sota Graduate School, and the industrial supporters of the University of Minnesota Polymerization and Polymer Process Engineering Center. The authors wish to acknowledge seeing the related article of R. J. J. Williams and C. I. Vallo[27] of the Institute of Materials Science and Technology (INTEMA), University of Mar del Plata and National Research Council (CONICET), Mar del Plata, Argentina, which alerted us to some errors in our work.

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(30) In our terminology, primary *chains* are obtained by ignoring all cross-links and couplings, but primary *molecules* are obtained by ignoring only cross-links. Primary *chains* are thus not affected by the termination mechanism and hence will have a geometric distribution. Primary *molecules*, however, are affected by the termination mechanism and will only have a geometric distribution if there is no combination. If combination is dominant, the primary molecules will have a self-convoluted geometric distribution (or a negative binomial distribution with $r = 2$; see: Feller, W. *An Introduction to Probability Theory and Its Applications*, 3rd ed.; Wiley: New York, 1968; Vol. 1).
(31) The original derivation[7] did not distinguish between the different cross-linker species and then said that $E(W_{\mathrm{A}f}{}^*) = M_{\mathrm{A}f} + (1 + ((f - 2)/2)p)2E(W_{\mathrm{A}}{}^{*\mathrm{out}})$. This is incorrect because it grabs cross-linker molecules not at random but by reacted bonds, and thus preferentially grabs more highly reacted cross-linkers. The authors acknowledge W. Merrill of the University of Minnesota for help in correcting this error.
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Statistics of Free-Radical Polymerizations Revisited Using a Fragment Approach. 1. Bifunctional Monomers

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ABSTRACT: A fragment approach is used to obtain statistical parameters for free-radical polymerizations of bifunctional monomers, allowing every possibility for chain termination, i.e., combination, disproportionation, and/or chain transfer. The method is based on (i) fragmentation of the system into all distinguishable units, comprising monomers and polymer fragments; (ii) determination of the concentration of every species and fragment in terms of kinetic parameters; and (iii) generation of average statistical parameters by joining the different fragments using a recursive algorithm. Number- and weight-average molecular weights result in a very simple way.

Introduction

Average statistical parameters of polymers produced by free-radical mechanisms, i.e., chainwise polymerizations, have been reported and discussed both for systems starting from bi- and polyfunctional monomers. In the former case, the resulting number- and weight-average degrees of polymerization of the polymer fraction, $\bar{x}_{\mathrm{n}}$ and $\bar{x}_{\mathrm{w}}$, can be derived from the molecular weight distribution obtained by assuming a random polymerization. For the case of termination by transfer and/or disproportionation, the following expressions are obtained (the derivation is reported in many standard polymer textbooks):

$$\bar{x}_{\mathrm{n}} = 1/(1 - q) \qquad (1)$$

$$\bar{x}_{\mathrm{w}} = (1 + q)/(1 - q) \qquad (2)$$

where

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$$q = r_p/(r_p + r_t + r_d) \tag{3}$$

(r_p, r_t, and r_d are rates of propagation, termination by chain transfer, and termination by disproportionation, respectively). For the case where chains terminate exclusively by combination, the corresponding equations are

$$\bar{x}_n = 2/(1 - q) \tag{4}$$

$$\bar{x}_w = (2 + q)/(1 - q) \tag{5}$$

where

$$q = r_p/(r_p + r_c) \tag{6}$$

(r_c is the rate of termination by combination).

The problem where all termination mechanisms take place simultaneously (as would happen, for example, when a chain-transfer agent is added to a system showing termination by combination) has also been solved,[1] using the distributions arising for $q = 1$. For this case, the polydispersity index is given by

$$\bar{x}_w/\bar{x}_n = (2 + \xi)(2 - \xi)/2 \tag{7}$$

where

$$\xi = r_c/(r_t + r_d + r_c) \tag{8}$$

On the other hand, reported average statistical parameters of networks arising from the free-radical polymerization of polyfunctional monomers were obtained by using the theory of stochastic branching processes in different, though equivalent, versions.[2-7] Derivations retain the classical simplifying assumptions: (i) all double bonds are equally reactive, (ii) there are no substitution effects, and (iii) no intramolecular reactions occur in finite species. The statistical description of these networks has been accomplished for the case where termination occurs by disproportionation and/or chain transfer.[3,4,6,7] However, when termination by combination is also present, no valid analysis has been reported (the approximation used in ref 3 and 4 is not correct, as may be easily shown by reducing the resulting equations for the case of a bifunctional monomer where chains are exclusively terminated by combination).

The aim of this part of the series is to show the simplicity with which a fragment approach may be used to derive average statistical parameters for free-radical polymerizations of bifunctional monomers. This constitutes an alternative derivation to the body of kinetic work done on the same subject and yielding similar results. Moreover, kinetic methods leads to molecular weight distributions while the present approach enables one to obtain just average values. However, the simplicity with which the fragment approach operates in simple systems will be used with advantage to analyze network-forming systems with several termination mechanisms (part 2 of the series).

The method is based on (i) fragmentation of the system into all distinguishable units comprising monomers and polymer fragments; (ii) determination of the concentration of every species and fragment along the polymerization using kinetic parameters (the fact that the parameter q is constant during the lifetime of chains is retained; this leads to the same instantaneous distributions derived from the quasi-steady-state assumption), and (iii) generation of average statistical parameters by joining the different fragments using a recursive algorithm. We have already used this method to analyze the formation of networks in several nonideal polymerizations, such as the production of phenolics,[8,9] the buildup of epoxy amine networks with simultaneous polyetherification,[10] the buildup of polymer networks by initiated polyreactions,[11] and the formation of polyurethane networks taking into account intramolecular reactions.[12]

Table I
Species and Fragments Identified When Termination Takes Place by Chain Transfer and/or Disproportionation

fragment	moles	mass	polymer mass fract.
unreacted monomer, ○	$A_2(1 - p)$	M	
chain propagator, ${}^{-}$–●–${}^{+}$	A_2pq	M	q
terminal unit, ${}^{-}$–●–|	$A_2p(1 - q)$	M	$1 - q$
initiator, □–${}^{+}$	$A_2p(1 - q)$	0	

The aim of the second part is to analyze the formation of networks by free-radical polymerizations, with the aid of the fragment approach, taking into account every possibility for chain termination, i.e., making use of the parameter ξ defined by eq 8.

For the sake of clarity, the present analysis will be performed beginning with particular cases and then deriving the general expressions.

Termination by Chain Transfer and/or Disproportionation

Table I shows the different species and fragments that must be identified in this case. At any conversion p, the number of moles of unreacted monomer is $A_2(1 - p)$, where A_2 is the initial number of moles. The probability that a reacted monomer becomes a chain propagator is A_2pq, where q is defined by eq 3. A reacted monomer becomes a terminal unit with a probability of $A_2p(1 - q)$. In this notation, linkages (+) are joined to linkages (−). Thus, the number of moles of initiators must be equal to the corresponding number of terminal units. As usual, it is assumed that the mass of the initiator does not contribute to the polymer mass; i.e., it is regarded as a fragment devoid of mass.

Once the concentration of every species and fragment has been stated, statistical parameters of the polymer chains may be obtained by using a recursive approach. Let us call $Y(+)$ and $Y(-)$ the average weights that are attached to linkages (+) and (−), respectively. These average weights are determined as $Y(+) = \sum_{\text{fragments}}$(probability of joining a particular fragment having one or more (−) linkages)(average weight contributed by the particular fragment) and $Y(-) = \sum_{\text{fragments}}$(probability of joining a particular fragment having one or more (+) linkages)(average weight contributed by the particular fragment). For example, the probability of joining a chain propagator with a (+) linkage is equal to the fraction of all (−) linkages of the system that belong to chain propagators; i.e., $(A_2pq)/[A_2pq + A_2p(1 - q)] = q$. The average weight contributed by the chain propagator when joined by its (−) linkage is $M + Y(+)$, i.e., the unknown $Y(+)$ reappears and gives place to the recursive nature of the calculation. Then,

$$Y(+) = q[M + Y(+)] + (1 - q)M \tag{9}$$

$$Y(+) = M/(1 - q) \tag{10}$$

$$Y(-) = q[M + Y(-)] + (1 - q)(0) \tag{11}$$

$$Y(-) = qM/(1 - q) \tag{12}$$

The weight-average molecular weight of the polymer fraction, $\bar{M}_w$, is defined as $\bar{M}_w = \sum_{\text{fragments}}$(mass fraction of a particular fragment belonging to the polymer)(average weight contributed by the particular fragment). Then,

$$\bar{M}_w = q[M + Y(+) + Y(-)] + (1 - q)[M + Y(-)] = M + qY(+) + Y(-) \tag{13}$$

By substituting eq 10 and 12 in 13, we get

$$\bar{x}_w = \bar{M}_w/M = (1 + q)/(1 - q) \tag{14}$$

Table II
Species and Fragments Identified When Termination Takes Place by Combination

fragment	moles	mass	polymer mass fract.
unreacted monomer, ○	$A_2(1-p)$	M	
chain propagator, $^{-}{-}\bullet{-}^{+}$	A_2pq	M	q
unit terminated by combination, $^{-}{-}\bullet{\rightarrow}$	$A_2p(1-q)$	M	$1-q$
initiator, $\square{-}^{+}$	$A_2p(1-q)$	0	

in agreement with the expected result (eq 2).

On the other hand, the number average molecular weight of the polymer fraction, $\bar{M}_n$, is defined as $\bar{M}_n$ = (total mass of fragments belonging to the polymer)/[(1/2) times the number of moles of chain ends (initiators + terminal units)]. Then,

$$\bar{M}_n = [A_2pqM + A_2p(1-q)M]/\{(1/2)[A_2p(1-q) + A_2p(1-q)]\} \quad (15)$$

$$\bar{M}_n = M/(1-q) \quad (16)$$

or

$$\bar{x}_n = \bar{M}_n/M = 1/(1-q) \quad (17)$$

as expected (eq 1).

Termination by Combination

Table II shows the species and fragments that must be identified in this particular case. Now, q is defined by eq 6. The fragment that has entered into a recombination step is identified with an arrow. In order to regenerate the structure, arrows must be joined among themselves, Z being the average weight attached to each arrow. As the number of (+) linkages must be always equal to the number of (−) linkages, the number of moles of initiators is $A_2p(1-q)$.

In this case, the average weights $Y(+)$, $Y(-)$, and Z are given by

$$Y(+) = q[M + Y(+)] + (1-q)[M + Z] = Z + M/(1-q) \quad (18)$$

$$Y(-) = q[M + Y(-)] + (1-q)(0) = qM/(1-q) \quad (19)$$

$$Z = M + Y(-) \quad (20)$$

By substituting eq 19 in 20 and the result in eq 18, we get

$$Z = M/(1-q) \quad (21)$$

$$Y(+) = 2M/(1-q) \quad (22)$$

The weight-average molecular weight of the polymer is given by

$$\bar{M}_w = q[M + Y(+) + Y(-)] + (1-q)[M + Y(-) + Z] \quad (23)$$

By replacing eq 19, 21, and 22, we get

$$\bar{x}_w = \bar{M}_w/M = (2+q)/(1-q) \quad (24)$$

which agrees with eq 5.

The number-average molecular weight of the polymer is calculated as

$$\bar{M}_n = [A_2pqM + A_2p(1-q)M]/[(1/2)A_2p(1-q)] = 2M/(1-q) \quad (25)$$

or

$$\bar{x}_n = \bar{M}_n/M = 2/(1-q) \quad (26)$$

as expected (eq 4).

Table III
Species and Fragments Identified in the General Case

fragment	moles	mass	polymer mass fract.
unreacted monomer, ○	$A_2(1-p)$	M	
chain propagator, $^{-}{-}\bullet{-}^{+}$	A_2pq	M	q
unit terminated by combination, $^{-}{-}\bullet{\rightarrow}$	$A_2p(1-q)\xi$	M	$(1-q)\xi$
unit terminated by transfer or disprop., $^{-}{-}\bullet{-}|$	$A_2p(1-q)(1-\xi)$	M	$(1-q)(1-\xi)$
initiator, $\square{-}^{+}$	$A_2p(1-q)$	0	

General Case

Table III shows the species and fragments that must be identified in the general case. Now, q is defined as

$$q = r_p/(r_p + r_t + r_d + r_c) \quad (27)$$

while ξ is given by eq 8 ($\xi = 0$ identifies termination by chain transfer and/or disproportionation, whereas $\xi = 1$ represents the case of termination by combination). The number of moles of initiator is always calculated by stating that the number of (+) linkages must equal the number of (−) linkages.

The average weights $Y(+)$, $Y(-)$, and Z are calculated as

$$Y(+) = q[M + Y(+)] + (1-q)\xi[M + Z] + (1-q)(1-\xi)M \quad (28)$$

$$Y(+) = \xi Z + M/(1-q) \quad (29)$$

$$Y(-) = q[M + Y(-)] + (1-q)(0) = qM/(1-q) \quad (30)$$

$$Z = M + Y(-) = M/(1-q) \quad (31)$$

From eq 29 and 31, we get

$$Y(+) = M(1+\xi)/(1-q) \quad (32)$$

The weight-average molecular weight is given by

$$\bar{M}_w = q[M + Y(+) + Y(-)] + (1-q)\xi[M + Y(-) + Z] + (1-q)(1-\xi)[M + Y(-)] \quad (33)$$

By substituting eq 30–32 in 33, we get

$$\bar{x}_w = \bar{M}_w/M = (1+q+\xi)/(1-q) \quad (34)$$

For $\xi = 0$ and 1, eq 14 and 24 are correctly obtained.

The number-average molecular weight is calculated as

$$\bar{M}_n = [A_2pqM + A_2p(1-q)\xi M + A_2p(1-q)(1-\xi)M]/\{(1/2)[A_2p(1-q)(1-\xi) + A_2p(1-q)]\} = 2M/[(1-q)(2-\xi)] \quad (35)$$

Then,

$$\bar{x}_n = \bar{M}_n/M = 2/[(1-q)(2-\xi)] \quad (36)$$

For $\xi = 0$ and 1, eq 17 and 26 are correctly predicted.

The polydispersity is defined as

$$\bar{x}_w/\bar{x}_n = (1+q+\xi)(2-\xi)/2 \quad (37)$$

which gives eq 7 for $q = 1$.

Conclusions

The fragment approach constitutes an extremely simple method to obtain statistical parameters of free-radical polymerizations involving different termination steps. The method may be conveniently applied to the case where polyfunctional monomers are also present, leading to the formation of networks.

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Statistics of Free-Radical Polymerizations Revisited Using a Fragment Approach. 2. Polyfunctional Monomers

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ABSTRACT: A fragment approach is used to derive statistical parameters of networks prepared from the free-radical polymerization of an $A_2 + A_f$ system, allowing different termination mechanisms to take place simultaneously. When the termination mechanism is shifted from chain transfer and/or disproportionation to combination, gelation is advanced by a factor 2/3, the amount of soluble material in the polymer fraction decreases, and the amount of elastic material in the polymer increases while showing a higher concentration of the cross-linking points of the highest possible functionality. Different macroscopic properties are, thus, expected for the resulting networks.

Introduction

Statistical parameters of networks arising from the free-radical polymerization of polyfunctional monomers have been derived by several authors,[1–6] using methods related to the theory of stochastic branching processes. A common limitation of these developments is that they do not consider, at least correctly, the case where different termination mechanisms take place simultaneously (the approximation used in ref 2 and 3, where termination by combination is considered statistically equivalent to propagation is not correct, as may be realized by analyzing the resulting expressions when combination is the exclusive termination mechanism).

Little is known about chain termination mechanisms for most monomers. Structural factors affecting the termination mechanism are the number of hydrogen atoms available for disproportionation and the bulkiness of substituents on the radical carbon atom. Increases in both factors enhance the termination by disproportionation. For example, in the case of styrene, it is generally agreed that termination takes place almost exclusively by combination over a wide range of temperatures. In the case of methyl methacrylate, both mechanisms are operative but the relative contribution of disproportionation increases with temperature (in this case there are bulky substituents and five hydrogens available for disproportionation). Chain transfer is obviously enhanced by adding a transfer agent. In any case, it is important to estimate the incidence of a shift in the termination mechanism on pre- and postgel properties of the polymer.

The aim of this part is to use the fragment approach previously developed[7] and to derive statistical parameters of networks prepared from the free-radical polymerization of an $A_2 + A_f$ system, allowing different termination mechanisms to take place simultaneously. As any double bond is a bifunctional unit, the functionality f of the polyfunctional monomer is always an even number. The present derivation retains the classical simplifying assumptions: (i) all double bonds are equally reactive, (ii) there are no substitution effects, and (iii) no intramolecular reactions occur in finite species. The validity of the last hypothesis may be questionable at the beginning of the reaction, when there is a finite probability for the radical at the end of a growing chain to react with double bonds pendant on its own chain.[8] The present analysis is then restricted to systems with a low concentration of the polyfunctional monomer A_f.

Fragment Approach

Table I shows the species and fragments that may be identified for a particular reaction extent p. An A_f molecule, with mass M_f, is fragmented into a skeleton with $f/2$ branches, devoid of mass, and $f/2$ double bonds, the mass of each one being $M_f(2/f)$. In order to regenerate the A_f structure, (α) linkages must be joined with (β) linkages.

The probability that a reacted double bond propagates the chain is defined as

$$q = r_p/(r_p + r_t + r_d + r_c) \tag{1}$$

where r_p is the propagation rate and r_t, r_d, and r_c are termination rates by chain transfer, disproportionation, and combination, respectively.

The probability that termination occurs by combination is defined as

$$\xi = r_c/(r_t + r_d + r_c) \tag{2}$$

By use of the definitions given by eq 1 and 2, the molar concentration of every species and fragment may be calculated, as is shown in Table I. In order to regenerate the structure, it must be taken into account that (+) linkages must be joined with (−) linkages, (α) linkages with (β) linkages, and arrows among themselves. As the concentration of (+) linkages must be equal to the one of (−) linkages, the concentration of initiator fragments must equal that of terminating units. Similarly, Table I shows that the concentration of (α) linkages is equal to the one of (β) linkages = $fA_f/2$.

At any reaction extent p, the unreacted A_f monomer verifies that not one of its $f/2$ double bonds has reacted. Then, its concentration is given by $A_f(1 - p)^{f/2}$, with an

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