Time Evolution to Similarity Solutions for Polymer Degradation

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The theory of polymer decomposition is basic in understanding polymer and plastics stability, durability, characterization, and recycling. Polymers degrade by chain scission occurring randomly along the chain, at the chain midpoint, at the chain end, or by a combination of random chain-scission and chain-end scission. Mathematical solutions for polymer degradation were previously constrained to particular stoichiometric kernels (usually random scission) and to specialized distributions (such as the exponential distribution). Because the first term in a Laguerre-polynomial expansion is the gamma distribution and the initial molecular-weight distributions (MWDs) of polymers can be represented as superposed gamma distributions, the mathematical solution is represented as the time evolution of generalized gamma distribution parameters. Such solutions show how the first three moments of the MWD evolve in time for each of the chain-scission models. The rate coefficient for random chain scission is assumed to depend on MW x as x^{λ}, and the stoichiometric kernel is symmetric as in random or midpoint chain scission. Except when $\lambda = 0$, the distribution evolves to a similarity solution with the MW and time appearing together in the dimensionless group, $x^{\lambda}/\beta(t)$. The case of chain-end scission, however, has no similarity solution.

Introduction

The theory of polymer degradation is important in understanding polymer stability (Hawkins, 1984), durability (Clough et al., 1996), characterization (Flynn and Florin, 1985), synthesis (Caeter and Goethals, 1995), and recycling (Miller, 1994). Polymer degradation usually occurs through binary fragmentation processes, which are also of interest in other engineering applications. Much of the current mathematical analysis applies, for example, to liquid–liquid drop breakup and particle fragmentation. The time evolution of the molecular-weight distribution (MWD) is fundamental to the study of polymer degradation. Numerous articles (Aris and Gavalas, 1966; McGrady and Ziff, 1988; Peterson, 1986; Ziff and McGrady, 1985; McCoy and Wang, 1994) have discussed mathematical solutions for fragmentation processes, such as polymer degradation (Browarzik and Kehlen, 1997; Wang et al., 1995; McCoy and Madras, 1997), hydrocarbon cracking (Browarzik and Kehlen, 1994), oxidative thermolysis (Madras and McCoy, 1997), and coal liquefaction (Wang et al., 1994). Though widely studied, most previous solutions are similarity solutions, applicable only for very long times or to specialized distributions (such as exponential distributions). Ziff (1991) showed how several similarity solutions, valid for long time and independent of initial conditions, could be generalized for a power-law rate-coefficient dependence on MW, $k'(x) = kx^{\lambda}$. The solutions have the form such that the MW x and the time t appear together in the similarity group, $x^{\lambda}/\beta(t)$.

The stoichiometric kernel provides the distribution of the chemical reaction products through the type of chain scission. Depending on the chemical structure and the degradation condition, polymers have been observed to degrade by chain scission occurring randomly along the chain (Madras and McCoy, 1996), or at the chain midpoint (Price and Smith, 1991), or at the chain end (Madras et al., 1996a,b), or by a combination of random chain scission and chain-end scission (Madras et al., 1995). A symmetric parabolic distribution of scission products has also been used (Ziff and McGrady, 1986). Inokuti (1963) examined the time evolution of the weight-average MW for polymers undergoing random scission with a generalized Poisson initial distribution. Yoon et

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al. (1996) showed for random chain scission how the polydispersity index evolves to a value of two, representing a similarity exponential distribution.

Initial MWDs and their evolution can be represented by a single distribution or more generally as a superposition of gamma distributions (Wang et al., 1995). The common MWDs, such as exponential, Poisson, Gaussian, delta, or rectangular distributions, are special cases of the gamma distribution. The gamma distribution, moreover, is the first term in a generalized Fourier expansion in Laguerre polynomials of the MWD (Hulburt and Katz, 1964). The gamma distribution, which is fully determined by its first three moments, can be generalized (Scott, 1974) so that x^λ appears in the exponential.

Usually in polymer degradation, depending on the extent of the reaction, the random-scission rate coefficient, $k_r'(x) = k_r x^\lambda$, is considered either a constant ($\lambda = 0$) or linearly dependent on the chain length or molecular weight ($\lambda = 1$). Although one might expect the probability of chain scission to be proportional to the chain length for a linear macromolecular ($\lambda = 1$), polymers can coil (Reich and Stivala, 1971) and form globules that protect inner bonds from cleavage. If the change in average MW is not large, an average rate constant independent of MW is satisfactory (Madras et al., 1995). Madras et al. (1997a) showed that a polynomial, $k_r'(x) = k_0 + k_1 x + k_2 x^2$, quantitatively described polystyrene degradation with large conversions.

The first three moments ($j = 0$, 1, 2) of the MWD are, respectively, molar concentration, mass concentration, and weight-average MW multiplied by mass concentration. These moments fully determine the gamma distribution, and hence represent many MWDs quite well. An *exact* solution for the MWD would satisfy the governing integrodifferential equation. The gamma distribution, however, satisfies the first three moment equations, and is therefore an approximation to the MWD. Under certain conditions, the gamma distribution is an exact similarity solution, as we will demonstrate.

The present objective is to formulate numerical and analytical solutions for several fragmentation equations and initial conditions applicable to polymer degradation when $\lambda \geq 0$. The mathematical modeling is guided by observations of polymer solution thermolysis in our laboratory and by experimental results from other sources (Chiantore et al., 1981; Price and Smith, 1991). Analytical solutions for the first three moments of the MWD, applicable for all $t \geq 0$, are derived for $\lambda = 0$ and 1. Continuous-distribution population balances provide the governing integrodifferential equations, which are converted to ordinary differential equations for the MW moments that can be solved numerically. The first three moments are expressed in terms of gamma distribution parameters, and the solutions for the time evolution of the MWD are obtained as functions of time-dependent gamma distribution parameters. For random chain scission, the well-known similarity solutions are recovered at long times for $\lambda > 0$. For midpoint chain scission, the solution evolves to a similarity solution not previously reported.

Theoretical Model

Continuous-distribution kinetics provide a straightforward technique to determine the dynamics of macromolecular reactions. The polymer, $P(x)$, is considered to be a mixture of a large number of homologous molecules with MW x as a continuous variable. Polymer degradation can be written as a combination of random chain scission,

$$P(x) \xrightarrow{k_r'} P(x') + P(x - x') \tag{1}$$

and chain-end scission,

$$P(x) \xrightarrow{k_i'} Q(x_i) + P(x - x_i), \tag{2}$$

where x_i is the MW of the specific product, Q.

With the continuous kinetics approach and for a first-order degradation, the rate equations for the polymer (Wang et al., 1995) can be written in terms of the reaction time, t, as follows:

$$\partial p(x,t)/\partial t = -k_r'(x)p(x,t) + 2\int_x^\infty k_r'(x')p(x',t)\Omega(x,x')dx' - k_i'(x)p(x,t) + \int_x^\infty k_i'(x')p(x',t)\Omega(x - x_i, x')\,dx'. \tag{3}$$

The initial condition is $p(x, t = 0) = p_0(x)$. The normalized stoichiometric kernel (McCoy and Wang, 1994) for a polymer of MW x that fragments into two products of MW, x' and $x - x'$, can be written as

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

where $m = 0$ and $m \to \infty$ correspond to random and midpoint chain scission, respectively (McCoy and Madras, 1997). The case $m = 1$ gives a parabolic distribution of scission products (Ziff and McGrady, 1986). The stoichiometric kernel for chain-end scission is

$$\Omega(x - x_i, x') = \delta[x - (x' - x_i)]. \tag{5}$$

We assume the rate coefficients depend on MW (Ziff, 1991) as

$$k_r'(x) = k_r x^\lambda \quad \text{and} \quad k_i'(x) = k_i x^\nu \tag{6}$$

The MW moments, $p^{(n)}$, are defined as

$$p^{(j)}(t) = \int_0^\infty x^j p(x,t)\,dx. \tag{7}$$

As the MW is proportional to the chain length for homologous polymers, chain-length moments are directly related to MW moments. Number- and weight-average MWs are defined as

$$M_n = p^{(1)}/p^{(0)} \quad \text{and} \quad M_w = p^{(2)}/p^{(1)}, \tag{8}$$

and the polydispersity index is $D = M_w/M_n$. Applying the moment operation, defined by Eq. 7, to Eq. 3 yields (McCoy and Madras, 1997)

$$dp^{(j)}/dt = -k_r p^{(j+\lambda)} + 2Z_{jm} k_r p^{(j+\lambda)} - k_i p^{(j+\nu)} + k_i \sum_{d=0}^{j} \binom{j}{d} p^{(j-d+\nu)}(-1)^d x_i^d, \quad (9)$$

where Z_{jm} is $1/(j+1)$ for random chain scission and $1/2^j$ for midpoint chain scission. The general expression (McCoy and Madras, 1997), $Z_{jm} = (m+1)_j/(2m+2)_j$, is a ratio of Pochhammer symbols $(m)_j = \Gamma(m+j)/\Gamma(m)$. We write the differential equations for the first three moments in terms of $\kappa = k_i x_i/k_r$ and the time variable, $\theta = k_r t$, which has units of $1/(\mathrm{MW})^\lambda$,

$$dp^{(0)}/d\theta = p^{(\lambda)} \quad (10)$$

$$dp^{(1)}/d\theta = -\kappa p^{(\nu)} \quad (11)$$

$$dp^{(2)}/d\theta = -(1/S)p^{(\lambda+2)} + \kappa(x_i p^{(\nu)} - 2p^{(\nu+1)}), \quad (12)$$

where $S = -1/(2Z_{jm} - 1)$, and $S = 3$ for random chain scission ($m = 0$) and $S = 2$ for midpoint chain scission ($m \to \infty$). For other values of m ($0 < m < \infty$), we have $2 < S < 3$, for example, $S = 5/2$ for the parabolic distribution of scission products. The effect of m appears only in the second and higher moments.

We require a solution that evolves to the similarity solution under appropriate conditions. The similarity solution for $\lambda > 0$ derived by Peterson (1986) and Ziff (1991) suggests the following generalization (Scott, 1971) of the gamma distribution with $u = x^\lambda/\beta$,

$$p(x,t) = Nu^{\alpha-1}\exp(-u). \quad (13)$$

The normalization factor, $N = p^{(1)}\lambda/[\beta^{2/\lambda}\Gamma(\alpha - 1 + 2/\lambda)]$, for convenience contains the first moment, which is time-invariant when $\kappa = 0$. For $\alpha = 1$ and for any $\lambda > 0$, Eq. 13 has the similarity solution form (Peterson, 1986; Ziff, 1991).

The MW moments, defined by Eq. 6, for the generalized distribution Eq. 13 are computed by substituting $x = (u\beta)^{1/\lambda}$,

$$p^{(j)} = p^{(1)}\beta^{(j-1)/\lambda}\Gamma(\alpha - 1 + (j+1)/\lambda)/\Gamma(\alpha - 1 + 2/\lambda), \quad (14)$$

where the gamma function has the property, $\Gamma(y+1) = y\Gamma(y)$. Thus, the number- and weight-average molecular weights and the polydispersity are

$$M_n = \beta^{1/\lambda}\Gamma(\alpha - 1 + 2/\lambda)/\Gamma(\alpha - 1 + 1/\lambda) \quad (15)$$

$$M_w = \beta^{1/\lambda}\Gamma(\alpha - 1 + 3/\lambda)/\Gamma(\alpha - 1 + 2/\lambda), \quad (16)$$

$$D = \beta^{1/\lambda}\Gamma(\alpha - 1 + 3/\lambda)\Gamma(\alpha - 1 + 1/\lambda)/\Gamma(\alpha - 1 + 2/\lambda)^2. \quad (17)$$

The generalized gamma distribution solution, Eq. 13, requires that we solve for three parameters, $\alpha(t)$, $\beta(t)$, and $p^{(1)}(t)$, whose time dependences are governed by the three moment differential equations (Eqs. 10–12).

We will consider the usual case when chain-end scission degradation rate is independent of the MW ($\nu = 0$) (Madras et al., 1996a). When the moment expressions for $j = 0$, 1, and 2 in Eq. 14 are substituted into three differential equations (Eqs. 10–12), we obtain

$$d\ln\{p^{(1)}\Gamma(\alpha - 1 + 1/\lambda)/[\beta^{1/\lambda}\Gamma(\alpha - 1 + 2/\lambda)]\}/d\theta = \beta(\alpha - 1 + 1/\lambda) \quad (18)$$

$$d\ln p^{(1)}/d\theta = -\kappa g_2 \quad (19)$$

$$d\ln[p^{(1)}\beta^{1/\lambda}\Gamma(\alpha - 1 + 3/\lambda)/\Gamma(\alpha - 1 + 2/\lambda)]/d\theta = -\beta(\alpha - 1 + 3/\lambda)/S + \kappa g_1, \quad (20)$$

where

$$g_1 = (g_2 - 2)\Gamma(\alpha - 1 + 2/\lambda)/[\beta^{1/\lambda}\Gamma(\alpha - 1 + 3/\lambda)] \quad (21)$$

and

$$g_2 = x_i\Gamma(\alpha - 1 + 1/\lambda)/[\beta^{1/\lambda}\Gamma(\alpha - 1 + 2/\lambda)]. \quad (22)$$

These can be reduced to two differential equations for $\alpha(\theta)$ and $\beta(\theta)$. Adding Eqs. 18 and 20 and using Eq. 19 gives

$$(d\alpha/d\theta)d\ln[\Gamma(\alpha - 1 + 1/\lambda)\Gamma(\alpha - 1 + 3/\lambda)/(\Gamma(\alpha - 1 + 2/\lambda)^2)]/d\alpha = \beta\{[(1 - 1/S)(\alpha - 1)] + [(S-3)/(S\lambda)]\} + \kappa(g_1 + 2g_2). \quad (23)$$

Rearranging Eq. 18 with Eq. 19 yields

$$d\beta/d\theta - \lambda\beta(d\alpha/d\theta)d\ln[\Gamma(\alpha - 1 + 1/\lambda)/\Gamma(\alpha - 1 + 2/\lambda)]/d\alpha = -\lambda\beta[\beta(\alpha - 1 + 1/\lambda) + \kappa g_2]. \quad (24)$$

Derived with the zero and the first moments only, Eq. 24 is independent of S. Equations 23 and 24 show the time dependence of the gamma distribution parameters, α and β, when $\lambda > 0$ and $\nu = 0$. Then Eq. 19 permits a solution for $p^{(1)}$ when $\alpha(\theta)$ and $\beta(\theta)$ are known.

A similarity solution is obtained when $d\alpha/d\theta = 0$, that is, when the righthand side of Eq. 23 is zero and α thus reaches a limiting value. When $\kappa = 0$ (no chain-end scission), the similarity solutions arise simply by equating $[(1 - 1/S)(\alpha - 1)] + [(S-3)/(S\lambda)]$ to zero, and solving for α,

$$\alpha = 1 + (3 - S)/[\lambda(S-1)]. \quad (25)$$

This expression contains $1/\lambda$, proving there is no similarity solution for $\lambda = 0$. For $S = 3$ (random chain scission only), $\alpha = 1$; for $S = 2$ (midpoint chain scission only), $\alpha = 1 + 1/\lambda$; and for $S = 5/2$ (parabolic product stoichiometry), $\alpha = 1 + 1/(3\lambda)$ provide the similarity solutions. The differential equation for $\beta(t)$ is obtained from Eq. 24 when $d\alpha/d\theta = 0$ and $\kappa = 0$,

$$d\beta/d\theta = -\lambda\beta^2(\alpha - 1 + 1/\lambda). \tag{26}$$

Integrating with the initial condition $\beta(\theta = 0) = \beta_0$ gives $\beta = \beta_0/(1+\beta_0\theta)$ for random scission, $\beta = \beta_0/(1+2\beta_0\theta)$ for midpoint scission, and $\beta = \beta_0/(1+4\beta_0\theta/3)$ for parabolic scission, all independent of λ.

For random-chain scission ($S = 0$, $\kappa = 0$), Peterson (1986) and Ziff (1991) derived the similarity solution ($\alpha = 1$ in Eq. 13),

$$p(x,t) = p^{(1)}\lambda\beta^{-2/\lambda}\exp(-x^\lambda/\beta)/\Gamma(2/\lambda) \tag{27}$$

by substituting the similarity form into the governing integrodifferential equation (Eq. 3 with $k_i'(x) = 0$). One can show that substituting the moment expression, Eq. 14, with $\alpha = 1$ into the moment equation, Eq. 9, yields $d\beta/d\theta = -\beta^2$. Because this is independent of the moment order j, the solution is valid for all j. Equation 27 is thus an exact solution *valid for all moments* ($j \geq 0$). The closure difficulty that arises for the moment differential equations when $\lambda > 0$ (Madras et al., 1997a) is surmounted in this case when $\lambda = 1$. If the solution is to be applied for all $t \geq 0$, however, the initial condition must be restricted to the generalized exponential distribution (Eq. 27) with $\beta = \beta_0$ and $p^{(1)} = p_0^{(1)}$.

When $\lambda = 1$, Eq. 13 becomes the usual gamma distribution (Abramowitz and Stegun, 1968),

$$\begin{aligned} p(x,t) &= p^{(1)}(t)(x/\beta)^{\alpha-1}\exp(-x/\beta)/[\beta^2\Gamma(\alpha+1)] \\ &= p^{(0)}(t)(x/\beta)^{\alpha-1}\exp(-x/\beta)/[\beta\Gamma(\alpha)], \end{aligned} \tag{28}$$

for which $M_n = \alpha\beta$, $M_w = (\alpha+1)\beta$, and $D = 1 + 1/\alpha$. When $\alpha = 1$ Eq. 28 is the exponential distribution,

$$p(x,t) = p^{(1)}\exp(-x/\beta)/\beta^2 = p^{(0)}\exp(-x/\beta)/\beta. \tag{28a}$$

This similarity solution, derived by Ziff (1991), Peterson (1985), and Madras and McCoy (1996), is equivalent to the "most probable distribution" (Scott, 1974). For vanishingly small x, one should write $p(x = 0,\ t) = 0$, as monomers of MW $x > 0$ are the smallest products of degradation. For a study of the oxidative degradation of polystyrene, Eq. 28 was also derived by Madras and McCoy (1997) by a Laplace transform procedure (Aris and Gavalas, 1966). The MWD of the degrading polymer, measured experimentally, was initially an exponential distribution and remained so for all times, and thus the polydispersity was always two. The mathematical model provided a solution for the declining peroxide concentration, as well as for the evolving MWD.

Even though Eqs. 23 and 24 can be solved numerically to obtain the time evolution of the moments for all $t > 0$, some special cases permit analytical solutions, as we demonstrate next.

Case 1: Polymer degrades by random chain scission only

Case 1.1. $\lambda = 1$. Polymers like polystyrene thermally degrade predominantly by random chain scission (Madras et al., 1997a). The MW dependence of the rate coefficient, $k(x)$, can be approximated as a linear function for some reactions over a wide range of MW (Madras et al., 1997a). To examine the evolution of the MWDs of such polymers, we evaluate the time evolution of the gamma distribution parameters. For random chain scission only ($k_i = 0$), Eqs. 10–12 can be rewritten with $\kappa = 0$ to obtain

$$dp^{(0)}/d\theta = p^{(1)} \tag{29}$$

$$dp^{(1)}/d\theta = 0 \tag{30}$$

$$dp^{(2)}/d\theta = -p^{(3)}/3. \tag{31}$$

Thus, $p^{(1)} = p_0^{(1)}$ and $p^{(0)} = p_0^{(0)} + \theta p_0^{(1)}$, so that the number-average MW declines as

$$M_n = \alpha\beta = M_{n0}/(1 + M_{n0}\theta), \tag{32}$$

where the subscript 0 denotes the initial condition. The time dependence of α is obtained directly from Eq. 23,

$$d\alpha/d\theta = 2M_n(1-\alpha^2)/3, \tag{33}$$

where M_n is given by Eq. 32. The solution to Eq. 33 is

$$\alpha = (1-A)/(1+A), \tag{34}$$

where $A = (\alpha_0 - 1)(1 + M_{n0}k_r t)^{-(4/3)}/(\alpha_0 + 1)$ and α_0 is the initial value of α. The time evolution of the gamma distribution parameter, β, can be found by dividing Eq. 32 by Eq. 34. After α reaches its limiting value of unity, the solution has the similarity form and β will continue to decrease as the polymer degrades, following $\beta = \beta_0/(1+\beta_0\theta)$, which is the solution to Eq. 26 mentioned earlier.

Case 1.2. $\lambda = 0$. For small conversions (small changes in average MW), the rate coefficients can be approximated as independent of MW, $\lambda = 0$ (Madras et al., 1997a). Then, Eqs. 10–12 for $j = 0$, 1, and 2 with $k_i = 0$ are

$$dp^{(0)}/d\theta = p^{(0)} \tag{35}$$

$$dp^{(1)}/d\theta = 0 \tag{36}$$

$$dp^{(2)}/d\theta = -p^{(2)}/S. \tag{37}$$

Solving Eqs. 35–37 yields

$$p^{(0)} = p_0^{(0)}\exp(-\theta) \tag{38}$$

$$p^{(1)} = p_0^{(1)} \tag{39}$$

$$p^{(2)} = p_0^{(2)}\exp(-\theta/3), \tag{40}$$

and the gamma distribution parameters can be derived as

$$M_n = p^{(1)}/p^{(0)} = \alpha\beta = \alpha_0\beta_0\exp(-\theta) \tag{41}$$

$$M_w = p^{(2)}/p^{(1)} = (\alpha+1)\beta = (\alpha_0+1)\beta_0\exp(-\theta/3). \tag{42}$$

Thus

$$\beta = M_w - M_n = \beta_0[(\alpha_0+1)\exp(-\theta/3) - \alpha_0\exp(-\theta)] \tag{43}$$

$$\alpha = \alpha_0 \beta_0 \exp(-\theta)/\beta. \tag{44}$$

As $t \to \infty$, the mathematical results show that $\beta \to 0$ and $\alpha \to 0$. Thus there is no similarity solution related to the gamma distribution when $\lambda = 0$. The assumption that the random rate coefficient, $k_r'(x)$, is independent of x is valid only if we consider it averaged over MW. This approximation is reasonable if the extent of conversion is small ($M_{n0}/M_n \ll 10$, Madras et al., 1997a), that is, if time is relatively short. For long times, however, the conversion can be large (Madras et al., 1997a), and the rate coefficient should be considered a function of MW ($\lambda \neq 0$).

Case 2: Polymer degrades by chain-end scission only

Rewriting Eqs. 10–12 for chain-end scission only with $\theta' = \kappa\theta = k_i x_i t$ yields the differential equations for the first three moments,

$$dp^{(0)}/d\theta' = 0 \tag{45}$$

$$dp^{(1)}/d\theta' = -p^{(\nu)} \tag{46}$$

$$dp^{(2)}/d\theta' = x_i p^{(\nu)} - 2p^{(\nu+1)}. \tag{47}$$

The chain-end scission rate of the polymer depends on the number of chain ends and is independent of the chain length. Thus, it is reasonable (Madras et al., 1996a,b; Wang et al., 1995) to assume that the chain-end scission rate coefficient is independent of MW ($\nu = 0$). Solving Eqs. 45–47, we have

$$p^{(0)} = p_0^{(0)} \tag{48}$$

$$p^{(1)} = p_0^{(1)} - p_0^{(0)}\theta' \tag{49}$$

$$p^{(2)} = p_0^{(2)} + p_0^{(0)}\theta'^2 + (x_i p_0^{(0)} - 2p_0^{(1)})\theta'. \tag{50}$$

Then if the polymer degrades by chain-end scission only ($k_r = 0$), the gamma distribution parameters can be derived as

$$M_n = \alpha\beta = \alpha_0 \beta_0 - \theta' \tag{51}$$

$$M_w = (\alpha + 1)\beta = \left[p_0^{(2)} + p_0^{(0)}\theta'^2 + (x_i p_0^{(0)} - 2p_0^{(1)})\theta'\right] / (p_0^{(1)} - p_0^{(0)}\theta'), \tag{52}$$

and thus

$$\beta = (x_i\theta' + \alpha_0\beta_0^2)/(\alpha_0\beta_0 - \theta') \tag{53}$$

$$\alpha = (\alpha_0\beta_0 - \theta')/\beta. \tag{54}$$

Equations 53 and 54 show the time dependence of the gamma distribution parameters for the polymer that degrades by chain-end scission only, and when the degradation rate coefficient is independent of MW. No similarity solution is known for chain-end scission. This is corroborated by substituting a generalized gamma distribution (Eq. 13 with $\lambda = \nu$) into the moment equations (Eqs. 45–47); then, setting $d\alpha/d\theta' = 0$ yields no similarity solution.

For chain-end scission $P(x)$ is the degrading polymer and $Q(x_i)$ is the monomer product. The rate equation for the product monomer can be written,

$$\partial q(x_i, t)/\partial t = \int_x^\infty k_i(x')p(x', t)\Omega(x_i, x')\,dx', \tag{55}$$

where $\Omega(x_i, x') = \delta(x - x_i)$. Applying the moment operation (Eq. 6) to Eq. 55 gives

$$dq^{(j)}/dt = k_i x_i^j p^{(\nu)}(t). \tag{56}$$

For chain-end scission, we are interested in the product, $Q(x_i)$, with MW x_i. Equation 56 with $\nu = 0$ and $j = 0$ gives

$$dq^{(0)}/dt = k_i p^{(0)}(t) = k_i p_0^{(0)}. \tag{57}$$

Thus, the zeroth moment of the product monomer is

$$q^{(0)} = k_i p_0^{(0)} t \tag{58}$$

and

$$q^{(j)} = x_i^j q^{(0)}. \tag{59}$$

The moments provide the average molecular weight and the variance,

$$q^{\text{avg}} = q^{(1)}/q^{(0)} = x_i \tag{60}$$

$$q^{\text{var}} = \sigma_i^2 = q^{(2)}/q^{(0)} - (q^{\text{avg}})^2 = 0. \tag{61}$$

These equations show that the specific-product MWD is a delta distribution, representing a monomer. Wang et al. (1995) have shown how several oligomer products of chain-end scission can be represented by a semicontinuous MWD.

Numerical Results

To obtain solutions that describe time evolution from arbitrary initial conditions, we consider simultaneous random chain scission and chain-end scission and assume the chain-end scission rate coefficient is independent of the MW ($\nu = 0$). The approach can be extended, however, to examine other kernels and $\nu > 0$.

Equations 23 and 24 can be solved numerically for any $\lambda > 0$ by using the digamma function (Abramowitz and Stegun, 1968),

$$\psi(y) = d \ln \Gamma(y)/dy, \tag{62}$$

which is a built-in function of software packages, such as Mathematica. We solved the equations by a straightforward Runge-Kutta routine for several values of $\lambda > 0$ and the initial conditions α_0 ($= 4$) and β_0 ($= 10^5$) for random chain scission ($S = 3$) and $\kappa = 0$. Because chain-end scission has only a small influence on the average MW of the polymer (Madras et al., 1997b), an appreciable effect on the gamma distribution parameters is observed only when κ is large. Results for the time evolution of α and β are shown in Figures

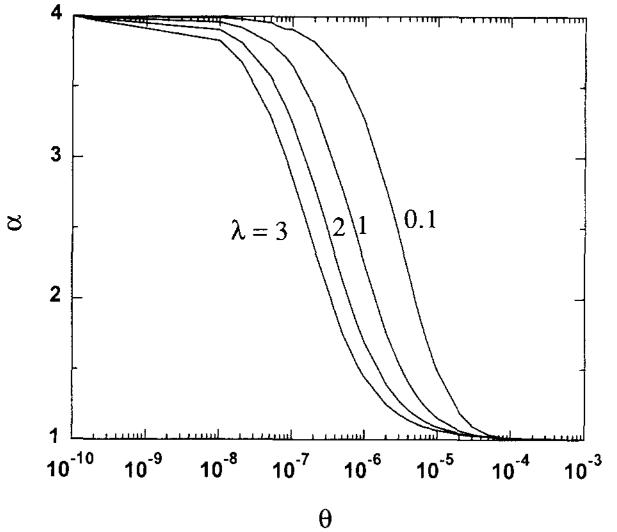

Figure 1. Gamma distribution parameter, α, vs. θ ($= k_r t$) for various λ (Eq. 23), with $\alpha_0 = 4$ when the polymer degrades by random chain scission only.

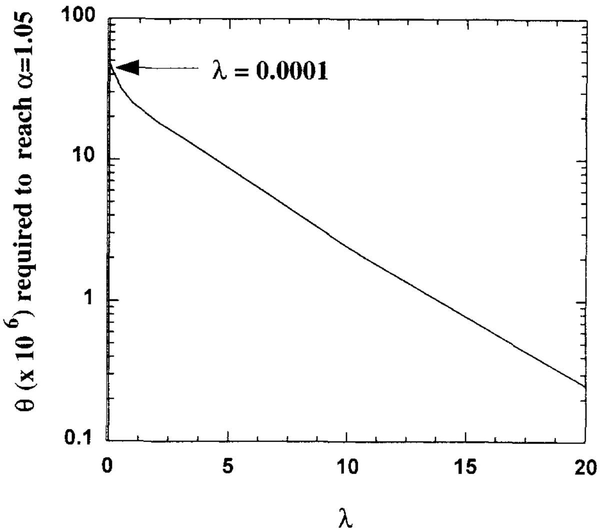

Figure 3. Time, θ ($= k_r t$), required to approach within 5% of the similarity solution ($\alpha = 1.05$) for various λ with $\alpha_0 = 4$.

1 and 2. The units of $\theta = k_r t$, which are suppressed in the figures, are $1/\text{MW}^{\lambda}$, or $(\text{g/gmol})^{-\lambda}$. The gamma distribution parameters (and the MWD) reach the λ-independent similarity solution ($\alpha = 1$) at times, $\theta = k_r t > 10^{-4}$. Long times are required when the rate coefficient is small. Figure 3 shows the effect of λ on the time required to approach within 5% of the similarity solution ($\alpha = 1.05$) for $\alpha_0 = 4$ and random chain scission. For smaller values of λ, exponentially larger times are required to reach the similarity solution. At $\lambda = 0$, the similarity solution does not exist.

Case 1.1 is when the polymer degrades by random chain scission, with the rate coefficient directly proportional to MW ($\lambda = 1$). Several polymers such as polyethylene and polystyrene (Madras et al., 1997a) thermally degrade predominantly by random chain scission, so that the MW of products of C–C bond cleavage are distributed randomly (Eq. 4 with $m = 0$) and the chain-end scission of the polymer can be neglected. We investigated Case 1.1 with $M_{n0} = 2\times10^5$ for three values of α_0 ($= 0.5$, 2, and 5) and the corresponding β_0 ($= 4\times10^5$, 1×10^5, 4×10^4). When $\lambda = 1$, Eq. 34 gives the time evolution of the gamma distribution parameter α. A plot of α vs. dimensionless time, $\theta_r = k_r M_{n0} t$ (Figure 4), shows that α, irrespective of its initial value, reaches unity (corresponding to a polydispersity of 2) at $\theta_r \sim 10$. For polystyrene degra-

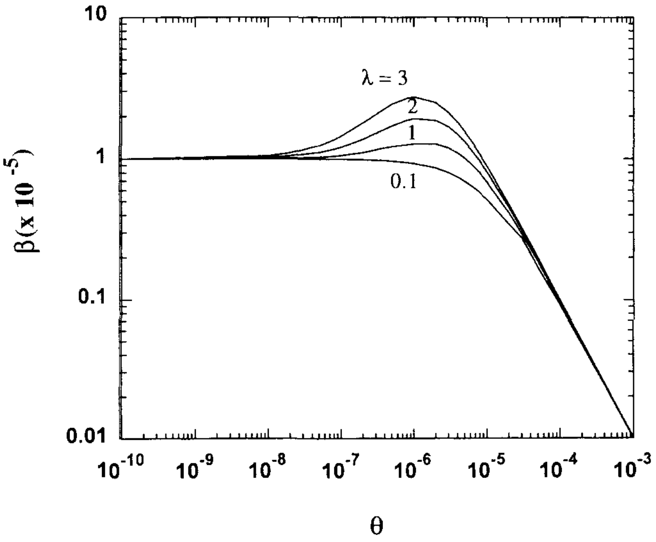

Figure 2. Gamma distribution parameter, β, vs. θ ($= k_r t$) for various λ (Eq. 24), with $\beta_0 = 10^5$ when the polymer degrades by random chain scission only.

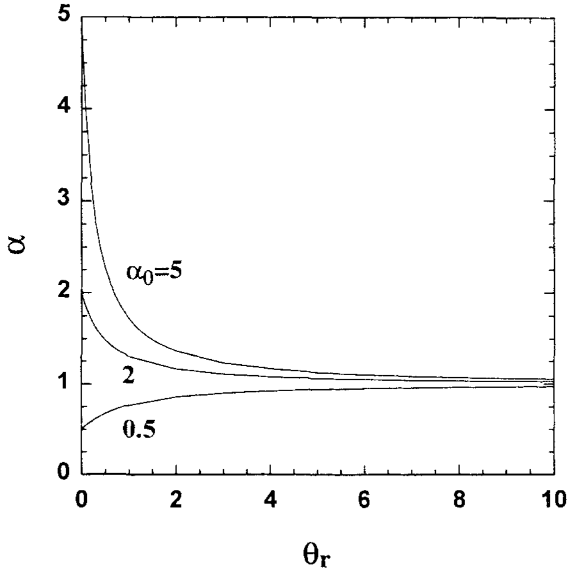

Figure 4. Gamma distribution parameter, α, vs. dimensionless θ_r ($= k_r M_{n0} t$) when the polymer degrades by random chain scission only and $\lambda = 1$ (Eq. 34) with $\alpha_0 = 0.5$, 2, and 5.

dation (275°C, $M_{n0} = 100{,}000$), $k_r M_{n0}$ is of the order 10^{-4} min^{-1} (Madras et al., 1997a), and a long time (~ 70 days) is required for the similarity solution to be reached. The slow approach of polydispersity to 2 has been observed experimentally (Yoon et al., 1996; Chiantore et al., 1981; Reich and Stivala, 1971) for polystyrene degradation. The gamma distribution with $\alpha = 1$ is an exponential distribution similarity solution when $\lambda = 1$ (Ziff, 1991). Thus, polymers that degrade by random chain scission, irrespective of initial polydispersity, slowly reach a similarity solution, the exponential MWD (most-probable distribution, Eq. 28a) (Yoon et al., 1996; Inokuti, 1963; Scott, 1974), with polydispersity 2 when $\lambda = 1$.

At initial times both α and β change with time, but at long times α reaches a constant value of unity while $\beta = \beta_0/(1 + \beta_0 \theta)$ continues to decrease inversely with time. Figure 5 shows the complete time evolution of β. Even though β rises slightly to a maximum for some values of λ, the decrease in α more than compensates to cause the average MW, $M_n = \alpha\beta$, to decrease.

Equations 23 and 24 can be solved for midpoint chain scission ($S = 2$), which dominates in the mechanical degradation of polymers (Price and Smith, 1991). The time evolution of the gamma distribution parameters is shown in Figures 6 and 7. The parameter α approaches the similarity solution given by $\alpha = 1 + 1/\lambda$. Thus, unlike random chain scission, the similarity solution for midpoint chain scission depends on λ.

We evaluated cases 1.2 and 2 with $\lambda = 0$ for typical values of $M_{n0} = 2 \times 10^5$, $x_i = 100$, two values of α_0 (= 0.5 and 2) and the corresponding β_0 ($= 4 \times 10^5$ and 1×10^5). Figure 8 shows how α, β, and M_n evolve in time when the polymer degrades by random chain scission and the rate coefficient is independent of MW, $\lambda = 0$ (Case 1.2). For this nonsimilarity solution, the parameters α and M_n decrease continuously with time (Eqs. 41 and 44). When $\alpha > 1$, β increases initially and then decreases (Eq. 43). This behavior has been observed experimentally when $\alpha_0 = 1.7$ (Wang et al., 1995). However, β decreases continuously when $\alpha_0 < 1$.

Figure 9 shows the nonsimilarity variation of α, β, and M_n with time when the polymer degrades only by chain-end scission for $\nu = 0$ (Case 2). Equations 53 and 54 indicate that if $\alpha_0 \beta_0 \gg k_i x_i t$, then α and β are constant. When $\theta' = k_i x_i t$ is comparable to $\alpha_0 \beta_0$, the number-average MW of the polymer, M_n, decreases linearly with time (Eq. 51), which has been observed experimentally (Madras et al., 1996a,b). Chain-end scission will cease when all the polymer has been converted to its monomer, when the average MW of the polymer equals the monomer MW ($M_n = x_i$). This will occur at a

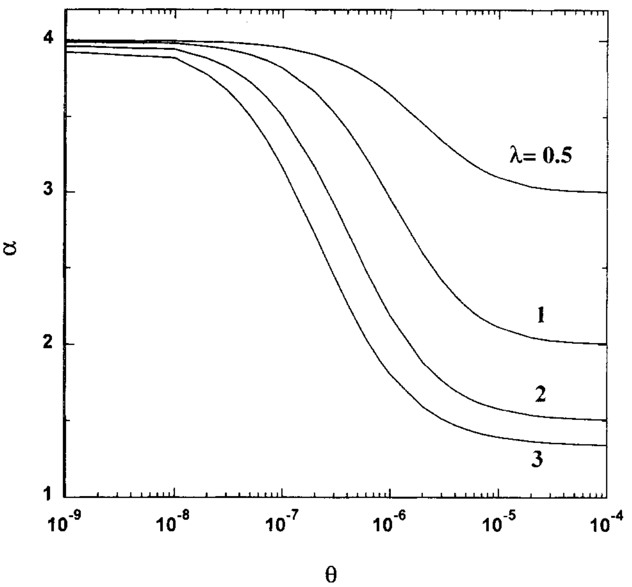

Figure 6. Gamma distribution parameter, α, vs. θ ($= k_r t$) for various λ (Eq. 23) with $\alpha_0 = 4$ when the polymer degrades by midpoint chain scission only.

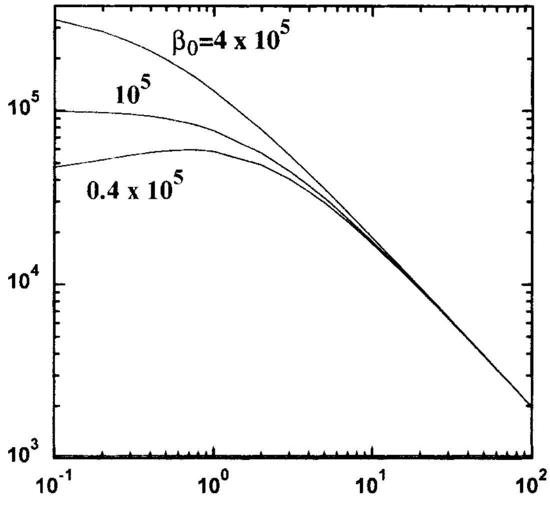

Figure 5. Gamma distribution parameter, β, vs. dimensionless θ_r ($= k_r M_{n0} t$) when the polymer degrades by random chain scission only and $\lambda = 1$ with β_0 ($\times 10^{-5}$) = 0.4, 1, and 4.

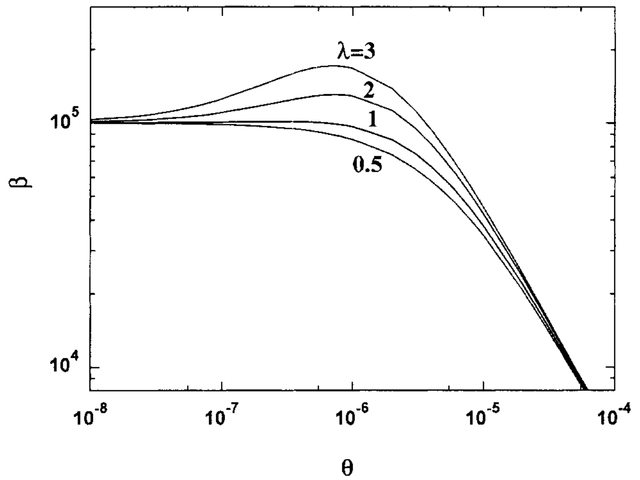

Figure 7. Gamma distribution parameter, β, vs. θ ($= k_r t$) for various λ (Eq. 24), with $\beta_0 = 10^5$ when the polymer degrades by midpoint chain scission only.

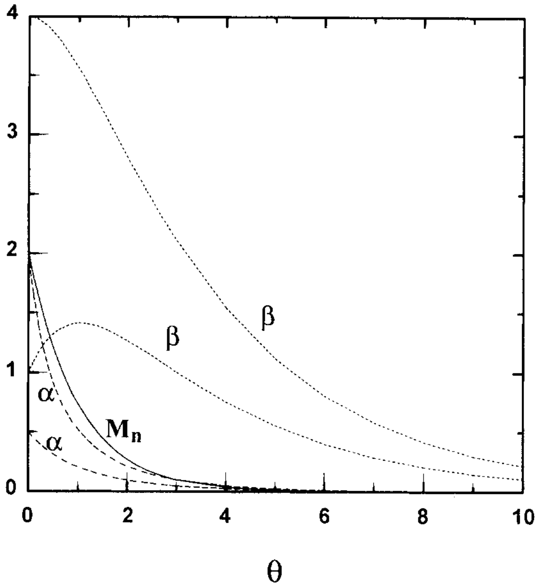

Figure 8. Gamma distribution parameters, α and β, and the number-average MW, M_n, vs. θ ($=k_r t$) when the polymer degrades by random chain scission only and $\lambda = 0$ (Eqs. 41, 43, and 44).

Solid line is time evolution of M_n; dashed line (– – –) is time evolution of α; dotted line (· · · ·) is time evolution of β.

finite value of time, $t_f = \alpha_0 \beta_0 / k_i x_i$ (McCoy and Madras, 1997). Figure 9 shows α and M_n decreasing with time and reaching zero at t_f, and β increasing without limit at t_f.

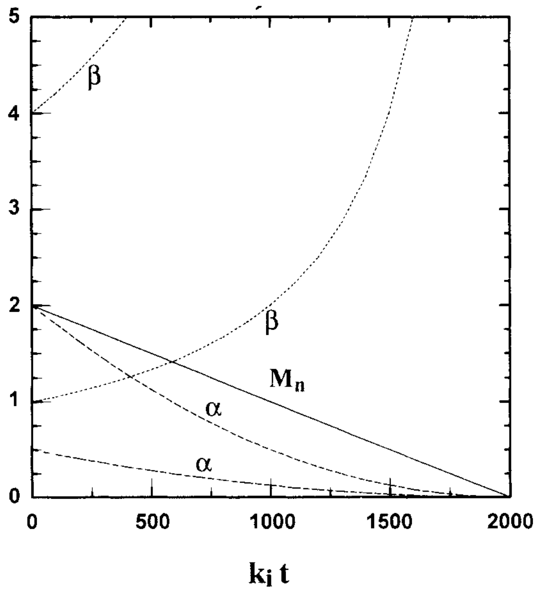

Figure 9. Gamma distribution parameters, α and β, and the number-average MW, M_n, vs. $k_i t$, with $x_i = 100$ when the polymer degrades by chain-end scission only and $\nu = 0$ (Eqs. 51, 53, and 54).

Solid line is time evolution of M_n; dashed line (– – –) is time evolution of α; dotted line (· · · ·) is time evolution of β.

Concluding Remarks

The current approach shows how the MWD, approximated as a gamma distribution, can evolve from a general initial condition to a similarity solution. When $\lambda = 0$ or $\nu = 0$, however, the solution is not of the similarity form. If the initial condition is already of the similarity solution form ($\alpha = 1$), then the similarity solution governs the time dependence for all time, $t > 0$. But for systems with arbitrary initial states ($\alpha \neq 1$), and when rate coefficients are small in magnitude, the evolution to the similarity solution requires a relatively long time. Experimental observations of such systems can be understood and described quantitatively by a time-dependent solution of the type described in this article.

Polymers can degrade by random, midpoint, or chain-end scission, as represented by the stoichiometric kernel. Solutions for the differential equations governing the first three moments of the polymer determine the number- and weight-average MW, and often provide a reasonable approximation to the MWD. When the polymer MWD is expressed as a generalized gamma distribution, the mathematical solution for the time evolution of the MWD can be derived in terms of gamma distribution parameters. General differential equations applicable for a rate coefficient, $k_r'(x) = k_r x^\lambda$, $\lambda > 0$, were derived and solved numerically. For random and midpoint chain scission, the MWD of the polymer, irrespective of its initial distribution, approaches a similarity solution (special case of a generalized gamma distribution). For midpoint-chain scission, the MWD approaches a similarity solution and the gamma distribution parameter α approaches $1 + 1/\lambda$. For random chain scission, α approaches unity, and for a parabolic product distribution, α approaches $1 + 1/(3\lambda)$. We have also derived analytical solutions for $\lambda = 0$ and 1 when the polymer degrades by random-chain scission only, and we discussed the time evolution of the gamma distribution parameters in these cases. The case of chain-end scission (with $\nu = 0$) also has an analytical nonsimilarity solution.

Acknowledgments

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. The authors thank Professor J. M. Smith for helpful discussions.

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Manuscript received July 18, 1997, and revision received Dec. 23, 1997.