Degradation Kinetics of Polymers in Solution: Time-Dependence of Molecular Weight Distributions

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Abstract

Polymer degradation occurs when polymer 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 the MWDs. The governing integro-differential 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 portray 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 polymer degradation processes.

Keywords: polymer degradation, depolymerization, continuous kinetics, molecular weight distributions, thermal decomposition, moments of molecular weight.

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, i.e., polymer chains with functional endgroups (Caeter and Goethals, 1995). Plastics recycling is yet another potential application of polymer degradation (Miller, 1994).

In the simplest conceptual approach, polymer degradation is a fragmentation phenomenon, a fundamental process long of interest to physicists and engineers. Population-balance integrodifferential equations are usually applied in fragmentation models to describe how the frequency distributions of different-sized 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). An approach to free-radical polymerization, similarly based on MWDs, was recently promoted by Clay and Gilbert (1995). 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 advocated by Laurence et al. (1994) for polymerization.

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). The outlook we propose here is that progress in basic understanding of polymer degradation kinetics can be

made by considering liquid-phase degradation. Some degradation processes are routinely studied in a single phase as liquid solution, for example, oxidation and mechanical degradation (Grassie and Scott, 1985). *Thermal* degradation in liquid phase requires high pressures to prevent vaporization (Wang et al., 1995; Madras et al., 1995, 1996a,b).

Our objective is to exploit a population-balance, or 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, e.g., by ultrasonic radiation (Price and Smith, 1993). The mathematical models for these scission mechanisms derive from distinctive expressions for the stoichiometric coefficient (or kernel) that appears in the integro-differential population balance equation.

We limit this study to decomposition processes controlled by polymer-backbone bond scission. For example, chain-end scission of a polymer can occur by three steps. The first step is initiation, where the polymer degrades into two radicals by breakage of the C-C bond in the β-position. This is followed by depropagation to yield the monomer. The termination step is either by disproportionation or recombination. Based on the stationary-state assumption for the radical concentrations, one can show that the rate of degradation is first-order in polymer concentration.

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 polydispersivity of the

MWD. The moments provide the essential data about the process behavior, but the time evolution of the complete distributions as a function of molecular weight (or chain length) also adds useful information. For example, during some degradation processes the MWD displays a *bimodal* shape (Florea, 1993; Price and Smith, 1991), which the lower moments may not reveal. The current study shows how the MWD can pass from unimodal to bimodal character.

Continuous Kinetics of Chain Scission

Polymer degradation can occur by several modes of chain scission. Chain-end scission of a homopolymer, by definition, occurs when scission produces a monomer and a polymer of molecular weight (MW) reduced by the monomer MW. This yields behavior different from the cases when chain scission occurs either randomly along the chain or precisely at the chain midpoint. For these mechanisms the consequent distributions of degradation products are 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.

Here we consider polymer degradation in solution, thus simplifying the system to a single liquid phase. We consider 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. We assume that molecular weight distributions (MWDs) of reactants and products can be monitored experimentally, e.g., 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

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

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'. 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 is (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 various values of m in Figure 1. When m = 1 the expression reduces to the quadratic form used by Prasad et al. (1986) for coal thermolysis,

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

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

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

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,

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

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,

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

The zero moment (n = 0) is the time-dependent total molar concentration (mol/vol) 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

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

and

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

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 polydispersivity 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, $M_n = p^{avg}$, 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., Darivakis et al., 1990; Wang et al., 1994), and is chosen to represent the MWDs,

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

and $p(x \leq x_{sj}) = 0$. The mean and variance are given by (Abramowitz and Stegun, 1968)

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

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 thus that $x' \geq x$ is valid in the interval of integration. With the initial condition

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

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 order of x and x' for the term on the rhs of Eq (14) is interchanged so that

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

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

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

with initial conditions, $p^{(n)}(t = 0) = p_o^{(n)}$ For the zero moments (n = 0) we have

$$dp^{(0)}/dt = 0 \quad \text{or} \quad p^{(0)}(t) = p_o^{(0)} \qquad (18)$$

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

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

which has the solution

$$p^{(1)}(t) = p_o^{(1)} - x_m\, p_o^{(0)}\, k\, t \qquad (20)$$

in terms of the the initial first and zero moments, $p_o^{(1)}$ and $p^{(0)}$. This shows that the polymer mass concentration decreases linearly in time with rate $kx_m p_o^{(0)}$. The average MW decreases with time according to

$$p^{avg}(t) = p_o^{avg} - x_m\, k\, t \qquad (21)$$

The degradation is complete (conversion is 100 percent) when the polymer mass approaches zero, i.e., when

$$t_f = p_o^{avg} / k\, x_m \qquad (22)$$

where $p_o^{avg} >> x_m$ for a high MW polymer. The second moment equation,

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

has the solution

$$p^{(2)}(t) = p_o^{(2)} + x_m^2\, p_o^{(0)}\, k\, t\, (1 + k\, t) - 2\, x_m\, p_o^{(1)} k\, t \qquad (24)$$

One can show that the variance of the MWD thus increases linearly with t,

$$p^{var}(t) = p_o^{var} + x_m^2 k t \tag{25}$$

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, $q(x,t = 0) = 0$. The moment equation can be written

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

The solution for any moment is simply

$$q^{(n)}(t) = x_m^n\, p_o^{(0)}\, k t \tag{28}$$

Thus the monomer molar concentration increases linearly with time,

$$q^{(0)}(t) = p_o^{(0)}\, k t \tag{29}$$

The mass concentration also increases linearly with time,

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

so that the MW of the monomer is constant,

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

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

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

We note that the time dependence of all moments is manifested through the dimensionless variable, kt.

Some of the results in this section for chain-end scission can be derived with a discrete model beginning with a polymer of given MW (Madras et al., 1996b) and using summations to formulate the moments. An advantage of the continuous approach is that it allows consideration of the more realistic 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 reactant polymer is separate from 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)

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

or as

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

when all rate constants are equal. The governing balance equations can be written for j = 0, 1, 2, ... , r-1 (with $k_o = k_r = 0$)

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

Since $k_r = 0$ the last differential equation 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

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

where, after expanding $(x' - x)^m$ as a binomial sum, we define

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

Some values of Z_{nm} are summarized in Table I. For n = 0 and 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, thus, only for the *second moment.*

For the batch reactor the moment equations are

$$dp_1^{(n)}/dt = -k p_1^{(n)} \tag{38}$$

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

and

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

with initial conditions

$$p_1^{(n)}(t = 0) = p_o^{(n)}$$
$$p_i^{(n)}(t = 0) = 0 \qquad \text{for } i > 1 \tag{41}$$

The differential equations have the solutions

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

for the reactant polymer, which leads to values of average, variance, and polydispersivity 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, i.e., 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 $p^{(0)}(t) / p_o^{(0)}$, the 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

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

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

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

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 $p_o^{(n)}$. 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

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

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,

$$q^{(1)}(t \rightarrow \infty) = p_o^{(1)} \quad (47)$$

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_o, by $x_o(r-2)!/2^{r-1}$.

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 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 $p_1(x,t)$ 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

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

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

$$q^{(n)} = p_o^{(n)} \exp(-kt) (\exp(2Z_{nm} k t) - 1) \quad (49)$$

valid for all values of $Z_{nm} k t$. 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 use of 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 $p_o^{(1)}/p_o^{(0)}$. According to Grassie and Scott, the difference of the inverses, λ(t), should vary linearly with time,

$$\lambda(t) = (p_1^{(0)}+q^{(0)})/(p_1^{(1)}+q^{(1)}) - p_o^{(0)}/p_o^{(1)} \quad (50)$$

Substituting our expressions for the moments yields the simple expression

$$\lambda(t) = (e^{kt} - 1)/p_o^{avg} \cong kt /p_o^{avg} \quad (51)$$

for kt << 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, λ(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 ($x \rightarrow 0$) 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): $\alpha_o = 1.7$, $\beta_o = 850$, $x_o = 1000$, $p_o^{(0)} = 1/2000$. 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, rather than plot time as t, it is convenient to use 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 $p_{tot}(x,t) = p_1(x,t) + q(x,t)$, 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

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

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

$$X^{var} = p_{tot}^{var} / p_o^{var} = [p_{tot}^{(2)} / p_{tot}^{(0)} - (p_{tot}^{avg})^2] / p_o^{var} \tag{54}$$

For chain-end scission (CES) and for random- (RCS) and midpoint-chain scission (MCS), Figure 2 displays the time dependence of these moments. For chain-end scission the moments are linear in t, and for random- and midpoint-chain scission the moments behave exponentially.

The polydispersivity 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 4 A, B, C show the effect of scission mechanism and the stoichiometric coefficient parameter m on the time dependence of the polymer MWDs. The reactant and product MWDs are represented as gamma MWDs and added together for chain scission. 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 $p_{tot}(x,t)/p_o^{(0)}$. Bimodal distributions are evident for all the scission modes. Chain-end scission (Figure 3A) yields a product monomer that is represented as a delta function growing in time. The polymer MWD decreases with time. As time approaches t_f, the polymer is entirely consumed and converted to monomer. Midpoint-chain scission with r=2 (3B), and random-chain scission with $r \rightarrow \infty$ (3C) 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, combinations of the mechanisms discussed in this paper may be operative.

Acknowledgement: The financial support of Pittsburgh Energy Technology Center Grant No. DOE DE-FG22-94PC94204 and EPA Grant No. CR 822990-01-0 is gratefully acknowledged.

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Notation

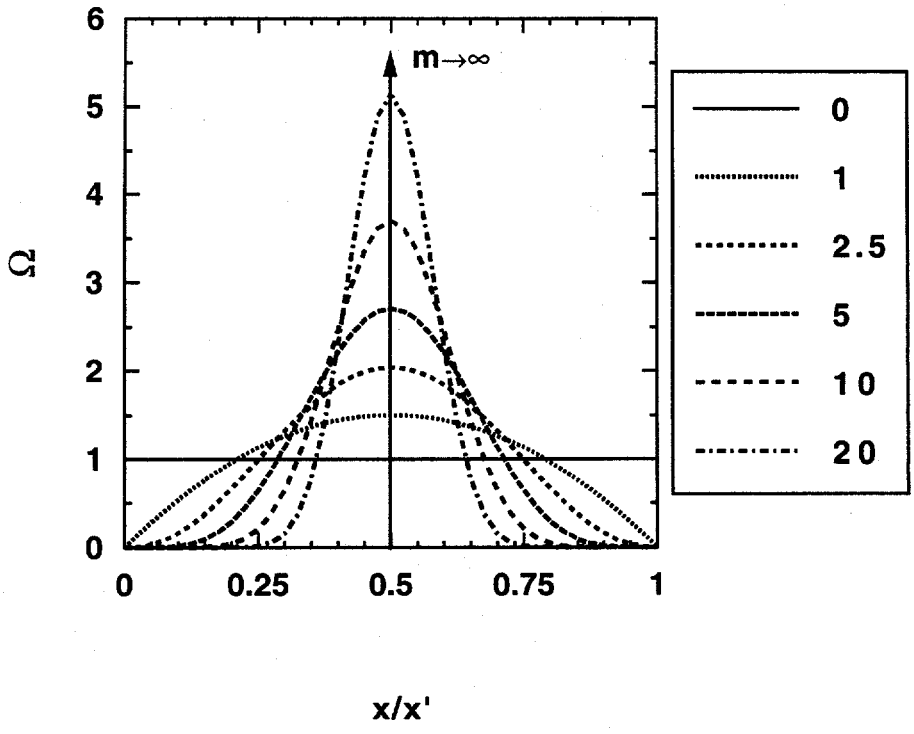
D	polydispersivity
k	degradation rate coefficient
m	parameter in stoichiometric coefficient expression, $\Omega(x,x')$
$p(x,t)$	molecular weight distribution (MWD) of polymer
$p_o(x,t)$	initial molecular weight distribution (MWD) of polymer
$p^{(n)}(t)$	the nth moment of $p(x,t)$
$p^{avg}(t)$	average MW of the MWD $p(x,t)$
$p^{var}(t)$	reduced second central moment (variance) of the MWD
$q(x,t)$	MWD for monomer or polymer product of chain scission
$q^{(n)}(t)$	the nth moment of $q(x,t)$
r	number of scissions in a sequence of events
t	time
x	molecular weight
x_o	molecular weight of the smallest polymer in an initial MWD
x_m	molecular weight of the monomer
$X^{(0)}$	$= p_{tot}^{(0)} / p_o^{(0)} = [p^{(0)}+q^{(0)}] / p_o^{(0)}$
X^{avg}	$= p_{tot}^{avg} / p_o^{avg} = [p^{(1)} + q^{(1)}]p_o^{(0)} / \{ [p^{(0)}+q^{(0)}]p_o^{(1)} \}$
X^{var}	$= p_{tot}^{var} / p_o^{var} = [p_{tot}^{(2)} / p_{tot}^{(0)} - (p_{tot}^{avg})2] / p_o^{var}$
y	dimensionless molecular weight in the gamma distribution
Z_{nm}	constant in the moment expression for MWD (Table I) based on the stoichiometric coefficient, $\Omega(x,x')$.
α_j	parameter in the gamma distribution
β_j	width parameter in the gamma distribution
$\delta(x)$	Dirac delta function of x
$\Omega(x,x')$	stoichiometry coefficient for scission process

Table 1. Values of Z_{nm}, defined in Eq (50).

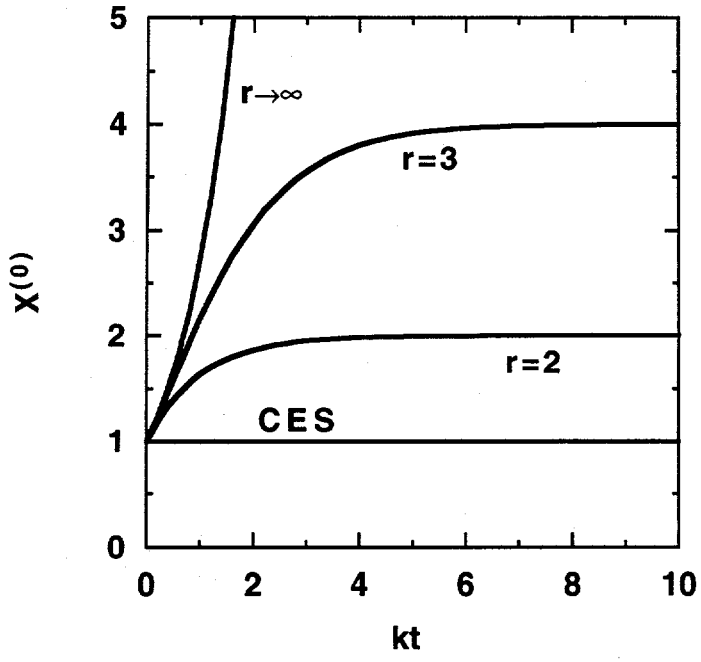
n \ m	0	1	2	...	∞
0	1	1	1	...	1
1	1/2	1/2	1/2	...	1/2
2	1/3	3/10	2/7	...	$1/2^2$
3	1/4	1/5	5/28	...	$1/2^3$

Figure Captions

1. The stoichiometric coefficient, Eq (4), for several values of m; random-chain scission is represented by m = 0, and midpoint-chain scission by $m \to \infty$.
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}. Let 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.
3. The time-evolution of the polydispersivity. Let CES, MCS, and RCS indicate chain-end, midpoint-, and random-chain scission, respectively.
4. Evolution of the MWD, $P^{tot} = p^{tot}(x,t)/p_o^{(0)}$, for a polymer undergoing (A) chain-end scission, (B) midpoint-chain scission with r=2, and (C) random-chain scission with $r \to \infty$.


6
5
4
3
2
1
0
Ω
m→∞
0
0.25
0.5
0.75
1
x/x'
0
1
2.5
5
10
20

2A



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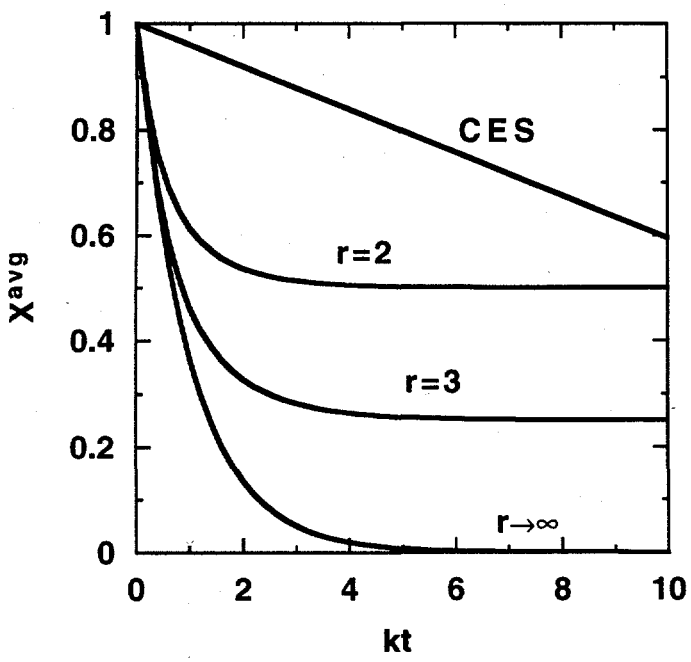

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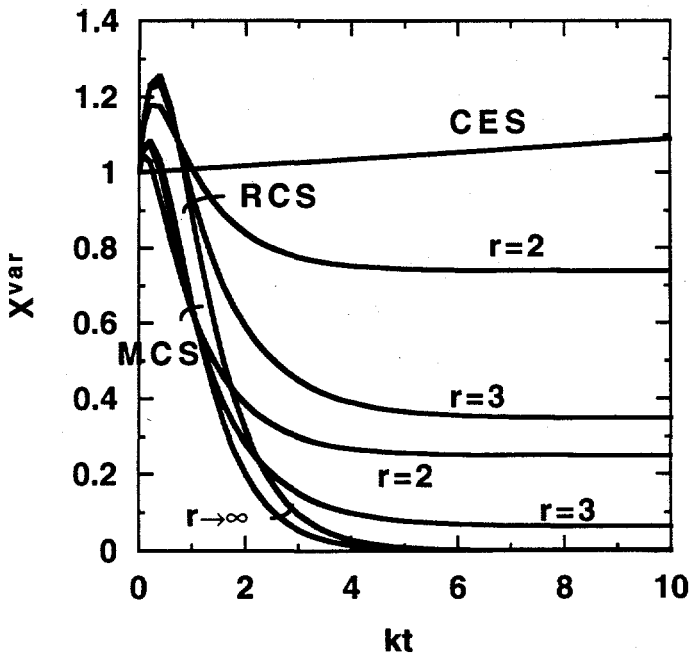
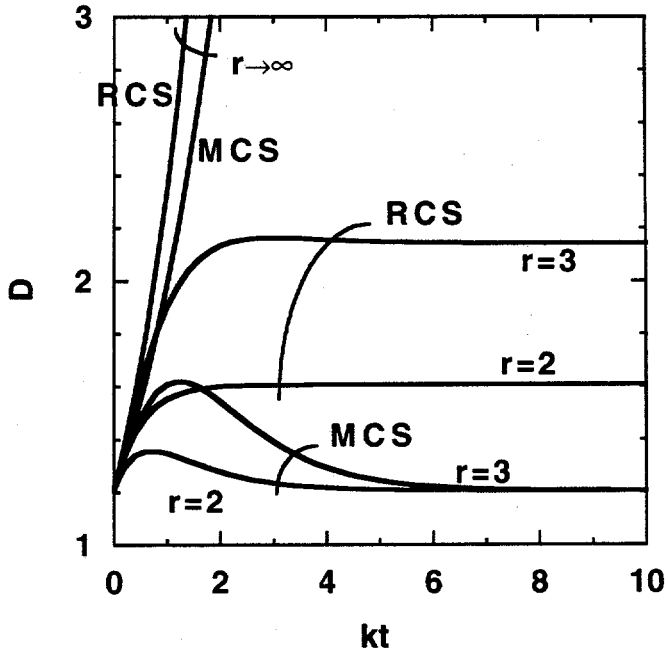
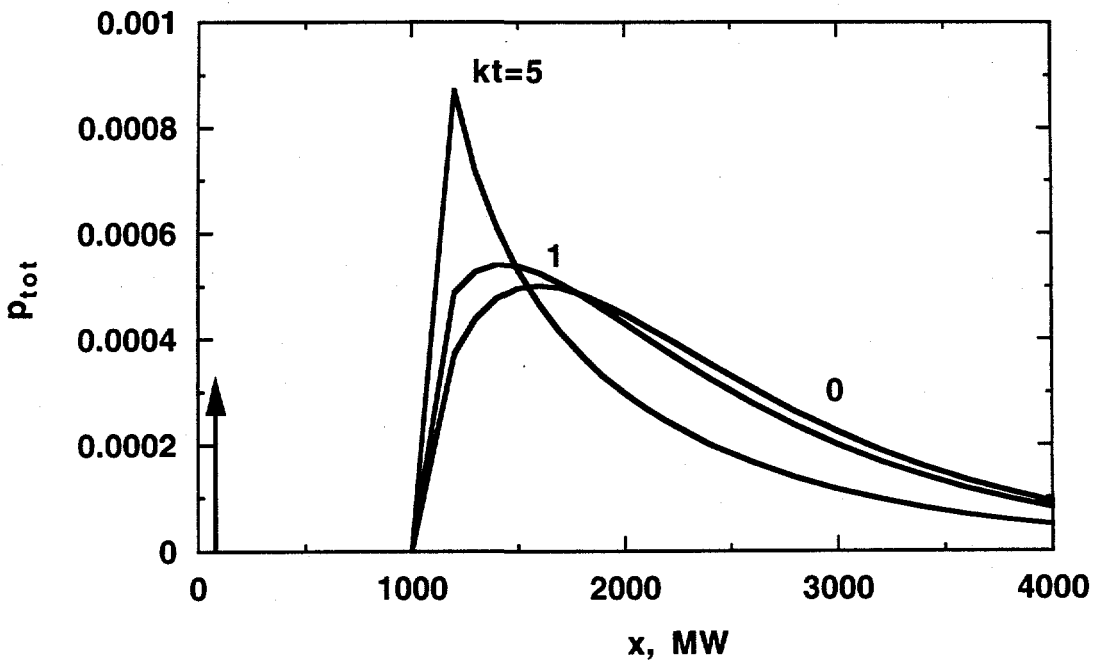



3
2
1
D
0
2
4
6
8
10
kt
r→∞
RCS
MCS
RCS
r=3
r=2
MCS
r=3
r=2

4A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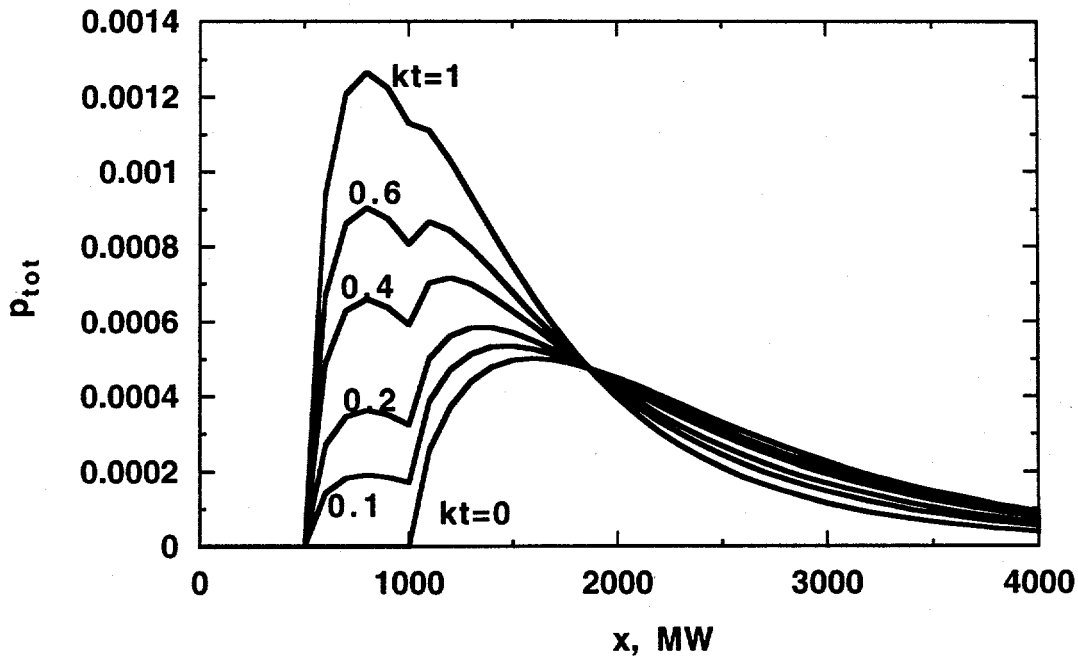
0.0008
0.0006
0.0004
0.0002
0
p_{tot}
kt=5
1
0
0
1000
2000
3000
4000
x, MW

4B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0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
p_{tot}
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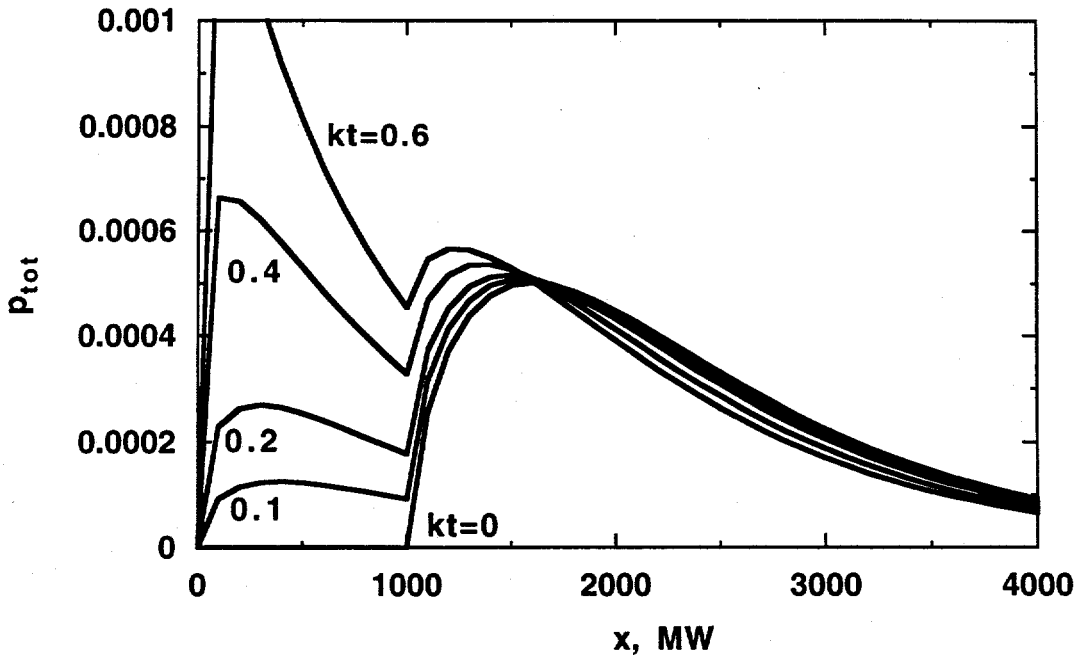
0.2
0.1
kt=0
0
1000
2000
3000
4000
x, MW

4C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0.0008
0.0006
0.0004
0.0002
0
p_{tot}
kt=0.6
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0.2
0.1
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0
1000
2000
3000
4000
x, MW