Degradation Kinetics of Polymers in Solution: Dynamics of Molecular Weight Distributions

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Polymer degradation occurs when macromolecular chains are broken under the influence of thermal, mechanical or chemical energy. Chain-end depolymerization and random- and midpoint-chain scission are mechanisms that have been observed in liquid-phase polymer degradation. Here we develop mathematical models, unified by continuous-mixture kinetics, to show how these different mechanisms affect polymer degradation in solution. Rate expressions for the fragmentation of molecular-weight distributions (MWDs) govern the evolution of MWDs. The governing integrodifferential equations can be solved analytically for realistic conditions. Moment analysis for first-order continuous kinetics shows the temporal behavior of MWDs. Chain-end depolymerization yields monomer product and polymer molecular-weight moments that vary linearly with time. In contrast, random- and midpoint-chain scission models display exponential time behavior. The mathematical results reasonably describe experimental observations for polymer degradation. This approach, based on the time evolution of continuous distributions of chain length or molecular weight, provides a framework for interpreting several types of macromolecular degradation processes, particularly how bimodal MWDs can evolve during degradation.

Introduction

Polymeric molecules decompose to smaller constituents under a variety of influences, including thermal and photochemical energy, mechanical stress, and oxidizing agents. Understanding polymer degradation is important not only to learn how to stabilize polymers against decomposition (Hawkins, 1984), but also as a means to characterize polymers by examining their degradation products (Flynn and Florin, 1985). Degradation by chain scission has been used to synthesize telechelic polymers, that is, polymer chains with functional endgroups (Caeter and Goethals, 1995). Plastics recycling is yet another potential application of polymer degradation (Miller, 1994).

Polymer degradation is a fragmentation phenomenon, a fundamental process of great interest in science and engineering. Population-balance equations are often applied in fragmentation models to describe how the frequency distributions of different-size entities, both parent and progeny, evolve. Most mathematical treatments of polymer degradation, however, have considered only average properties of the polymer chain-length distribution or molecular-weight distribution (MWD). The advantage of the population models is that they provide straightforward procedures to derive expressions for the moments of the frequency distributions. The MWD is a partial record of the kinetics and mechanism that influenced its evolution, and contains much more information than the lumped concentration (zero moment). Some population models can be solved directly for the distributions, but more often the moments are computed and then utilized to construct the distribution, as discussed by Laurence et al. (1994) and Dotson et al. (1996) for polymerization. The population balance equations can be written for discrete or continuous MWDs. Continuous kinetics is valid when the MWD allows integrals to represent averages (moments) of the distribution. This approach provides governing integrodifferential equations that can be straightforwardly solved by the moment method.

The typical thermal degradation experimental method is pyrolysis, which has the drawback that interactions between solid, liquid, and gas phases are usually involved, thus leading to experimental and theoretical difficulties (McCoy, 1996). Liquid-phase degradation is simpler to analyze. Some degradation processes are routinely studied in a single-phase liquid solution, for example, oxidation and mechanical degradation (Grassie and Scott, 1985). *Thermal* degradation in liquid phase may require high pressures to prevent solvent vaporization (Wang et al., 1995; Madras et al., 1995, 1996a,b). At temperatures above the polymer-ceiling temperature, where polymerization is thermodynamically limited (Odian, 1991), thermal degradation can be considered irreversible.

Our objective is to develop a unified continuous-kinetics approach to polymer degradation. The treatment focuses on scission in the polymer backbone, which can occur by scission (a) at any bond in the backbone chain (random-chain scission), (b) at the chain midpoint, or (c) at the end of the chain yielding a monomer (chain-end scission). We present several models, including chain-end scission and random- and midpoint-chain scission models. Chain-end scission occurs in certain depolymerization reactions, including thermal decomposition of poly(α-methyl styrene) (Madras et al., 1995). Random-chain scission is characteristic of oxidative degradation reactions (Jellinek, 1955). Midpoint-chain scission dominates in mechanical degradation, for example, by ultrasonic radiation (Price and Smith, 1993). The mathematical models for these scission mechanisms derive from expressions for the stoichiometric coefficient (or kernel) that appears in the integrodifferential population balance equation.

Polymer chain scission can occur by three steps. The initiation step forms radicals. This is followed by depropagation chain reactions (C-C bond cleavage by beta scission) to yield smaller molecular weight (MW) products. The termination step (by recombination, disproportionation, or hydrogen abstraction) neutralizes radicals. Based on the stationary-state assumption for the radical concentrations, one can show that the rate of degradation is first order in polymer concentration, which has been demonstrated experimentally (e.g., Madras et al., 1996a,b).

The MWD as a function of time t can be solved from the batch-reactor population-balance equation, and is identical to the steady-state plug-flow reactor result when t is replaced with residence time. MW moments of the molar MWD provide molar and mass concentrations (zero and first moments), as well as variance and polydispersity of the MWD. Moments provide the essential data about the process behavior, and are used to construct the complete distributions as a function of molecular weight (or chain length). During some degradation processes the MWD displays a *bimodal* shape (Florea, 1993; Price and Smith, 1991), and the current study shows how the MWD can pass from unimodal to bimodal character.

Continuous Kinetics of Chain Scission

Chain-end scission of homopolymer, by definition, occurs when scission produces a monomer and a polymer of MW reduced by the monomer MW. This is different from the cases when chain scission occurs either randomly along the chain or precisely at the chain midpoint. All distributions of degradation products can be described by a stoichiometric coefficient in an integral expression. As shown by McCoy and Wang (1994), the two cases of random- or midpoint-chain scission are extremes of a continuum of possible scission events. To describe experimental results for thermal degradation of the copolymer poly(styrene allyl alcohol), Wang et al. (1995) developed a model combining random-chain and chain-end scission events. The current treatment of chain-end scission is similar, but the Wang et al. (1995) derivation for random-chain scission utilized a single MWD and could not predict bimodal MWDs.

We consider polymer degradation in solution, thus simplifying the system to a single liquid phase. We assume that the rate coefficient for chain scission is independent of MW. Although we limit the discussion to homopolymers, Wang et al. (1995) showed how copolymers can be treated. MWDs of reactants and products often can be monitored experimentally, for example, by gel-permeation chromatography. The time-dependent MWD, denoted $p(x,t)$, is defined so that $p(x,t)\,dx$ is the molar concentration of polymer in the MW range $(x, x+dx)$. It is useful to distinguish the reactant and product MWDs by writing separate governing differential equations for their behavior (McCoy and Wang, 1994). For binary scission where the rate coefficient, k, is independent of x, the products of a binary fragmentation reaction (Aris and Gavalas, 1966) are governed by

$$R(x) = 2k\int_x^\infty \Omega(x,x')p(x',t)dx'. \tag{1}$$

The stoichiometric term $\Omega(x,x')$ represents a reaction in which a molecule fragments into two product molecules whose sizes, x and $x'-x$, sum to the reactant size, $x' \geq x$. The stoichiometric coefficient (or fraction) is defined to satisfy normalization and symmetry conditions,

$$\int_o^{x'} \Omega(x,x')\,dx = 1 \tag{2}$$

and

$$\Omega(x,x') = \Omega(x'-x,x'). \tag{3}$$

A general expression for the stoichiometric coefficient (McCoy and Wang, 1994),

$$\Omega(x,x') = x^m(x'-x)^m\Gamma(2m+2)/[\Gamma(m+1)^2(x')^{2m+1}] \tag{4}$$

is plotted for integer and noninteger values of m in Figure 1 for $x \leq x'$. Other forms were proposed by McGrady and Ziff (1988) and Ziff and McGrady (1985, 1986). When $m=1$ the expression reduces to the quadratic form used by Prasad et al. (1986) for coal thermolysis and by Ziff and McGrady (1986) for polymer degradation,

$$\Omega(x,x') = 6x(x'-x)/x'^3. \tag{5}$$

When $m=0$, the products are evenly distributed along all $x \leq x'$,

$$\Omega(x,x') = 1/x' \tag{6}$$

and the expression (Aris and Gavalas, 1966) is the totally random kernel. As $m \to \infty$, the stoichiometric coefficient describes scission that occurs at the chain midpoint,

$$\Omega(x,x') = \delta(x - x'/2). \tag{7}$$

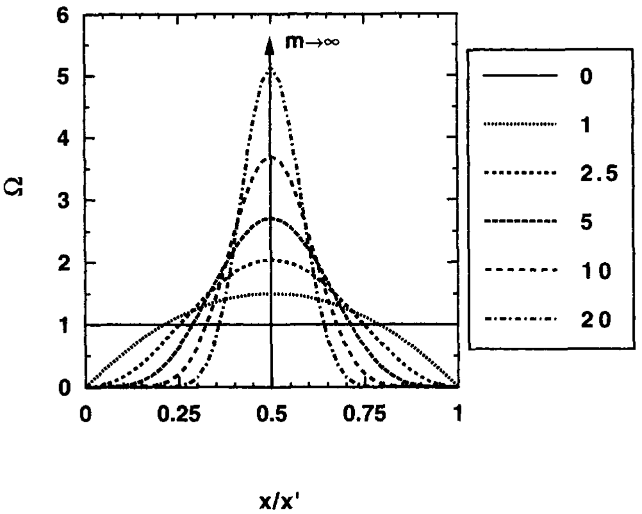

Figure 1. Stoichiometric coefficient, Eq. 4, for several values of *m*.

Random-chain scission is represented by $m = 0$, and midpoint-chain scission by $m \to \infty$.

Subsequent scissions can be accounted, as shown below, by multiple scission events occurring in sequence.

The moments of the MWDs are defined as the integrals over the MW, x,

$$p^{(n)}(t) = \int_0^\infty p(t,x)x^n \, dx. \tag{8}$$

The zero moment ($n = 0$) is the time-dependent total molar concentration (mol/volume) of the polymer. The first moment, $p^{(1)}(t)$, is the mass concentration (mass/volume). The normalized first moment (average MW) and the second central moment (variance of the MWD) are given, respectively, by

$$p^{\text{avg}} = p^{(1)}/p^{(0)} \tag{9}$$

and

$$p^{\text{var}} = p^{(2)}/p^{(0)} - [p^{\text{avg}}]^2. \tag{10}$$

The three moments, $p_j^{(0)}$, p_j^{avg}, and p_j^{var}, provide the shape characteristics of the jth MWD. These values are essential, and frequently sufficient, to represent the MWD. 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,

$$D = p^{(2)}p^{(0)}/[p^{(1)}]^2. \tag{11}$$

The gamma (Pearson type III) distribution function in terms of $y_j = (x - x_{sj})/\beta_j$ is a versatile representation of naturally distributed systems (e.g., Cotterman et al., 1985; Wang et al., 1994), and is chosen to represent the MWDs,

$$p_j(x) = p_j^{(0)} \exp(-y_j) y_j^{\alpha_j - 1}/[\beta_j \Gamma(\alpha_j)] \qquad \text{for } x \ge x_{sj} \tag{12}$$

and $p(x \le x_{sj}) = 0$. The mean and variance are given by

$$p_j^{\text{avg}} = x_{sj} + \alpha_j \beta_j \qquad \text{and} \qquad p_j^{\text{var}} = \alpha_j \beta_j^2. \tag{13}$$

The value of β_j strongly affects the variance. If $\alpha_j = 1$ and $x_{sj} = 0$, then the MWD is an exponential distribution. If $\beta_j = 1$ and $x_{sj} = 0$, then α_j is the parameter in the Poisson distribution.

Depolymerization by Chain-End Scission

During chain-end-scission degradation of polymers to form monomers of MW x_m, polymer molecules of MW x' are consumed while polymers of MW $(x' - x_m)$ are produced,

$$dp(x,t)/dt = -k\,p(x,t) + k\int_x^\infty p(x',t)\delta[x - (x' - x_m)] \, dx'. \tag{14}$$

The stoichiometric coefficient, $\delta[x - (x' - x_m)]$, ensures that a product has MW $x = (x' - x_m)$, and that $x' \ge x$ is valid in the interval of integration. With the initial condition

$$p(x,t=0) = p_0(x) \tag{15}$$

the time evolution of the polymer MWD can be developed by the moment method.

The moment operation, applied to Eq. 14 and interchanged with the time derivative, yields ordinary differential equations for moments. The integration of order of x and x' for the term on the righthand side of Eq. 14 is interchanged (Himmelblau and Bischoff, 1968) so that

$$\int_0^\infty dx' \, p(x',t) \int_0^{x'} dx \, x^n \delta[x - (x' - x_m)] = \int_0^\infty dx' \, (x' - x_m)^n p(x',t) \tag{16}$$

The differential equation for the moments $p^{(n)}(t)$, in terms of the binomial coefficient $\binom{n}{j} = n!/(n-j)!j!$, becomes

$$dp^{(n)}/dt = -k\,p^{(n)} + k\sum_{j=0}^{n} (-1)^{n-j}\binom{n}{j} x_m^{n-j} p^{(j)} \tag{17}$$

with initial conditions, $p^{(n)}(t=0) = p_0^{(n)}$. The equation for any nth moment in general depends on all lower moments $p^{(j)}$, $0 \le j < n$.

For the zero moments ($n = 0$) we have

$$dp^{(0)}/dt = 0 \qquad \text{or} \qquad p^{(0)}(t) = p_0^{(0)}. \tag{18}$$

Each scission event creates a monomer and a replacement polymer, thus the molar concentration of *polymer* is constant. The equation for the first moment ($n = 1$) is

$$dp^{(1)}/dt = -k\,x_m p^{(0)}, \tag{19}$$

which has the solution

$$p^{(1)}(t) = p_0^{(1)} - x_m p_0^{(0)} kt \tag{20}$$

in terms of the initial first and zero moments, $p_0^{(1)}$ and $p_0^{(0)}$. The polymer mass concentration decreases linearly in time with rate $k\,x_m p_0^{(0)}$. The average MW decreases linearly with time according to

$$p^{\text{avg}}(t) = p_0^{\text{avg}} - x_m kt. \tag{21}$$

The degradation is complete (conversion is 100% for irreversible degradation) when the polymer mass reaches zero, that is, when

$$t_f = p_0^{\text{avg}}/k\,x_m, \tag{22}$$

where $p_0^{\text{avg}} \gg x_m$ for a high MW polymer. The second moment equation,

$$dp^{(2)}/dt = k\,x_m^2 p^{(0)} - 2k\,x_m p^{(1)} \tag{23}$$

has the solution

$$p^{(2)}(t) = p_0^{(2)} + x_m^2 p_0^{(0)} kt(1+kt) - 2x_m p_0^{(1)} kt. \tag{24}$$

One can show that the variance of the MWD thus increases linearly with $t(\le t_f)$,

$$p^{\text{var}}(t) = p_0^{\text{var}} + x_m^2 kt. \tag{25}$$

The *monomer* MWD, $q(x,t)$, obeys a balance equation with an accumulation and a generation term,

$$dq(x,t)/dt = k\int_x^{\infty} p(x',t)\,\delta(x-x_m)\,dx' \tag{26}$$

and the initial condition, $q(x,t=0)=0$. When the order of integration over x' and x is reversed, the moment equation can be written

$$dq^{(n)}/dt = k\int_0^{\infty} dx'\; p(x',t)\int_0^{x'} dx\, x^n\delta(x-x_m) = k\,x_m^n p^{(0)}. \tag{27}$$

The solution for any moment is simply

$$q^{(n)}(t) = x_m^n p_0^{(0)} kt. \tag{28}$$

Thus the monomer molar concentration increases linearly with time $(t \le t_f)$,

$$q^{(0)}(t) = p_0^{(0)} kt. \tag{29}$$

The mass concentration also increases linearly with time,

$$q^{(1)}(t) = x_m p_0^{(0)} kt, \tag{30}$$

so that the MW of the monomer is constant,

$$q^{\text{avg}}(t) = q^{(1)}(t)/q^{(0)}(t) = x_m. \tag{31}$$

The sum of $p^{(1)}(t)$ and $q^{(1)}(t)$ is the total mass, which is constant and equal to the initial polymer mass, $p_0^{(1)}$, confirming that the equations are consistent. The variance of the monomer MWD is always zero, and thus the monomer MWD can be written as the Dirac delta function,

$$q(x,t) = q^{(0)}(t)\,\delta(x-x_m). \tag{32}$$

The time dependence of all moments is manifested through the dimensionless variable, kt, where $t \le t_f$.

Some of the results in this section for chain-end scission can be derived with a discrete model beginning with a polymer of single MW (Madras et al., 1996b) and using summations to formulate the moments. The continuous approach easily allows consideration of an initial *distribution* of reactant polymers. The interpretation of experimental MWDs for degradation of such polymers (Wang et al., 1995; Madras et al., 1996a,b) requires a model based on distributions.

Polymer Degradation by Chain Scission

The preceding chain-end scission model is based on the premise that product monomer can be distinguished from polymer. For example, gel-permeation chromatography analysis displays a narrow peak for monomer products that is distinct from the polymer (Madras et al., 1996a,b). The moment approach yields separate moments, and thus separate peaks, for monomer and polymer. For chain scission of a polymer, however, the products of the scission are two polymers that are not in general distinguishable from the reactant polymer. A moment theory that utilizes only the lower ($n = 0$, 1, 2) moments (e.g., Wang et al., 1995) could be used to reconstruct an evolving unimodal MWD, but not one that becomes bimodal unless the reactant polymer is separate from the product polymer. Bimodal MWDs have been observed for mechanical degradation of polymer (Price and Smith, 1991). Calculating higher moments and using them in a Gram–Charlier series to construct complex MWDs could potentially yield bimodal features. The convergence, however, of such series is slow, and many terms (and higher moments) would be needed for reliable results. A model is next developed, therefore, that allows the *reactant* polymer to be described by its moments, and the *products* of chain scission to be described by another set of moments. Each set of moments specifies a MWD whose sum can be either unimodal or bimodal. The basis for the development is further discussed in McCoy and Wang (1994).

Degradation with r scissions in sequence can be represented as (McCoy and Wang, 1994)

$$\begin{aligned}
&x_1 \rightarrow (x_1 - x_2) + x_2\\
&x_2 \rightarrow (x_2 - x_3) + x_3\\
&\vdots\\
&x_{r-1} \rightarrow (x_{r-1} - x_r) + x_r
\end{aligned}$$

or as

$$x_1 \rightarrow (x_1 - x_2) + (x_2 - x_3) + \cdots + (x_{r-1} - x_r) + x_r \tag{33}$$

when all rate constants are equal. The symmetry of $\Omega(x,x')$ (Eq. 3) ensures that either binary-scission product can further react. The governing balance equations can be written for $j = 0, 1, 2, \ldots, r-1$ (with $k_0 = k_r = 0$)

$$dp_{j+1}/dt = 2\int_{x_{j+1}}^{\infty} k_j \Omega(x_{j+1}, x_j) p_j \, dx_j - k_{j+1} p_{j+1}. \tag{34}$$

Since $k_r = 0$, the differential equation for $j = r-1$ is

$$dp_r/dt = 2\int_{x}^{\infty} k_{r-1} \Omega(x_r, x_{r-1}) p_{r-1} \, dx. \tag{35}$$

The moment equations are ordinary differential equations, from which sequential solutions can be developed for any value of $j+1$ from 1 to r.

The moment operation applied to the term involving $\Omega(x, x')$ deserves attention. Substituting the general expression 4 and interchanging x and x' in the integration, yields

$$2k\int_0^{\infty} dx' \, p(x',t) x'^{-(2m+1)} \int_0^{x'} dx \, x^{n+m} (x'-x)^m \Gamma(2m+2)/\Gamma(m+1)^2 = 2k p^{(n)}(t) Z_{nm}. \tag{36}$$

After expanding $(x'-x)^m$ as a binomial sum, we defined

$$Z_{nm} = [\Gamma(2m+2)/\Gamma(m+1)^2] \sum_{j=0}^{m} (-1)^{m-j} \tbinom{m}{j} / (2m+n-j+1) = \Gamma(2m+2)\Gamma(m+n+1)/[\Gamma(m+1)\Gamma(2m+n+2)], \tag{37}$$

which can be proved by mathematical induction. Some values of Z_{nm} are summarized in Table 1. For $n = 0$ or 1, $Z_{nm} = 1$ or 1/2, respectively, for all m. The limiting values for the second moments ($n = 2$) are $Z_{n0} = 1/3$ and $Z_{n\infty} = 1/4$. The difference between random- and midpoint-chain scission mechanisms is observed, therefore, for the *second moment*, but not for zero and first moments, and is indicated by the value of Z_{nm}.

For the batch reactor the moment equations are

$$dp_1^{(n)}/dt = -kp_1^{(n)} \tag{38}$$

Table 1. Values of Z_{nm}, Defined in Eq. 37*

$n\backslash m$	0	1	2	…	∞
0	1	1	1	…	1
1	1/2	1/2	1/2	…	1/2
2	1/3	3/10	2/7	…	$1/2^2$
3	1/4	1/5	5/28	…	$1/2^3$

*n denotes the nth moment, and $m = 0$ and $m \rightarrow \infty$ represent random and midpoint chain scission, respectively.

$$dp_i^{(n)}/dt = -kp_i^{(n)} + p_{i-1}^{(n)} 2kZ_{nm} \qquad i = 2, \ldots, r-1 \tag{39}$$

and

$$dp_r^{(n)}/dt = p_{r-1}^{(n)} 2kZ_{nm}, \tag{40}$$

with initial conditions

$$\begin{aligned} p_1^{(n)}(t=0) &= p_0^{(n)} \\ p_i^{(n)}(t=0) &= 0 \qquad \text{for } i > 1. \end{aligned} \tag{41}$$

The differential equations have the solutions

$$p_1^{(n)} = p_0^{(n)} \exp(-kt) \tag{42}$$

for the reactant polymer, which leads to values of average, variance, and polydispersity that are constants, and equal to their initial values (McCoy and Wang, 1994). Furthermore, if the initial MWD is a gamma distribution, then the *reactant* polymer $p_1(x,t)$ is always a gamma distribution.

For $r = 2$ (two scissions in the sequence) the product properties are simply related to the reactant properties, that is, x_{avg}, x_s, β, are one-half the reactant values. The value of α is constant. When the reactant molar concentration is normalized as $p^{(0)}(t)/p_0^{(0)}$, the similarly normalized product molar concentration increases to final values of 2 or 4 for $r = 2$ or 3, respectively.

The moments (McCoy and Wang, 1994) of intermediate product polymers are given by the solution to Eq. 39. Using q instead of p as the symbol for product polymer, we have

$$q_i^{(n)} = p_0^{(n)} e^{-kt} (2ktZ_{nm})^{i-1}/(i-1)!, \tag{43}$$

which all achieve a maximum and then vanish as t becomes very large. For the terminal scission ($i = r$) we have the following sequence:

$$\begin{aligned} q_{r=2}^{(n)} &= p_0^{(n)} 2Z_{nm}(1 - e^{-kt}) \\ q_{r=3}^{(n)} &= p_0^{(n)} (2Z_{nm})^2 [1 - (1 + kt)e^{-kt}]. \\ &\vdots \end{aligned} \tag{44}$$

The moments of *all* products of scission can be calculated as the sum

$$q^{(n)}(t) = \sum_{j=2}^{r} q_j^{(n)}(t). \tag{45}$$

All polymer moments are proportional to the initial polymer moments, so results can be scaled (and made dimensionless) by dividing by $p_0^{(n)}$. The exponential time behavior of chain scission degradation stands in contrast to the linear behavior of moments for chain-end scission.

Limiting values of the product moments as $t \rightarrow \infty$ are especially useful. For the zero moment, we have

$$q^{(0)}(t \rightarrow \infty) = p_0^{(0)} 2^{r-1}/(r-2)!, \tag{46}$$

indicating that (independent of m) the amount of final product is double the moles of reactant when $r = 2$, and quadruple the moles of reactant when $r = 3$. For the first moment,

$$q^{(1)}(t \to \infty) = p_0^{(1)}, \tag{47}$$

indicating that the mass of final product equals the mass of initial reactant, independent of m. The average MW of products, x_{avg}, is the ratio of the first to the zero moment, showing that for a single scission ($r = 2$) x_{avg} is half the initial value of x_{avg}. After double scission ($r = 3$), x_{avg} is 1/4 its initial value. As the number of scissions in a sequence is simply related to the ratio, $(r-2)!/2^{r-1}$, of the final to the initial average MW, this provides a way to determine the value of r. Similar reasoning indicates that the final smallest value of MW in the gamma MWD is given in terms of its initial value, x_0, by $x_0(r-2)!/2^{r-1}$.

The degradation process proceeds until termination of the reaction, usually occurring when the product molecules have reached a certain MW determined by the scission mechanism or available energy. At a sufficiently high temperature, some thermal degradation processes may last until only monomers remain. Mechanical scission will end when the average MW has reached a limiting value determined by the mechanical energy input, or ultrasonic intensity (Price and Smith, 1993). The value of r is thus a measure of the extent of reaction, providing the average number of scissions undergone by a polymer molecule.

The sequence, Eq. 33, of scission processes for $p_i(x,t)$ can be extended indefinitely for identical rate coefficients, k. The superposition of these governing equations is equivalent to the single-MWD model (McCoy and Wang, 1994). The MWD

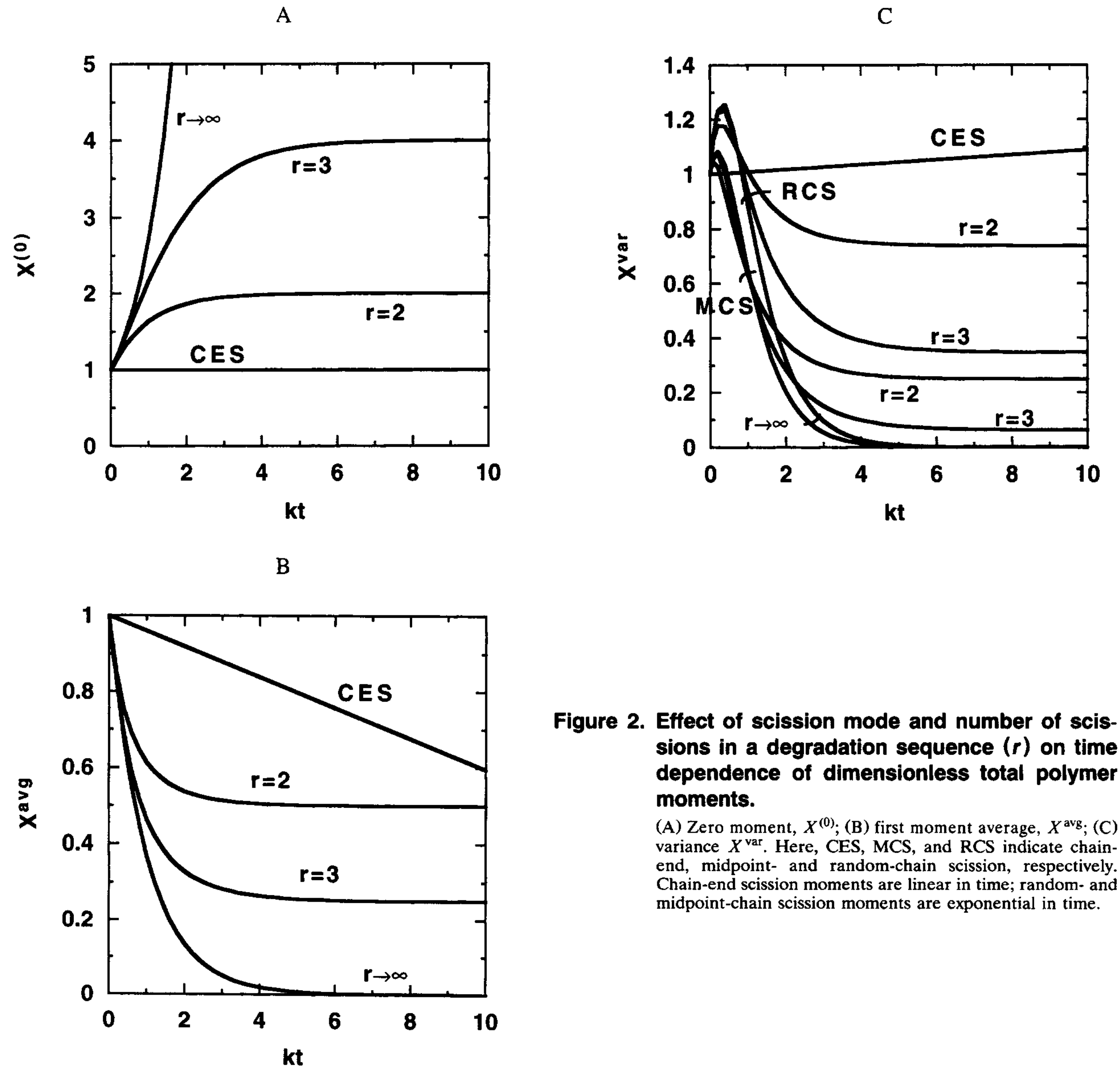

Figure 2. Effect of scission mode and number of scissions in a degradation sequence (r) on time dependence of dimensionless total polymer moments.

(A) Zero moment, $X^{(0)}$; (B) first moment average, X^{avg}; (C) variance X^{var}. Here, CES, MCS, and RCS indicate chain-end, midpoint- and random-chain scission, respectively. Chain-end scission moments are linear in time; random- and midpoint-chain scission moments are exponential in time.

$p_1(x,t)$ represents the reactant MWD at any time, while the sum of the other MWDs (from $j=2$ to ∞) refers to the polymer product, whose MWD can be defined as

$$q(x,t)=\sum_{j=2}^{\infty} p_j(x,t). \tag{48}$$

For the product polymers the moments $p_i^{(n)}$ are given by Eq. 43, which when summed from $i=2$ to ∞ yield

$$q^{(n)}=p_0^{(n)}\exp(-kt)[\exp(2Z_{nm}kt)-1], \tag{49}$$

valid for all values of $Z_{nm}kt$. The accuracy of the approximation was shown to be satisfactory except at very large or small values of time (McCoy and Wang, 1994). Small deviations from the exact MWD were due to the gamma MWD, which may not describe the actual MWD accurately over the entire range of t. As in the chain-end scission model, time dependence of the moments for random- and midpoint-chain scission is dimensionless through kt.

As reasoned by Grassie and Scott (1985), the inverse of average polymer chain length varies linearly with time over an initial range. The expression for average chain length in our notation is proportional to the average MW of the total polymer mixture, or $(p_1^{(1)}+q^{(1)})/(p_1^{(0)}+q^{(0)})$. Initially, the average MW is $p_0^{(1)}/p_0^{(0)}$. According to Grassie and Scott (1985), the difference of the inverses, $\lambda(t)$, should vary linearly with time,

$$\lambda(t)=(p_1^{(0)}+q^{(0)})/(p_1^{(1)}+q^{(1)})-p_0^{(0)}/p_0^{(1)}. \tag{50}$$

Substituting our expressions for the moments yields the simple expression

$$\lambda(t)=(e^{kt}-1)/p_0^{\text{avg}}\cong kt/p_0^{\text{avg}} \tag{51}$$

for $kt \ll 1$. In Figure 2.6 of Grassie and Scott (1985) the largest value of kt is less than 0.01, justifying the approximation. Thus the defined quantity, $\lambda(t)$, initially does indeed increase linearly with t. Further experimental confirmation of the chain-scission model was provided by Wang et al. (1995) and Madras et al. (1995).

To summarize, we note that the single MWD model can be replaced by an infinite cascade of sequential binary scission events. While the sequence mathematically yields products of infinitesimal size ($x \to 0$) after an infinitely long time, in reality the degradation stops when termination conditions for the particular process are met and the sequence is terminated. For the uniform rate constant the sequence shows behavior in agreement with the single MWD description (McCoy and Wang, 1995). The sequence representation has the benefit of allowing a moment procedure to be applied to the separate reactant and product MWDs. The peaks that are constructed by means of the zero, first, and second moments are good approximations to the MWD solution.

Results

We illustrate the degradation models by calculations showing how MWDs and their moments evolve in time. Values of the parameters used in the calculations are based on Wang et al. (1995): $\alpha_0=1.7$, $\beta_0=850$, $x_0=1{,}000$, $p_0^{(0)}=1/2{,}000$ mol/L for the initial gamma MWD. The MW of the smallest product of degradation (the monomer) is x_m ($=100$, the MW of methyl methacrylate) and is very small relative to the MWs of most polymers. The derived expressions can all be cast into dimensionless form to reduce the number of parameters that must be specified, for example, dimensionless kt. The total polymer MWD can be monitored as a function of time by gel-permeation chromatography of samples from the polymer mixture. The total polymer MWD for chain scission is $p_{\text{tot}}(x,t)=p_1(x,t)+q(x,t)$, and for chain-end scission, $p(x,t)$, because the monomer product can be distinguished from the polymer reactant. The total moments are made dimensionless by defining

$$X^{(0)}=p_{\text{tot}}^{(0)}/p_0^{(0)} \;=[p^{(0)}+q^{(0)}]/p_0^{(0)} \tag{52}$$

$$X^{\text{avg}}=p_{\text{tot}}^{\text{avg}}/p_0^{\text{avg}}=[p^{(1)}+q^{(1)}]p_0^{(0)}/\{[p^{(0)}+q^{(0)}]p_0^{(1)}\} \tag{53}$$

$$X^{\text{var}}=p_{\text{tot}}^{\text{var}}/p_0^{\text{var}}=\left[p_{\text{tot}}^{(2)}/p_{\text{tot}}^{(0)}-(p_{\text{tot}}^{\text{avg}})^2\right]/p_0^{\text{var}}. \tag{54}$$

For chain-end scission and for random- and midpoint-chain scission, Figure 2 displays the time dependence of these moments. For Figure 2A, we used Eq. 18 for chain-end scission and Eqs. 42–45 for various values of r in conjunction with Eq. 52. For Figure 2B, we used Eq. 21 for chain-end scission and Eqs. 42–45 for various values of r in conjunction with Eq. 53. For Figure 2C, we used Eq. 25 for chain-end scission and Eqs. 42–45 for various values of r in conjunction with Eq. 54. For chain-end scission the moments are linear in t, and for random- and midpoint-chain scission, the moments behave exponentially.

The polydispersity, D, Eq. 11, is graphed in Figure 3 as a function of time for various cases. As r increases, D increases because smaller MW products are formed by chain scission.

Figures 4A, 4B, 4C show the effect of scission mechanism and the stoichiometric coefficient parameter m on the time

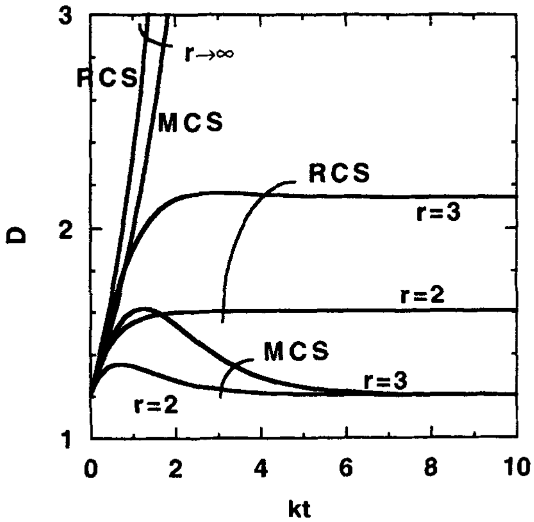

Figure 3. Time evolution of the polydispersivity.

Here, CES, MCS, and RCS indicate chain-end, midpoint- and random-chain scission, respectively.

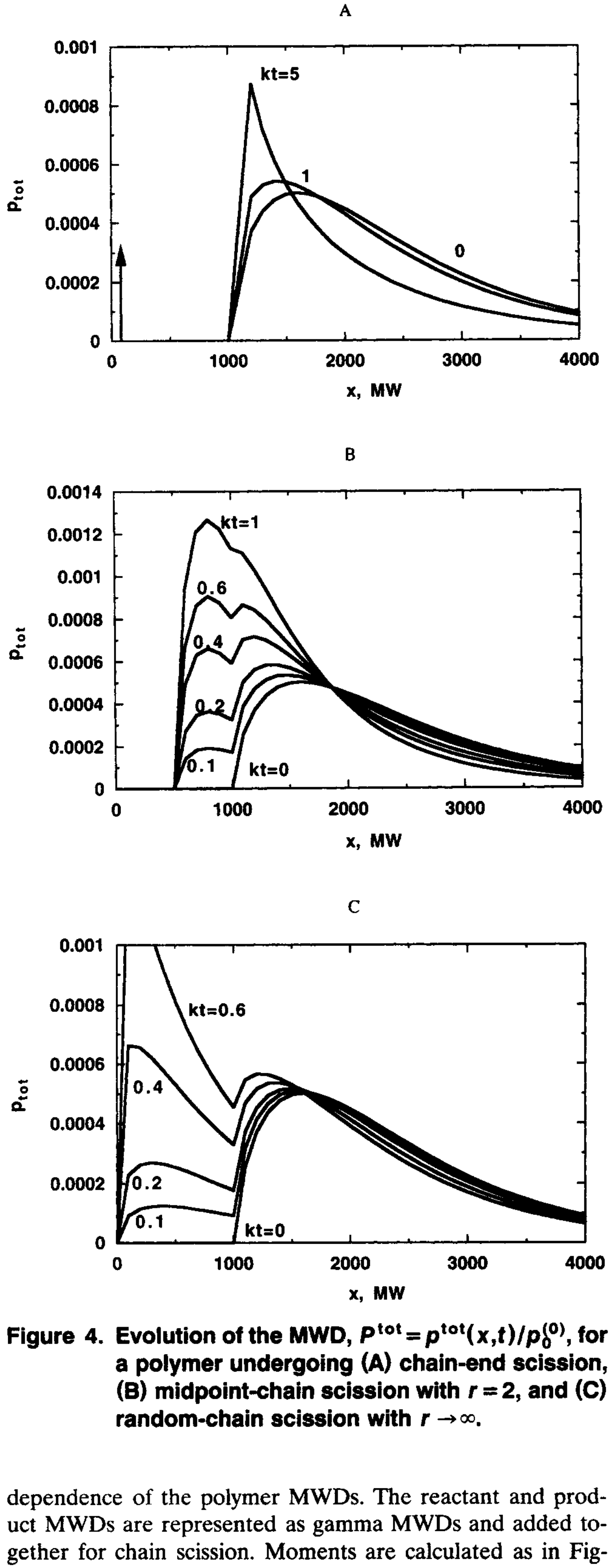

Figure 4. Evolution of the MWD, $P^{tot}=p^{tot}(x,t)/p_0^{(0)}$, for a polymer undergoing (A) chain-end scission, (B) midpoint-chain scission with $r=2$, and (C) random-chain scission with $r \rightarrow \infty$.

dependence of the polymer MWDs. The reactant and product MWDs are represented as gamma MWDs and added together for chain scission. Moments are calculated as in Figures 2A, 2B, 2C. The sum of $p_1(x,t)$ and $q(x,t)$ is the total molar MWD, $p_{tot}(x,t)$, which is related to the mass MWD measured by gel permeation chromatography. The dimensionless MWD is plotted as $p_{tot}(x,t)/p_0^{(0)}$. Bimodal distributions are evident for all the scission modes. Chain-end scission (Figure 4A) yields a product monomer that is represented as a delta function growing in time at $x=100$. The polymer MWD decreases with time. When time approaches its final value, t_f, the polymer is entirely consumed and converted to monomer. Midpoint-chain scission with $r=2$ (Figure 4B), and random-chain scission with $r \rightarrow \infty$ (Figure 4C) yield product distributions that increase nonlinearly with time.

The results of the moment analysis of the governing integrodifferential equations for the MWDs of degrading polymers have obvious implications for data interpretation. Monitoring the time dependence of the MWDs and their moments provides considerable information beyond the molecular-weight averages that are typically measured. Such data allows a sharper interpretation of the kinetics and mechanism of the degradation reactions. For real polymers and mixtures of polymers, the mechanisms discussed in this article can be readily combined.

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Notation

m = parameter in stoichiometric coefficient expression, $\Omega(x, x')$
$p_0(x,t)$ = initial molecular weight distribution (MWD) of polymer
y = dimensionless molecular weight in the gamma distribution
α_i = parameter in the gamma distribution
β_i = width parameter in the gamma distribution
$\delta(x)$ = Dirac delta function of x

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