Molecular-Weight Distribution Kinetics for Ultrasonic Reactions of Polymers

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Ultrasonic degradation of polymers is distinguished from thermal degradation by: midpoint rather than random chain scission; a lower limit of molecular weight (MW), x_f, below which the polymer will not undergo midpoint scission; and possible biomodal distribution evolving with time. The molecular-weight distribution (MWD) is governed by a population-balance equation whose time dependence is deduced from MW moments. To examine if ultrasonically induced reactions have similarity solutions, the moment equations were considered in terms of the time evolution of generalized gamma distribution parameters. The rate coefficient for chain scission is assumed to depend on MW, x, as $\kappa (x - x_f)$, where x_f is the limiting MW. The MWD approaches a similarity solution (with a polydispersity of 1.5) only when limiting MW x_f is zero. This study also provides an exact analytical solution for the MWD, showing how the MWD can evolve, with reaction time, from an unimodal distribution to a bimodal distribution. Numerical solutions are presented for cases when a polymer undergoes a reversible chain-end scission along with midpoint chain scission. The rate coefficients for chain-end scission and polymerization are assumed independent of MW. The theory satisfactorily explains experimental observations.

Introduction

The ultrasonic degradation of polymers has several unique characteristics that are of interest from both commercial and academic viewpoints (Price, 1990). Ultrasonic treatment has attracted considerable attention as a means of assisting and moderating physical and chemical processes. The effect of ultrasound can be attributed to cavitation, the growth and rapid collapse of the microbubbles as the ultrasound wave propagates through the solution (Price, 1990; Nguyen et al., 1997). Near the collapsing bubble, polymer chains are caught in the high-gradient shear field. Chain segments in this shear field will move at a higher velocity than those farther away from the collapsing cavity. The relative motion of the polymer segments and solvents produces stresses on the polymer chains that cause scission. Breaks are favored near the chain midpoint rather than near the chain ends, where the shorter chain segments undergo rapid reptation. The study of the kinetics of ultrasonic degradation is crucial in understanding the underlying mechanisms of degradation.

Two approaches have been generally followed for the calculation of rate coefficients. Earlier work relied solely on the measurement of the change in the number-average molecular weight (MW) with reaction time to estimate the number of bonds that were broken. Schmid (1940) considered the breakage of an initially monodisperse polymer and assumed the degradation rate proportional to $M_n - M_{\lim}$, where $M_{\lim}$ is the limiting number-average MW. Jellinek and White (1951) made similar assumptions and also hypothesized that the bonds in the chain were broken randomly. Mostafa (1956) extended this model for an initial polydisperse sample with a "most probable" distribution. Ovenall et al. (1958) applied a related approach but used a rate coefficient independent of the degree of polymerization. These methods have one or more drawbacks, such as the assumption of an initially monodisperse polymer, use of inappropriate chain-scission

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expressions, or neglect of the time evolution of the molecular-weight distribution (MWD). We will show that the degradation kinetics can be strongly influenced by these factors.

The first study that measured the change in MWD was that of Jellinek and White (1951), who calculated the distributions of ultrasonically degraded polystyrene in methyl ethyl ketone by fractional precipitation. Later, similar studies (Mostafa, 1958) showed that the polydispersity changed throughout the reaction. Glynn et al. (1972) defined a degradation index based on number-average MWs and developed a basic model in terms of probabilities. The predicted distributions compared poorly with the experimental MWD of polystyrene degraded in tetrahydrofuran. The model was later modified (Van der Hoff, 1974) to account for the limiting molecular weight. However, others (Linkens et al., 1978; Plaumann and Ho, 1987) found that the degradation index just defined was not a satisfactory parameter when applied to polymers with a wide distribution. With the advent of gel permeation chromatography, the overall change in the MWD has been monitored. Such studies include the degradation of poly(isobutylene) (Porter, 1967), poly(dimethyl siloxanes) (Shaw and Rodriguez, 1967), poly(alkyl methacrylates) (Malhotra, 1986), poly(methyl methacrylate) (Wu et al., 1977). Rate coefficients have recently been formulated based on continuous distribution kinetics applied to the time evolution of the MWDs (Madras et al., 2000; Madras and Karmore, 2001).

The time-evolution of the MWD is fundamental to the study of polymer degradation. Mathematical solutions for degradation dynamics have been discussed by Aris and Gavalas (1966), McCoy and Wang (1994), Wang et al. (1995), and McCoy and Madras (1997). 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 rate coefficient is considered either a constant or linearly dependent on the MW. If the change in average MW is not large, an average rate coefficient independent of MW is satisfactory (Madras et al., 1995), but for large conversions, it is necessary to consider the dependence of the rate coefficient on the MW (Madras et al., 1997). For the case when the limiting MW is relatively small, McCoy and Madras (1998) showed that a similarity solution exists when the rate coefficient is linearly dependent on MW.

The objective of the present study is to formulate general quantitative solutions for the evolution of MWDs with a stoichiometric kernel for midpoint chain scission. The model overcomes limitations of prior work (McCoy and Madras, 1998) by assuming the midpoint scission rate coefficient is linearly dependent on the MW *above the limiting MW*. Continuous-distribution population balances provide the governing integrodifferential equations that are converted to ordinary differential equations for the first three MW moments. The moments are expressed in terms of time-dependent gamma distribution parameters, and the solutions for the evolution of the MWD are obtained. The solution evolves to a similarity solution only when no limiting MW is assumed. In other cases, solutions that satisfy the first three moments are determined. For polymers with low initial polydispersity, we show how the initial MWD evolves to a bimodal distribution. We also present continuous distribution kinetic models and numerical solutions when the polymer undergoes a reversible chain-end scission along with midpoint chain scission. Thus, this article addresses the most relevant factors in the ultrasonic degradation of polymers (Nguyen et al., 1997): the type of chain scission, the degradation time, the effect of the initial polymer MW, and the temporal evolution of MWDs. The continuous distribution models are quite general and can be applied to particulate systems, biochemical systems, and mechanical degradation of polymers, where fission yields two equal-sized products.

Theoretical Model

In a discrete kinetics approach, the rate equations are complex because the polymer mixture of various chain lengths undergoes a series of parallel reactions at different rates. Continuous distribution models provide a simple yet effective technique to study the dynamics of macromolecular reactions. The polymer, $P(x)$, is considered to be a mixture of homologous molecules with MW, x, as a continuous variable. The polymer undergoing chain scission can be represented as

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

Based on molar concentration, we define the time-dependent MWD of $P(x)$, by $p(x,t)$. For chain scission the distribution kinetics equation with loss and gain terms on the righthand side (McCoy and Wang, 1994) is

$$\partial p(x,t)/\partial t = -k_d(x)p(x,t) + 2\int_{x_f}^{\infty} k_d(x')p(x',t)\Omega(x,x')\,dx', \tag{2}$$

where x_f is the limiting MW and $\Omega(x,x')$ is the stoichiometric kernel. McCoy (1993) has shown that for scission yielding precisely proportioned fragments, the stoichiometric kernel can be represented with Dirac delta functions. For equal-sized fragments, the stoichiometric kernel that satisfies the symmetry conditions is $\Omega(x,x') = \delta(x - x'/2)$. The MW moments for $x > x_f$ are defined as

$$p^{(j)}(t) = \int_{x_f}^{\infty} x^j p(x,t)\,dx. \tag{3}$$

The degradation rate coefficient depends on size (Madras et al., 1997). For scission with a limiting MW, the degradation rate coefficient can be assumed to be $k_d(x) = \kappa(x - x_f)^{\lambda}$. Applying the moment operation to Eq. 2, we obtain a differential equation for the moments, for $\lambda = 1$,

$$dp^{(j)}/dt = \kappa(2^{1-j} - 1)\left[p^{(j+1)} - x_f p^{(j)}\right]. \tag{4}$$

For $j = 0$, 1, 2, the preceding equation is

$$dp^{(0)}/dt = \kappa\left[p^{(1)} - x_f p^{(0)}\right] \tag{5}$$

$$dp^{(1)}/dt = 0 \tag{6}$$

$$dp^{(2)}/dt = (-\kappa/2)\left[p^{(3)} - x_f p^{(2)}\right]. \tag{7}$$

The differential equation for the zeroth moment, Eq. 5, is easily solved to show how the molar concentration increases from its initial condition, $p_o^{(0)}$, to its final value, $p^{(0)}(t\to\infty) = p_o^{(1)}/x_f$, in terms of the initial polymer mass concentration, $p_o^{(1)}$. This establishes that in the long-time limit the polymer is completely degraded to chains of the limiting MW, x_f. The number average MW, M_n, of the polymer is defined as $p^{(1)}/p^{(0)}$. By Eq. 6, the mass of the polymer, $p^{(1)} = p_o^{(1)}$, is constant. Thus M_n decreases from its initial value, M_{no}, to its final long-time value, x_f, as required.

Following previous analytical solution procedures (Ziff, 1991; McCoy and Madras, 1998), let us consider the gamma distribution as a possible similarity solution,

$$p(x,t) = p^{(0)}u^{\alpha-1}e^{-u}/[\beta\Gamma(\alpha)], \tag{8}$$

where $u = (x - x_f)/\beta$ ensures that x_f is the smallest MW in the MWD and in general both $\beta(t)$, and $\alpha(t)$ can be functions of time. For a similarity solution to exist, x must be combined with t into one variable that describes the solution as $t\to\infty$. For population balance equations, this occurs when α reaches a constant value, while β continues to change. The moments of the gamma distribution are

$$p^{(j)} = \left[p^{(0)}/\Gamma(\alpha)\right]\int_0^\infty (x_f+\beta u)^j u^{\alpha-1}e^{-u}du = \left[p^{(0)}/\Gamma(\alpha)\right]\sum_{d=0}^{j}\binom{j}{d}\beta^d x_f^{j-d}\Gamma(\alpha+d), \tag{9}$$

where $\binom{j}{d}$ refers to the binomial coefficient. The first and second moments of the gamma distribution are

$$p^{(1)} = p^{(0)}(x_f+\beta\alpha) \tag{10}$$

$$p^{(2)} = p^{(0)}\left[x_f^2 + 2\beta\alpha x_f + \alpha(\alpha+1)\beta^2\right]. \tag{11}$$

The number- and weight-average MWs and the polydispersity are

$$M_n = p^{(1)}/p^{(0)} = x_f + \beta\alpha \tag{12}$$

$$M_w = p^{(2)}/p^{(1)} = \left[x_f^2 + 2\beta\alpha x_f + \alpha(\alpha+1)\beta^2\right]/(x_f+\beta\alpha) \tag{13}$$

$$D = M_w/M_n = \left[x_f^2 + 2\beta\alpha x_f + \alpha(\alpha+1)\beta^2\right]/(x_f+\beta\alpha)^2 = 1 + \alpha\beta^2/(x_f+\beta\alpha^2). \tag{14}$$

A solution for the first three moments, given by Eqs. 5–7, can be obtained by rewriting the equations in terms of the gamma distribution parameters. The time dependence of the gamma distribution parameters can then be obtained. The first three moment equations, in terms of the gamma distribution parameters and $p^{(1)}$, are

$$d\ln h_1/dt = \kappa\alpha\beta \tag{15}$$

$$dp^{(1)}/dt = 0 \tag{16}$$

$$d\ln h_2/dt = (-\kappa/2)\left[p^{(3)}/p^{(2)} - x_f\right], \tag{17}$$

where $h_1 = p^{(1)}/(x_f+\beta\alpha)$ and $h_2 = p^{(1)}\,[x_f^2 + 2x_f\beta\alpha + \alpha(\alpha+1)\beta^2]/(x_f+\beta\alpha)$. The ratio $p^{(3)}/p^{(2)}$, in Eq. 17, can be written in terms of α and β using Eq. 9,

$$p^{(3)}/p^{(2)} = \left[x_f^3 + 3x_f^2\alpha\beta + 3x_f\alpha(\alpha+1)\beta^2 + \alpha(\alpha+1)(\alpha+2)\beta^3\right]/\left[x_f^2 + 2x_f\beta\alpha + (\alpha^2+\alpha)\beta^2\right]. \tag{18}$$

Equations 15–18 can be reduced to two equations in α and β and solved numerically.

Defining $\theta = \kappa t$, subtracting Eqs. 15 and 17, and applying Eq. 16, we get

$$-d\ln\left[x_f^2 + 2x_f\beta\alpha + \alpha(\alpha+1)\beta^2\right]/d\theta = \alpha\beta + \left[p^{(3)}/p^{(2)} - x_f\right]/2. \tag{19}$$

Equation 19 can be rewritten as

$$2x_f(\alpha\, d\beta/d\theta + \beta\, d\alpha/d\theta) + (2\alpha+1)\beta^2\, d\alpha/d\theta + 2(\alpha^2+\alpha)\beta\, d\beta/d\theta = -\left[x_f^2 + 2x_f\beta\alpha + (\alpha^2+\alpha)\beta^2\right]\left[\alpha\beta + \left(p^{(3)}/p^{(2)} - x_f\right)/2\right]. \tag{19a}$$

Rearranging Eqs. 15 and 16 yields,

$$d\ln(x_f+\beta\alpha)/d\theta = -\alpha\beta, \tag{20}$$

which is equivalent to

$$\alpha\, d\beta/d\theta + \beta d\alpha/d\theta = -\alpha\beta(x_f+\beta\alpha). \tag{20a}$$

Equations 19a and 20a govern the time dependence of the gamma distribution parameters. Computational results and discussion are presented below.

Exact solution for MWD evolution to bimodal distribution

Some investigators (Smith and Temple, 1968; Price and Smith, 1991) have observed the evolution of the MWD from a unimodal to a bimodal distribution for the ultrasonic degradation of polystyrene. This evolution can be simulated by considering separate population balances for the reactant and the product polymers, an approach suggested by McCoy and Madras (1997). Instead of a moment solution to the two population balance equations, we show that an analytical solution can be formulated when reactant polymers on average undergo at most one midpoint scission. For $x > x_f$ the distribution kinetics equation for reactants is

$$\partial p(x,t)/\partial t = -k_d(x)p(x,t), \tag{21}$$

with $k_d(x) = \kappa(x - x_f)$. With the initial condition, $p(x,t=0) = p_o(x)$, the solution to Eq. 21 is

$$p(x,t) = p_o(x)\exp\left[-\kappa(x-x_f)t\right], \tag{22}$$

which plots as a MWD that declines with time. As in Eq. 2, the equation for products is

$$\partial q(x,t)/\partial t = 2\int_x^\infty \kappa(x'-x_f)p(x',t)\delta(x-x'/2)dx', \tag{23}$$

where $x_f < x'/2 < x' < \infty$. The interval of integration covers the Dirac delta positioned at $x = x'/2$, which can also be written as $\delta(x' - 2x)$. Utilizing the selection property, $\int f(x)\delta(x-a)\,dx = f(a)$, yields

$$\partial q(x,t)/\partial t = 2\kappa(2x - x_f)p(2x,t). \tag{24}$$

Substituting $2x$ for x in Eq. 22 and applying the initial condition, $q(x,t=0) = 0$, gives a differential equation that can be solved for the product MWD,

$$q(x,t) = 2p_o(2x)\left\{1 - \exp\left[-\kappa(2x-x_f)t\right]\right\}. \tag{25}$$

The MWD that is measured by GPC is the sum of reactant and product polymers,

$$p_{\text{tot}}(x,t) = p(x,t) + q(x,t) = p_o(x)\exp\left[-\theta(x-x_f)\right] + 2p_o(2x)\left\{1 - \exp\left[-\theta(2x-x_f)\right]\right\}. \tag{26}$$

Equation 26 describes the evolution of the MWD with reaction time, $\theta = \kappa t$. Such an explicit solution for the MWD is possible only because midpoint scission is expressed as a Dirac delta stoichiometric kernel. The only constraint on this exact analytical solution for the MWD undergoing midpoint chain scission is that the initial average MW, M_{no}, should be no more than about twice the final value of M_n. This ensures that reactant polymers experience but one midpoint scission on average. Numerical solutions, however, can be developed for polymers that undergo multiple scissions (McCoy and Wang, 1994; McCoy and Madras, 1997).

Reversible chain end and midpoint scission

Experimental observations indicate that ultrasonic degradation can also yield chain-end products (monomers or oligomers) of low MW x_e in addition to midpoint chain-scission products (Kumar et al., 2001). The reversible chain-end reaction can be represented as

$$P(x) \underset{k_{ea}}{\overset{k_e}{\rightleftharpoons}} P(x-x_e) + Q(x_e), \tag{27}$$

where $Q(x_e)$ is the chain-end product. The chain-end rate coefficients are independent of x (McCoy and Madras, 1998) and may depend on thermodynamic conditions, such as temperature. Thus we assume for the chain-end scission rate coefficient, $k_e(x) = k_e$, and for the polymerization rate coefficient, $k_{ea}(x) = k_{ea}$. When the polymer experiences reversible chain-end scission as well as midpoint scission, the distribution kinetics equation for the reactant polymer is

$$\begin{aligned}\partial p(x,t)/\partial t = &-\kappa(x-x_f)p(x,t) \\ &+ 2\int_x^\infty \kappa(x'-x_f)p(x',t)\delta(x-x'/2)\,dx' - k_e p(x,t) \\ &+ k_e\int_x^\infty p(x',t)\delta\left(x-(x'-x_e)\right)\,dx' \\ &- k_{ea}p(x,t)\int_0^\infty q_e(x,t)dx + k_{ea}\int_0^x q_e(x',t)p(x-x',t)dx'.\end{aligned} \tag{28}$$

The species Q_e of specific MW x_e has a monodisperse distribution,

$$q_e(x,t) = q_e^{(0)}(t)\delta(x-x_e). \tag{28a}$$

In the last integral in Eq. 28 the position of the delta is $x' = x_e$, where $0 \le x' - x_e \le x$, so that the integration gives $k_{ea}p(x-x_e,t)q_e^{(0)}$. The differential equation for $p(x,t)$ becomes

$$\begin{aligned}\partial p(x,t)/\partial t = &-\left[\kappa(x-x_f) + k_e\right]p(x,t) \\ &+ 2\kappa(2x-x_f)p(2x,t) + k_e p(x+x_e,t) \\ &- k_{ea}p(x,t)q_e^{(0)} + k_{ea}p(x-x_e,t)q_e^{(0)}.\end{aligned} \tag{29}$$

If $x_e \ll x_f$, then $p(x \pm x_e,t) \approx p(x,t)$ and to a good approximation

$$\partial p(x,t)/\partial t = -\kappa(x-x_f)p(x,t)) + 2\kappa(2x-x_f)p(2x,t). \tag{29a}$$

The moment operation on Eq. 29a would yield an equation identical to Eq. 5. Therefore, in so far as chain-end scission and polymerization are secondary effects ($x_e \ll x_f$), they do not significantly influence the polymer MWD.

The general moment equation for the population balance Eq. 28 is

$$\begin{aligned}dp^{(j)}/dt = &-\kappa(2^{1-j}-1)\left(p^{(j+1)} - x_f p^{(j)}\right) - k_e p^{(j)} \\ &+ k_e\sum_{d=0}^{j}\binom{j}{d}p^{(j-d)}(-x_e)^d + k_{ea}\sum_{d=0}^{j}\binom{j}{d}p^{(j-d)}q_e^{(d)} \\ &- k_{ea}p^{(j)}q_e^{(0)}.\end{aligned} \tag{30}$$

The zeroth ($j = 0$ in Eq. 30) moment equation is

$$dp^{(0)}/dt = \kappa\left[p^{(1)} - x_f p^{(0)}\right]. \tag{31}$$

The governing distribution kinetics equation of the chain-end product is

$$\partial q_e(x,t)/\partial t = k_e \int_x^\infty p(x',t)\,\delta(x - x_e)\,dx' - k_{ea} q(x_e,t) \int_0^\infty p(x',t)\,dx'. \quad (32)$$

When Eq. 28a is substituted, $\delta(x - x_e)$ can be canceled as a common factor in Eq. 32, which gives

$$dq_e^{(0)}/dt = k_e p^{(0)} - k_{ea} p^{(0)} q_e^{(0)}, \quad (33)$$

or in terms of $\theta = \kappa t$,

$$dq_e^{(0)}/d\theta = -(k_e/\kappa) p^{(0)}\left(1 - q_e^{(0)} k_{ea}/k_e\right). \quad (33a)$$

When the time derivative vanishes, Eq. 33 shows that the final (long-time) end-product concentration is $q_e^{(0)}\ (t \to \infty) = k_e/k_{ea}$.

The equations for the first moment are

$$dq^{(1)}/dt = -dq^{(1)}/dt = -x_e\left(k_e p^{(0)} - k_{ea} p^{(0)} q_e^{(0)}\right), \quad (34)$$

which with the initial conditions, $p^{(1)}(t = 0) = p_o^{(1)}$ and $q_e^{(0)}(t = 0) = 0$, gives

$$p_o^{(1)} - p^{(1)} = x_e q_e^{(0)}. \quad (35)$$

Equation 35 confirms that the total polymer and chain-end mass is conserved. Equation 35 can be substituted in Eq. 31

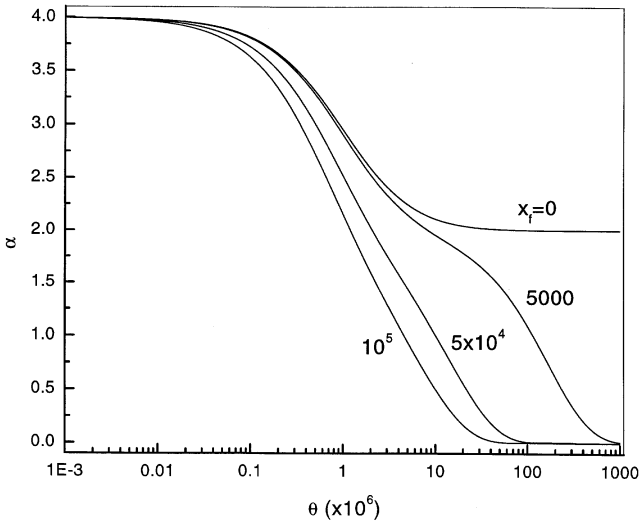

Figure 1. Gamma distribution parameter, α, vs. θ for various values of limiting MW, x_f, with $\alpha_o = 4$ and $\beta_o = 10^5$.

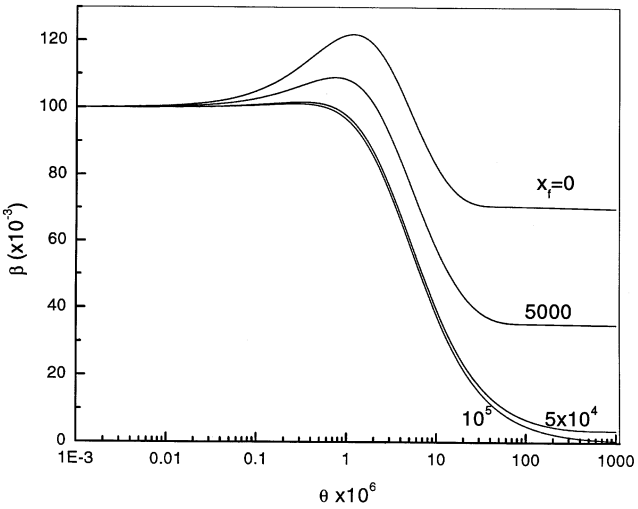

Figure 2. Variation of gamma distribution, β, with θ for various values of limiting MW, x_f, with $\alpha_o = 4$ and $\beta_o = 10^5$.

to obtain

$$dp^{(0)}/dt = \kappa\left[p_o^{(1)} - x_e q_e^{(0)} - x_f p^{(0)}\right]. \quad (36)$$

Rewriting Eq. 36 in terms of $\theta = \kappa t$ yields

$$dp^{(0)}/d\theta = \left[p_o^{(1)} - x_e q_e^{(0)} - x_f p^{(0)}\right]. \quad (36a)$$

When the time derivative vanishes, Eq. 36 shows that the final (long-time) polymer concentration is $p^{(0)}(t \to \infty) = (p_o^{(1)} - x_e k_e/k_{ea})/x_f$, which accounts for the mass loss of chain-end scission products. Equations 33a and 36a can be solved simultaneously by numerical methods to determine the time dependence of the polymer and chain-end product concentrations.

Results and Discussion

We numerically solved the differential Eqs. 19a and 20a with the initial conditions, $\alpha_o = 4$ and $\beta_o = 10^5$, for several values of the limiting MW, x_f. Figures 1 and 2 show how the gamma distribution parameters, α and β, evolve with time. When $x_f = 0$, these values of α_o and β_o correspond to an initial number-average MW of 4×10^5 and polydispersity of 1.25, values that are typical for commercially available polymers. Just as in prior work (McCoy and Madras, 1998), for the case of $x_f = 0$, a similarity solution is obtained with $\alpha = 2$. After α reaches this constant value, according to Eq. 20, β continues to decrease (slowly) with time as $\beta_o/(1 + 2\beta_o \kappa t)$. According to Eq. 8, this represents a similarity solution, as x appears only in concert with t as x/β. For other values of x_f, similarity solutions are not obtained and α and β decrease to zero (Figure 1). Figures 3 and 4 show the time evolution of the number-average MW, M_n, and polydispersity, D, according to Eqs. 19a and 20a. For the case $x_f = 0$, the polydispersity according to Eq. 14 is $1 + 1/\alpha$ and attains a constant value

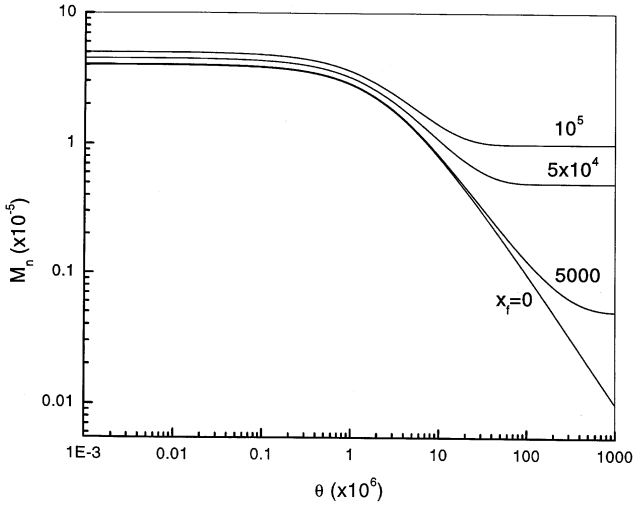

Figure 3. Number average MW, M_n, vs. θ for various values of limiting MW, x_f, with $\alpha_o = 4$, $\beta_o = 10^5$.

($D = 1.5$) corresponding to $\alpha = 2$. When $x_f \neq 0$, the long-time behavior is quite different, as α goes to zero (Figure 1) and the polydispersity goes to 1 (Figure 4). Figure 4 thus shows that, at long reaction times, when $x_f = 0$, a similarity solution is reached and the polydispersity of the polymer attains a constant value of 1.5. When x_f is not zero (as observed for ultrasonic degradation), the polydispersity continues to decrease until it is unity and there is no similarity solution.

Wu et al. (1977) studied the degradation of poly(methyl methacrylate) in tetrahydrofuran and found that initially narrow polydispersity fractions became broader with degradation before narrowing at long sonication times. This phenomenon was also observed for the degradation of polystyrene and poly(vinyl acetate) by Madras et al. (2000). This is consistent with the present theory. As shown in Figure 4, the polydispersity initially increases and then decreases approaching unity at long sonication times for a finite limiting MW. Independent of the initial polydispersity, the final polydispersity approaches unity when x_f is finite. Shaw and Rodriguez (1967) studied the degradation of poly(dimethyl siloxanes) and found that the same value, $D = 1$, was approached at long reaction times and was independent of the initial polydispersity.

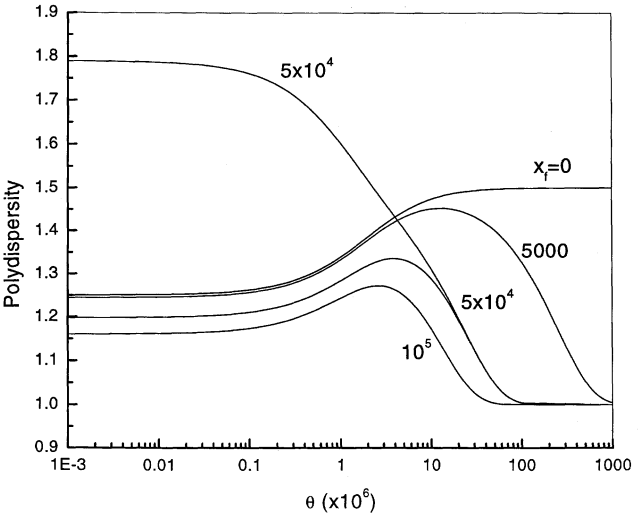

Figure 4. Evolution of polydispersity with θ for various values of limiting MW, x_f, with $\alpha_o = 4$ and $\beta_o = 10^5$ and with $\alpha_o = 1$, $\beta_o = 4 \times 10^5$, and x_f = 50,000.

To determine the influence of the initial polydispersity, we determined the evolution of polydispersity for two cases with the same initial M_n (= 450,000), but different initial polydispersities ($D = 1.2$ and 1.79) that evolve to the same limiting MW, $x_f = 50{,}000$. We choose $\alpha_o = 4$, $\beta_0 = 10^5$ in the first case and $\alpha_o = 1$, $\beta_o = 4 \times 10^5$ for the second case. Figure 4 shows that polydispersity in the first case initially increases and then decreases, but in the second case polydispersity decreases monotonically for the wide-distribution polymer. This is consistent with the experimental results reported by Porter (1967) and Wu et al. (1977), who observed that ultrasonication of initially wide-distribution polymers shows only a narrowing of the polydispersity.

Bimodal distribution

Our previous model (McCoy and Madras, 1997) assumed a constant degradation rate coefficient and showed how a unimodal distribution evolves to a bimodal distribution. Such a constant rate coefficient is satisfactory for low conversions, but cannot simulate a large change in M_n/M_{n0} (Madras et al., 1997). Equation 26, which assumes that the degradation rate is proportional to the chain length above the limiting MW, can simulate the MWD evolution. We consider a process with limiting MW $x_f = 40{,}000$ and an initial distribution with polydispersity 1.025, $\alpha_o = 10$, and $\beta_o = 4\,000$. The initial number-average MW is 80,000, which is twice x_f, and thus (on average) the reactant polymers can undergo only one scission. According to the exact solution, Eq. 26, the MWD evolves to a final value $M_n = 40{,}000$ through a bimodal distribution for various θ, as shown in Figure 5. This is consistent with the experimental observation that ultrasonic degradation of polymers with low polydispersities ($D < 1.1$) evolve as bimodal distribution (Smith and Temple, 1968; Price and Smith, 1991). This exact solution for the MWD is unusual, as most solutions for population-balance equations are expressed in terms of moments.

For an initial distribution ($\alpha_o = 1$, $\beta_o = 40{,}000$) having the same number-average MW but a higher polydispersity (D = 1.25) the calculated MWD does not evolve as a bimodal MWD. Numerous investigators (Madras et al., 2000; Porter et al., 1967; Wu et al., 1997) reported that polymers having a high initial polydispersity (> 1.2) do not evolve to a bimodal distribution. The appropriate dependence on initial conditions is a significant result of our theory. For example, we have chosen two polydispersities ($D = 1.025$ and $D = 1.25$) for the same initial number-average MW of 80,000. Price and Smith (1991) have shown for a very low polydispersity (D = 1.03) that the MWD evolves to a bimodal distribution. We observe the same results theoretically for $D = 1.025$. When

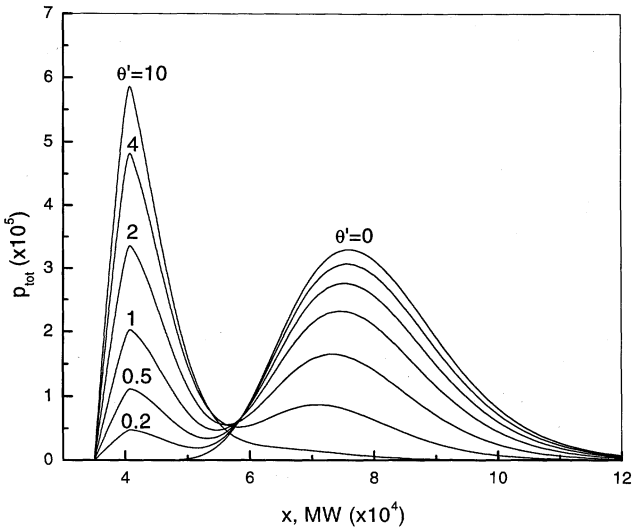

Figure 5. Evolution of MWD into a bimodal distribution for various θ' ($=10^5\ \theta$), with $\alpha_o = 10$ and $\beta_o = 4{,}000$.

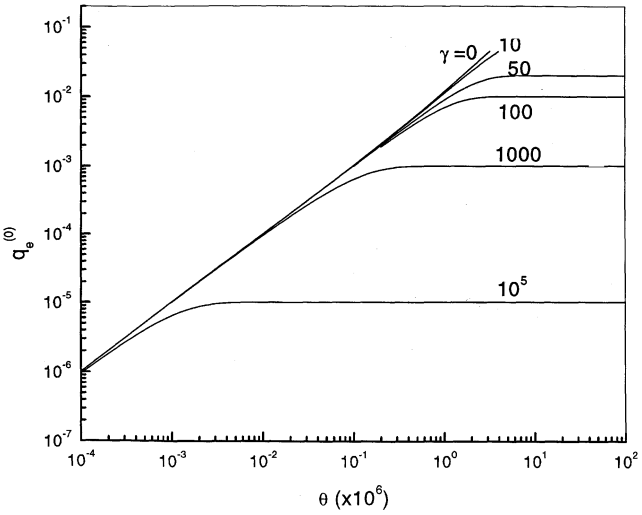

Figure 7. Molar concentration of the chain end product, $q_e^{(0)}$, vs. θ for various values of $\gamma = k_{ea}/k_e$, with $k_e = 100$, $\kappa = 10^{-7}$, $x_e = 100$, $x_f = 50{,}000$, $p_o^{(1)} = 4.5$, and $p_o^{(0)} = 10^{-5}$.

the polymers had a high initial polydispersity ($D > 1.2$), the polymers did not evolve to a bimodal distribution in the Price and Smith experiments. Madras and Karmore (2001) likewise did not observe a bimodal distribution when poly(methyl methacrylate) of initial number-average MW of 80,000 and polydispersity of 1.3 was degraded to a limiting MW of 40,000. These results are also consistent with our theory when the initial polydispersity of $D = 1.2$. The experimentally observed results are thus explained by the current theory.

Reversible chain-end and midpoint scission

Equations 33a and 36a were solved numerically with the initial conditions, $p_o^{(1)} = 4.5$ and $p_o^{(0)} = 10^{-5}$, and the limiting MW, $x_f = 50{,}000$, for several values of $\gamma = k_{ea}/k_e$, with $k_e = 100$ and $\kappa = 10^{-7}$. The monomer MW, $x_e = 100$, is much smaller than the limiting MW, x_f, that is, $x_e \ll x_f$. Figure 6 shows the variation of the number-average MW, M_n, with time. When γ is zero or small ($= 10$), $M_n = (p_o^{(1)} - x_e q_e^{(0)})/p^{(0)}$ decreases from the initial value, $M_{no} = p_o^{(1)}/p_o^{(0)}$, to its final value of zero. When $p_o^{(1)} = x_e q_e^{(0)} = q_e^{(1)}$ M_n approaches zero sharply, that is, when all the polymer is consumed. When γ is very large ($\geq 10^5$), the variation in M_n is identical to that shown in Figure 3 for $k_e = k_{ea} = 0$ and M_n reaches the limiting MW of 50,000. This indicates that when chain-end degradation is dominated by polymerization, the effect on the equilibrium number-average MW is not significant. This behavior is expected, because all the products formed by chain-end scission repolymerize, which is equivalent to the case when no chain-end scission occurs.

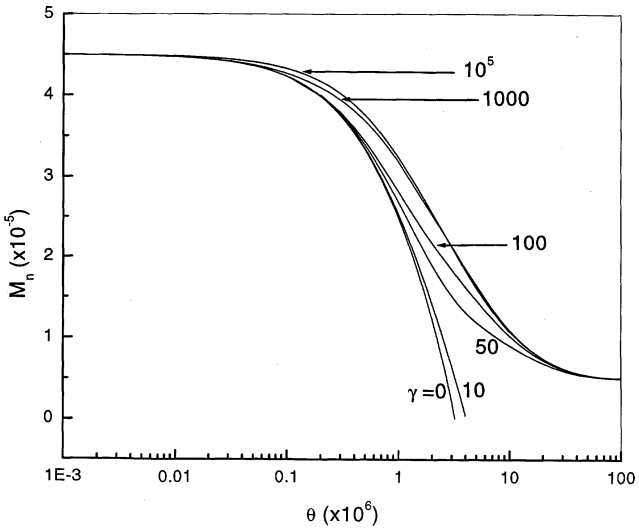

Figure 6. Variation of the number average MW, M_n, with θ for various values of $\gamma = k_{ea}/k_e$, with $k_e = 100$, $\kappa = 10^{-7}$, $x_e = 100$, $x_f = 50{,}000$, $p_o^{(1)} = 4.5$, and $p_o^{(0)} = 10^{-5}$.

Figure 7 depicts the variation of molar concentration of the chain-end products, $q_e^{(0)}$, with time. When $\gamma = k_{ea}/k_e$ is large, the molar concentration of the chain-end products reaches the equilibrium value, k_e/k_{ea}, at long times. When $k_{ea}/k_e = 0$ and 10, $q_e^{(0)}$ continues to increase till it reaches $p_o^{(1)}/x_e$, that is, when M_n of the polymer becomes zero. The equilibrium value of 0.1, however, is not reached when $k_{ea}/k_e = 10$, because the polymer is completely consumed before $q_e^{(0)}$ attains the equilibrium value.

Conclusions

The objective of this article was to provide an overall framework for determining the time evolution of MWDs for the degradation of polymers by ultrasonic waves. Ultrasonication in liquids causes cavitating bubbles to form and then collapse with high shear rates and strong viscous heating. A linear polymer in the shear field can be stressed to the point of breaking at its midpoint. A particular concern was to develop a theory that describes the major observations of ultrasonic

polymer reactions (a bimodal MWD evolving to a limiting average MW) by accounting for the essential chemical kinetics—midpoint chain scission with a MW-dependent rate coefficient, possibly combined with reversible chain-end scission with MW-independent rate coefficients. We have used continuous distribution kinetics and represented the system by an integrodifferential population balance equation. This was transformed into a set of ordinary differential equations for MW moments and represented in terms of time-dependent gamma distribution parameters.

The major results of ultrasonic experiments for polymer degradation are that the lower limit of MW, x_f, is a function of the input ultrasonic energy and the MWD evolves through bimodal distributions when the polydispersity is large ($D > 1.2$), but not when the polydispersity is small ($D < 1.1$). The present theory utilizes a stoichiometric kernel for chain scission occurring precisely at the midpoint, and a scission rate coefficient that is linear in $x - x_f$. We have determined the change in the number-average MW and polydispersity with reaction time and showed that the results obtained by our theory are consistent with a range of experimental observations. We have also shown that the MWD evolves to a similarity solution only when there is no limiting MW ($x_f = 0$).

Notation

k_d = midpoint chain scission rate coefficient
k_e = chain end scission rate coefficient
k_{ea} = chain end polymerization rate coefficient
$p(x,t)$ = MWD of the unreacted polymer
$p^{(j)}(t)$ = jth moment of the polymer MWD
$q(x,t)$ = MWD of the midpoint scission products
$q^{(j)}(t)$ = jth moment of the midpoint scission product MWD
$q_e(x,t)$ = MWD of the chain end scission products
$q_e^{(j)}(t)$ = jth moment of the chain end scission product MWD
t = time, min
x_f = limiting (final) MW
x_e = MW of the chain end product

Greek letters

α, β = gamma distribution parameters
θ = reaction time, κt
$\gamma = k_{ea}/k_e$

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