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Notes

Statistical Analysis of Free-Radical Copolymerization/Cross-Linking Reactions Using Probability Generating Functions: Reaction Directionality and General Termination

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The free-radical copolymerization/cross-linking reaction of a monomer containing one polymerizable double bond with small amounts of a cross-linking agent containing two double bonds may be used to produce polymeric networks for a variety of applications. Many authors[1-10] have found that the statistical approach for modeling polymerization reactions is useful for describing structural development during the course of this network-forming reaction. Several statistical computational schemes are based on the same underlying model which incorporates the assumptions of ideal random cross-linking, including conversion-independent kinetics, termination by chain transfer or disproportionation, equal reactivity, and no cyclization. Recently, the statistical approach has been extended to account for nonidealities in the reaction. Statistical analyses have been reported which include conversion-dependent kinetics[10] and approximate treatments of cyclization.[6,9]

Most statistical analyses reported in the literature have neglected the importance of the directionality of the free-radical mechanism, treating the two directions along the polymer chain as statistically equivalent. Actually the free-radical polymerization reaction begins with initiation and ends with termination, and the two directions may be unequivalent if, for example, termination occurs by combination rather than disproportionation. Recently, Dotson et al.[10] and Williams and Vallo[8] have treated termination by combination using the Macosko–Miller recursive technique[1,2] and a fragment approach, respectively. These authors considered the free-radical copolymerization of a bifunctional monomer with a multifunctional cross-linking agent ($A_2 + A_f$). Burchard and collaborators[11-13] considered the importance of reaction directionality for free-radical network formation occurring by virtue of multifunctional chain-transfer agents. Finally, Galina[14] included the free-radical reaction directionality and termination by combination in a statistical description of linear copolymerizations.

In this note, free-radical reaction directionality and termination by multiple mechanisms are included in a statistical description of the copolymerization/cross-linking reaction using the probability generating function approach. The analysis shown here provides an alternative derivation of relationships derived previously using the Macosko–Miller recursive technique[10] and the statistical fragment approach.[8] The probability generating function approach, based on the mathematical framework of the theory of branching or cascade processes,[15-17] allows expressions for structural averages to be obtained very efficiently and systematically once the link probability generating functions have been formulated. When termination by combination is included in the analysis, one statistically distinct type of zeroth-generation monomer unit and two types of first-generation units can be identified for each comonomer; therefore, the dimensionalities of the corresponding generating functions are different. The analysis shown here illustrates the versatility of the theory of branching or cascade processes for describing free-radical polymerization reactions.

Copolymerization/Cross-Linking Reactions with General Termination

The theory of branching or cascade processes has been the subject of several books.[15-17] A general feature of the mathematical framework is the use of probability or enumeration generating functions. The framework was first applied to polymerization reactions by Gordon,[5] who defined the link probability generating functions, which are summed over all possible reacted states of the monomer units under consideration. Gordon illustrated that the link probability generating functions could be used to construct other generating functions useful for calculating structural averages. After the appropriate generating functions were constructed, averages could be obtained by simple differential operations. Expressions for many polymerization structural averages have been formulated directly in terms of the link probability generating functions.[5,18,19] Excellent descriptions of the application of the theory of branching or cascade processes to polymer systems are given by Burchard[20] and Dusek.[21]

Link Probability Generating Functions. For the copolymerization/cross-linking reaction with general termination, the link probability generating function for the zeroth generation, $\mathbf{F}_0(\mathbf{s})$, is a two-component vector with a component corresponding to each chemical type of monomer unit.

$$\mathbf{F}_0(\mathbf{s}) = [F_{01}(\mathbf{s}), F_{02}(\mathbf{s})]^{\mathrm{T}} \tag{1}$$

Here, the subscript 1 refers to the monounsaturated monomer, while the subscript 2 refers to the diunsaturated cross-linking agent.

The component generating functions which make up $\mathbf{F}_0(\mathbf{s})$ are shown below:

$$F_{01}(\mathbf{s}) = 1 - a + a[1 - p + p((1-r)s_{b1} + rs_{b2})][(1-p)\{1 - k + k((1-r)s_{b1} + rs_{b2})\} + p((1-r)s_{c1} + rs_{c2})] \tag{2}$$

$$F_{02}(\mathbf{s}) = F_{01}^2 \tag{3}$$

Here, the subscript c corresponds to a bond issued to the next generation in the direction of propagation, while the subscript b corresponds to a bond issued in the opposite direction. As in a previous publication,[6] the symbol a

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represents the conversion of double bonds in the system, p is the probability that a growing radical will add at least one more monomer unit before terminating, and r is equal to the fraction of the double bonds belonging to untis of the cross-linking agent.

Since four statistically distinct types of bonds can be formed with the next generation, the dummy variable vector, **s**, has the following four components:

$$\mathbf{s} = [s_{b1}, s_{c1}, s_{b2}, s_{c2}] \tag{4}$$

Likewise, the link probability generating function for all generations other than the zeroth, **F**(**s**), is a four-component vector:

$$\mathbf{F}(\mathbf{s}) = [F_{b1}(\mathbf{s}), F_{c1}(\mathbf{s}), F_{b2}(\mathbf{s}), F_{c2}(\mathbf{s})]^T \tag{5}$$

The component generating functions which make up **F**(**s**) are as follows:

$$F_{b1}(\mathbf{s}) = 1 - p + p((1 - r)s_{b1} + rs_{b2}) \tag{6}$$

$$F_{c1}(\mathbf{s}) = (1 - p)\{1 - k + k((1 - r)s_{b1} + rs_{b2})\} + p((1 - r)s_{c1} + rs_{c2}) \tag{7}$$

$$F_{b2}(\mathbf{s}) = F_{b1}F_{01} \tag{8}$$

$$F_{c2}(\mathbf{s}) = F_{c1}F_{01} \tag{9}$$

Number-Average Molecular Weight. The number-average molecular weight of the reaction system, $\bar{M}_n$, may be calculated with the following equation:[18]

$$\bar{M}_n = \frac{2\mathbf{n}\cdot\mathbf{M}}{2 - \mathbf{F}'_0(1)\cdot\mathbf{n}} \tag{10}$$

Here, **n** and **M** are the mole fraction vector and the molecular weight vector, respectively.

$$\mathbf{n} = [n_1, n_2]^T \tag{11}$$

$$\mathbf{M} = [M_1, M_2]^T \tag{12}$$

Here, the derivative of the zeroth-generation link probability generating function, **F**′(1), is a vector with the following two components:

$$F'_{01}(1) = \left(\frac{\partial F_{01}(\mathbf{s})}{\partial s_{b1}} + \frac{\partial F_{01}(\mathbf{s})}{\partial s_{c1}} + \frac{\partial F_{01}(\mathbf{s})}{\partial s_{b2}} + \frac{\partial F_{01}(\mathbf{s})}{\partial s_{c2}}\right)_{\mathbf{s}=1} \tag{13}$$

$$F'_{02}(1) = \left(\frac{\partial F_{02}(\mathbf{s})}{\partial s_{b1}} + \frac{\partial F_{02}(\mathbf{s})}{\partial s_{c1}} + \frac{\partial F_{02}(\mathbf{s})}{\partial s_{b2}} + \frac{\partial F_{02}(\mathbf{s})}{\partial s_{c2}}\right)_{\mathbf{s}=1} \tag{14}$$

Substitution of eqs 2 and 3 into eq 10 yields the following equation for $\bar{M}_n$:

$$\bar{M}_n = \frac{2n_1M_1 + 2n_2M_2}{2 - (n_1 + 2n_2)[2ap + ak(1 - p)]} \tag{15}$$

When $k = 0$, eq 15 reduces to the previously reported[6] solution for termination by disproportionation and/or chain transfer.

Weight-Average Molecular Weight. The equation for the reaction system weight-average molecular weight in terms of the link probability generating functions is as follows:[18]

$$\bar{M}_w = \mathbf{M}^T(\Delta + (\Delta - \Gamma)^{-1}\Gamma_0)\mathbf{m} \tag{16}$$

Here, Γ_0 and Γ_1 are the transposed Jacobian matrices[22] of $\mathbf{F}_0(\mathbf{s})$ and $\mathbf{F}_1(\mathbf{s})$, evaluated with $\mathbf{s} = 1$. Also, Δ is a four by four unitary matrix, and **m** is the weight fraction vector.

Equation 16 was originally derived[5] for the case in which the matrices Δ, Γ_0, and Γ have the same dimensionality. For a typical copolymerization reaction, these matrices have two rows and two columns. For the free-radical copolymerization/cross-linking reaction with general termination, however, these matrices have different dimensionalities due to the directionality of the free-radical reaction. Therefore, eq 16 must be modified to the following equation.

$$\bar{M}_w = \mathbf{M}^T(\Delta_2 + \Lambda(\Delta_4 - \Gamma)^{-1}\Gamma_0)\mathbf{m} \tag{17}$$

Here, Δ_2 is the two by two unitary matrix, while Δ_4 is the four by four unitary matrix. The transposed Jacobian of $\mathbf{F}_0(\mathbf{s})$, Γ_0, is an four by two matrix, while Γ is a four by four matrix. Λ is the following two by four matrix:

$$\Lambda = \begin{bmatrix} 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 \end{bmatrix} \tag{18}$$

Substitution of eq 2–9 into eq 17 yields the following equation for $\bar{M}_w$:

$$\bar{M}_w = \{m_1[M_1(1 - p + a(2p + k)(1 - 2r)) + M_2ar(2p + k)] + m_2[2M_1a(2p + k)(1 - r) + M_2(1 - p + ar(2p + k))]\}/\{1 - p - (2ap + ak)r\} \tag{19}$$

This equation is equivalent to eq 22 of ref 8, which was derived by using the fragment method. Again, eq 19 has the correct limit when $k = 0$.

Critical Conversion for Gelation. Since the weight-average molecular weight diverges at the gel point, an expression for the gel point conversion is readily obtained from eq 17. At the gel point, the denominator in eq 17 is equal to zero:

$$|\Delta_4 - \Gamma| = 0 \tag{20}$$

Combination of eqs 6–9 with eq 20 yields the following expression for the gel point conversion:

$$a_c = \frac{1 - p}{2pr + kr} \tag{21}$$

Again, eq 21 agrees with results obtained with the statistical fragment approach.[8]

Extinction Probability. The extinction probability is the probability that a bond has no paths to the infinite network. The extinction probability is useful for calculating some postgel statistical averages and is the smallest positive root of the following equation:[18]

$$\mathbf{v} = \mathbf{F}(\mathbf{v}) \tag{22}$$

Here, **v** is the extinction probability vector, and **F**(**v**) is the probability generating function vector for all generations higher than the zeroth evaluated with $\mathbf{s} = \mathbf{v}$. Equation 22 provides a set of four coupled algebraic equations which may be solved for the four components of the extinction probability vector.

Sol Weight Fractions. The sol weight fraction, w_s, may be calculated with the following equation:[18]

$$w_s = m_1F_{01}(\mathbf{v}) + m_2F_{02}(\mathbf{v}) \tag{23}$$

Here, each bond between monomer units is weighted by the probability that it does not have any paths to the network.

Substitution of the zeroth-generation generating functions into eq 23 yields the following expression for the sol weight fraction:

$$w_s = m_1\{1 - a + a[1 - p + p((1 - r)v_{b1} + rv_{b2})][(1 - p)\{1 - k + k((1 - r)v_{b1} + rv_{b2})\} + p((1 - r)v_{c1} + rv_{c2})]\} + m_2\{1 - a + a[1 - p + p((1 - r)v_{b1} + rv_{b2})][(1 - p)\{1 - k + k((1 - r)v_{b1} + rv_{b2})\} + p((1 - r)v_{c1} + rv_{c2})]\}^2 \quad (24)$$

Elastically Active Network Chains (EANC). An elastically active network chain connects two effective cross-links (an effective cross-link issues at least three bonds which eventually lead to the gel). The number of EANC may be calculated by constructing the probability generating function for bonds leading to the gel[21], $\mathbf{T}(\mathbf{s})$. This generating function is related to the link probability generating function by the following equation:

$$\mathbf{T}(\mathbf{s}) = \mathbf{F}_0(\mathbf{v}+(1-\mathbf{v})\mathbf{s}) = [T_1(\mathbf{s}), T_2(\mathbf{s})] \quad (25)$$

Here, each bond in the link probability generating functions is weighted by the probability that the bond eventually leads to the gel.

The number of EANC can be calculated with the following equation:[6]

$$N_e = {}^1/_2[T'_2(1) - T'_2(0) - T''_2(0)] \quad (26)$$

Expressions for the derivatives of $T_s(\mathbf{s})$ will be given later.

Molecular Weight between Cross-Links. The molecular weight between cross-links, $\bar{M}_c$, may be defined as the average molecular weight between effective cross-links or, equivalently, the average weight of an elastically active network chain. This network structural average may be calculated by using the generating function $\mathbf{T}(\mathbf{s})$ defined previously.[19]

$$\bar{M}_c = \frac{\bar{M}[{}^1/_2 n_1 T''_1(0) + n_2(T'_2(1) - T'_2(0) - {}^1/_2 T''_2(0))]}{N_e} \quad (27)$$

Here

$$\bar{M} = \frac{n_1 M_1 + n_2 M_2}{n_1 + n_2} \quad (28)$$

The derivatives of $\mathbf{T}(\mathbf{s})$ are useful for calculating network structural averages such as the number of elastically active network chains and the molecular weight between cross-links. Combining eqs 2, 3, and 25 and differentiating yield the following results for these derivatives:

$$T'_1(0) = a[1 - p + p((1 - r)v_{b1} + rv_{b2})]\{p[(1 - r)(1 - v_{c1}) + r(1 - v_{c2})] + k(1 - p)[(1 - r)(1 - v_{b1}) + r(1 - v_{b2})]\} + ap[(1 - r)(1 - v_{b1}) + r(1 - v_{b2})][(1 - p)\{1 - k + k[(1 - r)v_{b1} + rv_{b2}]\} + p\{(1 - r)v_{c1} + rv_{c2}\}] \quad (29)$$

$$T'_1(1) = ap[(1 - r)(2 - v_{b1} - v_{c1}) + r(2 - v_{b2} - v_{c2})] + ak(1 - p)[(1 - r)(1 - v_{b1}) + r(1 - v_{b2})] \quad (30)$$

$$T''_1(0) = 2a[p(1 - r)(1 - v_{b1}) + r(1 - v_{b2})]\{p[(1 - r)(1 - v_{c1}) + r(1 - v_{c2})] + k(1 - p)[(1 - r)(1 - v_{b1}) + r(1 - v_{b2})]\} \quad (31)$$

$$T'_2(0) = 2T_1(0)T'_1(0) \quad (32)$$

$$T'_2(1) = 2T'_1(1) \quad (33)$$

$$T''_2(0) = 2[T'_1(0)]^2 + 2T_1(0)T''_1(0) \quad (34)$$

Here, $T_1(0) = F_{01}(\mathbf{v})$.

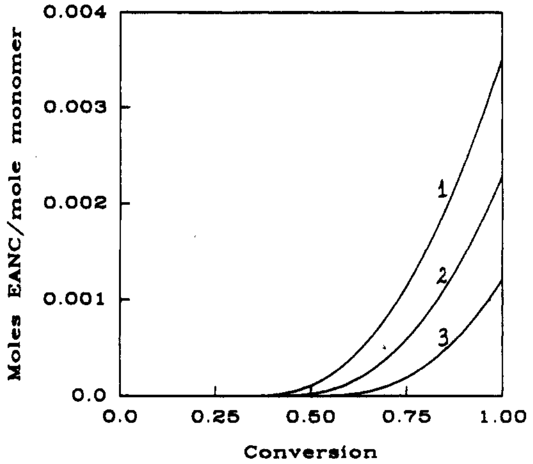

Figure 1. Simulation results for the number of elastically active network chains as a function of conversion with $p = 0.99$, $r = 0.01$, $M_1 = 130$ g/mol, and $M_2 = 198$ g/mol. Curve 1, $k = 1.0$; curve 2, $k = 0.5$; curve 3, $k = 0$.

Results and Discussion

The above analysis illustrates the efficiency with which expressions for a variety of structural averages can be derived once the link probability generating functions have been formulated. The expressions for the number- and weight-average molecular weights, the critical conversion for gelation, and the sol weight fraction are equivalent to those derived by Williams and Vallo[8] and will be discussed only briefly. Equations 15, 19, and 21 illustrate that the number- and weight-average molecular weights increase monotonically as the probability of combination increases, while the critical conversion for gelation decreases monotonically. These trends may be explained by the effect of combination of the length of the primary polymer chains (the linear chains that would remain if all cross-links were cut). If termination occurs entirely by combination rather than disproportionation and/or chain transfer, the number- and weight-average primary chain lengths increase by factors of 2 and approximately 1.5, respectively. This increase in the primary chain length results in an increase in the molecular weight of the cross-linked polymer molecules but also increases the probability of forming a polymer network at a lower conversion. Hence the ratio of the conversion for gelation for termination solely by combination to that for disproportionation and/or chain transfer is $2p/(2p + 1)$, or approximately two-thirds.[8]

Simulation results for the number of elastically active network chains and the molecular weight between cross-links are shown in Figures 1 and 2, respectively. These profiles were obtained by using the following values for the reaction parameters: $p = 0.99$, $r = 0.01$, $M_1 = 130$ g/mol, and $M_2 = 198$ g/mol. This value for the parameter r corresponds to a reaction system containing 0.5025 mol % cross-linking agent. Figures 1 and 2 illustrate the effect of termination by combination on the internal network structure. Figure 1 illustrates that an increase in the probability of combination results in an increase in the number of elastically active network chains at a given conversion. Polymer strands which would exist as dangling chain ends if termination occurred by disproportionation and/or chain transfer are elastically active when combination occurs. Figure 2 illustrates that termination by combination results in a more tightly cross-linked network since the molecular weight between cross-links at a given conversion decreases as the fraction of combination increases.

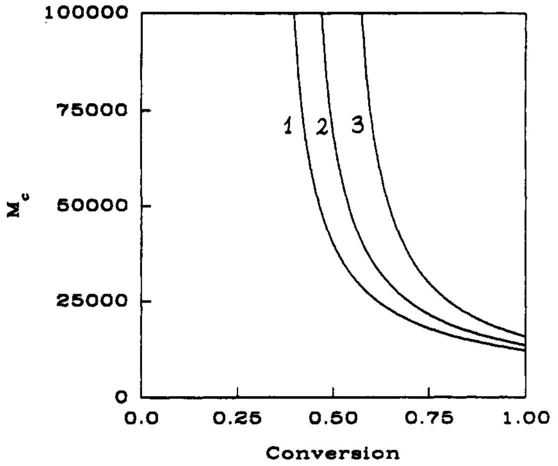

Figure 2. Simulation results for the molecular weight between cross-links as a function of conversion with $p = 0.99$, $r = 0.01$, $M_1 = 130$ g/mol, and $M_2 = 198$ g/mol. Curve 1, $k = 1.0$; curve 2, $k = 0.5$; curve 3, $k = 0$.

Conclusions

Reaction directionality and termination by multiple mechanisms were included in a statistical description of free-radical copolymerization/cross-linking reactions using the probability generating function approach. The use of probability generating functions allowed expressions for structural averages to be obtained efficiently and coveniently using a general mathematical framework. When termination occurs by combination, the numbers of statistically distinct types of monomers units in the zeroth and first topological generations differ, and the dimensionalities of the corresponding link probability generating functions are therefore different. Expressions for a variety of structural averages were obtained. The analysis shown here illustrates the versatility of the theory of cascade or branching processes for the description polymerization reactions and is equivalent to previously reported analyses based upon the Macosko–Miller recursive method[10] and the statistical fragment approach.[8]

Simulation results indicate that termination by combination can have a dramatic effect on structural averages. As the probability of combination increases, the pregel weight-average molecular weight at a given conversion increases and the conversion required for the formation of a network decreases. In the postgel region, the fraction of monomer units incorporated into the network at a given conversion increases as the probability of combination increases. Termination by combination also influences the internal network structure. Combination allows polymer strands that would exist as dangling chain ends if termination occurred by disproportionation and/or chain transfer to be elastically active. Therefore, as the probability of termination increases, the number of elastically active network chains increases, and the molecular weight between cross-links decreases.

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References and Notes

(1) Macosko, C. W.; Miller, D. R. *Macromolecules* **1976**, *9*, 199.
(2) Miller, D. R.; Macosko, C. W. *Macromolecules* **1976**, *9*, 206.
(3) Durand, D.; Bruneau, C. M. *Eur. Polym. J.* **1985**, *21*, 527.
(4) Durand, D.; Bruneau, C. M. *Eur. Polym. J.* **1985**, *21*, 611.
(5) Gordon, M. *Proc. R. Soc. London* **1962**, *A268*, 240.
(6) Scranton, A. B.; Peppas, N. A. *J. Polym. Sci., Polym. Chem. Ed.* **1990**, *28*, 39.
(7) Williams, R. J. J. *Macromolecules* **1988**, *21*, 2568.
(8) Williams, R. J. J.; Vallo, C. I. *Macromolecules* **1988**, *21*, 2571.
(9) Landin, D. T.; Macosko, C. W. In *Characterization of Highly Crosslinked Polymers*; Labana, S. S., Ed.; ACS Symposium Series 243; American Chemical Society: Washington, DC, 1984; p 33.
(10) Dotson, N. A.; Galvan, R.; Macosko, C. W. *Macromolecules* **1988**, *21*, 2560.
(11) Burchard, W.; Ullisch, B.; Wolf, C. *Faraday Discuss. Chem. Soc.* **1973**, *57*, 56.
(12) Ullisch, B.; Burchard, W. *Makromol. Chem.* **1977**, *178*, 1403.
(13) Wolf, C.; Burchard, W. *Makromol. Chem.* **1976**, *177*, 2519.
(14) Galina, H. *Eur. Polym. J.* **1986**, *22*, 665.
(15) Harris, T. E. *The Theory of Branching Processes*; Prentice-Hall: Englewood Cliffs, NJ, 1963.
(16) Mode, C. J. *Multitype Branching Processes*; Elsevier: New York, 1971.
(17) Athreya, K. B.; Ney, P. E. *Branching Processes*; Springer-Verlag: New York, 1972.
(18) Gordon, M.; Malcolm, G. N. *Proc. R. Soc. London* **1966**, *A295*, 29.
(19) Dobson, G. R.; Gordon, M. *J. Chem. Phys.* **1965**, *43*, 705.
(20) Burchard, W. *Adv. Polym. Sci.* **1983**, *48*, 1.
(21) Dusek, K. *Adv. Polym. Sci.* **1986**, *78*, 1.
(22) Tsou, A.; Peppas, N. A. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 2043.