Dynamics of Molecular Weight Distributions for Polymer Scission

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The dynamics of molecular weight distributions (MWDs) for polymer degradation is of interest to various applications. The time evolutions of MWDs can be determined by solving the governing population balance equations, which are generally solved by moment techniques wherein the initial distribution is represented by a gamma distribution. The evolution of MWD is determined by the time dependence of the gamma distribution parameters. The population balance equations (PBEs) can also be solved numerically by converting them to partial differential equations (PDEs). The degradation rate coefficient in the PBE depends on the molecular weight x as $(x - x_o)^\lambda$ *or as a quadratic polynomial in x. The solutions obtained with the moment technique, which are inaccurate for certain cases, are compared with the solutions determined by solving the PDEs. The utility of the numerical scheme is also discussed for cases where the initial distribution cannot be represented satisfactorily by a gamma distribution.*

Introduction

The study of the degradation of polymers is an important aspect of polymer science and engineering, the applications of which include polymer recycling (Miller, 1994) and characterization (Flynn and Florin, 1985). Practical problems like low heat-transfer rates and high viscosity of melting polymers have shifted the focus of degradation of polymers by pyrolysis to the degradation of polymers in solution, which promises to be a better technology for controlled degradation of polymers (Sato et al., 1990).

A polymer is a mixture of molecules with varying sizes and, therefore, a molecular weight distribution (MWD) is needed to describe the polymer. MWDs can be characterized by the moments of the distribution of the molecules. A finite number of such molecules implies that the moments are the sums over the molecules in the polymer that constitute the distribution. However, sums are difficult to evaluate compared to integrals and, therefore, continuous distribution kinetics is generally employed to analyze the time evolution of MWDs of reacting polymers (McCoy and Madras, 2001). Continuous distribution models have been previously used to model polymer degradation (Aris and Gavalas, 1966; McCoy and Wang, 1994; Madras and McCoy, 1998). Rate coefficients are measured for the degradation of polymers by examining the time evolution of the MWDs of the reacting polymers. (Madras et al., 1997; Wang et al., 1995). The rate coefficients of the degradation reactions depend on the molecular chain length and thus on the molecular weight x. For small conversions, the rate coefficients can be assumed to be independent of the molecular weight of the reacting polymer (McCoy and Wang, 1994). However, this assumption fails when the change in the molecular weight of the reacting mixture is significant (Madras et al., 1997). McCoy and Madras (1998) assume the molecular weight dependence of the rate coefficient as x^λ, so that the rate coefficient can be constant, linear, or quadratic depending on the value of λ. A more general form of the dependence of the rate coefficient on molecular weight dependence is $k_0 + k_1 x + k_2 x^2$ (Madras et al., 1997).

For polymer degradation, the population balance equations (PBEs) govern the behavior of the MWDs of the reacting polymer (Aris and Gavalas, 1966; Ramkrishna, 1985). Depending on the type of the polymer and operating conditions, polymers fragment to yield a random or parabolic distribution of the binary daughter products or a specific distribution of products (McCoy and Madras, 1997). The stoichiometric kernel in the PBE incorporates the information on the distributions of products of the fragmentation process. Ternary or higher scission events are usually not considered as they can be described as multiple sequential binary scissions (McCoy and Wang, 1994).

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Several articles have discussed the mathematical solutions for the governing population balance equations for a variety of special cases (Aris and Gavalas, 1966; McCoy and Wang, 1994; Wang et al., 1995; McCoy and Madras, 1998; Vigil and Ziff, 1989). McCoy and and Madras (1998) present the solutions to the population balance equations in the context of similarity solutions or self-preserving solutions (Ramkrishna, 1985) by using the moment solutions techniques for a general rate dependence of the form x^{λ}.

The governing PBEs, in the form of integro–differential equations, are generally solved by moment techniques by converting them to ordinary differential equations for the molecular-weight moments. The initial MWD is assumed to be a gamma distribution, which is a versatile representation of distributions (Abramowitz and Stegun, 1968). The gamma distribution fit can be constructed by knowing the zeroth, first, and second moments. The moments are then expressed in terms of the generalized gamma distribution parameters $\alpha(t)$ and $\beta(t)$ (McCoy and Madras, 1998). Therefore, the time evolution of these parameters provides the dynamic behavior of the MWDs of the reacting polymers.

The gamma distribution is actually the first term in the generalized expansion of the MWD function in orthogonal Laguerre polynomials with higher-order terms related to the third and the higher moments of the distribution. Higher-order moments are hence neglected in considering a gamma distribution. The moment solutions are, therefore, approximations to the original solutions that can be made more accurate by considering further terms in the expansions of the orthogonal polynomials.

In the case of quadratic polynomial dependency of the rate coefficients (Madras et al., 1997), other simplifying assumptions are made to solve the ordinary differential equations that result from the application of the moment operations to the population balance equations.

The objective of the current investigation is to formulate a general numerical solution for the evolution of MWDs for a random scission stoichiometric kernel such as for the case where the degradation products are randomly distributed. Continuous distribution kinetics provide the governing PBEs, and these equations are converted to partial differential equations (PDEs). The molecular weight dependency is taken as $k_s(x) = (x - x_o)^{\lambda}$, which provides the generalized rate coefficient and reduces to the rate coefficient of $k_d x^{\lambda}$ assumed by Madras and McCoy (1998) for $x_o = 0$. Solutions are also obtained for the case of a rate coefficient of the form $k_0 + k_1 x + k_2 x^2$. The results obtained by solving the PDEs are compared with the appropriate moment solutions. The solution obtained by the method of moments is an approximation and, as shown in this study, this approximation is not valid in some cases. We also investigate the time evolution of MWDs for cases wherein the initial distribution cannot be represented by a single gamma distribution.

Theoretical Model

In continuous distribution kinetics, the polymer $P(x)$ is considered as a mixture of a large number of different size molecules with MW, and x is taken as a continuous variable. The MWD is defined such that $p(x, t)$ represents the molar concentration of polymer of MW in the interval $(x, x + dx)$ at any given time t. Thus, integration of $p(x,t)$ and $xp(x,t)$ over x yields the molar and mass concentration of the polymer, respectively. For a random chain scission and binary fragmentation, the reaction of the polymer can be expressed as

$$P(x) \rightarrow P(x') + P(x - x')$$

For a first-order reaction with a rate coefficient $k'_d(x)$ in a batch reactor, the governing equation is (Aris and Gavalas, 1966)

$$\partial p(x, t)/\partial t = -k'_d(x) p(x, t) + 2\int_x^{\infty} k'_d(x') p(x', t) \Omega(x, x') dx' \quad (1)$$

where $\Omega(x, x')$ is the stoichiometric kernel that determines the distribution of scission products and represents a reaction in which a polymer molecule cleaves into two product molecules of size x and $x - x'$. For a *totally* random distribution of degradation products, the stoichiometric kernel is (McCoy and Wang, 1994)

$$\Omega(x, x') = 1/x' \quad (2)$$

The rate coefficient in Eq. 1 can be considered a composite rate coefficient of various radical reactions (Kodera and McCoy, 1997). The general form of rate coefficient $k'_d(x)$ is (McCoy and Wang, 1994)

$$k'_d(x) = k_d(x - x_o)^{\lambda}. \quad (3)$$

Equations 2 and 3 reduce the population balance equation (PBE) (Eq. 1) to

$$\partial p(x, t)/\partial \theta = -(x - x_o)^{\lambda} p(x, \theta) + 2\int_x^{\infty} (x' - x_o)^{\lambda} p(x', \theta)(1/x') dx' \quad (4)$$

where $\theta = t k_d$. This integrodifferential equation can be converted to a partial differential equation by differentiating it with respect to x using the Leibnitz rule

$$\partial^2 p(x, \theta)/\partial\theta\partial x + (x - x_o)^{\lambda} \partial p(x, \theta)/\partial x + \left(2x^{-1}(x - x_o)^{\lambda} + \lambda(x - x_o)^{\lambda - 1}\right) p(x, \theta) = 0. \quad (5)$$

For complex mixtures or when the degradation is very high, the degradation rate dependence on MW can be represented by a polynomial in x (Madras et al., 1997)

$$k'_d(x) = k_0 + k_1 x + k_2 x^2. \quad (6)$$

Substituting Eq. 6 in Eq. 1 yields

$$\partial p(x,t)/\partial t = -\left(k_0 + k_1 x + k_2 x^2\right) p(x,t) + 2\int_x^{\infty} \left(x'^{-1} k_0 + k_1 + k_2 x'\right) p(x',t) dx'. \quad (7)$$

Equation 7 can be converted to a partial differential equation

$$\partial^2 p(x,t)/\partial t \partial x + \left(k_0 + k_1 x + k_2 x^2\right) \partial p(x,t)/\partial x + \left(2x^{-1}k_o + 3k_1 + 4k_2 x\right) p(x,t) = 0. \quad (8)$$

Partial differential equation (Eqs. 5 and 8) can be solved numerically with appropriate initial and boundary conditions to obtain the solution to the PBE (Eq. 1).

Moment solutions

A frequently used approach to the solution of the PBE is to convert it into moment equations and solve the resulting ordinary differential equations by assuming the moments as functions of gamma distribution parameters (McCoy and Madras, 1998; Wang et al., 1995). The moments for a distribution $p(x,t)$ are defined as

$$p^{(j)}(t) = \int_0^\infty x^j p(x,t)\,dx \quad (9)$$

where $p^{(j)}$ is the jth moment of the distribution. The zeroth moment $p^{(0)}(t)$ is the time-dependent total molar concentration of polymer, and the first moment $p^{(1)}(t)$ is the mass concentration. The number-average and weight-average molecular weights of the polymer mixture are defined in terms of the moments of the MWD

$$M_n = p^{(1)}/p^{(0)} \quad (10)$$

$$M_w = p^{(2)}/p^{(1)}. \quad (11)$$

The polydispersity of the polymer is defined as

$$D = M_w/M_n. \quad (12)$$

Assuming the molecular weight dependency of the rate coefficient given by Eq. 3, the moment operation defined by Eq. 9, applied on Eq. 1 gives

$$dp^{(j)}/d\theta = S \sum_{d=0}^{\lambda} \binom{\lambda}{d} p^{(j+\lambda-d)}(-x_o)^d \quad (13)$$

where $S = -(j-1)/(j+1)$ and $\binom{\lambda}{d}$ is the binomial expression, $\lambda!/[d!(\lambda-d)!]$. For $j = 0$, 1 and 2, Eq. 13 is

$$dp^{(0)}/d\theta = \sum_{d=0}^{\lambda} \binom{\lambda}{d} p^{(\lambda-d)}(-x_o)^d \quad (14a)$$

$$dp^{(1)}/d\theta = 0 \quad (14b)$$

$$dp^{(2)}/d\theta = -1/3 \sum_{d=0}^{\lambda} \binom{\lambda}{d} p^{(2+\lambda-d)}(-x_o)^d \quad (14c)$$

Equation 14b ensures that the mass of the reacting mixture is conserved, and $p^{(1)}$ is invariant with time in accordance with the batch operation. Similar solutions are obtained when the MW x appears together with time t in the similarity group (Ramkrishna, 1985). The distributions can be expressed as gamma distributions in the form of a similarity variable $(x - x_o)^\lambda/\beta(t)$, (McCoy and Madras, 1998; Ziff, 1991) and written as

$$p(x,t) = N u^{\alpha-1} \exp(-u) \quad (15)$$

where u is the similarity variable form $(x - x_o)^\lambda/\beta(t)$ and $\alpha(t)$, $\beta(t)$ are the time-dependent gamma distribution parameters, and N is the time-dependent normalizing factor. Applying moment operations to Eq. 15 yields the moments in terms of the gamma distribution parameters

$$p^{(j)} = N\lambda^{-1}\beta^{(j+1)/\lambda} \sum_{d=0}^{j} \binom{j}{d} \Gamma \times (\alpha + (j-d+1)/\lambda - 1)\left(x_o/\beta^{1/\lambda}\right)^d \quad (16)$$

where $\Gamma(x)$ is the gamma function and the time-dependent normalizing factor N is

$$N = p^{(1)}\lambda/\left[\beta^{2/\lambda}\left(\Gamma(\alpha + 2/\lambda - 1) + x_o/\beta^{1/\lambda}\Gamma(\alpha + 1/\lambda - 1)\right)\right]. \quad (17)$$

The number-average and the weight-average molecular weight are obtained by substituting Eq. 16 in Eqs. 10 and 11.

$$M_n = \beta^{1/\lambda}\left[\Gamma(\alpha + 2/\lambda - 1) + \left(x_o/\beta^{1/\lambda}\right)\Gamma(\alpha + 1/\lambda - 1)\right]/\Gamma(\alpha + 1/\lambda - 1) \quad (18)$$

$$M_w = \beta^{1/\lambda}\left[\Gamma(\alpha + 3/\lambda - 1) + 2\left(x_o/\beta^{1/\lambda}\right)\Gamma(\alpha + 2/\lambda - 1) + \left(x_o/\beta^{1/\lambda}\right)^2\Gamma(\alpha + 1/\lambda - 1)\right]/\left[\Gamma(\alpha + 2/\lambda - 1) + \left(x_o/\beta^{1/\lambda}\right)\Gamma(\alpha + 1/\lambda - 1)\right]. \quad (19)$$

The polydispersity is given by the ratio of Eqs. 19 and 18 and is

$$D = \left[\Gamma(\alpha + 3/\lambda - 1) + 2\left(x_o/\beta^{1/\lambda}\right)\Gamma(\alpha + 2/\lambda - 1) + \left(x_o/\beta^{1/\lambda}\right)^2\Gamma(\alpha + 1/\lambda - 1)\right]\left[\Gamma(\alpha + 1/\lambda - 1)\right]/ \left[\Gamma(\alpha + 2/\lambda - 1) + \left(x_o/\beta^{1/\lambda}\right)\Gamma(\alpha + 1/\lambda - 1)\right]^2. \quad (20)$$

Equations 15–17 are then substituted in the moment equations (Eqs. 14a–14c) to obtain a set of ordinary differential equations in terms of the gamma distribution parameters, $\alpha(t)$ and $\beta(t)$. For $\lambda = 1$, $k_d'(x) = k_d(x - x_o)$, the equations reduce to

$$d\left[1/(\beta\Gamma(\alpha+1)/\Gamma(\alpha) + x_o)\right]/d\theta = \Gamma(\alpha+1)/(\Gamma(\alpha+1) + (x_o/\beta)\Gamma(\alpha)) \quad (21a)$$

$$d\left[\left\{\beta(\Gamma(\alpha+2)+2(x_o/\beta)\Gamma(\alpha+1)+(x_o/\beta)^2\Gamma(\alpha)\right\}/\right.$$
$$(\Gamma(\alpha+1)+(x_o/\beta)\Gamma(\alpha))\big]/d\theta=-1/3\big[\{\beta^2\Gamma(\alpha+3)$$
$$+2\beta x_o\Gamma(\alpha+2)+x_o^2\Gamma(\alpha+1)\}/(\Gamma(\alpha+1)$$
$$\left.+(x_o/\beta)\Gamma(\alpha))\right]. \quad (21b)$$

For $\lambda=2$, $k'_d(x)=k_d(x-x_o)^2$, Eqs. 14a–14c become

$$d\left[1/(\beta^{1/2}\Gamma(\alpha)/\Gamma(\alpha-0.5)+x_o)\right]/d\theta=\beta^{1/2}(\alpha-0.5)/$$
$$\left[\Gamma(\alpha)/\Gamma(\alpha-0.5)+x_o/\beta^{1/2}\right] \quad (22a)$$

$$d\left[\beta^{1/2}\left\{(\alpha-0.5)+2\left(x_o/\beta^{1/2}\right)\Gamma(\alpha)/\Gamma(\alpha-0.5)+x_o^2/\beta\right\}/\right.$$
$$\left.\left(\Gamma(\alpha)/\Gamma(\alpha-0.5)+x_o/\beta^{1/2}\right)\right]/d\theta=-1/3\left[\beta^{3/2}(\alpha+0.5)\right.$$
$$\left.(\alpha-0.5)+2\alpha\beta x_o\Gamma(\alpha)/\Gamma(\alpha-0.5)+x_o^2\beta^{1/2}(\alpha-0.5)\right]/$$
$$\left[\Gamma(\alpha)/\Gamma(\alpha-0.5)+x_o/\beta^{1/2}\right] \quad (22b)$$

For the case of quadratic dependency of the rate coefficient, $k'_d(x)=k_0+k_1x+k_2x^2$, the moment equations are (Madras et al., 1997)

$$dp^{(0)}/dt=k_0p^{(0)}+k_1p^{(1)}+k_2p^{(2)} \quad (23a)$$

$$dp^{(1)}/dt=0 \quad (23b)$$

$$dp^{(2)}/dt=-1/3\left[k_0p^{(2)}+k_1p^{(3)}+k_2p^{(4)}\right] \quad (23c)$$

$$dp^{(3)}/dt=-1/2\left[k_0p^{(3)}+k_1p^{(4)}+k_2p^{(5)}\right] \quad (23d)$$

$$dp^{(4)}/dt=-3/5\left[k_0p^{(4)}+k_1p^{(5)}+k_2p^{(6)}\right] \quad (23e)$$

Results and Discussion

The PBE (Eq. 1) was solved for various λ, x_o and $k_d(x)$ by the moment technique and compared with the solution determined by solving the PDE. The domain of the variable x in Eq. 5 was converted to the interval [0,1) by a new variable y

$$x-x_0=Y=ay/(1-y) \quad (24)$$

The constant a (= 50,000) was introduced to keep the grid points in y such that it spans the meaningful range of the original MW variable x. The PDE (Eq. 5) in terms of y is

$$\partial^2p(y,\theta/)\partial\theta\partial y+Y^{\lambda}\partial p(y,\theta)/\partial y$$
$$+a(1-y)^{-2}\left[2Y^{\lambda}(x_o+Y)^{-1}+\lambda Y^{\lambda-1}\right]p(y,t)=0 \quad (25)$$

The partial differential equation, Eq. 25, was discretized by the finite difference scheme. A forward difference in time was used with 1×10^{-14} as the step size. The y variable was discretized into 500 intervals. The equation was solved with the boundary condition $p(y=1,t)=0$ various values of λ and x_o. The numerical scheme was verified by determining the molecular weight distribution for the case of $\lambda=1$ and $x_o=0$. An analytical solution for this case has been provided by McCoy and Madras (1998). The MWD determined by the numerical scheme matches exactly with the analytical solution indicating the validity of the numerical scheme.

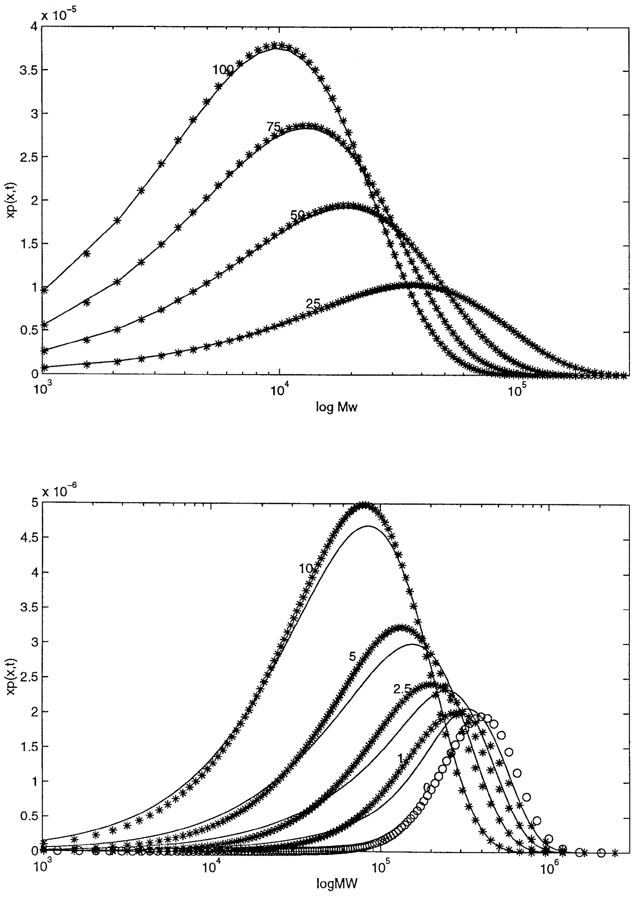

Figure 1. Time evolution of MWD $p(x, t)$ for various $\gamma(=10^6\ \theta)$ with $\lambda=1$ and $x_o=0$.

Moment solution (Eq. 21); —: PDE solution (Eq. 5); ○: Initial distribution.

For $\lambda=1$ and $x_o=0$, the PDE, Eq. 25, was solved and compared with the corresponding moment solution. The moment solutions are obtained by solving the set of ordinary differential equations, Eqs. 21a and 21b, that require the use of gamma $\Gamma(\phi)$ and digamma $d\Gamma(\phi)/d\phi$ functions. Because these functions are inbuilt in Mathematica it was used to solve Eqs. 21a and 21b. The initial MWD was chosen to be a gamma distribution (Eq. 15) with $\alpha(t=0)=4$ and $\beta(t=0)=10^5$, corresponding to M_n of 4×10^5 and D of 1.25, values that are realistic for commercially available polymers. McCoy and Madras (1998) have mathematically proved that, when $\lambda=1$ and $x_o=0$, the moment solution is the *exact* similarity solution and all initial distributions evolve to a similarity solution with $\alpha=1$, that is, equal to a polydispersity of 2, indicative of the most probable distribution (Flory, 1963). When $\alpha=1$, both the PDE solution and the moment solution should, therefore, be identical. Figure 1 depicts the evolution of the MWD for case of $\lambda=1$, $x_o=0$ for various γ ($=10^6\ \theta$). It is clearly seen that at long times, the MWD evolves to a similarity solution with $\alpha=1$ and both the PDE solution and the moment solution are identical, indicating the validity of the

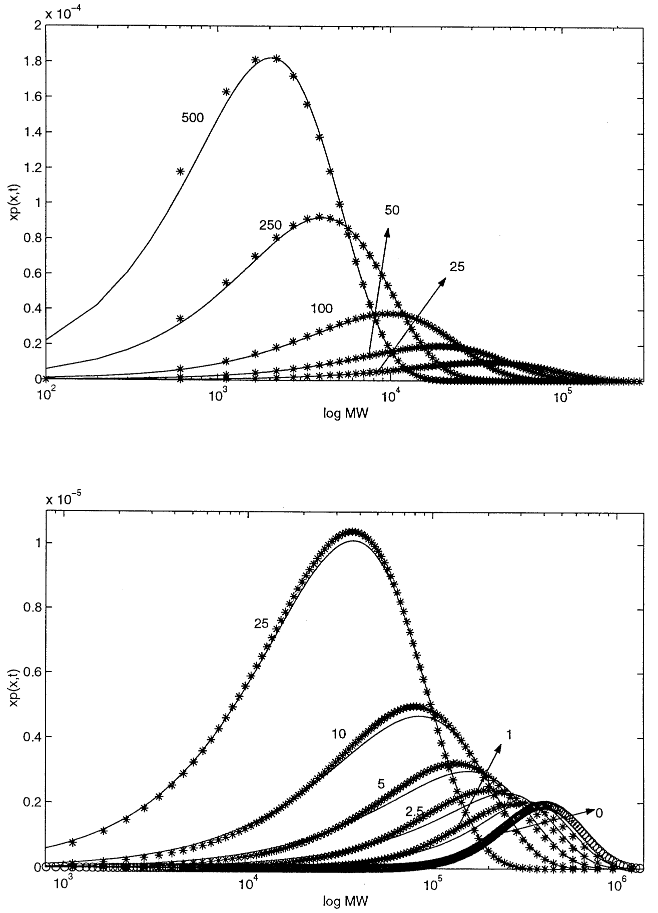

Figure 2. Dynamics of MWD $p(x, t)$ for various $\gamma(=10^6\ \theta)$ with $\lambda = 1$ and $x_o = 100$.

Moment solution (Eq. 21); —: PDE solution (Eq. 5); ○: Initial distribution.

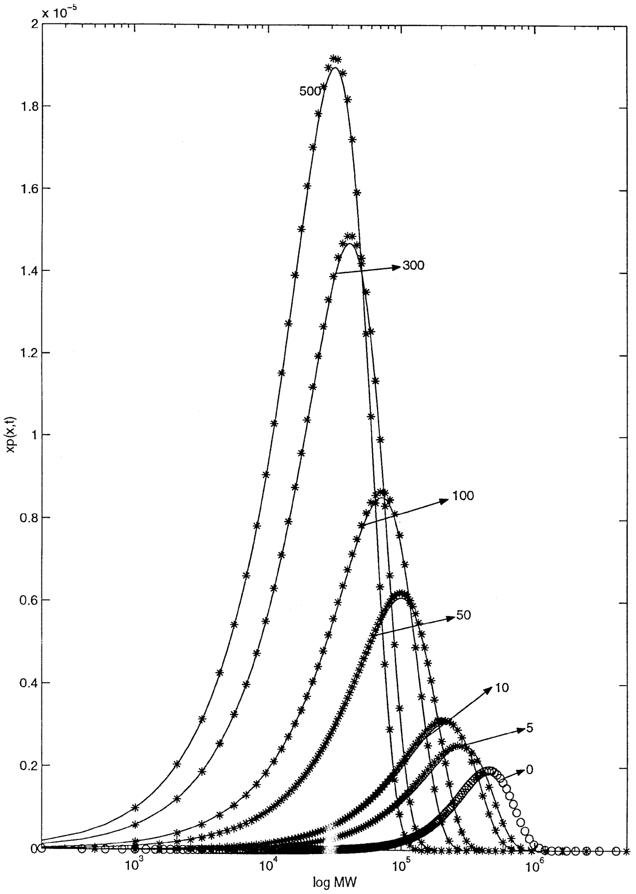

Figure 3. Time evolution of MWD $p(x, t)$ with initial gamma distribution parameter $\alpha(t = 0) = 1.588$ for various values of time $(=10^{12}\ \theta)$ with $\lambda = 2$ and $x_o = 0$.

Moment solution (Eq. 22); —: PDE solution (Eq. 25); ○: Initial distribution.

numerical scheme. However, the moment solutions differ from the PDE solutions at low γ (<25). When $\lambda = 1$, the degradation rate coefficients k_d of polymers are usually around 10^{-9} g^{-1} min^{-1} mol (Madras et al., 1997) and, thus, $\gamma = 1$ itself corresponds to long reaction times ($\approx 1{,}000$ min). This indicates that, although the similarity solution is exact for $\lambda = 1$ and $x_o = 0$, the moment and PDE solutions are not identical until the similarity solution is reached.

When $\lambda = 1$ and x_o is finite, there is no similarity solution. This case was investigated for the same initial distribution by solving PDE (Eq. 25) and the moment equations, Eqs. 21a–21b, with $x_o = 100$ (indicative of the monomer MW). Figure 2 compares the time evolution of the MWD obtained by the moment technique and the evolution determined by solving the PDEs. At high γ (>50), both the solutions match reasonably well. However, at low γ both the solutions differ, indicating that the moment technique is slightly inaccurate. Because there is no similarity solution, the polydispersity starts increasing from its initial value of 1.25 to nearly 2 ($D = 1.975$ at $\gamma = 100$) and then decreases ($D = 1.94$ at $\gamma = 500$) ultimately reaching unity (not shown in the figure), indicating that all of the polymer has degraded to monomer.

The solution of the PBE was determined for $\lambda = 2$ and $x_o = 0$. The initial distribution is assumed to be a gamma distribution and both the PDE and moment solutions are determined for two different initial distributions. For the case $\alpha(t = 0) = 1.588$, $\beta(t = 0) = 10^{10}$ such that the initial polydispersity is 1.25 and $M_n = 4 \times 10^5$, the moment solution is in reasonable agreement with the PDE solution for $\theta \geq 10^{-11}$ (Figure 3). When the initial distribution is assumed to be $\alpha(t = 0) = 3.108$ and $\beta(t = 0) = 10^{10}$ corresponding to M_n of 1.53×10^5 and D of 1.1, the moment solution is considerably different from the PDE solution (Figure 4) for even $\theta \geq 10^{-11}$. Since when $\lambda = 2$, the degradation rate coefficient k_d of polymers is usually around 10^{-13} min^{-1} g^{-2} mol^2 (Madras et al., 1997), this corresponds to a reaction time of 100 min. This indicates that higher moments are required for describing the dynamics of MWD, especially when the value of the gamma distribution parameters α is much different than 1. When $\alpha(t)$ approaches 1, the moment solution is a good approximation, but is not an exact solution. This is consistent with the results of Madras and McCoy (1998) that, when $\lambda = 2$, the similarity solution $\alpha = 1$ satisfies the first three moments, but is not an exact solution to the PBE, given by Eq. 1.

When the rate coefficient depends as a quadratic polynomial in MW, x, the PDE is given by Eq. 8 and the moment solutions can be determined by solving Eqs. 23a–23e. Equation 8 is discretized by finite difference scheme by converting the variable x in terms of another variable z as

$$x = az/(1 - z). \tag{26}$$

The resulting equation is then solved with the appropriate initial and boundary conditions. However, Eqs. 23a–23e governing the moment solution cannot be solved directly due to lack of "closure," that is, the differential equation for the fourth moment (Eq. 23e) depends on the fifth and sixth moments. Madras et al. (1997) have solved the equation by assuming a monodisperse distribution

$$p^{(5)}(t) = p^{(4)}(t)p^{(1)}/p^{(0)}(t) \tag{27a}$$

$$p^{(5)}(t) = p^{(4)}(t)\left[p^{(1)}/p^{(0)}(t)\right]^2 \tag{27b}$$

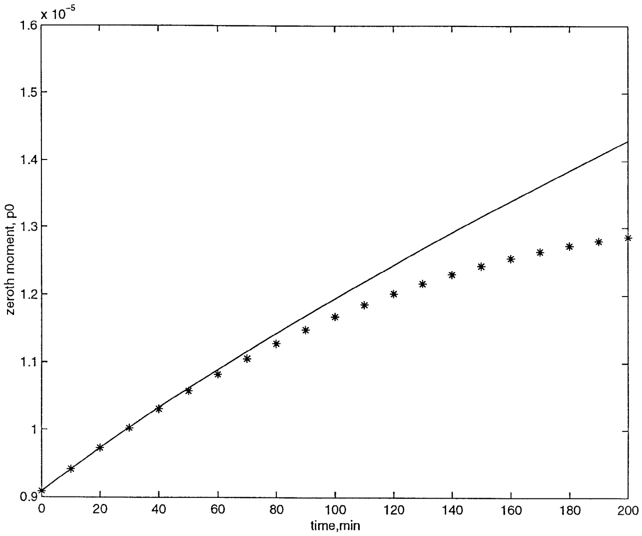

Figure 5. Variation of zeroth moment with time when the rate coefficient is given by $k_0 + k_1x + k_2x^2$.

Moment solution (Eq. 23); —: PDE solution (Eq. 8).

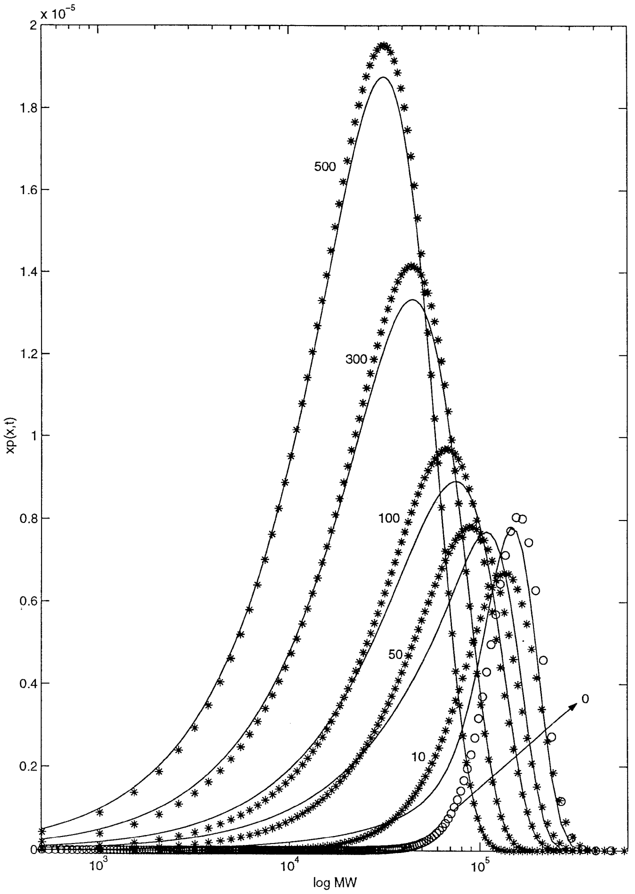

Figure 4. Time evolution of MWD $p(x, t)$ with initial gamma distribution parameter $\alpha(t = 0) = 3.108$ and for various values of time ($10^{12}\ \theta$) with $\lambda = 2$ and $x_o = 0$.

Moment solution (Eq. 22); —: PDE solution (Eq. 25); ○: Initial distribution.

Equations 23a–23e were solved with the assumptions given by Eqs. 27a and 27b and compared with the solution obtained by solving the PDE (Eq. 8) discretized by Eq. 26. The initial conditions were chosen to be a gamma distribution based on the experimental data of Madras et al. (1997) with $M_n = 110{,}000$ and $D = 1.8$ with the rate coefficient $k_d(x) = 2.0 \times 10^{-4} + 2.0 \times 10^{-9}x + 1.5 \times 10^{-13}x^2$. Figures 5 and 6 compare the solutions determined by the two methods by depicting the time variation of zeroth and second moments of the MWD. It is seen that the monodisperse assumption is erroneous, especially for second moments.

The partial differential equation is capable of predicting the time evolution of MWDs regardless of the initial distribution unlike the method of moments that require the initial distribution to be represented by a gamma distribution. The versatility of the PDE technique can be illustrated by considering initial MWDs that cannot be represented satisfactorily by a gamma distribution.

A polymer with a very narrow initial distribution (near monodisperse) with polydispersity D ($= 1.0034$) and M_n ($= 4 \times 10^5$) is considered. A gamma distribution fit (Eq. 15) to this MWD will result in high values for the parameter $\alpha(t = 0)$, as for a monodisperse polymer $\alpha \to \infty$. Modeling of the MWD based on the time evolution of the gamma distribution parameters would be erroneous and a gamma distribution representation would be faulty. However, the time evolution of the MWD can be determined by solving the PDE with this initial distribution. Figure 7 shows the time evolution of a distribution, when $\lambda = 1$, that is indicative of a near monodisperse polymer. The distribution evolves to a similarity solution ($D = 2$) at long times confirming the observation of McCoy and Madras (1998) that, for random scission, all distributions evolve to a similarity solution regardless of their initial polydispersity.

Multimodal distributions are often encountered in polymers and the polymers have to be pretreated by chemical fractionation to make the distribution unimodal (Wang et al., 1995). Gamma distribution with two parameters, given by Eq. 15, can represent only unimodal distributions and the mo-

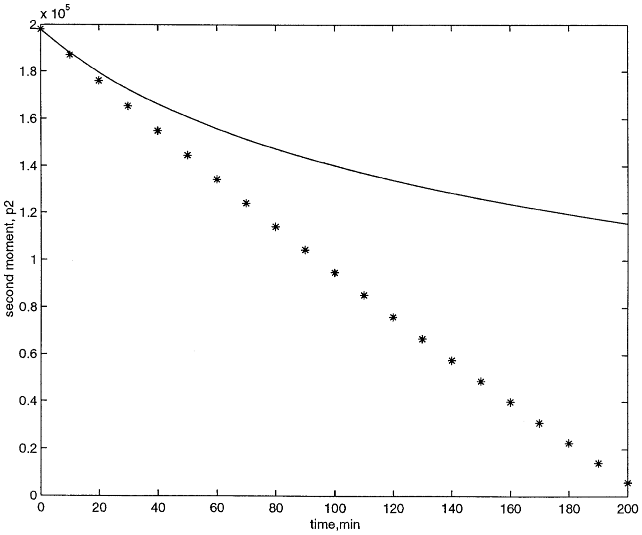

Figure 6. Change in second moment with time for a quadratic dependency of the rate coefficient.

Moment solution (Eq. 23); —: PDE solution (Eq. 8).

ment technique has to be suitably modified before it can be applied to the case of multimodal distributions. The initial condition in this case has to be represented as the superposition of two or more distinct gamma distributions and the resulting equations may be difficult to solve. As an example, we solve the PDE (Eq. 25) with a bimodal initial distribution. Figure 8 shows the time evolution of a bimodal distribution when $\lambda = 1$. The inset of the figure shows the initial bimodal distribution evolving to a unimodal distribution. The distribution eventually evolves to the similarity solution with polydispersity $D = 2$.

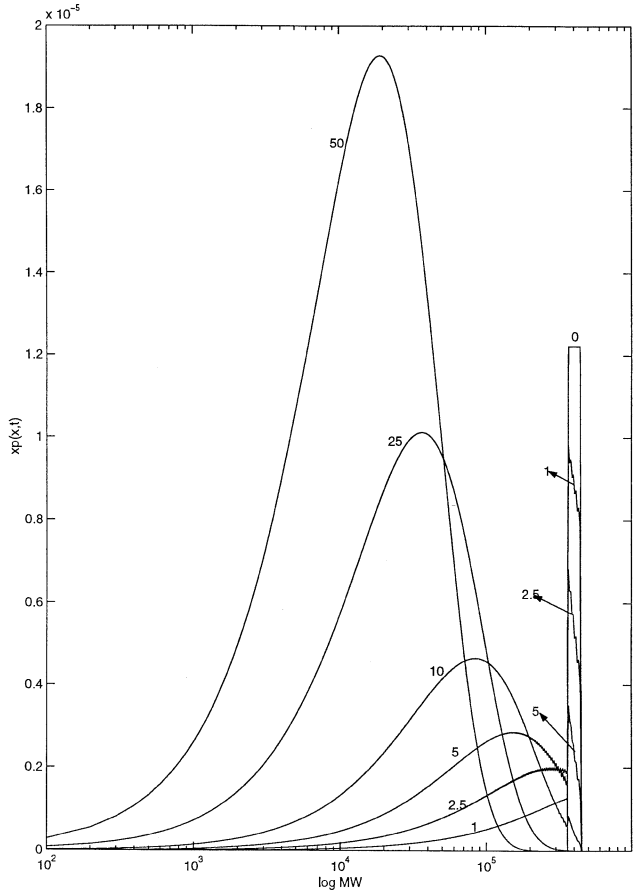

Figure 7. Time evolution of a near monodisperse MWD of $D = 1.003$ for various values of time $\gamma (= 10^6\ \theta)$.

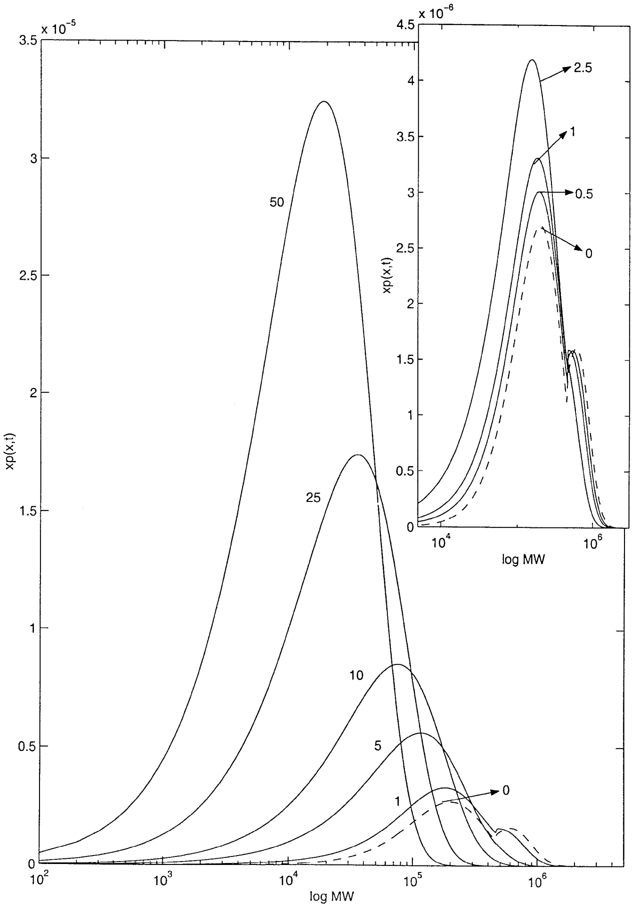

Figure 8. Evolution of a bimodal initial MWD for different values of time $\gamma (= 10^6\ \theta)$.

Inset shows the evolution of bimodal to a unimodal distribution. The dotted line denotes the initial distribution.

Figure 9 shows a general broad distribution, with $M_n = 3 \times 10^5$ and polydispersity of 1.667, which is not satisfactorily represented by a gamma distribution. Such broad distributions are observed in some commercially available polymers including polyethylene. This distribution can be represented by an addition of two gamma distributions (shown by broken lines in Figure 9). Since the resulting equations may be difficult to solve, this distribution can be represented by a single gamma distribution with $\alpha(t = 0)\ (= 1.5)$ and $\beta(t = 0)$ $(= 2 \times 10^5)$ determined from the initial number- and weight-average MW by Eqs. 18 and 19 with $\lambda = 1$. The evolution of this MWD was investigated by the moment method by using the single gamma distribution and by solving the PDEs without making any assumptions on the initial distribution. Figure 10 shows the time evolution of the MWD distri-

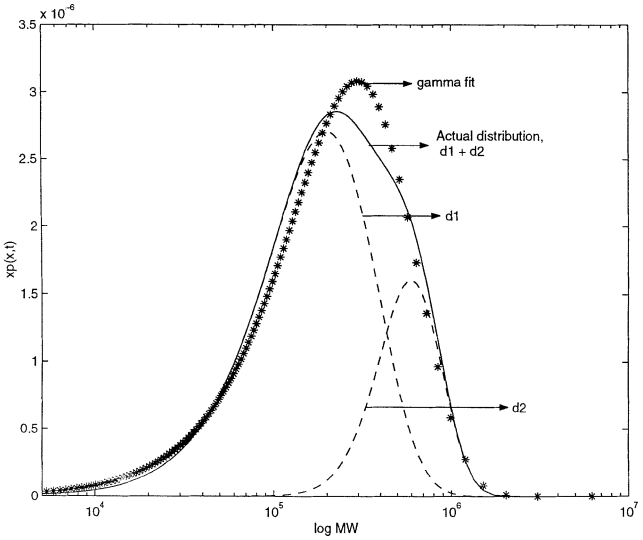

Figure 9. Gamma distribution fit for a broad MWD where the initial MWD can be represented as an addition of two gamma distributions.

Gamma distribution fit; —actual distribution; – – gamma distributions comprising the distribution.

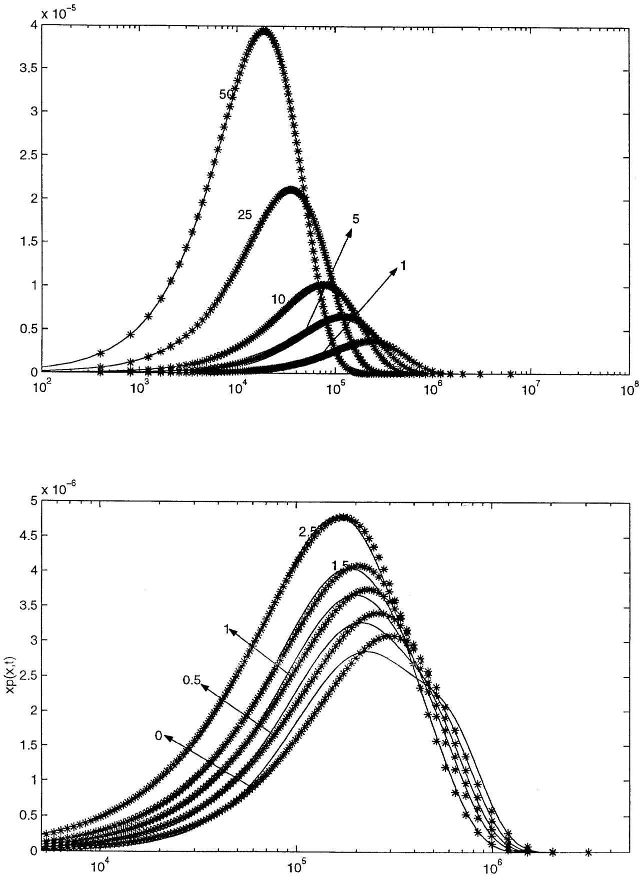

Figure 10. Comparison of the moment solution and the PDE solution for time evolution of distribution in Figure 9.

Moment solution (Eq. 21); —: PDE solution (Eq. 5); ○: Initial distribution.

bution obtained by both the methods. As expected, the prediction of the time evolution of MWDs by the moment method is poor. However, for large θ the polymer reacts and evolves to a MWD that conforms to a gamma distribution and the moment solution in agreement with the PDE solution.

Conclusions

Two different techniques were compared for solving the PBEs that result from modeling of the polymer degradation reactions undergoing random scission. The PBEs can either be solved by the method of moments, or by converting them to PDEs. We show that, although the similarity solution obtained by the moment method is identical to the solution obtained by solving the PDE when $\lambda = 1$ and $x_o = 0$, the solutions are not identical at low θ, corresponding to reaction times of 100–1,000 min. The solutions are also compared for other values of λ and x_o, and it is shown that the moment solutions can be erroneous in certain cases. Although the first three moments determined by the moment technique and the numerical scheme do not differ much and can be used for determination for the rate coefficients from experimental data, the numerical scheme must be preferred for prediction or fitting MWDs. We have also determined the time evolution of MWDs when the initial distribution is biomodal, or narrow, or broad distribution, wherein the initial condition cannot be satisfactorily represented by a gamma distribution. Therefore, this method of determining the solution by numerically solving the PDEs is a powerful technique for solving PBEs that result from the random degradation of the polymer.

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