangling chains (C, D), 1; sol, 0.

In the theory of branching processes, the distribution of units in the whole system according the number of issuing bonds (irrespective of whether they have a finite or infinite continuation) is given by the *probability generating function* (pgf) $F_0(\Theta)$, and for the units in the first or higher generations by the pgf $F_1(\Theta)$ (cf. reg 13–16)

$$F_0(\Theta) = \sum_{i=0}^{f} a_i \Theta^i \tag{1}$$

$$F_1(\Theta) = \sum_{i=1}^{f} i a_i \Theta^{i-1} \Big/ \sum_{i=1}^{f} i a_i \tag{2}$$

a_i is the fraction of units in which i functional groups of the total number f have reacted and participate in i bonds; Θ is the dummy variable of the pgf. Beyond the gel point, these units are nonrandomly distributed between the sol and gel. It should be noted that we disregard here a possible formation of elastically inactive cycles, but an approximate method for treating this problem is available.[24]

The crucial parameter for the distribution of units beyond the gel point is the probability that a bond has a finite or infinite continuation. In TBP, the former is called the extinction probability v, defined by

$$v = F_1(v) \tag{3}$$

For the assumption of the uncorrelated structure of the gel, one can get a new bivariate pgf for the units $P_0(\Theta_v, \Theta_{1-v})$ which gives the distribution of units with respect to the number of bonds with finite and infinite continuation. F_0 is transformed into P_0 by substituting for Θ in $F_0(\Theta)$ the expression $v\Theta_v + (1 - v)\Theta_{1-v}$

$$P_0(\Theta_v,\Theta_{1-v}) = \sum_{ij} p_{ij}\Theta_v{}^i\Theta_{1-v}{}^j = F_0(v\Theta_v + (1-v)\Theta_{1-v}) = \sum_i a_i(v\Theta_v + (1-v)\Theta_{1-v})^i \quad (4)$$

where the coefficient p_{ij} is equal to the probability of finding a unit with $i + j$ bonds of which i have finite and j infinite continuation. The pgf P_0 is related to the whole system, including the sol. Since the gel does not contain any unit of the sol (the sol fraction is given by $\sum p_{i0} = F_0(v)$), the pgf for the distribution of units in the gel, P_g, reads as follows:

$$P_g(\Theta_v,\Theta_{1-v}) = \sum_{ij} g_{ij}\Theta_v{}^i\Theta_{1-v}{}^j = \frac{F_0(v\Theta_v + (1-v)\Theta_{1-v}) - F_0(v\Theta_v)}{1 - F_0(v)} \quad (5)$$

The denominator on the right-hand side of eq 5 is equal to the gel fraction ($\sum p_{ij}$ ($j > 0$)).

The pgf for units in the first and higher generation depends on whether the unit is situated in a finite or infinite branch. If the branch is finite, all issuing bonds must have a finite continuation and the pgf reads

$$P_v(\Theta) = F_1(v\Theta_v)/F_1(v) = F_1(v\Theta_v)/v \quad (6)$$

If the branch is infinite, all possibilities of its continuation are included in the pgf P_{1-v}

$$P_{1-v}(\Theta) = \frac{F_1(v\Theta_v + (1-v)\Theta_{1-v}) - F_1(v\Theta_v)}{1 - F_1(v)} \quad (7)$$

For generation of selected walks, e.g., along a dangling chain in the infinite direction or along an EANC, the corresponding pgf's have been modified as shown below.

Once the explicit form of the pgf $F_0(\Theta)$ is given (its coefficients are a function of an independent variable (conversion or time), all statistical averages can be expressed through the values of derivatives of the pgf's. Let us denote for this purpose the values of derivatives of the pgf Y_{xz} as follows:

$$Y_{xz}{}^m(a,b) \equiv \left[\frac{\partial Y_{xz}(\Theta_m,\Theta_n)}{\partial\Theta_m}\right]_{\Theta_m=a,\Theta_n=b}$$

$$Y_{xz}{}^{m,n}(a,b) \equiv \left[\frac{\partial_2 Y_{xz}(\Theta_m,\Theta_n)}{\partial\Theta_m\partial\Theta_n}\right]_{\Theta_m=a,\Theta_n=b} \quad (7a)$$

For the pgf P_0, the values of the pgf itself and of its first and second derivatives are given below.

$$\begin{array}{ll}
P_0(0,0) = p_{00} & P_0{}^v(0,0) = p_{10} \\
P_0(1,0) = \sum p_{i0} & P_0{}^v(1,0) = \sum ip_{i0} \\
P_0(0,1) = \sum p_{0j} & P_0{}^v(0,1) = \sum p_{1j} \\
P_0(1,1) = 1 & P_0{}^v(1,1) = \sum ip_{ij} \\
P_0{}^{1-v}(0,0) = p_{01} & P_0{}^{v,v}(0,0) = 2p_{20} \\
P_0{}^{1-v}(1,0) = \sum p_{i1} & P_0{}^{v,v}(1,0) = \sum i(i-1)p_{i0} \\
P_0{}^{1-v}(0,1) = \sum jp_{0j} & P_0{}^{v,v}(0,1) = 2\sum p_{2j} \\
P_0{}^{1-v}(1,1) = \sum jp_{ij} & P_0{}^{v,v}(1,1) = \sum i(i-1)p_{ij} \\
P_0{}^{1-v,1-v}(0,0) = 2p_{02} & P_0{}^{1-v,v}(0,0) = p_{11} \\
P_0{}^{1-v,1-v}(1,0) = 2\sum p_{i2} & P_0{}^{1-v,v}(1,0) = \sum ip_{i1} \\
P_0{}^{1-v,1-v}(0,1) = \sum j(j-1)p_{0j} & P_0{}^{1-v,v}(0,1) = \sum jp_{1j} \\
P_0{}^{1-v,1-v}(1,1) = \sum j(j-1)p_{ij} & P_0{}^{1-v,v}(1,1) = \sum ijp_{ij}
\end{array}$$

Number-Average Size of Network Chains

It has been shown by Dobson and Gordon[12] that the number of EANC's per monomer unit, N_e, is derived from the number of active branch units; each such unit contributes by half of its number of bonds with infinite continuation

$$N_e = (1/2)\sum_{\substack{i=0\\j=3}} jp_{ij} = (1/2)(P_0{}^{1-v}(1,1) - P_0{}^{1-v}(1,0) - P_0{}^{1-v,1-v}(1,0)) \quad (8)$$

The frequently used expression for the DP of EANC's

$$(P_C)_n = 1/N_e \quad (9)$$

has no physical meaning unless the network is perfect. If it is not, the units in dangling chains and in the sol are also counted.

One of the realistic definitions counts backbone units of an EANC, e.g., B_1–B_8 in Figure 1, placed between active branch units A_1 and A_2. All these backbone units must issue two and only two bonds with infinite continuation. Therefore

$$(P_{CB})_n = \sum_{i=0} p_{i2}/N_e = (1/2)P_0{}^{1-v,1-v}(1,0)/N_e \quad (10)$$

Parts of active branch units can also be included in the backbone of an EANC. If all branch units are added, the corresponding number average reads

$$(P_{CB}')_n = \sum_{\substack{i=0\\j=2}} P_{ij}/N_e = [1 - P_0(1,0) - P_0{}^{1-v}(1,0)]/N_e \quad (11)$$

If only $1/f$ part of the active branch unit is considered to contribute, one gets an average suitable for star-shaped monomer units

$$(P_{CB}'')_n = [\sum_{i=0} p_{i2} + \sum_{\substack{i=0\\j=3}} jp_{ij}/f]/N_e = (P_{CB})_n + 2/f \quad (12)$$

The dynamic behavior of EANC's is determined not only by the number of backbone units but also by the dangling chains attached to the backbone. The number-average DP of an EANC including its dangling chains can be derived as follows: The number of units in all dangling chains is equal to $\sum p_{i1}$, but some of the dangling chains issue from active branch points. The dangling chains have the same average size irrespective of the type of unit they issue from. Therefore, the fractions of units in dangling chains issuing from EANC's is

$$X = \frac{\sum_{i=1} ip_{i2}}{\sum_{\substack{i=1\\j=2}} ip_{ij}} = \frac{P_0{}^{v,1-v,1-v}(1,0)}{P_0{}^v(1,1) - P_0{}^v(1,0) - P_0{}^{v,1-v}(1,0)}$$

and the number average is given by the relation

$$(P_{CBD})_n = [\sum_{i=0} p_{i2} + X\sum_{i=0} p_{i1}]/N_e \quad (13)$$

where

$$\sum_{i=0} p_{i2} = P^{1-v,1-v}(1,0)/2$$

and

$$\sum_{i=0} p_{i1} = P_0{}^{1-v}(1,0)$$

The number-average DP of dangling chains, $(P_D)_n$, is given by the number of p_{i1} units per bond with finite continuation issuing from a unit in EANC or from an active branch unit

$$(P_{\mathrm{D}})_{\mathrm{n}} = \sum_{i=0} p_{i1} / \sum_{\substack{j=1\\ j=2}} i p_{ij} \qquad (14)$$

Degree of Polymerization Distribution of Network Chains and Higher Degree of Polymerization Averages

The number-, weight-, z-, etc. fraction distributions are conveniently expressed through the number- ($N(\Theta)$), weight- ($W(\Theta)$), and z- ($Z(\Theta)$), fraction generating functions, defined as follows:

$$N(\Theta) \equiv \sum_{x=1} n_x \Theta^x \qquad (15)$$

$$W(\Theta) \equiv \sum_{x=1} w_x \Theta^x \qquad (16)$$

$$Z(\Theta) \equiv \sum_{x=1} z_x \Theta^x \qquad (17)$$

Once one of these pgf's is obtained, the remaining distributions and averages can be obtained by the following transformations:

$$W(\Theta) = \Theta N'(\Theta)/P_{\mathrm{n}} \qquad (18)$$

$$Z(\Theta) = \Theta W'(\Theta)/P_{\mathrm{w}} \qquad (19)$$

$$N(\Theta) = P_{\mathrm{n}} \int_0^{\Theta} (W(\Theta)/\Theta)\, \mathrm{d}\Theta \qquad (20)$$

where $N'(\Theta)$ and $W'(\Theta)$ are derivatives of N and W with respect to Θ and $N'(1)$ and $W'(1)$ are their values for $\Theta = 1$; $P_{\mathrm{n}} = N'(1)$, $P_{\mathrm{w}} = W'(1)$, and $P_z = Z'(1)$ are the number-, weight-, and z-average degrees of polymerization; eq 20 is valid if $x \geq 1$.

In order to obtain the degree of polymerization distribution, we can proceed formally in two ways: (1) to derive the number fractions and the corresponding pgf $N(\Theta)$, or (2) to obtain the weight-fraction gf $W(\Theta)$ by cascade substitution in a routine way. To this purpose, we define the probability that from a unit of EANC or from an active branch point a bond does not lead to another active branch point. The number of such possibilities is given by $2\sum p_{i2}$ of the total number of possibilities $\sum_{j=2} j p_{ij}$ so that one gets for z

$$z = (2\sum_{i=0} p_{i2})/(\sum_{\substack{i=0\\ j=2}} j p_{ij}) \qquad (21)$$

Since for $z = 1$, the DP of an EANC is zero, we have

$$n_x = (1 - z) z^x \qquad (22)$$

and

$$N_{\mathrm{B}}(\Theta) = (1 - z)/(1 - z\Theta) \qquad (23)$$

which gives

$$(P_{\mathrm{CB}})_{\mathrm{n}} = z/(1 - z) \qquad (24)$$

This relation is identical with eq 10 if one substitutes for z from eq 21.

Using transformation (18), one obtains

$$W_{\mathrm{B}}(\Theta) = (1 - z)^2 \Theta/(1 - z\Theta)^2 \qquad (25)$$

and

$$(P_{\mathrm{CB}})_{\mathrm{w}} = (1 + z)/(1 - z) \qquad (26)$$

The same $W_{\mathrm{B}}(\Theta)$ and the weight-average of DP of EANC's $(P_{\mathrm{CB}})_{\mathrm{w}}$ can be derived by cascade substitution

$$W_{\mathrm{B}}(\Theta) = \Theta F_0(u) = \Theta(1 - z + zu)^2 \qquad (27)$$

$$u = \Theta F_1(u) = \Theta(1 - z + zu)$$

since in the bifunctional case $u = (1 - z)\Theta/(1 - z\Theta)$.

The definition of the DP of EANC's such that for the case of a bond between two active branch units the DP of the EANC is equal to zero makes the polydispersity expressed as $(P_{\mathrm{CBw}}/(P_{\mathrm{CB}})_{\mathrm{n}}$ diverge for $z = 0$, because in the weight-fraction distribution $w_0 = 0$ by definition and the distribution is normalized.

To characterize the polydispersity, one should either use the ratios of higher DP averages or redefine the number-fraction distribution to cover the range $(1, \infty)$

$$n_x^* = (1 - z) z^{x-1}$$

which yields

$$N_{\mathrm{B}}^*(\Theta) = (1 - z)\Theta/(1 - z\Theta)$$

and

$$(P_{\mathrm{CB}}^*)_{\mathrm{n}} = 1/(1 - z) \qquad (28)$$

which is the number-fraction gf for the most probable distribution.

The z-fraction distribution and average are obtained by the transformation (19)

$$(P_{\mathrm{CB}})_z = (z^2 + 4z + 1)/(1 - z^2) \qquad (29)$$

Degree of Polymerization Distribution of EANC's Including Dangling Chains

Each backbone unit of an EANC bears $f - 2$ groups that either are in the unreacted state or have reacted and participate in bonds with finite continuation. Each such bond makes a connection to a dangling chain. Therefore, the probability that a unit issues i finite paths (p_{i2}) is to be multiplied by the ith power of the weight-fraction gf of a dangling chain $F_{\mathrm{w}}(\Theta)$, which is derived below. The cascade substitution yields the weight-fraction gf as

$$W_{\mathrm{BD}}(\Theta) = \Theta(1 - z + uz(F_{\mathrm{w}}(\Theta)))^2 \qquad (30)$$

$$u = \Theta(1 - z + uz(F_{\mathrm{w}}(\Theta))) \qquad (31)$$

where

$$z(F_{\mathrm{w}}(\Theta)) = 2\sum_{i=0} p_{i2}(F_{\mathrm{w}}(\Theta))^i / \sum_{\substack{i=0\\ j=2}} j p_{ij}$$

$$z(1) = z$$

which yields

$$W_{\mathrm{BD}}(\Theta) = (1 - z)^2 \Theta/(1 - \Theta z(F_{\mathrm{w}}(\Theta)))^2 \qquad (32)$$

By differentiation one obtains

$$(P_{\mathrm{CBD}})_{\mathrm{w}} = W'(1) = (1 + z + 2z')/(1 - z) \qquad (33)$$

where

$$z' = (\partial z(F_{\mathrm{w}}(\Theta))/\partial F_{\mathrm{w}}(\Theta))_{\Theta=1} F'_{\mathrm{w}}$$

and

$$F_{\mathrm{w}}' = (\partial F_{\mathrm{w}}(\Theta)/\partial\Theta)_{\Theta=1}$$

The transformation (19) followed by differentiation yields expressions for z-fraction gf and z-average degree of polymerization

$$Z_{\mathrm{BD}}(\Theta) = \frac{(1 - z)^3[1 + \Theta z(F_{\mathrm{w}}(\Theta)) + 2\Theta^2 z'(F_{\mathrm{w}}(\Theta))]\Theta}{(1 - \Theta z(F_{\mathrm{w}}(\Theta)))^3(1 + z + z')} \qquad (34)$$

$$(P_{\mathrm{CBD}})_z = \frac{1 + 2z + 7z' + 2z''}{1 + z + 2z'} + \frac{3(z + z')}{1 - z} \qquad (35)$$

where

$$z'(F_{\mathrm{w}}(\Theta)) = \frac{\partial z(F_{\mathrm{w}}(\Theta))}{\partial F_{\mathrm{w}}(\Theta)} \frac{\partial F_{\mathrm{w}}(\Theta)}{\partial\Theta}$$

z' and z'' are the values of the first and second derivatives

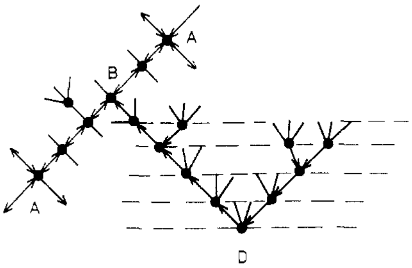

Figure 2. Scheme for the generation of a dangling chain. The chain is rooted by one of its units (D). The arrows denote the direction of continuation to infinity (direction $1 - v$); the opposite direction is the direction of finite continuation. The dangling chain is attached to an EANC at the point B.

of $z(F_w(\Theta))$ with respect to Θ for $\Theta = 1$ (see below).

The Function F_w and the Degree of Polymerization Averages of Dangling Chains

The dangling chains are composed of units issuing one bond with infinite continuation and the remaining $f - 1$ groups either are in the unreacted state or have reacted and participate in bonds with finite continuation. The bonds with infinite continuation are oriented in the direction of the EANC and the bonds with finite continuation are oriented out of the coupling point with the EANC. A dangling chain is schematically shown in Figure 2 as an oriented graph in which one distinguishes between the finite (v) and infinite ($1 - v$) directions. In formulating the pgf for the dangling chain, one has to take these specific directions (variables Θ_v and J_{1-v}) into account. The pgf for the number of bonds issuing from a unit in the root of the tree (a randomly selected unit) reads

$$F_0(\Theta) = \sum_{i=0} p_{i1}\Theta_v^{\,i}(1 - \psi + \psi\Theta_{1-v}) / \sum_{i=0} p_{i1} \tag{36}$$

where ψ is the probability that the neighbor of a randomly chosen unit of the dangling end in the infinite direction is another unit of the dangling chain (i.e., a unit with only one bond issuing into the infinite direction). In addition to these units, units of the EANC and active branch units also may be found among the neighbors, if they themselves issue at least one bond in the finite direction. If this happens to be the case, the dangling chains end at that point (probability $1 - \psi$).

Therefore

$$\psi = \sum_{i=1} p_{i1} / (\sum_{j=1} p_{i1} + \sum_{\substack{i=1\\ j=2}} ip_{ij}) \tag{37}$$

because the number of possibilities for the units with $j \geq 2$ to be coupled with the end of a dangling chain is proportional to i.

The pgf's for units in the generation higher than one, $F_v(\Theta)$ and $F_{1-v}(\Theta)$, are different for the finite and infinite directions

$$F_v(\Theta) = \sum_{i=0} p_{i1}\Theta_v^{\,i} / \sum_{i=0} p_{i1} \tag{38}$$

$$F_{1-v}(\Theta) = \sum_{i=1} ip_{i1}\Theta_v^{\,i-1}(1 - \psi + \psi\,\Theta_{1-v}) / \sum_{i=0} ip_{i1} \tag{39}$$

and have been obtained by differentiation of the pgf $F_0(\Theta)$ (eq 36). The cascade substitution then yields the desired pgf $F_w(\Theta)$

$$F_w(\Theta) = \Theta F_0(\mathbf{u}) \tag{40}$$

$$u_v = \Theta F_v(\mathbf{u}) \tag{41}$$

$$u_{1-v} = \Theta_{1-v}F_{1-v}(\mathbf{u}) \tag{42}$$

The pgf $F_w(\Theta)$ (eq 32) is to be used in the weight-fraction gf for EANC's including their dangling chains, where for the sake of simplicity the variable Θ has not been given as a vector. The variable Θ by which $F_0(u)$ is multiplied to yield $F_w(\Theta)$ does not bear any subscript because the multiplication is performed in order to take into consideration the unit in the root which issues bonds in both directions. The derivatives $F_w'(\Theta)$ and $F_w''(\Theta)$ are defined as follows:

$$F_w'(\Theta) = F_0(\mathbf{u}) + \Theta\left[\frac{\partial F_0(\mathbf{u})}{\partial u_v}u_v' + \frac{\partial F_0(\mathbf{u})}{\partial u_{1-v}}u_{1-v}'\right] \tag{43}$$

where

$$u_v' = \frac{\partial u_v}{\partial \Theta_v} + \frac{\partial u_v}{\partial \Theta_{1-v}} \tag{44}$$

(the second term is, however, equal to zero—cf. eq 37), and

$$u_{1-v}' = \frac{\partial u_{1-v}}{\partial \Theta_v} + \frac{\partial u_{1-v}}{\partial \Theta_{1-v}} \tag{45}$$

The second derivative $F_w''(\Theta)$ is obtained from $F_w'(\Theta)$ analogically. Equations 38, 39, 41, and 42 yield the derivatives of $\mathbf{u}$ (cf. the way of abbreviation given by eq 7a)

$$u_v^{\,v}(\Theta) = \frac{F_v(\mathbf{u})}{1 - \Theta_v F_v^{\,v}(\mathbf{u})}$$

$$u_v^{\,1-v}(\Theta) = 0$$

$$u_{1-v}^{\,1-v}(\Theta) = \frac{F_{1-v}(\mathbf{u})}{1 - \Theta_{1-v}F_{1-v}^{\,1-v}(\mathbf{u})}$$

$$u_{1-v}^{\,v}(\Theta) = \frac{\Theta_{1-v}F_{1-v}^{\,v}(u)F_v(u)}{(1 - \Theta_v F_v^{\,v}(\mathbf{u})(1 - \Theta_{1-v}F_{1-v}^{\,1-v}(\mathbf{u}))} \tag{46}$$

and serve also for the derivation of the second derivatives $u_v^{\,v,v}$, $u_{1-v}^{\,1-v,1-v}$, $u_{1-v}^{\,1-v,v}$, $u_{1-v}^{\,v,1-v}$, and $u_{1-v}^{\,v,v}$ necessary for the derivation of the z-averages of DP. The explicit forms are not given here because of their complexity.

The pgf $F_w(\Theta)$ is at the same time the weight-fraction gf for the dangling chain, so that

$$(P_D)_w = F_w'(1)$$

and $F_w'(1)$ (eq 43) is obtained with the help of eq 44–47 or by using the matrix transformation (cf. ref 14 and 16)

$$(P_D)_w = 1 + (1,\,1)\begin{pmatrix} 1 - F_v^{\,v} & -F_{1-v}^{\,v} \\ 0 & 1 - F_{1-v}^{\,1-v} \end{pmatrix}^{-1}\begin{pmatrix} F_0^{\,v} \\ F_0^{\,1-v} \end{pmatrix} \tag{47}$$

where the operator -1 indicates matrix inversion. After substituting from eq 36–39

$$(P_D)_w = 1 + \frac{1}{D}\left[(1 - 2\psi)\frac{\sum ip_{i1}}{\sum p_{i1}} + \psi\frac{\sum i(i-1)p_{ij}}{\sum ip_{i1}}\right] \tag{48}$$

$$D = \left(1 - \frac{\sum ip_{i1}}{\sum p_{i1}}\right)(1 - \psi)$$

$(P_D)_w$ diverges for $D \rightarrow 0$, which occurs at the gel point, where both components of D converge to zero.

Application and Possible Extension of the Procedure

For characterization of the average size of EANC's the number averages are well suited and one can select one of the definitions of EANC given by one of eq 10, 11, and 12, if dangling chains are not counted. The differences can be noticed only in the region of relatively short EANC's, a region that is more difficult to correlate with viscoelastic properties. From the structural point of view, the dif-

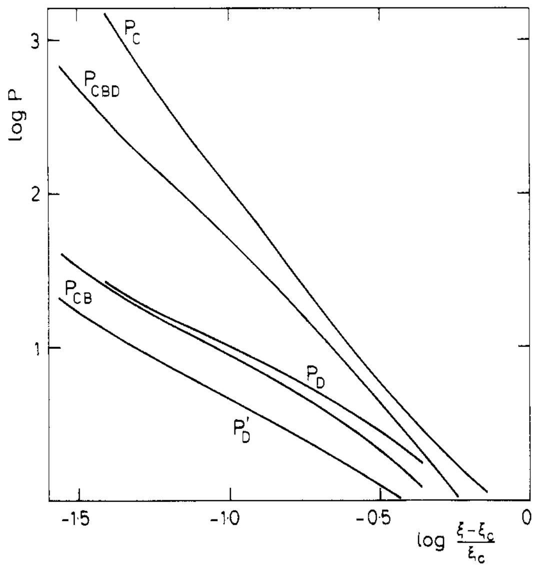

Figure 3. Changes in the number-average DP of elastically active network chains and dangling chains for the random trifunctional polycondensation as a function of the relative molar conversion. ξ is the molar conversion of functional groups and ξ_c is its value at the gel point. The number averages of P_C, P_{CB}, P_{CBD}, and P_D are calculated, respectively, according to eq 9, 10, 13, and 14. $P_D' = [(P_{CBD})_n - (P_{CB})_n]/(P_{CB})_n$ and is equal to the number-average DP of dangling chains, if any unit of an EANC not bearing a dangling chain is counted as a dangling chain of DP zero.

ference between these expressions lies in the different way of counting contributions to EANC's coming from active branch units, and the selection of the way of counting depends on the chemical structure of the unit. For longer EANC's, the difference between the results obtained in various ways disappears.

The polydispersity can be conveniently expressed through the ratios of various DP averages. However, since the averages $(P_{CB})_n$ and $(P_{CBD})_n$ include the fraction of network chains with zero DP and the higher averages by definition do not include this fraction, the number average has to be redefined to exclude the fraction with DP zero. This modification has been performed for $(P_{CB})_n$ in eq 28. For the average $(P_{CBD})_n$ given by eq 13, the number of EANC's and their dangling chain units are to be divided not by a total number of EANC's (according to the definition the connections between two active branch points are included in EANC's) but by the number of EANC's composed of at least one unit having two bonds with infinite continuation. This fraction is just equal to X appearing in eq 13. The modified number-average $(P_{CBD}^*)_n$ is equal to

$$(P_{CBD}^*)_n = (P_{CBD})_n/X \tag{49}$$

For practical application, it is necessary to find the coefficients p_{ij} given by the pgf (4) and these, for the uncorrelated network, are fully determined by the coefficients a_i of the pgf $F_0(\Theta)$ (eq 1), which gives the distribution of monomer units with i bonds. For the first-shell substitution effect (the reactivity of a group depends on how many neighboring groups have reacted), the set of a_i is obtained by solving the corresponding set of kinetic differential equations based on the mass action law (cf., e.g., ref 24). For an equal and independent reactivity of functional groups, the situation becomes very simple, because the pgf $F_0(\Theta)$ assumes the form

$$F_0(\Theta) = (1 - \xi + \xi\Theta)^f \tag{50}$$

where ξ is the fraction of groups that have reacted (molar conversion) and f is the functionality of the monomer unit.

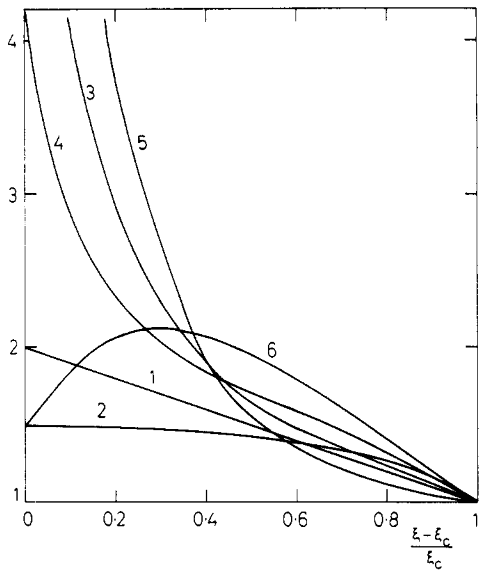

Figure 4. Changes in polydispersity of EANC's and dangling chains in random trifunctional polycondensation as a function of relative molar conversion. The polydispersity is expressed by the ratios of weight-average DP to number-average DP and z-average DP to weight-average DP. (1) $(P_{CB})_w/(P_{CB}^*)_n$; (2) $(P_{CB})_z/(P_{CB})_w$; (3) $(P_D)_w/(P_D)_n$; (4) $(P_D)_z/(P_D)_w$; (5) $(P_{CBD})_w/(P_{CBD}^*)_n$; (6) $(P_{CBD})_z/(P_{CBD})_w$.

The coefficients a_i and p_{ij} can be obtained by binomial expansion, but more conveniently by differentiation of the pgf $P_0(\Theta_\upsilon,\Theta_{1-\upsilon})$ (eq 4), because the values of the derivatives yield directly the necessary sums.

Figures 3 and 4 illustrate changes in the number-average DP and polydispersity as a function of increasing conversion for a system with an equal and independent reactivity of functional groups and functionality $f = 3$. It can be seen that the often assumed inverse proportionality between the number of EANC's and their length given by P_C strongly overestimates the DP of EANC's. Another conclusion that can be drawn from Figure 3 is the substantial contribution to the DP of EANC's made due to dangling chains. For $f = 3$, the dangling chains are almost equal in size to the backbone of EANC's. The polydispersity expressed by P_w/P_n for the backbone EANC's decreases almost linearly with increasing conversion; it reaches the value 2 at the gel point, which is characteristic of the most probable distribution. P_w/P_n diverges for the dangling chains and EANC's, including the dangling chains, in a similar way as it does for the whole system if ξ increases up to ξ_c. The ratios P_z/P_w are always finite at the gel point. The difference in the dependence for P_D and P_{CB} vs. ξ is reflected in a maximum of the dependence of $(P_{CBD})_z/(P_{CBD})_w$ on conversion. In the pregel region, the ratio P_z/P_w also converges to a finite value, if ξ approaches ξ_c.

An extension of the approach to other polyfunctional systems is of interest. For systems composed of different monomer units and containing different types of bonds, the procedure is very similar. One has, however, to consider the molecular weight averages, rather than the DP averages. The simplest way is the use of vectorial pgf's and stoichiometric arguments for the number averages and the cascade substitution for obtaining the weight-fraction gf and higher averages in the following form:

$$W(\Theta) = \sum_K W_K(\Theta)m_K \tag{51}$$

where m_k is the weight fraction of the units of type K, and the components of the vectorial pgf, $\mathbf{W}(\Theta)$, can be expressed as

Macromolecules **1984,** *17,* 722–727

$$W_K(\Theta) = \Theta_K{}^{M_K} F_{0K}(\mathbf{u}) \tag{52}$$

$$\mathbf{u} = (\mathbf{u}_A, ..., \mathbf{u}_K ...)$$

$$\mathbf{u}_K = (u_{K,\upsilon}, u_{K,1-\upsilon})$$

$$u_{K,\upsilon} = \Theta_{K,\upsilon}{}^{M_K} F_{K,\upsilon}(\mathbf{u})$$

$$u_{K,1-\upsilon} = \Theta_{K,1-\upsilon}{}^{M_K} F_{K,1-\upsilon}(\mathbf{u})$$

$$\Theta_K = \upsilon_K \Theta_{K,\upsilon} + (1 - \upsilon_K)\Theta_{K,1-\upsilon}$$

where M_K is the molecular weight of the unit of type K, F_K is the pgf for the number of bonds issuing from a unit of type K on generation g to a unit on generation $g + 1$, provided $g > 0$. The weight-average molecular weight is then obtained by the differentiation of eq 52 with respect to all variables given by the vector Θ for $\Theta = 1$.

Another case of interest is the vulcanization of chains with an arbitrary degree of polymerization distribution. It is possible to take the whole primary chains as roots, a method suggested originally by Dobson and Gordon,[12] and to find the number of active branch points, units of EANC's, and of dangling chains assuming a random distribution of cross-linked units along the primary chain, which determines the degree of polymerization distribution of parts of primary chains between cross-links.

The other possibility for determining the DP averages of EANC's and dangling chains can be found by taking every monomer unit of primary chains as a root and constructing the weight-fraction gf in the same way as that employed in treating cross-linking and degradation.[25] The latter method is more straightforward for calculating the higher moments of the DP distribution.

References and Notes

(1) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1976,** *351,* 351.
(2) Flory, P. J. *Polymer* **1979,** *20,* 1317.
(3) Flory, P. J. *Macromolecules* **1982,** *15,* 99.
(4) Dušek, *Makromol. Chem.* **1979,** *Suppl. 2,* 35.
(5) Dušek, K. *Rubber Chem. Technol.* **1982,** *55,* 1.
(6) Ferry, J. D. "Viscoelastic Properties of Polymers"; Wiley: New York, 1970.
(7) Mooney, M. *J. Polym. Sci.* **1959,** *34,* 599.
(8) Cohen, R. E.; Tschoegl, N. W. *Int. J. Polym. Mater.* **1972,** *2,* 49; **1973,** *3,* 205.
(9) Bibbô, M. A.; Vallês, E. M. *Macromolecules* **1982,** *15,* 1300.
(10) Havránek, A.; Nedbal, J.; Berčík, Č.; Ilavský, M.; Dušek, K. *Polym. Bull.* **1980,** *3,* 497; unpublished results.
(11) Flory, P. J. "Principles of Polymer Chemistry"; Cornell University Press: Ithaca, NY, 1950.
(12) Dobson, G. R.; Gordon, M. *J. Chem. Phys.* **1965,** *43,* 705.
(13) Gordon, M. *Proc. R. Soc. London, Ser. A* **1962,** *268,* 240.
(14) Gordon, M.; Malcolm, G. N. *Proc. R. Soc. London* **1966,** *295,* 29.
(15) Dušek, K.; Prins, W. *Adv. Polym. Sci.* **1969,** *6,* 1.
(16) Burchard, W. *Adv. Polym. Sci.* **1983,** *48,* 1.
(17) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976,** *9,* 199.
(18) Miller, D. R.; Macosko, C. W. *Macromolecules* **1976,** *9,* 206.
(19) Stockmayer, W. H. *J. Chem. Phys.* **1943,** *11,* 45.
(20) Stockmayer, W. H. *J. Chem. Phys.* **1944,** *12,* 125.
(21) Kuchanov, S. I. "Methods of Kinetic Calculations in Polymer Chemistry"; Khimiya: Moscow, 1978 (in Russian).
(22) Dušek, K. *Polym. Bull.* **1979,** *1,* 523.
(23) Mikeš, J.; Dušek, K. *Macromolecules* **1982,** *15,* 99.
(24) Dušek, K.; Gordon, M.; Ross-Murphy, S. B. *Macromolecules* **1978,** *11,* 236.
(25) Dušek, K.; Demjanenko, M. *Macromolecules* **1980,** *13,* 571.

Further Studies of Spin Relaxation and Local Motion in Dissolved Polycarbonates

John J. Connolly, Edward Gordon, and Alan Anthony Jones*

Jeppson Laboratory, Department of Chemistry, Clark University, Worcester, Massachusetts 01610.

Received June 14, 1983

ABSTRACT: Both proton and carbon-13 spin–lattice relaxation times at two fields are reported for dilute solutions of two polycarbonates. For the polycarbonate of 2,2-propanediylbis(4-hydroxyphenyl) carbonate, the relaxation measurements were made as a function of concentration in $C_2D_2Cl_4$ and temperature while for the polycarbonate of 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene the measurements were made at a concentration of 10 wt % in $C_2D_2Cl_4$ and as a function of temperature. A partially deuterated analogue of the first polycarbonate was made to remove cross-relaxation effects from the proton relaxation. The proton and carbon-13 relaxation times are interpreted in terms of three local motions: segmental motion, phenyl group rotation, and methyl group rotation. Two different correlation functions are employed for segmental motion. An older function based on the three-bond jump and a new function by Weber and Helfand gave successful interpretations, yielding surprising similar conclusions concerning segmental motion. Both segmental interpretations relied primarily on cooperative backbone transitions, yielding similar time scales and apparent activation energies for this type of motion. Estimates of the time scale for phenyl group rotation and methyl group rotation did not depend on the model used for segmental motion. By and large the time scale for phenyl group rotation paralleled the time scale for segmental motion as temperature and concentration changed while methyl group rotation displayed a weaker concentration dependence.

Introduction

Two reports of spin relaxation and local motion of dissolved polycarbonates have already been made[1,2] but a more complete series of observations is presented now to verify and expand the previous interpretations. In addition, a new correlation function for segmental motion developed by Weber and Helfand[3] is tested and compared to an earlier function based on the three bond jump.[4] The large data base given for polycarbonates is well suited for test applications of models though the repeat unit structure of the polycarbonates is more complex than the basis of either model.

Specific improvements in the data set relative to the earlier reports[1,2] include the addition of carbon-13 spin–

0024-9297/84/2217-0722$01.50/0