Distribution Kinetics of Radical Mechanisms: Reversible Polymer Decomposition

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For polymers and other homologous mixtures that span a molecular weight (MW) range, many reaction mechanisms involve the formation, addition and decomposition of free radicals. In the chain reactions of polymerization and depolymerization, radicals and polymer molecules interact by a variety of primary reactions. We postulate that these radicals and molecules can be described by continuous molecular weight distributions (MWDs). Their chemical interactions are developed from generic, reversible addition or bond scission reactions. Distribution balance equations are proposed for initiation-termination and propagation-depropagation reactions, such as hydrogen abstraction, disproportionation, chain cleavage, and radical coupling. A comprehensive model including all these events conforms to the special mechanisms for chain-end depolymerization and for random-scission polymer degradation. The evolution of an MWD from initial state to final equilibrium is described by the time dependence of MW moments. Irreversible degradation or polymerization relationships are obtained as limiting cases. First-order rate constants observed in pyrolysis and thermolysis reactions are composed of algebraic groups of primary reaction rate constants.

Introduction

The chemistry of radicals is fundamental to many reactions of hydrocarbons and polymers, such as pyrolysis, thermolysis, and polymerization. These processes involve bond scission (fragmentation) and addition (polymerization) reactions, which lead to mixtures spanning a range of molecular weights. According to the Rice-Herzfeld chain reaction (Gavalas, 1966; Nigam et al., 1994), the elementary steps are initiation, propagation, hydrogen (H-) abstraction, and termination. The elementary components engaging in the chain reaction are paraffins and olefins in the forms of monomers, oligomers, and polymers and the corresponding radicals. We will distinguish between end and midchain radicals, where the unpaired electron is located at the chain end or elsewhere along the chain. H-abstraction reactions allow radicals to be quenched (stabilized) by capturing a hydrogen atom from a stable position. Such H-abstraction reactions may be intermolecular (typically biomolecular) or intramolecular (for example, backbiting).

Complex mixtures of homologous components can be characterized by the moments of their distributions. The finite number of chemical components in a mixture implies that moments should be defined as sums over the components in the frequency distribution, constituting the molecular-weight, or chain-length, distribution. However, sums can be difficult to evaluate compared to integrals. Continuous-distribution kinetics is valid when the MWD allows integrals to represent averages of the distribution. As in numerical integration, a sum over mixture species can be approximated by an integral when we have sufficient smoothness and a large enough number of intervals (chemical components). The smooth nature of gel permeation chromatographs supports the notion that continuous MWDs may be appropriate for many polymer processes. The theoretical results of the discrete and continuous models should be identical for mixtures with many components. The continuous-distribution theory has been applied to the dynamics of polymer reactions by, for example, Gloor et al. (1994), Wang et al. (1995), and Browarzik and Kehlen (1997).

The objective of the present work was to develop a continuous-distribution approach for chain reactions of interacting

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molecules and radicals. The chemical interactions are generic reversible addition or chain scission reactions between distributions of paraffins, olefins, and end- and midchain radicals. Distribution (population) balance equations for MWDs are proposed for initiation-termination and propagation-depropagation reactions, such as H-abstraction, disproportionation, chain cleavage, and radical coupling. We ignore solution density changes (volume contraction) and gel effects. If the change in average MW of the polymer mixture is not too great, one can consider that the rate coefficient k is independent of x (Madras et al., 1997); hence, we will develop the present theory by assuming k is constant with x. The integrodifferential governing equations are solved in terms of molecular-weight moments. The moments form a hierarchy of ordinary differential equations, which can be solved numerically up to the desired moment order, usually up to second moments. In the present treatment we invoke two common approximations and solve analytically for algebraic moment expressions. The long-chain approximation (LCA) (Gavalas, 1966; Nigam et al., 1994) maintains that initiation and termination reaction events are infrequent and therefore their rates are negligible relative to H-abstraction and propagation-depropagation chain reaction rates. The quasi-stationary-state approximation (QSSA) is valid when the concentration of free radicals is extremely small, so that their rate of change with time is negligible compared to other rates. For either chain-end or random scission, the results show that reversible processes reduce to irreversible decomposition reactions when the addition (repolymerization) rate coefficients are relatively very small. Previously derived and experimentally verified expressions for polymer degradation are thus recovered from the generalized theory. When addition (recombination) reactions dominate over decomposition, well-known polymerization results are recovered.

General Reactions of Polymers

We consider that macromolecules can react in three ways: by transforming without change in molar concentration, by undergoing chain scission, and by combining to form higher MW compounds. For generality, we allow that each compound in a given reaction is distinguishable, and then specify for particular cases when the compounds are indistinguishable within a class, such as the class of radicals or of stable macromolecules. We indicate the chemical species with the capital letters $P(x)$, $Q(x)$, $R(x)$, where x represents a continuous variable, either the MW or chain length. The MWDs of these species are $p(x,t)$, $q(x,t)$, and $r(x,t)$, respectively, where at time t, for example, $p(x,t)dx$ is the molar concentration (mol/volume) of species P having values of x in the range x to $x+dx$.

Simple transformation reaction

A transformation without change in chain length or with negligible change in MW, such as from a radical to a stable polymer, can be written as

$$R(x) \rightarrow P(x) \tag{1}$$

If $k(x)$ is the rate coefficient for this reaction, then the rates of change of the two species are

$$\partial p/\partial t = k(x)\, r(x,t) = -\,\partial r/\partial t \tag{2}$$

Chain scission reaction

When a chain is cleaved by bond scission, the two products have MWs, x and $x'-x$, that add to the reactant MW, x',

$$P(x') \rightarrow Q(x) + R(x'-x) \tag{3}$$

The rates of change of the three species are

$$\partial p/\partial t = -k(x)p(x,t) \tag{4}$$

$$\partial q/\partial t = \partial r/\partial t = \int_x^\infty k(x')\Omega(x,x')p(x',t)dx' \tag{5}$$

The rates for q and r have equivalent forms because the scission stoichiometric coefficient, or kernel, is symmetric (Aris and Gavalas, 1966), $\Omega(x,x') = \Omega(x'-x,x')$. The kernel represents a reaction in which a molecule cleaves into two product molecules whose sizes, x and $x'-x$, sum to the reactant size, $x' \geq x$. This leads to the normalization

$$\int_0^{x'} \Omega(x,x')dx = 1 \tag{6}$$

A general expression for the stoichiometric coefficient is (McCoy and Wang, 1994; McCoy and Madras, 1997)

$$\Omega(x,x') = x^m(x'-x)^m\Gamma(2m+2)/[\Gamma(m+1)^2(x')^{2m+1}] \tag{7}$$

When $m=1$, this expression reduces to the quadratic form used by Prasad et al. (1986) for coal thermolysis and by Ziff and McGrady (1986) for polymer degradation, $\Omega(x,x') = 6x(x'-x)/x'^3$. When $m=0$ the products are evenly distributed along all $x \leq x'$, that is, $\Omega(x,x') = 1/x'$, which describes the totally random kernel (Aris and Gavalas, 1966). As $m \rightarrow \infty$, the stoichiometric coefficient describes scission that occurs at the chain midpoint, $\Omega(x,x') = \delta(x - x'/2)$. For chain-end scission when a specific product of fixed MW x_s and a chain of MW $x' - x_s$ are formed, the stoichiometric kernels are $\delta(x - x_s)$ and $\delta(x - (x' - x_s))$, respectively. By definition, such Dirac delta functions are symmetric and normalized to unity.

Addition reaction

Two macromolecules of MW x' and $x-x'$ can join together by bimolecular chain addition or cross-linking to form a product of MW x

$$P(x') + Q(x-x') \rightarrow R(x) \tag{8}$$

The rates depend on concentrations of both reactants and hence are second-order

$$\partial p/\partial t = -k(x)\,p(x)\int_0^\infty q(x')\,dx' \tag{9}$$

$$\partial q/\partial t = -k(x)\,q(x)\int_0^\infty p(x')\,dx' \tag{10}$$

$$\partial r/\partial t = \int_0^x k(x')\,p(x')\,q(x-x')\,dx' \tag{11}$$

Moment solution

Integral forms of the above rate expressions lend themselves to moment calculations. Moments of the MWDs are defined as the integrals over the MW x; for example,

$$p^{(n)}(t) = \int_0^\infty p(x,t)x^n\,dx \tag{12}$$

The zeroth moment ($n = 0$) is the time-dependent total molar concentration (mol/volume) of the macromolecule. The first moment $p^{(1)}(t)$ is the mass concentration (mass/volume). The normalized first moment (average MW) and second central moment (variance of the MWD) are given, respectively, by $p^{\text{avg}} = p^{(1)}/p^{(0)}$ and $p^{\text{var}} = p^{(2)}/p^{(0)} - [p^{\text{avg}}]^2$. The polydispersity is defined as the ratio of the mass (or weight) average MW, $M_w = p^{(2)}/p^{(1)}$, to the molar (or number) average MW, $M_n = p^{\text{avg}}$, that is, $D = p^{(2)}p^{(0)}/[p^{(1)}]^2$. The three moments $p^{(0)}$, p^{avg}, and p^{var} provide the shape characteristics of the MWD, and can be used to construct the MWD. When the initial MWD is $p(x,t=0) = p_o(x)$, its moments are $p^{(n)}(t=0) = p_o^{(n)}$. The Γ distribution function is a versatile representation of distributions (Cotterman et al., 1985; Wang et al., 1994, 1995) that can be constructed from the zeroth, first, and second moments.

General Model for Radical Reactions

We will consider that branched and linear polymers undergo (H-)abstraction, disproportionation, chain cleavage, and radical coupling reactions with mathematical representations in terms of MWDs. Chain scission is bond scission in the backbone of a polymer or radical, whether linear or branched, proceeding either with random or specific (for chain-end scission) distribution of products. Addition reactions occur between radicals and olefins. We adopt the notation in Table 1 for the general model of radical reactions.

Table 1. Species Symbol and MWD Notation for Macromolecule and Radical Reactions

Species	MWD	Definition
$P(x)$	$p(x,t)$	n-alkane or isoalkane polymer
$Q(x)$	$q(x,t)$	Polymer with at least one unsaturated C-C bond (alkene)
$Q_s(x)$	$q_s(x,t)$	Monomer or oligomer of MW x_s, such as an alkane or alkene specific product of chain-end scission
$R_e^{\cdot}(x)$	$r_e(x,t)$	Radical with an unpaired electron at the chain end
$R_r^{\cdot}(x)$	$r_r(x,t)$	Radical with unpaired electron at a random position on a main chain carbon
$R_s^{\cdot}(x)$	$r_s(x,t)$	Radical formed by intramolecular isomerization (backbiting reaction) of $R_e\cdot$
$R_{es}^{\cdot}(x)$	$r_{es}(x,t)$	End-radical given by fragmentation of $R_s^{\cdot}$

The initiation and termination of radicals are represented by the reversible reaction

$$P(x) \underset{k_t}{\overset{k_f}{\rightleftharpoons}} R_e^{\cdot}(x') + R_e^{\cdot}(x-x') \tag{13}$$

The forward reaction represents an initiation reaction by C-C bond scission, with rate coefficient k_f, forming two end-radicals. The reverse reaction with rate coefficient k_t is termination by radical coupling. According to the long chain-reaction approximation (LCA), these reactions, although necessary in the complete mechanism, have a negligible effect on the overall *rate* of the reaction (Gavalas, 1966; Nigam et al., 1994).

The reversible chain scission of radicals (propagation-depropagation) and H-abstraction occur orders of magnitude more frequently than initiation-termination events. The Fabuss-Satterfield-Smith mechanism, where intermolecular H-abstraction is an important elementary reaction, has been applied to high-pressure thermal treatment (Khorasheh et al., 1993). Radical-promoted abstraction of a hydrogen atom from a polymer gives both an end-radical and a midchain (random) radical,

$$P(x) \underset{k_{He}}{\overset{k_{he}}{\rightleftharpoons}} R_e^{\cdot}(x) \tag{14}$$

$$P(x) \underset{k_{Hr}}{\overset{k_{hr}}{\rightleftharpoons}} R_r^{\cdot}(x) \tag{15}$$

The quasi-steady-state approximation (QSSA) for radical species allows these reactions to be expressed as pseudo-first-order reactions. H-abstraction may be expressed as a disproportionation with a transition-state species $S^{\cdot}$,

$$P(x) + R^{\cdot}(x') \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} S^{\cdot}(x+x') \xrightarrow{k_2} R^{\cdot}(x) + P(x') \tag{16}$$

The moment method of solution of the MWD balance equations, or a conventional chemical kinetics procedure for molar concentration, provides the equations for the zeroth moments,

$$dp^{(0)}/dt = dr^{(0)}/dt = -ds^{(0)}/dt = -k_1\,p^{(0)}r^{(0)} + (k_1' + k_2)s^{(0)} \tag{17}$$

Applying QSSA as $ds^{(0)}/dt = 0$ yields $k_1\,p^{(0)}r^{(0)} = (k_1' + k_2)s^{(0)}$, from which it follows that

$$dp^{(0)}/dt = -k_h\,p^{(0)} + k_H\,r^{(0)} = 0 \tag{18}$$

where $k_h = k_1\,r^{(0)}$ and $k_H = k_1\,p^{(0)}$. It follows that $k_h/k_H = r^{(0)}/p^{(0)} \ll 1$, which is precisely the relationship one obtains from applying QSSA to the reaction

$$P(x) \underset{k_H}{\overset{k_h}{\rightleftharpoons}} R^{\cdot}(x) \tag{19}$$

because Eq. 11 applies. Thus, we can use Eq. 19 as a simplification of Eq. 16 to represent H-abstraction.

Radical chain scission yielding an olefin and a radical, and recombination to form a radical are represented as

$$R_r^{\cdot}(x) \rightarrow Q(x') + R_e^{\cdot}(x - x') \tag{20}$$

$$R_e^{\cdot}(x) + Q(x') \rightarrow R_r^{\cdot}(x + x') \tag{21}$$

$$R_r^{\cdot}(x) + Q(x') \rightarrow R_r^{\cdot}(x + x') \tag{22}$$

Random chain scission is expressed as β-scission of a random radical, yielding an alkene and an end-radical (Eq. 20). An alkene can undergo recombination with a radical by addition to form a branched radical (Eqs. 21 and 22) denoted as a random radical.

Chain-end scission yields specific products, such as a monomer (C2 fragment of a main chain such as ethylene or styrene) or an oligomer of MW x_s, denoted as $Q_s(x_s)$. Monomer formation can be given by both β-scission of an end-radical (Eq. 23) and β-scission of a specific radical that is the result of a 1,2-radical shift of an end-radical (Eqs. 25 and 26).

$$R_e^{\cdot}(x) \leftrightarrow Q_s(x_s) + R_e^{\cdot}(x - x_s) \tag{23}$$

$$R_r^{\cdot}(x) + Q_s(x_s) \rightarrow R_r^{\cdot}(x + x_s) \tag{24}$$

An end radical is strongly reactive and undergoes chain-end scission resulting in the formation of the C2 fragment monomer (such as ethylene or styrene) as in Eq. 23. The reverse, or recombination, reaction is the addition of the monomer to the chain-end radical to yield a higher MW chain-end radical. A random radical can also combine with the monomer (Eq. 24) to give the corresponding branched radical, treated here as a random radical when the branching is short.

Reactions of oligomer radicals and nonradicals are written as follows:

$$R_e^{\cdot}(x) \underset{k_{iH}}{\overset{k_{ih}}{\longleftrightarrow}} R_s^{\cdot}(x) \tag{25}$$

$$R_s^{\cdot}(x) \underset{k_{as}}{\overset{k_{bs}}{\longleftrightarrow}} Q_s(x_s) + R_e^{\cdot}(x - x_s) \tag{26}$$

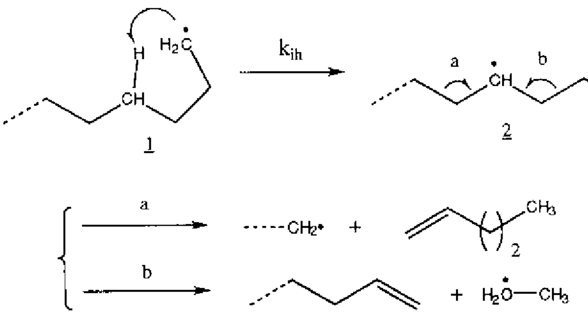
$$R_r^{\cdot}(x) + Q_s(x_s) \xrightarrow{k_{as2}} R_r^{\cdot}(x + x_s) \tag{27}$$

$$R_s^{\cdot}(x) \xrightarrow{k_{bs2}} R_{es}^{\cdot}(x_s) + Q(x - x_s) \tag{28}$$

$$R_{es}^{\cdot}(x_s) \xrightarrow{k_{hr}} Q_s(x_s) \tag{29}$$

An end-radical can undergo intramolecular isomerization to form a specific radical $R_s^{\cdot}$ (Eq. 25), that is, the end-radical stabilizes to the corresponding radical. Such an intramolecular transformation can be a 1,2-, 1,4-, 1,5-, or 1,6-shift reaction depending on the chemical structure. The resulting radical species can undergo β-scission affording specific compounds (Eq. 26), usually with large rate coefficients or low activation energy. Addition of the alkene specific product to an end-radical is the reverse (Eq. 26). Addition of a specific product to a random radical is shown in Eq. 27. Formation of specific compound $Q_s(x_s)$ via H-abstraction of the end-radical $R_{es}^{\cdot}$ is depicted in Eqs. 28 and 29.

A mechanism for intramolecular radical isomerization (backbiting) of n-alkane via a cyclic transition state (Ravve, 1995; Mita, 1978) is included in the Rice-Kossiakoff mechanism (Kossiakoff and Rice, 1943)



(30)

The intramolecular isomerization of the end-radical (1) by the five-membered transition state gives a specific radical (2), subsequently followed by two modes of fragmentation. One mode (a) yields an alkyl radical and 1-pentene. Another mode (b) yields a 1-alkene and ethyl radical, which can give ethylene and ethane via disproportionation and n-butane via coupling. Similarly, specific chain scission via a six-membered transition state can afford 1-hexene and propyl radical, a precursor of C3 and C6 species as specific products. The actual reaction will depend on the polymer chemical structure.

Distribution balance equations can be written for all the reactions in the general model. MWDs can in principle be measured by a combination of HPLC-GPC and GC-MS. The analytical chemistry difficulties are comparable to those approaches that use lumping procedures (Nigam et al., 1994; Nigam and Klein, 1993; Savage and Klein, 1989). The advantages of our proposal may be that computational demands are reduced (no matrix inversions are needed) and closed-form algebraic results allow straightforward recognition of parametric effects. Aside from the specific products, the continuous-distribution method describes the macromolecular components as averages (MW moments), rather than as individual concentrations at each MW. To illustrate the conceptual method, we will present examples of derivations. The system of equations is simplified by recognizing that the usual GPC analysis does not distinguish between alkanes and alkenes; hence, we combine them together as $P(x)$. For random scission, we further treat all radicals as similar, and denote them as $R^{\cdot}(x)$. The chemical reactions then condense to initiation-termination, H-abstraction, and propagation-depropagation steps for random and chain-end scission. We will derive for these simplifications the kinetic expressions that are known to describe experimental data (Wang et al., 1995; Madras et al., 1995, 1996a,b).

Reversible Random Chain Scission and H-Abstraction

Polymer degradation or solvolysis can occur in some circumstances solely by random chain scission, and so in this section we ignore chain-end scission. Below the ceiling temperature, recombination (polymerization) chain reactions can produce higher MW polymer. The following scheme includes the major elementary steps in the Rice-Herzfeld mechanism, as discussed by Gavalas (1966) and Nigam et al. (1994) for high-temperature hydrocarbon conversions

$$P(x)\underset{k_t}{\overset{k_f}{\longleftrightarrow}}R^{\cdot}(x')+R^{\cdot}(x-x') \tag{31}$$

$$P(x)\underset{k_H}{\overset{k_h}{\longleftrightarrow}}R^{\cdot}(x) \tag{32}$$

$$R^{\cdot}(x)\underset{k_a}{\overset{k_b}{\longleftrightarrow}}P(x')+R^{\cdot}(x-x') \tag{33}$$

The symbol $P(x)$ here represents both alkane and alkene, and $p(x,t)$ is the corresponding MWD. The distribution balance equations for $p(x,t)$ and for radical MWD, $r(x,t)$, are as follows

$$\begin{aligned}\partial p/\partial t = & -k_f\,p(x)+k_t\int_0^x r(x')r(x-x')dx'-k_h\,p(x)\\ & +k_H\,r(x)+k_b\int_x^\infty r(x')\Omega(x,x')dx'-k_a\,p(x)\int_0^\infty r(x')dx'\end{aligned} \tag{34}$$

$$\begin{aligned}\partial r/\partial t = & \,2k_f\int_x^\infty p(x')\Omega(x,x')dx'-2k_t\,r(x)\int_0^\infty r(x')dx'\\ & +k_h\,p(x)-k_H\,r(x)-k_b\,r(x)+k_b\int_x^\infty r(x')\Omega(x,x')dx'\\ & +k_a\int_0^x r(x-x')p(x')dx'-k_a\,r(x)\int_0^\infty p(x')dx'\end{aligned} \tag{35}$$

The initial conditions are $p(x,t=0)=p_o(x)$ and $r(x,t)=0$. Applying the moment operation (McCoy, 1993; McCoy and Madras, 1997), $\int_0^\infty[\;]\,x^n\,dx$, to both integrodifferential equations yields

$$\begin{aligned}dp^{(n)}/dt = & -k_f\,p^{(n)}+k_t\sum_{j=0}^{n}\binom{n}{j}r^{(j)}r^{(n-j)}-k_h p^{(n)}+k_H\,r^{(n)}\\ & +k_b\,Z_{nm}\,r^{(n)}-k_a p^{(n)}r^{(0)}\end{aligned} \tag{36}$$

$$\begin{aligned}dr^{(n)}/dt = & \,2\,k_f\,Z_{nm}\,p^{(n)}-2\,k_t\,r^{(n)}r^{(0)}+k_h\,p^{(n)}-k_H\,r^{(n)}\\ & -k_b\,r^{(n)}+k_b Z_{nm}\,r^{(n)}+k_a\sum_{j=0}^{n}\binom{n}{j}r^{(j)}p^{(n-j)}-k_a\,r^{(n)}p^{(0)}\end{aligned} \tag{37}$$

For random scission, $Z_{n0}=1/(n+1)$. The initial conditions for moments are $p^{(n)}(t=0)=p_o^{(n)}$ and $r^{(n)}(t=0)=0$.

The LCA is based on the negligible effect of initiation and termination reactions compared with the predominant influence of the chain (propagation-depropagation) reactions. We assume accordingly that terms involving k_f and k_t can be set to zero. This assumption is based on the relatively insignificant magnitude of k_f and the extremely low probability of addition reactions between radicals at small concentrations.

The basis of the QSSA is the small number of radicals, and therefore the negligible change with time of the radical MWD,

$$\partial r(x,t)/\partial t = 0 \tag{38}$$

It follows that the rate of change of moments for the radical MWD is vanishingly small, $dr^{(n)}/dt=0$. For the radical concentration to be small implies that $k_h/k_H \ll 1$, so that the H-abstraction to quench radicals is much faster than their formation. Applying the QSSA for $r^{(0)}$ demonstrates that $r^{(0)} \ll p^{(0)}$

$$r^{(0)}=(k_h/k_H)p^{(0)} \tag{39}$$

and therefore

$$dp^{(0)}/dt=(k_b-k_a p^{(0)})r^{(0)}=(k_b-k_a p^{(0)})(k_h/k_H)p^{(0)} \tag{40}$$

Integrating with the initial condition yields

$$p^{(0)}(t)=e^{kt}/[(e^{kt}-1)k_a/k_b+1/p_o^{(0)}] \tag{41}$$

where $k=k_b k_h/k_H$. The equilibrium relation is found from the long time limit

$$p^{(0)}(t\rightarrow\infty)=p_\infty^{(0)}=k_b/k_a \tag{42}$$

The summation of *first moments* $(n=1)$ for polymer and radicals (total mass concentration) is

$$d[r^{(1)}+p^{(1)}]/dt=0 \tag{43}$$

confirming the conservation of polymer mass. This mass conservation requirement applies for all models as a check that distribution balance equations have been properly stated and algebraic manipulations have been performed without errors. Applying the QSSA gives $dr^{(1)}/dt=0$; it follows that $dp^{(1)}/dt=0$, which integrates with the initial condition to

$$p^{(1)}(t)=p_o^{(1)} \tag{44}$$

The radical mass concentration becomes

$$r^{(1)}=(k_h+k_a r^{(0)})p_o^{(1)}/(k_H+k_b/2) \tag{45}$$

The time-dependence of *second moments* with the QSSA is given by

$$dp^{(2)}/dt=-k_h\,p^{(2)}+k_H\,r^{(2)}+(k_b/3)r^{(2)}-k_a\,p^{(2)}r^{(0)} \tag{46}$$

$$\begin{aligned}dr^{(2)}/dt= & \,k_h\,p^{(2)}-k_H\,r^{(2)}-(2k_b/3)r^{(2)}\\ & +k_a(p^{(2)}r^{(0)}+2\,p^{(1)}r^{(1)})=0\end{aligned} \tag{47}$$

Summation of these equations gives

$$dp^{(2)}/dt=-(k_b/3)r^{(2)}+2\,k_a\,p^{(1)}r^{(1)} \tag{48}$$

and from Eq. 25

$$r^{(2)}=[(k_h+k_a\,r^{(0)})\,p^{(2)}+2\,k_a\,p^{(1)}r^{(1)}]/(k_H+2\,k_b/3) \tag{49}$$

Substitution of $p^{(1)}$, $r^{(1)}$, and $r^{(2)}$ in Eq. 48 and integrating with the initial condition yields

$$p^{(2)}(t) = [4k_a(k_b+3k_H)p_o^{(1)2}/k_b(k_b+2k_H)] + [p_o^{(2)} - 4k_a(k_b+3k_H)p_o^{(1)2}/(k_b(k_b+2k_H))] \exp\{k_b[-k_h t + \ln k_b - \ln\{k_b - k_a p_o^{(0)}[1-\exp(kt)]\}/(2k_b+3k_H)]\} \quad (50)$$

in terms of $k = k_b k_h / k_H$. The equilibrium limit is

$$p^{(2)}(t \to \infty) = p_\infty^{(2)} = [4k_a(k_b+3k_H)p_o^{(1)2}/k_b(k_b+2k_H)] \quad (51)$$

The equilibrium values of number-average and mass-average MW and of polydispersity are

$$M_{n\infty} = p_o^{(1)}(k_a/k_b) \quad (52)$$

$$M_{w\infty} = 4p_o^{(1)}k_a(k_b+3k_H)/k_b(k_b+2k_H) \quad (53)$$

$$D_\infty = 4(k_b+3k_H)/(k_b+2k_H) \quad (54)$$

The equilibrium polydispersity is independent of initial conditions. Also, since usually $k_H \gg k_b$, we have $M_{w\infty} = 6p_o^{(1)}k_a/k_b$ and $D_\infty = 6$, which indicates that MWD broadening occurs when random chain scission and recombination reach a dynamic equilibrium after a long time. Other treatments of reversible chain scission were limited to the mass or molar concentration (such as Blatz and Tobolsky, 1945; Odian, 1991) and did not provide expressions for higher moments. A shortcoming of the long-time results is our assumption that all rate coefficients are independent of x. Conversions increase with time, and for large conversions chain-scission rate coefficients should be functions of x (Madras et al., 1997). The broadening is exaggerated ($D \to 6$ rather than 2), because larger molecules are not cleaved as often as when the rate coefficient increases with MW. For small conversions observed in experiments conducted over several hours, however, rate coefficients independent of x are adequate.

One cannot distinguish between polymer reactants and products in the continuous-distribution model of polymers undergoing chain scission and addition reactions. Thus, a single MWD $p(x,t)$ represents the polymer mixture at any time t. The zeroth moment $p_\infty^{(0)}$, which is the equilibrium molar concentration given by Eq. 42, serves in the place of the mass-action form of the chemical-reaction equilibrium constant. With $k_b = k_{bo}e^{-E_b/RT}$ and $k_a = k_{ao}e^{-E_a/RT}$, in terms of the energies of activation, E_b and E_a, for chain scission and addition, respectively, we obtain from Eq. 42 a result related to the van't Hoff equation

$$p_\infty^{(0)} = K_o e^{-\Delta H/RT} \quad (55)$$

where $K_o = k_{bo}/k_{ao}$ and $\Delta H = E_b - E_a$ is the heat of reaction. Polymer degradation is typically endothermic $\Delta H > 0$.

If the molar free energy of polymers is $\mu(x)$ (Cotterman et al., 1985), the total free energy of the (reacting) solution is

$$G(t) = \int_0^\infty p(x,t)\,\mu(x)\,dx \quad (56)$$

When $\mu(x)$ can be represented as a polynomial in x, the free energy is the sum of MW moments of $p(x,t)$, and G is minimized when the moment derivatives vanish at equilibrium.

Irreversible random chain scission

In the absence of recombination ($k_a \ll k_b$) the zeroth and second moment expressions (Eqs. 41 and 50) reduce to

$$p^{(0)}(t) = p_o^{(0)} e^{kt} \quad (57)$$

$$p^{(2)}(t) = p_o^{(2)} \exp[-k_b k_h t/(3k_H + 2k_b)] \simeq p_o^{(2)} e^{-kt/3} \quad (58)$$

when $k_H \gg k_b$. These results are identical with earlier reports (Wang et al., 1995; Madras et al., 1995), which did not account for the radical mechanism, but merely allowed for random-chain fragmentation, as in

$$P(x') \xrightarrow{k} P(x) + P(x'-x) \quad (59)$$

Since $E_b \simeq 29$ (Song et al., 1994), $E_h \simeq 8$ (activation energy for intermolecular H-abstraction, Kerr et al., 1951), and $E_H = 0$ kcal/mol (activation energy for radical stabilization, Lehni et al., 1979), the activation energy for the degradation, $E_b + E_h - E_H \simeq 29 + 8 - 0 = 37$ kcal/mol, is in general agreement with experimental values (Wang et al., 1995). Differences in chemical structure, such as side groups and branching, will affect the activation energy.

Irreversible addition reaction

This case (reverse of random chain scission) is analogous to irreversible step-growth polymerization. In the absence of chain scission ($k_b \ll k_a$) the zeroth and second moment expressions (Eqs. 41 and 50) reduce as follows, where $k_p = k_a k_h / k_H$

$$p^{(0)}(t) = p_o^{(0)}/\left[1 + p_o^{(0)}k_p t\right] \quad (60)$$

and

$$p^{(2)}(t) = p_o^{(2)} + 2k_p p_o^{(1)2}\left[t + (1/k_h)\ln\left(1 + p_o^{(0)}k_p t\right)\right] \quad (61)$$

One can readily show that the expression for polydispersity for large time is asymptotic to $D = 2$, the classic result for the most probable MWD in polymerization (Dotson et al., 1996; Odian, 1991). The continuous distribution approach is thus consistent with discrete step-growth polymerization kinetics, when the addition rate coefficient is assumed independent of x (Dotson et al., 1996, page 84).

Reversible Chain-End Scission and H-Abstraction

The end radical plays an important role in depolymerization by chain-end scission, which yields either monomer or other low-MW specific products. For poly(methyl methacrylate) (PMMA) or poly(α-methyl styrene) (PAMS), only chain-end scission to monomer occurs at the temperatures investigated by Madras et al. (1996a,b). The end-radical can undergo radical isomerization to form a specific radical via a radical-shift reaction. As a result, polymers such as poly(styrene allyl alcohol) (PSA) and polystyrene yield low MW products in addition to the monomer. For example, PSA not only undergoes random scission, but also gives monomers, dimers, and trimers by chain-end scissions with lower activation energies than the corresponding values for random chain scission (Wang et al., 1995; Madras et al., 1995). Our analysis shows that expressions comparable to those in Madras et al. (1996a,b) are obtained. Isomerization of the radical proceeds via a cyclic transition state, such as a six-membered ring (Ravve, 1995). Fragmentation by β-scission of the resulting radical always gives small molecules as the specific compounds. The essential feature in chain-end scission is radical isomerization of the end-radical to a more stable radical, called a specific radical in our notation.

According to the LCA, contributions of initiation and termination reactions to the overall rate are negligible. Thus we have the three reversible reactions

$$P(x) \underset{k_{He}}{\overset{k_{he}}{\longleftrightarrow}} R_e^{\cdot}(x) \tag{62}$$

$$R_e^{\cdot}(x) \underset{k_{iH}}{\overset{k_{ih}}{\longleftrightarrow}} R_s^{\cdot}(x) \tag{63}$$

$$R_s^{\cdot}(x) \underset{k_{as}}{\overset{k_{bs}}{\longleftrightarrow}} Q_s(x_s) + R_e^{\cdot}(x - x_s) \tag{64}$$

For simplicity, Q_s stands for any specific (discrete) compound, and in a complete treatment a reaction like Eq. 64 would be written for each specific product. Formation and reactions of a random radical are excluded from these schemes because the absence of random chain scission products in the typical experiments of PMMA and PAMS suggest no formation of a random radical, or no reaction of a random radical to the product Q_s.

The balance equations for $p(x,t)$, $q_s(x,t)$, $r_e(x,t)$, and $r_s(x,t)$ are

$$\partial p/\partial t = -k_{he}\, p(x) + k_{He}\, r_e(x) \tag{65}$$

$$\partial q_s/\partial t = k_{bs}\int_x^{\infty} r_s(x')\,\delta(x' - x_s)\,dx' - k_{as}\, q_s(x_s)\int_0^{\infty} r_e(x')dx' \tag{66}$$

$$\begin{aligned}\partial r_e/\partial t = {} & k_{he}p(x) - k_{He}\, r_e(x) - k_{ih}\, r_e(x) + k_{iH}\, r_s(x) \\ & + k_{bs}\int_x^{\infty} r_s(x')\,\delta[x - (x' - x_s)]\,dx' - k_{as}\, r_e(x)\int_0^{\infty} q_s(x')dx'\end{aligned} \tag{67}$$

$$\begin{aligned}\partial r_s/\partial t = {} & k_{ih}\, r_e(x) - k_{iH}\, r_s(x) - k_{bs}\, r_s(x) \\ & + k_{as}\int_0^{x} r_e(x' - x_s)\, q_s(x_s)dx'\end{aligned} \tag{68}$$

The initial conditions are $p(x, t=0) = p_o(x)$, $q_s(x, t=0) = q_{so}(x)$, and $r_e(x, t=0) = r_s(x, t=0) = 0$. Applying the moment operation to each balance equation yields moment equations

$$dp^{(n)}/dt = -k_{he}\, p^{(n)} + k_{He}\, r_e^{(n)} \tag{69}$$

$$dq_s^{(n)}/dt = k_{bs}\, x_s^n\, r_s^{(0)} - k_{as}\, q_s^{(n)} r_e^{(0)} \tag{70}$$

$$\begin{aligned}dr_e^{(n)}/dt = {} & k_{he}\, p^{(n)} - k_{He}\, r_e^{(n)} - k_{ih}\, r_e^{(n)} + k_{iH}\, r_s^{(n)} \\ & + k_{bs}\sum_{j=0}^{n} \binom{n}{j}(x_s)^j(-1)^j\, r_s^{(n-j)} - k_{as}\, r_e^{(n)} q_s^{(0)}\end{aligned} \tag{71}$$

$$dr_s^{(n)}/dt = k_{ih}\, r_e^{(n)} - k_{iH}\, r_s^{(n)} - k_{bs}\, r_s^{(n)} + k_{as}\sum_{j=0}^{n} \binom{n}{j} r_e^{(j)} q_s^{(n-j)} \tag{72}$$

The specific product has the unique MW x_s, so that $q_s(x, t = q_s^{(0)}(t)\delta(x - x_s)$, and therefore $q_s^{(n)} = x_s^n q_s^{(0)}$. For this specific product, we need to solve for the zeroth moment only. If several specific compounds are present, they are expressed as a summation over the index s in the balance equations; then, the complete MWD is semicontinuous (Cotterman et al., 1985).

Zeroth moments are governed by the following differential equations, where the QSSA for radical species has been applied

$$dp^{(0)}/dt = -k_{he}\, p^{(0)} + k_{He}\, r_e(0) \tag{73}$$

$$dq_s^{(0)}/dt = k_{bs}\, r_s^{(0)} - k_{as}\, q_s^{(0)} r_e^{(0)} \tag{74}$$

$$\begin{aligned}dr_e^{(0)}/dt = {} & k_{he}\, p^{(0)} - k_{He}\, r_e^{(0)} - k_{ih}\, r_e^{(0)} + k_{iH}\, r_s^{(0)} \\ & + k_{bs}\, r_s^{(0)} - k_{as}\, r_e^{(0)} q_s^{(0)} = 0\end{aligned} \tag{75}$$

$$dr_s^{(0)}/dt = k_{ih}\, r_e^{(0)} - k_{iH}\, r_s^{(0)} - k_{bs}\, r_s^{(0)} + k_{as}\, r_e^{(0)} q_s^{(0)} = 0 \tag{76}$$

Adding Eqs. 75 and 76 yields

$$r_e^{(0)} = (k_{he}/k_{He})p^{(0)} \tag{77}$$

so that by Eq. 73, $dp^{(0)}/dt = 0$, which integrates with the initial condition to

$$p^{(0)}(t) = p_o^{(0)} \tag{78}$$

The molar concentration of polymer is unchanged by chain-end scission, which produces a specific product and a polymer. Equation 74 gives

$$r_s^{(0)} = r_e^{(0)}(k_{ih} + k_{as}\, q_s^{(0)})/(k_{bs} + k_{iH}) \tag{79}$$

Then,

$$\begin{aligned}dq_s^{(0)}/dt & = k_{bs}\, r_s^{(0)} - k_{as}\, q_s^{(0)} r_e^{(0)} \\ & = (k_{bs}k_{ih} - k_{as}\, k_{iH}\, q_s^{(0)})k_{he}\, p_o^{(0)}/k_{He}(k_{bs} + k_{iH})\end{aligned} \tag{80}$$

and

$$\begin{aligned}q_s^{(0)}(t) = {} & q_{so}^{(0)}\exp\left(-k_g\, p_o^{(0)} t\right) \\ & + (k_{bs}\, k_{ih}/k_{as}\, k_{iH})\left[1 - \exp\left(-k_g\, p_o^{(0)} t\right)\right]\end{aligned} \tag{81}$$

where $k_g = k_{as}\, k_{he} k_{iH}/k_{He}(k_{bs} + k_{iH})$.

First moment equations for each species with the QSSA for radical species are

$$dp^{(1)}/dt = -k_{he}p^{(1)} + k_{He}r_e^{(1)} \qquad (82)$$

$$\begin{aligned} dr_e^{(1)}/dt = k_{he}p^{(1)} - k_{He}r_e^{(1)} - k_{ih}r_e^{(1)} \\ + k_{iH}r_s^{(1)} + k_{bs}(r_s^{(1)} - x_s r_s^{(0)}) - k_{as}r_e^{(1)}q_s^{(0)} = 0 \qquad (83) \end{aligned}$$

$$\begin{aligned} dr_s^{(1)}/dt = k_{ih}r_e^{(1)} - k_{iH}r_s^{(1)} - k_{bs}r_s^{(1)} \\ + k_{as}(r_e^{(1)}q_s^{(0)} + r_e^{(0)}q_s^{(1)}) = 0 \qquad (84) \end{aligned}$$

The summation of first moments for polymer and radicals yields $d[p^{(1)} + q_s^{(1)} + r_e^{(1)} + r_s^{(1)}/dt = 0$, confirming the conservation of polymer mass. With QSSA for the radicals, the mass concentration of polymer and specific product $p^{(1)} + q_s^{(1)}$ is constant in time

$$p^{(1)}(t) = p_o^{(1)} - x_s[q_s^{(0)}(t) - q_{so}^{(0)}] \qquad (85)$$

The second moment equations for each species with the QSSA for radical species are

$$dp^{(2)}/dt = -k_{he}p^{(2)} + k_{He}r_e^{(2)} \qquad (86)$$

$$\begin{aligned} dr_e^{(2)}/dt = k_{he}p^{(2)} - k_{He}r_e^{(2)} - k_{ih}r_e^{(2)} + k_{iH}r_s^{(2)} \\ + k_{bs}(x_s^2 r_s^{(0)} - 2x_s r_s^{(1)} + r_s^{(2)}) - k_{as}r_e^{(2)}p_s^{(0)} \qquad (87) \end{aligned}$$

$$\begin{aligned} dr_s^{(2)}/dt = k_{ih}r_e^{(2)} - k_{iH}r_s^{(2)} - k_{bs}r_s^{(2)} + k_{as}(r_e^{(2)}q_s^{(0)} \\ + 2r_e^{(1)}q_s^{(1)} + r_e^{(0)}q_s^{(2)}) \qquad (88) \end{aligned}$$

A summation of Eqs. 87 and 88 gives

$$\begin{aligned} k_{he}p^{(2)} - k_{He}r_e^{(2)} + k_{bs}(x_s^2 r_s^{(0)} - 2x_s r_s^{(1)}) \\ + k_{as}(2r_e^{(1)}q_s^{(1)} + r_e^{(0)}q_s^{(2)}) = 0 \end{aligned}$$

Then

$$\begin{aligned} dp^{(2)}/dt = -k_{he}p^{(2)} + k_{He}r_e^{(2)} = k_{bs}x_s(x_s r_s^{(0)} - 2r_s^{(1)}) \\ + k_{as}x_s q_s^{(0)}(2r_e^{(1)} + x_s r_e^{(0)}) \qquad (89) \end{aligned}$$

A summation of Eqs. 83 and 84 gives

$$k_{he}p^{(1)} - k_{He}r_e^{(1)} - k_{bs}x_s r_s^{(0)} + k_{as}r_e^{(0)}q_s^{(1)} = 0 \qquad (90)$$

Applying Eqs. 77, 79 and 85 to 90 gives

$$\begin{aligned} r_e^{(1)} = (k_{he}/k_{He})\Big\{p_o^{(1)} + x_s q_{so}^{(0)} - [k_{bs}k_{ih}/k_{He}(k_{bs} + k_{iH})]x_s p_o^{(0)} \\ + \Big[k_g p_o^{(0)}/k_{he} - 1\Big]x_s q_s^{(0)}\Big\} \qquad (91) \end{aligned}$$

Equation 84 provides an expression for $r_s^{(1)}$, which is combined with Eqs. 77, 81 and 91 to yield

$$\begin{aligned} r_s^{(1)} = [k_{he}/(k_{iH} + k_{bs})]\{k_{ih} + k_{as}q_s^{(0)}(t)\}[p_o^{(1)} + x_s q_{so}^{(0)} \\ - [k_{bs}k_{ih}/k_{He}(k_{bs} + k_{iH})]x_s p_o^{(0)} + \Big(k_g p_o^{(0)}/k_{he} - 1\Big)x_s q_s^{(0)}(t)\Big] \\ + \Big[\Big(k_g p_o^{(0)}/k_{he}\Big)x_s q_s^{(0)}(t)\Big] \qquad (92) \end{aligned}$$

Applying Eqs. 77, 79, 81, 91 and 92 to 89 followed by integration gives

$$\begin{aligned} p^{(2)}(t) = p_0^{(2)} + x_s t[2k_{as}k_{he}/k_{He}(k_{bs} + k_{iH})][k_{as}k_{bs}k_{ih}k_{iH} \\ \times(p_o^{(1)} + x_s p_o^{(0)} + x_s q_o^{(0)}) + k_{as}^2 k_{iH}^2(p_o^{(1)} + x_s p_o^{(0)} + x_s q_o^{(0)}) \\ + k_{as}k_{ih}k_{iH}^2 x_s p_o^{(0)} - k_{bs}^2 k_{ih}^2 x_s] \\ + \Big[(k_{as}k_{iH}q_o^{(0)} - k_{bs}k_{ih})^2 x_s^2/k_{as}^2 k_{He}k_{iH}^3 p_o^{(0)}\Big] \\ \times(k_{bs}k_{He} + k_{He}k_{iH} + k_{as}k_{iH}p_o^{(0)}) \\ \times\{\exp[-(2k_{as}k_{he}/k_{He}(k_{bs} + k_{iH}))p_o^{(0)}t] - 1\} \\ + [(k_{as}k_{iH}q_o^{(0)} - k_{bs}k_{ih})x_s/k_{as}^2 k_{He}k_{iH}^3(k_{bs} + k_{iH})p_o^{(0)}] \\ \times[-2k_{as}k_{bs}^2 k_{He}k_{iH}(p_o^{(1)} + x_s p_o^{(0)} + x_s q_o^{(0)}) \\ - k_{as}k_{bs}k_{He}k_{iH}^2(4p_o^{(1)} + 3x_s p_o^{(0)} + 4x_s q_o^{(0)}) \\ - 2k_{as}k_{bs}^2 k_{ih}k_{iH}x_s p_o^{(0)} - k_{as}k_{He}k_{iH}^3(2p_o^{(1)} + x_s p_o^{(0)} + 2x_s q_o^{(0)}) \\ + 6k_{bs}^2 k_{He}k_{ih}k_{iH}x_s + 2k_{bs}k_{He}k_{ih}k_{iH}^2 x_s \\ + 4k_{bs}^3 k_{He}k_{ih}x_s + 2k_{as}^2 k_{bs}k_{iH}^2 x_s p_o^{(0)}] \\ \times\{\exp[-(k_{as}k_{he}/k_{He}(k_{bs} + k_{iH}))p_o^{(0)}t] - 1\} \qquad (93) \end{aligned}$$

Irreversible chain-end scission

In the absence of recombination ($k_{as} \ll k_{bs}$), the polymer zeroth moment is constant and the first moment satisfies Eq. 85. For the second moment, Eqs. 79, 89, and 92 give

$$dp^{(2)}/dt = k_{bs}x_s(x_s r_s^{(0)} - 2r_s^{(1)}) \qquad (94)$$

$$r_s^{(0)} = r_e^{(0)}k_{ih}/(k_{bs} + k_{iH}) \qquad (95)$$

$$\begin{aligned} r_s^{(1)} = [k_{he}k_{ih}/(k_{iH} + k_{bs})k_{He}][p_o^{(1)} + x_s q_{so}^{(0)} \\ - [k_{bs}k_{ih}/k_{He}(k_{bs} + k_{iH})]x_s p_o^{(0)} - x_s q_s^{(0)}] \qquad (96) \end{aligned}$$

When $k_{as} \approx 0$ and $q_s^{(0)}(t = 0) = 0$, Eq. 81 for the specific product concentration is reduced to

$$q_s^{(0)}(t) = k_d p_o^{(0)}t \qquad (97)$$

where $k_d = k_{bs}k_{he}k_{ih}/k_{He}(k_{bs} + k_{iH})$. The linear time dependence of the specific product moment $q_s^{(0)}(t)$ is exactly what was derived by a simpler mechanism to describe experimental data (Madras et al., 1996a,b). From Eq. 85 we have

$$p^{(1)}(t) = p_o^{(1)} - x_s k_d p_o^{(0)}t \qquad (98)$$

Applying Eqs. 95, 96 and 97 to 94 followed by integration gives

$$p^{(2)}(t) = p_o^{(2)} + k_d x_s^2 p_o^{(0)} t(1 + k_d t) - 2k_d x_s [p_o^{(1)} t - (k_d/k_{he}) p_o^{(0)}] \quad (99)$$

These results of $p^{(0)}$, $p^{(1)}$, and $p^{(2)}$ are consistent with the corresponding results of McCoy and Madras (1997), except for the term $(k_d/k_{he})p_o^{(0)}$ in Eq. 94. This negligible term arises from the additional radical R_s, which is a transient species given by the conversion of very small amounts of R_e as indicated by Eq. 95.

When $k_{bs} \gg k_{iH}$, the activation energy for degradation corresponds to $E_{he} + E_{ih} - E_{He} \simeq 8 + 8 - 0 = 16$ kcal/mol, since $E_{he} \simeq E_{ih} \simeq 8$ (Kerr and Trotman-Dickenson, 1951) and $E_{He} = 0$ (Lehni et al., 1979). Although the values of activation energies depend on the particular chemical structures, the experimental data corroborate this generally low value for chain-end scission relative to that for random chain scission (30–40 kcal/mol). It should be noted that the radical isomerization, Eq. 63, with a rate constant E_{ih}, is required so that the energy of activation corresponds to observed low values.

Irreversible chain-end addition

Chain-end addition (chain polymerization) in the absence of decomposition ($k_{bs} \ll k_{as}$), according to Eq. 81, can be described by

$$q_s^{(0)}(t) = q_{so}^{(0)} \exp\left[- k_{ps} p_o^{(0)} t \right] \quad (100)$$

where $k_{ps} = (k_{as} k_{he}/k_{He})$ and by Eq. 78

$$p^{(0)}(t) = p_o^{(0)} \quad (101)$$

The monomer concentration decreases exponentially, and the polymer concentration is constant. A convenient substitution (Dotson et al., 1996, p. 109) for time is $d\theta = k_{ps} q_s^{(0)} dt$, which integrates to

$$\theta = \left[1 - \exp\left(- k_{ps} p_o^{(0)} t\right)\right] q_{so}^{(0)}/p_o^{(0)} \quad (102)$$

Then, the first moment expression (Eq. 85) simplifies to

$$p^{(1)}(t) = p_o^{(1)} + x_s p_o^{(0)} \theta \quad (103)$$

The interesting case for the second moment is when $k_{He} \gg k_{as}$, that is, when the radical concentration is small and consistent with QSSA. When Eq. 86 is integrated, one then obtains

$$p^{(2)}(t) = p_o^{(2)} + x_s p_o^{(0)} \theta [2p_o^{\text{avg}} + x_s(\theta + 1)] \quad (104)$$

The time dependence of the polymer variance from Eqs. 103 and 104 can be expressed as

$$p^{\text{var}} = p_o^{\text{var}} + x_s^2 \theta \quad (105)$$

To show the moments are consistent with accepted results, consider the polymer delta distribution initial condition, that is, $p_o^{\text{var}} = 0$, and sufficiently large polymerization time so that $p_o^{\text{avg}} \ll p^{\text{avg}}$. The average and variance are made dimensionless by dividing by x_s and x_s^2, respectively, and are *both* equal to θ. This is a defining property of the Poisson distribution, which is the solution of the difference-differential equation for discrete chain-growth polymerization. If we represent such polymerization without radicals in the mechanism

$$P(x) + Q_s(x_s) \xrightarrow{k_{ps}} P(x + x_s) \quad (106)$$

then the continuous-distribution population balance equation is

$$\partial p/\partial t = - k_{ps} p(x) q^{(0)} + k_{ps} q^{(0)} \int_0^x \delta(x' - x_s) p(x - x') dx' \quad (107)$$

If we define $d\theta$ as above, then integrate over x', we find

$$\partial p/\partial \theta = - p(x) + p(x - x_s) \quad (108)$$

Once can discretize with the integer index $j = x/x_s$, which gives the difference-differential equation that yields the Poisson distribution with mean and variance θ, identical to the continuous-distribution approach. An advantage of the continuous approach is that the moment solution applies when the initial condition for $p(x,t)$ is *any* distribution, whereas the difference-differential equation is usually solved for a delta distribution. Generally, we should expect that the discrete and continuous theories will yield identical results when a large number of components make up the distribution.

An expansion of $p(x - x_s)$ in Eq. 107 as a Taylor series around x leads to a partial differential equation that is an *approximation* to the exact population balance equation (Dotson et al., 1996, page 112). Rather, one should solve the integrodifferential equation itself, either by a moment method, or by the Laplace transformation (Aris and Gavalas, 1966), or by a similarity method (Ziff and McGrady, 1986).

Conclusions

We have demonstrated that the continuous-distribution approach to macromolecular reactions can describe reversible H-abstraction and chain scission. The method allows an understanding of the MWD time evolution to equilibrium, even though the chain-scission rate coefficient cannot be independent of MW for long times as we have assumed. Results are simplified by the long chain-reaction approximation (initiation and termination steps have negligible effect on the rate) and the quasi-steady-state approximation (radical rates of change are vanishingly small). With these assumptions, zeroth, first, and second MW moments have explicit expressions for reversible random chain scission and for reversible chain-end scission. The irreversible random and chain-end scission results agree with experimentally verified rate equations. The results for irreversible step-growth polymerization (reverse of random chain scission) and chain-growth polymerization (reverse of chain-end scission) are also in accord with accepted concepts. The advantage of the continuous, as compared to the discrete, distribution approach is that the moment equations are readily derived from the distribution balance equations for the primary reactions of macromolecules and their radicals.

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