Polymer Bulletin 17, 239–245 (1987)

Polymer Bulletin

Theoretical treatment of network formation by a multistage process

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SUMMARY

A general scheme for a multistage process of network formation is formulated in which the Galton-Watson or universal consistency relation is assumed to be valid. The scheme is elaborated with the theory of branching processes with cascade substitution. Cyclization is postulated not to occur, substitution effects are allowed and can be incorporated in the probability generating functions (pgf).

INTRODUCTION

Recent advances in the development of the statistical theories of branching processes have made it possible to treat a number of complex crosslinking processes which are of technological importance. These processes include curing of epoxy resins (1), formation of polyurethane networks including possible side reactions (2,3), crosslinking of functional polydimethylsiloxanes (4) and of urea-formaldehyde coatings (5).

Technologically very important are multistage processes in which prepolymers are formed in one or several stages, upon which a network is obtained by crosslinking the functional prepolymers. Alternatively, a network formed in an intermediate stage can be further modified.

In this contribution a method is formulated to describe such a multistage process. The method is based on the statistical theory with cascade subsitution. However, it is not limited to the statistical theory because also stages treated by the kinetic method can be included.

APPLICABILITY OF THE STATISTICAL THEORIES

Before we treat the general scheme of a multistage process of network formation it is necessary to analyse the applicability of the statistical theories to real systems (cf. also Ref. 6). This applicability is limited to situations where no long-range correlations are operative. The long-range correlations may be due to a specific reaction mechanism such as the substitution effect (7) or initiated polyreactions (8). If the substitution effect is operative in units from which the networks is built up, the kinetic method should be used and application of the statistical theory yields only approximate results. However, in polymer chemistry the long-range correlations are usually interrupted by groups of independent reactivity and, consequently, become short range (6). Thus, before applying a statistical theory it has to be realized whether the treatment is rigorous or only yields a good approximation. The other type of long-range correlations, cyclization, is not considered here.

In the branching theory with cascade substitution, the distribution of units differing in number and type of bonds in which they are engaged is

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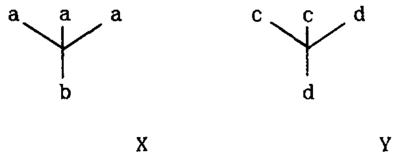
described by a vectorial probability generating function (pgf) $\underline{F}_0(\underline{z})$, where the subscript 0 refers to the root of the probability tree, see e.g. refs. (1,9). Its component $F_{0X}(\underline{z})$ is the pgf for the type and number of bonds issuing from unit X. The components of the dummy vector $\underline{z}$, which differ in their subscripts, denote the various types of bonds. Another pgf, $\underline{F}(\underline{z})$, describes the distribution of bonds issuing from a unit in generation g (g > 0) to units in generation g+1. This pgf characterizes the propagation ability of the system (1,9).

The formulation of $\underline{z}$ and $\underline{F}(\underline{z})$ depends on whether the formation of a new bond is influenced by the type and state of other groups in the same unit. Consider the following example of monomers X and Y:



The probability of formation of a bond between X in generation g and X or Y in generation g+1 depends on the type of group X is connected with (rooted in) in generation g-1. Obviously, if X is rooted in the group b, b cannot take part in bond formation from X to a unit in generation g+1. Also, the propagation ability depends on whether the bond extends to X or Y. Therefore, in multifunctional systems involving units with different functional groups and possibly first-shell substitution effects the subscripts of z and F should specify the passage from one unit to another by identifying the type of the bond, such as XacY, XbdY, XbbX, etc.. Thus, we have in general: z_{XijY} and $F_{XijY}(\underline{z}) = N(\partial F_{0Y}/\partial z_{YjiX})$. The subscript of z means a passage from unit X via an i-j bond to unit Y. F_{XijY} means the pgf for unit Y rooted in unit X via an j-i bond (seen from unit Y) and N is a normalizer.

In many systems simplifications are possible. For instance, if each monomer has only one type of group, the type of bond is determined by the type of group. Moreover, if no substitution effect is operative, the Galton-Watson or universal consistency relation (9) between F_X and F_{0X} (which averages the propagation ability over all possible situations):

$$F_X(\underline{z}) = \sum_i \partial F_{0X}(\underline{z})/\partial z_i \Big/ \Big[\sum_j \partial F_{0X}(\underline{z})/\partial z_j\Big]_{\underline{z}=\underline{1}} \qquad (1)$$

is rigorous. If a substitution effect exists in one of the monomers in an n-component ($n \geqslant 3$) system, the distribution of triads obtained from kinetic differential equations is required (10). However, the Galton-Watson formulation appears to be a good approximation for a number of systems with substitution effects.

In the next paragraph we present a general scheme for a multistage process of network formation in which the Galton-Watson formulation is assumed to be valid. This limitation is not a requirement but keeps the formulae relatively simple. In principle the more general derivation can be made in a similar way. In addition, cyclization or other long-range spatial correlations are postulated not to occur. Substitution effects, however, are allowed and can be incorporated in the pgf's.

SCHEME OF A MULTISTAGE PROCESS

Let us consider a process for a multicomponent system in which the monomers are converted into the final network in several consecutive stages:

stage	components
1	monomers 1 $\xrightarrow{\text{reactions 1}}$ products 1
2	products 1 + monomers 2 $\xrightarrow{\text{reactions 2}}$ products 2
ℓ	products ℓ-1 + monomers ℓ $\xrightarrow{\text{reactions } \ell}$ products ℓ

We only consider situations in which the statistical methods are valid or yield a good approximation. Our strategy is that the products of stage i become building units in stage i+1. The mathematics are simpler when we assume that the reactions which were possible in stage i are no longer possible in stage i+1. This implies that the unreacted groups remaining in the products of stage i may take part in subsequent reactions in the next stage with newly added monomers. Throughout the process, track is being kept of the number and type of unreacted (= free) groups by introducing dummy variables for these, collected in the pgf vector $\underline{z}_f$. The calculation procedure for a multistage process is as follows:

STAGE 1

We formulate the pgf for the number of reacted (related to variable $\underline{z}$) and unreacted (related to $\underline{z}_f$) groups for each monomer X in stage 1 in the zeroth generation:

$$_{(1)}F_{0X}(\underline{z}, \underline{z}_f) \tag{1-1}$$

and derive the pgf for unit X in the subsequent generations with (1,9):

$$_{(1)}F_X(\underline{z}, \underline{z}_f) = \sum_i \partial F_{0X}(\underline{z}, \underline{z}_f)/\partial z_i \Big/ [\sum_j \partial F_{0X}(\underline{z}, \underline{z}_f)/\partial z_j]_{\underline{z}=1,\ \underline{z}_f=\underline{1}} \ . \tag{1-2}$$

Next, the mass fraction generating function ${}_{(1)}W(z, \underline{z}_f)$ is derived with

$$ {}_{(1)}W(z, \underline{z}_f) = \sum_X {}_{(1)}m_X \; {}_{(1)}W_X(z, \underline{z}_f) \qquad (1\text{-}3) $$

where each component of the vector $\underline{z}$ is replaced by the scalar z since we are not explicitly interested in the distribution according to the type of unit. The mass fraction of component X is ${}_{(1)}m_X$ and the mass fraction generating function for this component is defined by

$$ {}_{(1)}W_X(z, \underline{z}_f) = z^{M_X} \; {}_{(1)}F_{0X}({}_{(1)}\underline{u}, \underline{z}_f) \qquad (1\text{-}4) $$

in which the component ${}_{(1)}u_Y$ of ${}_{(1)}\underline{u}$ is given by the implicit relationship

$$ {}_{(1)}u_Y = z^{M_Y} \; {}_{(1)}F_Y({}_{(1)}\underline{u}, \underline{z}_f) \quad . \qquad (1\text{-}5) $$

Here, M_X and M_Y are the molecular masses of units X and Y, respectively, and the cascade substitution vector ${}_{(1)}\underline{u}$ has the components ${}_{(1)}u_Y$ (the coefficients of z^I in ${}_{(1)}W_X \equiv \Sigma \, {}_{(1)}m_I \, z^I$ are the mass fractions of molecules having a molecular mass equal to I). Subsequently we want to convert ${}_{(1)}W(z, \underline{z}_f)$ into the number fraction generating function ${}_{(1)}N(z, \underline{z}_f)$, defined by

$$ {}_{(1)}N(z, \underline{z}_f) = \sum_X n_X \; {}_{(1)}N_X(z, \underline{z}_f) \qquad (1\text{-}6) $$

where n_X represents the number or mole fraction of component X and $N_X(z, \underline{z}_f)$ its number fraction generating function. This ${}_{(1)}N(z, \underline{z}_f)$ will be used to formulate the pgf for the next stage, in which the products of the first stage represent the building units. The transformation of W to N proceeds as follows:

$$ {}_{(1)}N(z, \underline{z}_f) = {}_{(1)}\bar{M}_n \int_0^z \frac{{}_{(1)}W(z', \underline{z}_f)}{z'} \, dz' \qquad (1\text{-}7) $$

where the number average molecular mass of the product of stage 1, ${}_{(1)}\bar{M}_n$, is given by

$$ {}_{(1)}\bar{M}_n = \frac{\sum\limits_X n_X M_X}{1 - \sum\limits_X n_X \; {}_{(1)}F_{0X}/2} \qquad (1\text{-}8) $$

with

$$ {}_{(1)}F_{0X} = \Big[\sum_y \partial F_{0X}(\underline{z}, \underline{z}_f)/\partial z_y\Big]_{\underline{z}=1, \; \underline{z}_f=\underline{1}} \quad . \qquad (1\text{-}9) $$

Next, we check whether the condition for gelation has not yet been reached, i.e. whether eq. (1.10) is still valid:

$$D = \det \left| \delta_X^{\,i} - F_X^{\,i} \right| < 0 \qquad (1\text{-}10)$$

with $\delta_X^{\,i} = 1$ for $i = X$ and zero otherwise and

$$F_X^{\,i} = [\partial F_X(\underline{z}, \underline{z}_f)/\partial z_i]_{\underline{z}=\underline{1},\ \underline{z}_f=\underline{1}} \qquad (1\text{-}11)$$

Finally, if we are below the gel point, we calculate the mass average molecular mass of the products of stage 1 with

$${}_{(1)}\bar{M}_w = [\sum_X m_X\ \partial\, {}_{(1)}W_X(z, \underline{z}_f)/\partial z]_{z=1,\ \underline{z}_f=\underline{1}} \qquad (1\text{-}12)$$

and the number average free functionality of type i, ${}_{(1)}\bar{\Phi}_{ni}$

$${}_{(1)}\bar{\Phi}_{ni} = [\partial\, {}_{(1)}N(z, \underline{z}_f)/\partial z_{fi}]_{z=1,\ \underline{z}_f=\underline{1}} \qquad (1\text{-}13)$$

STAGE 2

The products of stage 1 are subsequently mixed with newly added monomers 2 in stage 2. Together they are related to the components of the vectorial pgf in stage 2, ${}_{(2)}\underline{F}_0$. For the products of stage 1 the pgf reads

$${}_{(2)}F_{0P}(\underline{z}, \underline{z}_f) = {}_{(1)}N(\underline{1}, \underline{z}_f) \qquad (2\text{-}1)$$

where $\underline{z}$ and $\underline{z}_f$ are not the same vectors as in stage 1 because dummy variables for the new components are added to $\underline{z}$ and $\underline{z}_f$, whereas those for components which do not react in this stage are removed from $\underline{z}$.

Assume a reaction between the unreacted groups Y of products P with the newly added monomers 2. We then have to perform the following substitution in Eq. (2-1):

$$z_{fY} = (1 - {}_{(2)}\alpha_{YK})\ z_{fY} + {}_{(2)}\alpha_{YK}\ z_K \qquad (2\text{-}2)$$

where ${}_{(2)}\alpha_{YK}$ is the partial conversion of groups Y in stage 2 yielding bonds of type YK, and z_K is the variable for the newly added monomers 2 (with eq. (2-2) it is assumed that no substitution effects are present in the monomers with the Y groups; if these are present, a modified cascade substitution is used). Next, we derive the other components of ${}_{(2)}\underline{F}_0$ and all components of ${}_{(2)}\underline{F}$ in the same way as has been done for stage 1. Subsequently, the mass fraction generating function ${}_{(2)}W(z, \underline{z}_f)$ is derived as for stage 1 but with

$$W_P(z, \underline{z}_f) = {}_{(1)}W(z, \underline{z}_f) \qquad (2\text{-}3)$$

$$u_P(z, \underline{z}_f) = \sum_K \frac{\partial\, {}_{(1)}N[z, \underline{z}_f(\underline{u})]}{\partial z_K} \Bigg/ \left[\sum_K \frac{\partial\, {}_{(1)}N[z, \underline{z}_f]}{\partial z_K} \right]_{z=1,\ \underline{z}_f=\underline{1}} \qquad (2\text{-}4)$$

with

$$z_{fY}(u_K) = (1 - {}_{(2)}\alpha_{YK})\ z_{fY} + {}_{(2)}\alpha_{YK}\ u_K \qquad (2\text{-}5)$$

where the summations over K take into account the various types of monomers 2 that react with unreacted groups of product P. Again, the Galton-Watson approximation has been used in formulating eq. (2-4). The number fraction generating function ${}_{(2)}N(z, \underline{z}_f)$ is derived in the same way as for stage 1. Again it can be checked whether or not the condition for gelation has been reached in stage 2. Subsequently the number and mass average molecular masses and the number average free functionalities can be calculated in a similar way as for stage 1, though of course all formulae become more complex.

STAGE ℓ

The products of stage ℓ-1 are mixed with newly added monomers ℓ. The vectiorial pgf's ${}_{(\ell)}\underline{F}_0(\underline{z}, \underline{z}_f)$ and ${}_{(\ell)}\underline{F}(\underline{z}, \underline{z}_f)$ are derived in a similar way as for stage 2. The condition for gelation is checked with Eq. (1-12). If D > 0, gelation occurs and the extinction probabilities are calculated by solving the set of coupled nonlinear equations:

$$ {}_{(\ell)}v_X = {}_{(\ell)}F_X({}_{(\ell)}\underline{v}) \tag{ℓ-1} $$

The sol fraction is calculated with

$$ {}_{(\ell)}w_s = \sum_X {}_{(\ell)}m_X \; {}_{(\ell)}F_{0X}(\underline{z}={}_{(\ell)}\underline{v}, \; \underline{z}_f=\underline{1}) \tag{ℓ-2} $$

The concentration of elastically active network chains depends on its definition in the particular system, but this quantity can be derived from the following pgf:

$$ {}_{(\ell)}T_X(z) = {}_{(\ell)}F_{0X}(\underline{z} = {}_{(\ell)}\underline{v} + (\underline{1} - {}_{(\ell)}\underline{v})z, \; \underline{z}_f = \underline{1}) \tag{ℓ-3} $$

which contains the probabilities for the number of bonds having infinite continuation (i.e. ties) issuing from an X-unit in the zeroth generation. Other quantities of interest can also be derived in a routine way, see e.g. ref. (1).

DISCUSSION

The key transformations and operations in this scheme are the following: the unreacted functionalities in the generating functions are labelled and kept track of. They are transformed in the next reaction stage by making the substitution $z_f = (1 - \alpha)\, z_f + \alpha\, z$. In addition, the mass fraction generating function W(z) is converted into the number fraction generating function N(z) by integration of W(z)/z. N(z) and W(z) are used in the following stage to formulate the new pgf's. Later it will be shown that in a number of cases this conversion is possible by solving the integration analytically (11).

The procedure suggested here can also be used if in one or several steps a kinetic treatment is required. If the kinetic theory is applied, use can be made of the simplification mentioned before (8), which implies cutting the connections between reactive groups in such monomers that the reactivity of the groups becomes independent. Subsequently, the structures are generated from the resulting fragments. Finally, the broken connections are reformed in a random way.

ACKNOWLEDGEMENTS

The authors are grateful to Dr. R. van der Linde for indicating the general problem and for the many stimulating discussions.

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Accepted February 10, 1987 C