Distribution Kinetics of Thermolytic Macromolecular Reactions

W. Jerome Sterling and Benjamin J. McCoy
Dept. of Chemical Engineering and Materials Science, The University of California-Davis, Davis, CA 95616

Essential elements of thermolytic reaction kinetics for distributions of polymers are reviewed. Bond scission, occurring randomly along a chain backbone or at the chain end, is the major reaction process in polymer thermolysis. Underlying this bond scission are free radical mechanisms, including initiation and termination, hydrogen abstraction, and beta scission. Population-balance equations for the molecular-weight distributions of macromolecules or their radicals describe the dynamics of the reactions. The governing integrodifferential equations for continuous distributions can be solved by moment methods, similarity techniques, other analytical procedures, or numerical methods. The approach has been applied to analytical thermolysis and pyrolysis, polymer degradation for stability characterization or plastics recycling, and coal thermolysis to produce fuels and feedstocks. Experiments have demonstrated the usefulness of the continuous distribution kinetics approach for polymer thermolysis with additives, including hydrogen donors, peroxides, and other polymers. Molecular-weight distributions and their moments can be measured by size exclusion chromatography. Experimental data can be interpreted by evaluating rate parameters, which may be composites of rate coefficients for elementary steps in complex reaction mechanisms.

Introduction

Distribution kinetics describes chemical or physical processes occurring in discrete or continuously distributed systems. Polydisperse systems are ubiquitous in chemical processing of macromolecules, including polymer melts and solutions, liquefied coal, and petroleum. Each macromolecule in an homologous family comprises a discrete number of repeat units, so the molecular-weight distribution (MWD) is in general discrete. Macromolecules, however, typically contain very many repeat units, so that the MW of each macromolecule is much larger than the MW of a repeat unit. As the number of repeat units becomes large, the population distribution becomes continuous. Continuous distribution functions are approximations that allow direct application of characterization data and often lead to substantial simplification in mathematical analyses. DeDonder (1931), Amundson (1980), and Aris and Gavalas (1966) were among the first to consider multicomponent systems as continuously distributed rather than as sums of discrete components (Dotson et al., 1996; Laurence et al., 1994). Krambeck (1994), in a general discussion of complex mixture kinetics and thermodynamics, pointed out the similarity between the continuous and discrete approaches. More recently, McCoy and Madras (2001) showed that the discrete and continuous approaches lead to equivalent results for polymerization and depolymerization, and further that the discrete approach can be considered a special case of the continuous approach. Equilibrium thermodynamics of continuously distributed systems, based on the fundamental concept of the distribution of molecular properties, has advantages relative to a discrete approach for complex systems (Gualtieri et al., 1982; Salacuse and Stell, 1982; Briano and Glandt, 1983; Ratzsch and Kehlen, 1983; Cotterman et al., 1985; Evans et al., 1998; Choi and Bae, 1999; McCoy and Sterling, 2000). The lumping approach to study chemical reactions or phase separations in polydisperse systems divides the homologous components into discrete collections of pseudocomponents or lumps (Astarita and Sandler, 1991). The continuous approach conceptually increases the number of pseudocomponents, or decreases the size of the discretization, to the limit where the sum of discrete components can be replaced by integration over the distributed quantity. This

---

Correspondence concerning this article should be addressed to B. J. McCoy.

facilitates the understanding of reactions occurring in polydisperse mixtures, such as for polymers (Gloor et al., 1994; Wang et al., 1995; Browarzik and Kehlen, 1997) or hydrocarbons (Browarzik and Kehlen, 1994). The appropriate choice of distributed variable depends on the characteristics of the system. Possible variables for distributions are MW, number of repeat units (chain length), degree of branching, degree of cross-linking, extent of dehydrogenation, particle diameter, and cell size.

For dynamic systems, population-balance equations (PBEs) govern the temporal and spatial dependence of distributions. PBEs describe, in addition to reaction kinetics, a variety of particle processes, such as crystallization, comminution, aerosol science, granulation, gas–liquid and liquid–liquid contacting, bed fluidization, and microbial fermentation (Hulburt and Katz, 1964; Himmelblau and Bischoff, 1968; Ramkrishna, 1985, 2000). The same PBE approach discussed in this review has been recently applied to vapor nucleation and droplet growth (McCoy, 2000), ultrasonication (Madras and McCoy, 2001), and chromatography (Goto and McCoy, 2000).

In this article we review the essential elements of distribution kinetics, with particular emphasis on the use of continuous distribution functions in understanding the mechanisms of macromolecular thermal degradation. We begin by discussing the general reaction mechanisms of such processes and how the reaction kernel and rate parameter dependence on molecular size are based on molecular structure fundamentals for kinetic studies. Next, the formulation of PBEs from the reaction mechanism is covered, followed by common assumptions applied to simplify the PBEs. Methods for solving the system of PBEs are explained, with emphasis on the moment technique. Finally, systems to which distribution kinetics has been gainfully applied are discussed, as well as possible areas for future efforts. The Appendix explains some of the mathematical intricacies in detail.

General Macromolecular Reactions

Macromolecules can react by transformation, scission, or addition. Chemical species are indicated as $P(x)$, $Q(x)$, and $R(x)$, where x represents the continuous variable MW. The MWDs of these species are $p(x,t)$, $q(x,t)$, and $r(x,t)$, respectively, where at time t, $p(x,t)dx$ is the molar concentration of species P having MW in the range from x to $x+dx$. A distribution is a partial record of the mechanism and kinetics that influenced its evolution, governed by a PBE.

Transformation reaction

Macromolecules can transform with little or no change in MW, such as from a radical to a stable molecule, an alkane to an alkene, or a transformation among isomers. The reaction can be expressed as

$$\mathrm{R}(x) \xrightarrow{k_{tr}} \mathrm{P}(x). \tag{1}$$

The rate coefficient is generally a function of MW, $k_{tr}(x)$, and the species concentration rates are

$$\partial p/\partial t = k_{tr}(x) r(x,t) = -\partial r/\partial t. \tag{2}$$

Addition reaction

Two macromolecules can join by chain addition or cross-linking to form a macromolecule whose mass is the sum for the two joining molecules,

$$\mathrm{P}(x') + \mathrm{Q}(x-x') \xrightarrow{k_a} \mathrm{R}(x). \tag{3}$$

The reaction rates depend upon the concentration of each reactant and are therefore second order,

$$\partial p/\partial t = -k_a(x) p(x) \int_0^\infty q(x')\, dx', \tag{4}$$

$$\partial q/\partial t = -k_a(x) q(x) \int_0^\infty p(x')\, dx', \tag{5}$$

and

$$\partial r/\partial t = \int_0^x k_a(x') p(x') q(x-x')\, dx'. \tag{6}$$

The reacting species within the integral can have a range specified by the integration limits. To understand the reaction rate of P (Eq. 4), consider that a particular P of MW x, $p(x)$, may react with any Q, $\int_0^\infty q(x')\, dx'$, with rate coefficient $k_a(x)$. The reaction for addition of species of the same type is

$$\mathrm{P}(x') + \mathrm{P}(x-x') \to \mathrm{P}(x). \tag{7}$$

The reaction for polymerization by monomer addition is

$$\mathrm{P}(x-x_s) + \mathrm{Q}(x_s) \to \mathrm{P}(x). \tag{8}$$

where x_s is the MW of the monomer.

Scission reaction

A macromolecule can break into two smaller molecules in a scission reaction,

$$\mathrm{P}(x') \xrightarrow{k_d} \mathrm{Q}(x) + \mathrm{R}(x'-x). \tag{9}$$

The reaction rates are

$$\partial p/\partial t = -k_d(x) p(x,t) \tag{10}$$

$$\partial q/\partial t = \partial r/\partial t = \int_x^\infty k_d(x') \Omega(x,x') p(x',t)\, dx', \tag{11}$$

where the stoichiometric coefficient or reaction kernel, $\Omega(x,x')$, indicates the likelihood of obtaining a scission product of MW x from a larger molecule x'. The scission of a macromolecule into more than two smaller molecules can be represented as a series of biomolecular scissions.

General Reaction Mechanism

The reaction mechanism (Rice and Herzfeld, 1939; Kossiakoff and Rice, 1943; Flory, 1953) commonly used to describe the growth and/or degradation of macromolecules, comprises three reversible elementary steps: initiation-termination of radicals, propagation–depropagation (addition–scission, growth–decay), and hydrogen abstraction (Kodera and McCoy, 1997). Radical mechanisms are commonly employed for qualitative and semiquantitative interpretations of experimental observations (Jellinek, 1955; Price and Smith, 1991; McCaffrey et al., 1996), but quantitative interpretation requires that mechanisms be reduced to mathematical equations. Distribution kinetics can be applied to a radical mechanism through the convenient notation devised by Kodera and McCoy (1997). $P(x)$ represents a macromolecule with MW x, $R\cdot(x)$ represents a radical, and $Q(x_s)$ represents an oligomer. In a scission reaction a molecule, say $P(x)$, may be the molecule undergoing scission or it may be a product. The $P(x)$ molecule may occupy three different places in the reaction, and the reaction-rate equation in general will have three terms. When deriving the rate expressions, it is helpful to rewrite the reaction equation for each of the possible roles. The reaction rate coefficients, k_i, generally depend on MW, but can be assumed constant when the change in average MW is not large.

Initiation and termination of radicals

The initiation of radicals, usually caused by addition of heat, radiation, or chemical agent, occurs when a neutral molecule is cleaved into two radicals (Odian, 1991). Two radicals may combine to form one neutral molecule in a termination reaction, the reverse of the initiation reaction. The reaction equation for initiation and termination of radicals is

$$P(x) \underset{k_t}{\overset{k_i}{\rightleftharpoons}} R^{\bullet}(x') + R^{\bullet}(x-x'). \tag{12}$$

Termination also occurs by disproportionation when two radicals form an intermediate complex and then separate as stable molecules (Odian, 1991). Disproportionation usually occurs much less frequently than termination by combination (Odian, 1991), and its representation by distribution kinetics is straightforward.

Reversible addition and scission

The two molecules joining in an addition process may have the same MW, one may be an oligomer, or they may be of different MWs but neither an oligomer. As scission, or reverse addition events, the three different reactions are called midpoint, chain-end, and random, respectively. Midpoint scission is dominant in certain mechanical degradation processes (Price and Smith, 1991; McCoy and Madras, 1997), chain-end scission occurs in depolymerization processes (Madras et al., 1995), and random scission is characteristic of oxidative and thermal degradation reactions (Jellinek, 1955; Madras and McCoy, 1997).

Reversible random chain scission

Random scission involves splitting a macromolecule of MW x into two smaller macromolecules,

$$P(x) \underset{k_a}{\overset{k_d}{\rightleftharpoons}} P(x-x') + P(x'). \tag{13}$$

The reaction-rate expression is

$$\begin{aligned}\partial p/\partial t &= 2k_d \int_x^\infty p(x')\Omega(x,x')\,dx' - k_d p(x) \\ &\quad -2k_a p(x)\int_0^\infty p(x')\,dx' + k_a \int_0^x p(x')p(x-x')\,dx'. \end{aligned}\tag{14}$$

The terms account for obtaining an x by scission (the x could be either product of the scission), losing an x by scission, losing an x by addition (the x could be either reactant in the addition), and obtaining an x by addition, respectively. The reaction-rate coefficient is not a function of MW for addition or for random scission over a small conversion range. The stoichiometric kernel for a random scission reaction is based on the equal probability of scission at each bond.

Reversible chain-end scission

Chain-end scission involves the loss or removal of one oligomer from the end of the macromolecular chain. Monomer can evolve from a chain-end radical through β-scission, but for larger oligomer evolution to occur, intramolecular hydrogen abstraction by the end radical must precede the β-scission. Intramolecular hydrogen abstraction (or backbiting) processes typically occur near the sixth carbon from the chain end (Odian, 1991), suggesting an upper size limit for oligomers derived from chain-end scission. The reversible reaction equation is

$$P(x) \underset{k_a}{\overset{k_d}{\rightleftharpoons}} P(x-x_s) + Q(x_s). \tag{15}$$

When chain-end scission yields multiple specific products, $Q(x_s)$, each must be accounted for independently. The rate expressions for each specific product are

$$\begin{aligned}\partial p/\partial t &= k_d \int_x^\infty p(x')\Omega(x_s,x')\,dx' - k_d p(x) \\ &\quad - k_a p(x)\int_0^\infty q(x')\,dx' + k_a \int_0^x p(x')q(x_s)\,dx', \end{aligned}\tag{16a}$$

and

$$\partial q/\partial t = k_d \int_0^\infty p(x')\Omega(x_s,x')\,dx' - k_a q(x_s)\int_0^\infty p(x')\,dx'. \tag{16b}$$

The stoichiometric kernel for chain-end scission is a Dirac distribution, $\Omega(x_s,x') = \delta(x'-x_s)$, because the reaction yields a specific product species whose MW is x_s.

Hydrogen abstraction

Hydrogen abstraction (chain transfer) occurs when a radical takes a hydrogen atom away from a neutral molecule or another section of its own molecule, becoming neutral itself, and changing the unpaired electron to another location. The radical is moved, typically, to a more stable location, but no significant change in MW occurs. Intramolecular hydrogen abstraction (backbiting) usually converts a chain-end radical to one where the unpaired electron is only a few carbon atoms away from the end. Backbiting reactions typically lead to isomerization (Odian, 1991) or chain-end scission to produce oligomer. Chain-end radicals are more likely than internal radicals to participate in hydrogen abstraction, because they are the least stable and most reactive (Solomons, 1986).

The reaction path for intermolecular hydrogen abstraction involves an intermediate macromolecular complex,

$$R^{\bullet}(x)+P(x') \rightarrow I^{\bullet}(x+x') \rightarrow P(x)+R^{\bullet}(x'). \quad (17)$$

Because the intermediate is short-lived, effectively $R^{\bullet}(x)$ is converted to $P(x)$ and $P(x')$ is converted to $R^{\bullet}(x')$; thus the reaction equation can be written as

$$R^{\bullet}(x) \rightleftharpoons P(x), \quad (18)$$

and the reaction rate is pseudo first-order (Kodera and McCoy, 1997). The MW of the hydrogen atom is considered negligible relative to the MW of the macromolecule. Intermolecular hydrogen abstraction can lead to β-scission of the radicals (Solomons, 1986). An example reaction equation for an alkane radical undergoing β-scission to form an alkene and a smaller alkane radical is (Kodera and McCoy, 1997)

$$R(CH_2)(CH)^{\bullet}-(CH_2)(CH_2)R' \rightarrow R(CH_2)(CH)=(CH_2) + R'(CH_2)^{\bullet}. \quad (19)$$

Simplified Reaction Mechanism

Long-chain approximation

The creation of two radicals in an initiation reaction has a large activation energy (80–90 kcal/mol; Song et al., 1994). The initiation rate is thus small relative to the propagation (polymerization) or depropagation (degradation) rates (Kodera and McCoy, 1997), which will be large because radicals are highly reactive. The termination reaction rate is also small due to the low concentration of radicals. Initiation and termination reaction rates are thus negligible and can be ignored for large molecules (Gavalas, 1966) that undergo many propagation events (Dotson et al., 1996; Odian, 1991). By omitting initiation and termination rates, the long-chain approximation (LCA) simplifies reaction kinetics analysis. Nigam et al. (1994) developed an approximate linear rate law to depict the Rice-Herzfeld mechanism when the propagation rate does not strongly dominate the initiation and termination rates, and discussed some conditions under which this alternate approach might be necessary.

Quasi-steady-state approximation

The concentration of radicals in the macromolecular system is very small, and the rate of initiation (formation of radicals) is approximately equal to the rate of termination (loss of radicals), so the rate of change in radical concentration is very small (Odian, 1991). Mathematically, $\partial r/\partial t \ll \partial p/\partial t$, and therefore the radical concentration rate of change can be ignored for most analyses (Dotson et al., 1996; Kodera and McCoy, 1997). If such a quasi-steady-state approximation (QSSA) is inadequate, the governing nonlinear differential equations must be solved. This may be necessary when gel effects occur, in which case the stiff nonlinear equations can be solved numerically (Venkateshwaran and Kumar, 1992).

Simplified mechanism

Applying LCA and QSSA to the reaction mechanism is reasonable for most thermolytic polymer reactions, and yields a considerable simplification in the kinetics analysis (Kodera and McCoy, 1997). The LCA allows the initiation–termination reaction to be omitted from the analysis of macromolecular growth and/or decay. The QSSA allows the remaining reaction equations to be reduced to the reversible scission reactions, Eq. 13 or 15 (Kodera and McCoy, 1997). Although LCA and QSSA are widely applied, special conditions relating rate coefficients and their activation energies, temperature, and degree of gellation or polymerization should be carefully considered.

Reaction-rate coefficients

Although rate coefficients in general are functions of the MW of the reactants, over a useful range, they are relatively unvarying with respect to MW (Kodera and McCoy, 1997). For polymerization, molecules are equally likely to participate in the free radical mechanism, and rate coefficients are usually assumed independent of MW (equal reactivity principle) (Dotson et al., 1996). The chain-end scission rate coefficient is also not a function of MW, but rather a function of the number of chain ends per molecule.

The random scission rate coefficient is expected to increase with the number of bonds that can be broken. If the average MW does not vary greatly (such as small conversion or short reaction times), the random scission rate coefficient (k_d) can be assumed constant. For large conversion it must be represented as a function of MW (Kodera and McCoy, 1997; Madras et al., 1997a). Even if the reactant is initially monodisperse, random scission yields polydisperse reaction products and k_d will depend on MW (Madras et al., 1997a). Numerous studies have assumed $k_d(x)=\kappa_{\lambda}x^{\lambda}$ (McCoy and Wang, 1994), for example, $\lambda=0$ was used for reversible oligomerization (McCoy, 1993), $\lambda=1$ for oxidative degradation of polystyrene (Madras and McCoy, 1997) and coal thermolysis (Wang et al., 1993), and $\lambda=2$ for chemical cracking (Aris and Gavalas, 1966). To avoid the accumulation of an infinite number of *zero-mass* products, McCoy and Wang (1994) proposed $k_d(x)=\kappa_{\lambda}(x-x_0)^{\lambda}$, where the smallest product of random scission has MW x_0. A polynomial form expressing the random scission rate coefficient as a function of MW, $k_d(x)=\Sigma_{j=0}^{m}k_j x^j$, was suggested by Madras et al. (1997a), who used a second-order polynominal ($m=2$) to represent the thermal degradation of polysytyrene. As discussed below, taking k_d proportional to x^{λ} permits similar solutions that in some cases are exact solutions to the PBEs.

However, chemical mechanistic fundamentals, rather than mathematical convenience, should be used to guide rate-coefficient expression form.

Population-Balance Equation Solutions

The dynamic behavior of distributions is governed by integrodifferential PBEs, which are solved by moment techniques, Laplace transformation, method of characteristics, similarity methods, or numerical techniques. Simulation techniques, such as Monte Carlo or molecular dynamics, may prove valuable for multivariate distribution reactions (Ramkrishna, 1985).

Moment approach

The moments of MWDs, defined as

$$p^{(n)}(t) = \int_0^\infty p(x,t)x^n dx, \tag{20}$$

give specific physical information (Kodera and McCoy, 1997). The zeroth moment ($n = 0$) and the first moment ($n = 1$) are the molar concentration (moles/volume) and the mass concentration (mass/volume), respectively. The number-average MW is the normalized first moment ($M_n = p^{\text{avg}} = p^{(1)}/p^{(0)}$), and the weight-average MW is the ratio of the second to first moments ($M_w = p^{(2)}/p^{(1)}$). The polydispersity is the ratio of weight-average to number-average MWs ($D = M_w/M_n = p^{(2)}p^{(0)}/[p^{(1)}]^2$). The variance of the MW distribution is the second central moment ($p^{\text{var}} = p^{(2)}/p^{(0)} - [p^{\text{avg}}]^2$). The first three moments ($p^{(0)}$, p^{avg}, p^{var}) describe shape characteristics of the distribution and can be used to construct the distribution in gamma distribution form, for example (Cotterman et al., 1985; Wang et al., 1994a). Several common distributions, such as the Gaussian, Poisson, Dirac delta, and exponential (or most probable) distributions, are special cases of the gamma distribution (Abramowitz and Stegun, 1968), which is the first term in a generalized Fourier expansion in Laguerre polynomials (Hulburt and Katz, 1964). Perturbations to the Gaussian distribution are commonly represented by an expansion in Hermite polynomials (Hulburt and Katz, 1964). If the first three moments do not give satisfactory representation of experimental observations, higher-order terms in the expansion can be related to higher-order moments of the distribution to improve the fit. The third moment is a measure of skewness (asymmetry), so that a symmetrical peak centered at the origin has $p^{(3)} = 0$. The fourth moment is a measure of kurtosis (peakedness) (Croxton, 1953). Usually only the zeroth moment is required to determine a rate coefficient from experimental data (McCoy and Madras, 1998).

The moment definition (Eq. 20) can be applied to the reversible addition reaction rate equation (Eq. 14) term-by-term. The stoichometric kernel for random scission is $\Omega(x', x) = 1/x'$ (Aris and Gavalas, 1966). If the reaction-rate coefficients are constant, the moment-rate equations form a closed set. If the reaction-rate coefficients are functions of MW, a closure problem may arise (McCoy and Madras, 1998), and an approximation may be needed to close the system of equations. The moment expression for reversible random addition with constant rate coefficients becomes

$$dp^{(n)}/dt = -[(n-1)/(n+1)]k_d p^{(n)} - 2k_a p^{(n)}p^{(0)} + k_a \Sigma_{j=0}^{n} \binom{n}{j} p^{(n-j)}p^{(j)}. \tag{21}$$

Experimental data, for example gel permeation chromatograms, are analyzed to provide the moments of the mass or molar distribution function. The distribution is then represented in terms of its moments. The molar gamma distribution is (Wang et al., 1995)

$$p(x) = [p^{(0)}/\beta\Gamma(\alpha)]y^{\alpha-1}\exp(-y), \tag{22}$$

where $y = (x - x_o)/\beta$, x_o represents the minimum size of a molecule with $p(x) = 0$ for $y \leq 0$, and $p^{(0)}$ is the total molar concentration. The time dependence of $p(x)$ is expressed through $p^{(0)}(t)$, $\alpha(t)$, and $\beta(t)$. The weight-fraction gamma distribution function is $p_w(x) = xp(x)$. The average position x^{avg}, and peak width, σ, are (Abramowitz and Stegun, 1968; Wang et al., 1995)

$$x^{\text{avg}} = x_o + \alpha\beta = p^{\text{avg}} = p^{(1)}/p^{(0)} \tag{23}$$

and

$$\sigma^2 = \alpha\beta^2 = p^{\text{var}} = p^{(2)}/p^{(0)} - (p^{\text{avg}})^2. \tag{24}$$

The position of the peak maximum, x_p, is (Wang et al., 1995)

$$x_p = x_o + (\alpha - 1)\beta. \tag{25}$$

The gamma distribution becomes the exponential (most probable) distribution when $\alpha = 1$ and $x_o = 0$, or the Poisson distribution when $\beta = 1$ and $x_o = 0$ (McCoy and Madras, 1997).

Similarity solutions

Similarity (self-similar, scaling, or self-preserving) solutions to PBEs combine the variables x and t into a single algebraic expression and thus allow data to be represented concisely (Ramkrishna, 1985). Ramkrishna (2000) emphasizes similarity solutions to invert PBEs to find fundamental rate coefficients. McCoy and Madras (1998) discussed conditions under which such solutions exist. Many of the analytical solutions found for scission processes are similarity solutions, but are valid only for long times, specialized distributions, or specific forms of the reaction kernel. These solutions, generalized for scission by a rate coefficient dependent upon MW through a power law relation, $k_d(x) = k_\lambda x^\lambda$, combine MW and time together in a similarity group, $u(x,t) = x^\lambda/\beta(t)$ (Ziff, 1991; Madras and McCoy, 1998b). A study of random scission showed the evolution of the polydispersity ($D = M_w/M_n$) to a value of two at long times (Yoon, 1996), which represents an exponential distribution similarity solution (Madras and McCoy, 1998b).

Realistic reversible systems must evolve through time to a steady-state or equilibrium condition, but irreversible dynamic systems continue until reactant is depleted. McCoy and Madras (1998) presented a general approach to finding simi-

Table 1. Similarity Solutions in Poisson Distribution Form

	λ	α	$\beta(t)$
Random scission only	>0	1	$\beta_0/(1+\beta_0 k_d t)$
Random addition only	>0	1	$\beta_0 + k_a t$
Reversible random scission and addition	1	1	$\eta^{1/2}(\xi - 1)/(\xi + 1)$

Source: McCoy and Madras, 1998.
Here $\xi = [(\eta^{1/2} + \beta_0)/(\eta^{1/2} - \beta_0)] - 1 + \exp(2\eta^{1/2} k_d t)$, with $\eta = k_a p_0^{(1)}/k_d$

larity solutions for irreversible scission, irreversible addition, and reversible scission-addition, using the power-law rate-coefficient relation for scission, and the preceding similarity group $u(x,t)$. They showed how the solutions with $\alpha(t)$ evolve from a general initial condition to the similarity solutions where α is constant and β depends on time. McCoy and Madras (1998) compiled the known similarity solutions, all of which have the Poisson distribution form,

$$p(x,t) = \left[p^{(1)}\lambda/\beta^{2/\lambda}\Gamma(\alpha - 1 + (2/\lambda)) \right] u^{\alpha-1} e^{-u}, \quad (26)$$

for which some representative results are displayed in Table 1. The solutions in Table 1 have the expected value of the polydispersity, $D = 2$, whereas moment solutions for scission with $\lambda = 0$ yield the unrealistic value, $D = 6$ (McCoy and Madras, 1998). They showed that when $\lambda = 1$, the self-similar solution satisfies all the moments of the PBE. But when $\lambda \neq 1$, the similarity solution satisfies only the first three moments, and therefore is not an exact solution to the PBE. Although the self-similar solutions simplify the analysis of experimental data, more general solutions are needed to examine the range of possible dynamic behavior.

Other solution techniques

The moment method together with a Laguerre expansion is a special case of the general *method of weighted residuals* (MWR), which involves expanding an unknown distribution in terms of trial functions that are substituted into governing PBE to obtain the residual functions (Ramkrishna, 1971). The residual functions are orthogonalized by weighting functions such that the accumulation of residuals is nearly zero over the interval of the independent variable. If Laguerre polynomials are trial functions, and x^n are weighting functions, the result for minimizing the residual functions is the moment (Ramkrishna, 1971, Tobito and Ito, 1992).

The integrodifferential-rate equation can be discretized (McCoy and Madras, 2001), leading to a discontinuous or pseudocomponent description. Numerical methods have proven valuable in many continuous and discrete distribution kinetics studies (Gloor et al., 1994; Browarzik, 1997; Ng, 1995; Nicmanis and Hounslow, 1998).

The rate equation may be solved by a power series representation of the solution (Kehlen et al., 1988). An algorithm is established whereby the number of terms in the assumed solution form is increased until desired accuracy is attained. If the number of terms is large, the mathematical complexities may be similar to the discrete approach (Kehlen et al., 1988). The power-series solution suffers from the need to truncate the series to obtain an analytic result, although in a first-order degradation study a convergent solution was reported (Kehlen et al., 1988).

An alternative to distribution kinetics methods is the use of reaction families or groups (Woo and Broadbelt, 1998). In computer simulations of pyrolysis of a poly (α-methylstyrene) (PAMS) and polystyrene mixture, several hundred model components were considered to undergo several thousand reactions. Activation energies for the groups (polymers and their radicals) were estimated by linear free-energy relationships, which represent values of the activation energy in terms of reactivity indices, such as the heats of reaction. Various other reasonable assumptions (Woo and Broadbelt, 1998) are made to implement the method. A critical comparison of this method and its results with the distribution kinetics approach has not yet appeared.

Comparison of discrete to continuous kinetics

Macromolecular reactions can be described by a discrete or by a continuous approach (McCoy and Madras, 2001), so that a mass balance provides either a difference-differential or an integrodifferential equation, respectively. The continuous kinetics result will be identical to the discrete result for a system with many similar components, except for small average MW or degree of polymerization (McCoy and Madras, 2001). The continuous (integrodifferential) equation replaces

Table 2. Comparison of Discrete and Continuous Representation for Reaction Equations and Kinetic Expressions

Reaction	Discrete	Continuous
Transformation	$P_J \rightarrow Q_j$ Gain $= -$loss $= k_{tf} p_j$	$P(x) \rightarrow Q(x)$ Gain $= -$loss $= k_{tf} p(x)$
Addition reactant	$P_j + P_i \rightarrow P_{j+i}$ Loss $= -2k_a p_j \Sigma_{i=1}^{\infty} p_i$	$P(x) + P(x') \rightarrow P(x+x')$ Loss $= -2k_a p(x) \int_0^{\infty} p(x')\, dx'$
Addition product	$P_i + P_{j-i} \rightarrow P_j$ Gain $= k_a \Sigma_{j=1}^{i-1} p_j p_{j-i}$	$P(x') + P(x-x') \rightarrow P(x)$ Gain $= k_a \int_0^x p(x') p(x-x')\, dx'$
Random scission reactant	$P_j \rightarrow P_{j-i} + P_i$ Loss $= -k_d p_j$	$P(x) \rightarrow P(x') + P(x-x')$ Loss $= -k_d p(x)$
Random scission product	$P_i \rightarrow P_j + P_{i-j}$ Gain $= k_d \Sigma_{i=1}^{\infty} p_i \Omega_{ji}$	$P(x') \rightarrow P(x) + P(x'-x)$ Gain $= k_d \int_x^{\infty} p(x') \Omega(x,x')\, dx'$

Note: Rate terms refer to the gain or loss of P_j or $P(x)$. Here we assume rate coefficients are independent of MW. Corresponding terms for chain-end addition and scission are obtained by appropriately replacing polymer molecules with monomer or oligomer.

the discrete equation in the same way the Riemann integral replaces a summation. Table 2 shows the comparable expressions for the discrete and continuous approaches. The continuous approach is favored in most cases because integrals are simpler to manipulate than summations, and because moment solutions can be easily obtained (see the Appendix). Laurence et al. (1994) and Dotson et al. (1996) focused on the discrete approach. Analytical comparisons of the continuous kinetics to the discrete results were made for polymerization (Krambeck, 1994; Kodera and McCoy, 1997), for chain-end scission (Madras et al., 1996a), and for reversible chain polymerization (McCoy and Madras, 2001).

The discrete description of a multicomponent system can be considered a special case of the continuous description. The distribution function represents a sum of terms, one for each discrete component, proportional to a Dirac delta distribution (Astarita and Ocone, 1988). The continuous and discrete representations are therefore related by simple mathematical expressions (McCoy and Goto, 1994). If the continuous concentration distribution is $p(x,t)$, then the total (lumped) concentration, $p^{(0)}(t)$, is the integral over the entire range of x:

$$p^{(0)}(t) = \int_0^\infty p(x,t)\, dx. \tag{27}$$

The continuous representation reduces to the discrete representation if

$$p(x,t) = \Sigma p_i^{(0)}(t)\,\delta(x - x_i), \tag{28}$$

where the x_i are the discontinuous values of x. Once the continuous case is solved, the discrete case solution is found by applying the preceding relation. The total concentration is then the sum over all the discrete species in the mixture,

$$p^{(0)}(t) = \Sigma p_i^{(0)}(t). \tag{29}$$

Attention has been directed to the question of how lumping yields overall nth-order kinetics for various continuous-mixture reactions (Ho and Aris, 1987; Ho, 1991). McCoy (2001) has shown that realistic chain scission and recombination reactions that occur in temperature-programmed pyrolysis of polymers lead to rate expressions for moments that can be represented as reactions of order $n = 1/2$, 1, or 2. Zero- and first-moment equations have a solution that is identical to an empirical kinetics expression that represents isothermal thermogravimetric analysis (TGA) data (McCoy, 2001). Such thermogravimetric analysis of homologous molecules is well-suited for the distribution kinetics treatment, and may have advantages over the usual approach, assuming parallel reactions with distributed activation energies. Both isothermal and constant heating rate TGA data have structural details and shape properties (Burnham, 2000; Burnham and Braun, 1999) that constitute a useful test of kinetics models.

Applications

Chemical reactors

Distribution kinetics can describe reactions in chemical reactors through mass (or mol) balances:

$$[\text{Net accumulation}] = [\text{Net flow in}] + [\text{Net generation}]. \tag{30}$$

For irreversible scission in a reaction medium with $p(x,\boldsymbol{r},t)$ the differential form of the mass balance is (McCoy and Wang, 1994)

$$\partial p/\partial t + \boldsymbol{v}\cdot\nabla p = 2\int_x^\infty k(x')p(t,\boldsymbol{r},x')\Omega(x,x')\,dx' - k(x)p(t,\boldsymbol{r},x), \tag{31}$$

where $\boldsymbol{v}$ is the hydrodynamic velocity and $\boldsymbol{r}$ is the spatial coordinate.

The steady plug-flow reactor equation is obtained when the steady-state condition, $\partial p/\partial t = 0$, and the inlet condition (boundary condition), $p(x,z=0) = p_o(x)$, are applied (McCoy and Wang, 1994). A steady plug-flow reactor was used to study thermolysis of poly(styrene-allyl alcohol) copolymer (Wang et al., 1995; Madras et al., 1995), poly(methyl methacrylate) (Madras et al., 1996a), and poly(α-methyl styrene) (Madras et al., 1996b). A differential packed-bed reactor equation, a special case of the plug-flow reactor equation, was applied to coal liquefaction and thermolysis (Wang et al., 1993; Wang et al., 1994a).

The batch-reactor equation, with the initial condition, $p(t=0,x) = p_o(x)$, comes from the mass balance, Eq. 30, with no flow (McCoy and Wang, 1994). A well-mixed batch reactor was used for thermal degradation of polystyrene (Madras et al., 1997a,b; Madras and McCoy, 1998a; Sterling et al., 2001b) and polystyrene mixtures with poly(α-methyl styrene) (PAMS) (Madras and McCoy, 1999). A well-mixed reactor, with removal of volatiles, was used for polyethylene pyrolysis (Sezgi et al., 1998; McCaffrey et al., 1996). Peroxide-enhanced thermal degradation of batch solutions of polystyrene (Madras and McCoy, 1997; Kim and McCoy, 2000), PAMS (Sterling et al., 2001a), and polymethylmethacrylate (PMMA) (Madras and Karmore, 2001) has also been studied. The batch-reactor equation is equivalent to the steady plug-flow reactor equation when time t is replaced with residence time τ (McCoy and Madras, 1997). The continuous-flow stirred-tank reactor (CSTR) equation for distribution kinetics develops from the well-mixed batch reactor equation by adding inlet and outlet flow terms (McCoy and Wang, 1994).

Irreversible reactions

Experiments for irreversible thermal degradation of poly(styrene-allyl alcohol) (PSA), poly(methyl methacrylate) (PMMA), and poly(α-methyl styrene) (PAMS) in solution provided reaction-rate parameters and activation energies (Wang et al., 1995; Madras et al., 1996a,b). The degradation reactions were conducted in a tube reactor at various temperatures and residence times (or flow rates). The reaction

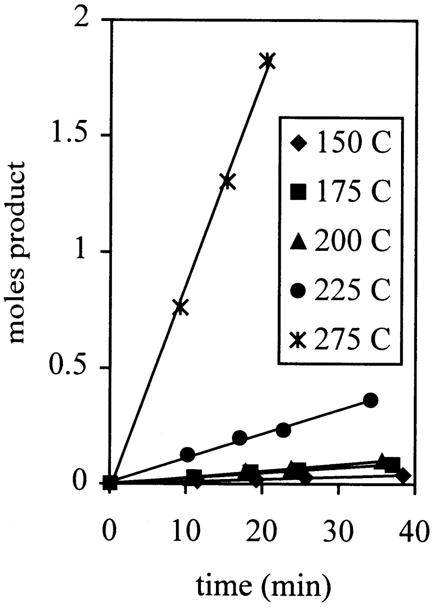

Figure 1. Evolution of chain-end product in thermal degradation of PAMS at different temperatures (Madras et al., 1996a).

The number of moles of end product is normalized by the number of moles of polymer.

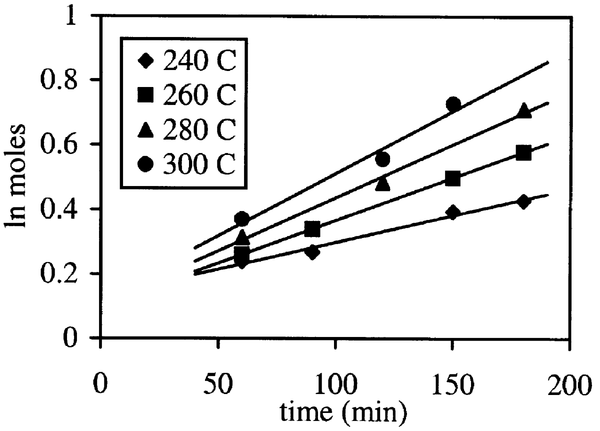

Figure 2. Polystyrene random degradation of strong links at four different temperatures (Madras et al., 1997b).

Moles of polymer are normalized by initial moles of polymer.

rates were first order in polymer concentration. Small residence times were studied so the reaction-rate coefficients were independent of MW. Short reaction times also exclude reverse reactions and provide a linear relation between the residence time and the zeroth moment (molar concentration) of chain-end product formed. Chain-end scission products accumulate in a Dirac delta distribution. The normalized zeroth moment of each specific product in the reactor effluent was plotted vs. residence time to give the reaction-rate coefficient for the generation of the specific product as the plot slope, as shown in Figure 1. PMMA and PAMS showed chain-end degradation only, and the random degradation-rate coefficient for PSA was obtained as a fitted parameter in a gamma distribution. Broadening of the reactant MWD toward lower MWs is evidence of random degradation, and the temporal change of the reactant MWD gives the random degradation kinetic parameters. Arrhenius plots yielded the activation energy for each reaction. The activation energies observed for thermolysis in solution indicate that scission is the rate-limiting step (Madras et al., 1996a).

Madras et al. (1995) studied the thermal degradation of PSA in solution in the presence of a hydrogen donor (tetralin) in a tubular reactor. Through a distribution kinetics analysis, the hydrogen-donor enhancement of degradation rate was observed to be first order at low concentration but zero order at high concentration, and therefore was modeled in the Langmuir form,

$$k = k_t C_t/(1 + KC_t). \qquad (32)$$

Here, C_t is the tetralin concentration, and K and k_t are model parameters. Depending on the particular polymer, adding hydrogen donors may increase, decrease, or have no effect on degradation rate. For example, the addition of 6-hydroxy tetralin retarded the polystyrene random degradation rate in a mineral oil solution (Madras and McCoy, 1998a). Distribution kinetics of the radical mechanism for chain scission can explain the different observed effects through relative rates of hydrogen abstraction steps (Madras and McCoy, 1998a).

Madras et al. (1997b) and Sterling et al. (2001b) investigated polystyrene degradation in solution in a batch reactor. Karmore and Madras (2000) extended the investigation to supercritical fluid solutions. Polystyrene degrades by random and, to a lesser degree, chain-end scission. The reaction-rate coefficient and activation energy for polystyrene chain-end scission were determined in the same manner as PMMA and PAMS degradation. The analysis of random polystyrene degradation is complicated by the existence of weak links in the polymer backbone that arise during manufacture. The weak links are responsible for the observed initial rapid random scission. The random reaction-rate coefficients for weak-link and strong-link scission are found as the segmented slopes of the logarithm of molar conversion plotted vs. time, as shown in Figure 2. Sterling et al. (2001b) combined the mechanisms for chain-end and random degradation into a single model that reduced to the individual mechanisms in limiting situations. They found the zeroth and first polymer molar moments to have trigonometric temporal behavior for the combined model, put physical constraints limited the cyclic solution to the early, monotonic portion of the curves. In general, random scission yields MWD moments that display exponential time behavior, but chain-end scission yields MWD moments that vary linearly with time (McCoy and Madras, 1997).

The effect of MW on the reaction rate coefficient for polystyrene thermolysis in solution was investigated with a batch reactor (Madras et al., 1997a). Due to the rapid weak-link degradation of monodisperse feed, the strong-link degradation initial condition was polydisperse. The random strong-link degradation coefficient was modeled as a polynomial function of MW, $k(x) = \sum_j k_j x^j$, and the moment expression of the reactor equation for any moment included terms of higher-order moments. Truncation after the fourth moment in a second-order polynomial expression for $k(x)$ provided satisfactory results. The theoretical expressions for the normalized zeroth and second moments were fitted to experimental-rate data to determine the polynomial coefficients (Madras et al., 1997a).

The thermal degradation behavior of polyethylene in batch solution occurs by a random scission mechanism (Guy and Fixari, 1999; Kumar et al., 2001). Guy and Fixari (1999) studied HDPE degradation in phenyl ether solution at moderate pressures, while Kumar et al. (2001) studied LDPE degradation in liquid paraffin at atmospheric pressure. Both continuous models considered that the degradation rate increases linearly with molecular size and ignored branching effects, which were judged to have small effect. The hydrogen donor solvent tetralin was found to diminish the degradation rate of polyethylene in solution (Guy and Fixari, 1999).

Madras and McCoy (1997) and Kim and McCoy (2000) studied the oxidative degradation of polystyrene in solution in a batch reactor when peroxide was added. Distribution kinetics analysis revealed the polystyrene random degradation rate to be first order in both polystyrene concentration and di-*t*-butyl peroxide concentration, or second order overall. The reaction-rate coefficient was modeled as a linear function of polystyrene MW. The reaction occurred quickly, and no chain-end products were observed. A similarity solution provided satisfactory interpretation of experimental data. Rate coefficients for peroxide decomposition, hydrogen abstraction by peroxide radicals, hydrogen transfer, and random scission were estimated from experimental data. The proposed mechanism explains the time dependence of the reaction. Madras and Karmore (2001) found the oxidative degradation behavior of PMMA could be represented with the same model as for polystyrene.

Sterling et al. (2001a) studied the peroxide-enhanced thermal degradation of PAMS in batch solution. A complex distribution kinetics model, which followed the temporal populations of polymer and radical species, was necessary to successfully represent the experimental data. Because the model involved coupled nonlinear differential equations for the species moments, an analytical solution was not possible and numerical methods were utilized. Under the influence of the free radical initiator, PAMS degraded by both random and chain-end processes, in contrast to the purely chain-end mechanism observed with heat alone. These results, along with those for polystyrene discussed earlier, show that the initiator increases the randomness of the degradation, while the backbone disubstitution favors the end process. These effects can be explained in terms of radical stability, which is dictated by molecular structure. Sterling et al. (2001a) found their model to be less successful under very aggressive degradation conditions, and suggested the deficiency may be due to increased radical populations leading to failure of the steady-state hypothesis for radical populations.

Dextran degradation by acid hydrolysis, ultrasound, and enzyme attack was studied by Browarzik and Koch (1996) and Browarzik (1997) with a reaction kernel that included fitting parameters. The form of the distribution was assumed to remain consistent throughout the reactions. Numerical methods gave values of the fitting parameters, providing good agreement between the model and the experimental data. The parameter values indicate that dextran molecules degrade preferentially near the ends, and that smaller molecules degrade faster than large ones (Browarzik, 1997; Browarzik and Koch, 1996).

Ultrasonic degradation of polymers is an example of mechanochemistry (Nguyen et al., 1997), which has attracted attention as a means of initiating and moderating chemical reactions. As in simple elongational shear fields, macromolecules subjected to ultrasound tend to undergo midpoint rather than chain scission. Distribution kinetics can explain the evolution of polydispersity and average MW observed in experiments (Madras et al., 2000). Ultrasound waves passing through a liquid cause cavitation bubbles to form and collapse, inducing severe shearing and high temperatures. A detailed mathematical description of how the shear field causes midpoint scission to produce macromolecular free radicals remains to be developed. Such a theory should explain the observed effects of polymer concentration, development of a bimodal MWD, and the lower limit of final average MW that depends on ultrasound intensity (Madras and McCoy, 2001). The quantitative effects of temperature, solvent, dissolved gases, and radical scavengers also present research projects for the near future.

Reversible reactions

The distribution kinetics of reversible reactions shows that the observed first-order rate coefficients comprise algebraic groups of primary reaction-rate coefficients (Gloor et al., 1994; Kodera and McCoy, 1997). A reversible free radical reaction mechanism is

$$\mathrm{P}(x) + \mathrm{R}^\bullet(x'-x) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} \mathrm{R}^\bullet(x') \tag{33}$$

and

$$\mathrm{P}(x) \underset{k_H}{\overset{k_h}{\rightleftharpoons}} \mathrm{R}^\bullet(x), \tag{34}$$

where the long-chain approximation excludes the initiation and termination steps. The moment operation is applied to the reaction rate expressions, and the quasi-stationary-state approximation provides the relation between the radical and polymer zeroth moments (molar concentration) (Kodera and McCoy, 1997)

$$r^{(0)} = (k_h/k_H)\, p^{(0)}. \tag{35}$$

Integrating the zeroth-moment polymer expression with the initial condition, $p^{(0)}(t=0,x) = p_o^{(0)}(x)$, gives (Kodera and McCoy, 1997)

$$p^{(0)}(t) = e^{kt} / \left[(e^{kt}-1) k_a/k_d + 1/p^{(0)} \right]. \tag{36}$$

where $k = k_d k_h / k_H$. In the long-time limit, the equilibrium relation is (Kodera and McCoy, 1997)

$$p^{(0)}\,(t \to \infty) = p_\infty^{(0)} = k_d/k_a. \tag{37}$$

The ratio of the reaction-rate coefficients for a reversible addition/scission reaction is found experimentally as the long-time limit of the molar concentration. The reaction-rate coefficients are written in Arrhenius form

$$k_a = k_{ao} e^{-Ea/RT} \tag{38a}$$

and

$$k_d = k_{do} e^{-Ed/RT}, \tag{38b}$$

in terms of the energies of activation for addition (E_a) and scission (E_d). A result related to the van't Hoff equation,

$$p_\infty^{(0)} = K_o e^{-\Delta H/RT}, \tag{39}$$

is obtained when $K_o = k_{do}/k_{ao}$ and $\Delta H = E_d - E_a$ is the heat of reaction (Kodera and McCoy, 1997). The total free energy of the system is the sum of the MW moments when the molar free energy of the molecules, $\mu(x)$ (Cotterman et al., 1985), is expressed as a polynomial (Kodera and McCoy, 1997),

$$G(t) = \int_0^\infty p(x,t)\mu(x)\,dx. \tag{40}$$

The free energy is minimized at equilibrium ($dp^{(n)}/dt \to 0$) (Kodera and McCoy, 1997).

Sezgi et al. (1998) investigated the characteristics of polyethylene thermal degradation, or pyrolysis, in an open batch reactor with separate collection of condensable and noncondensable volatiles. The reaction-rate coefficient for chain-end scission was determined from the molar production of the noncondensable products. The volatilization effects were taken into account by an overall mass-transfer coefficient presumed to decrease linearly with MW, and an interphase driving force given by the concentration distribution difference and a phase-equilibrium coefficient in polynomial form. The experimental and modeling study was an attempt to examine a multiphase pyrolysis process using fundamental distribution kinetics based on actual chemical reactions, rather than empirical representations. An advantage over pyrolysis data from TGA experiments was that the MWD of the remaining polymer could be analyzed. As mentioned earlier, however, TGA systems are well-developed and provide precise and detailed data that can in principle be used to test chemical kinetics models of complex macromolecules. Recently, McCoy (2001) showed how distribution kinetics can be applied to TGA experiments to elucidate the rates of the mechanistic steps during polymer degradation. Pyrolysis is required before combustion of most liquid and solid fuels can occur, and thus is of fundamental importance, not only as a method of chemical analysis.

Gloor et al. (1994) studied distribution kinetics for random scission and simultaneous random cross-linking of polyolefins during reactive extrusion. Numerical methods were favored over the moment method due to a closure problem beyond the gel point. The model was able to predict polyethylene gel fraction and average MW as related to oxidant concentration.

The expressions for reversible processes reduce to the expressions for irreversible degradation reactions when the addition (or repolymerization) -rate coefficients are relatively small. The irreversible decomposition expressions are thereby recovered from the more general available analysis. When the scission reactions are negligible compared to the addition reactions, the well-known polymerization expressions appear.

Complex macrmolecular systems

The preceding theoretical development and experimental discussion has been based on single-variable distributions. Much work remains to be done to extend the principles to more complex systems, including multivariate distributions and interacting mixtures. Kodera and coworkers recently applied the distribution kinetics methods described here to asphaltene hydrocracking (Kodera et al., 2000). The evolution of multiple specific scission products was effectively modeled as the summation of Dirac delta distributions in a study of copolymer thermolysis (Wang et al., 1995). Madras and McCoy (1999) studied binary polymer mixture degradation by representing the mixture as a sum of continuous distributions. The degree and type of interacting between the degrading polymers depends on the polymer concentrations and on the reaction-rate parameters in the free radical mechanism, and therefore temperature and pressure. The effect of PAMS on the thermal degradation of polystyrene in batch solution was studied at low polystyrene concentrations to preserve a pseudo-first-order reaction rate (Madras and McCoy, 1999). Polystyrene degrades mainly by random scission, but PAMS degrades by a chain-end process. The polystyrene degradation rate decreased with increasing PAMS concentration, as shown in Figure 3, similar to the effect of a hydrogen donor, suggesting the interaction involves hydrogen abstraction. Thermolysis of polymer mixtures has interesting potential applications for plastics recycling and for heat-resistant blends. Analyzing the temperature stability of such polymer mixtures requires an understanding of radical mechanisms for MWDs.

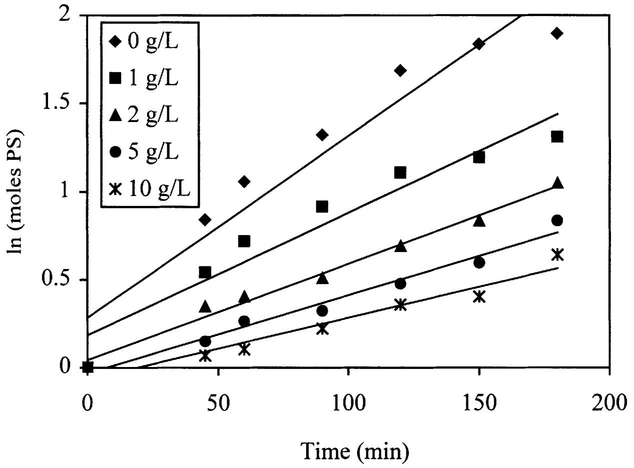

Figure 3. Effect of PAMS on thermal degradation of polystyrene (Madras and McCoy, 1999).

Moles polystyrene normalized with initial moles polystyrene.

Coal liquefaction has been simulated by random and chain-end scission reactions in coal networks to form distributions of soluble macromolecules (Wang et al., 1993, 1994a,b). The governing integrodifferential equations include reaction and mass transfer terms. Reaction rate coefficients and gamma distribution parameters for the semicontinuous product distribution were determined from experimental and literature data (Wang et al., 1993, 1994a,b). The addition of a hydrogen-donor solvent (tetralin) to the system increased the thermolysis rate due to enhanced hydrogenation of the coal structure (Wang et al., 1994b).

Modeling of reactions of branched macromolecules is a challenge for chemical-reaction engineering. Metallocene-catalyzed polymerization of branched polymers has been addressed (Chu et al., 2000; Wang et al., 1998, 1999). Formation of hyperbranched and fractal dendrimers has also been considered (McCoy, 1999b). However, degradation of branched polymers, important for synthetic and natural macromolecular systems, remains a difficult objective. Catalytic degradation of branched as well as unbranched polymers will require concerted experimental and theoretical efforts.

Future work

Many systems of scientific and engineering interest are composed of entities that are distributed with respect to a property, and therefore can be described by a distribution whose time and space dependence is governed by a PBE. Methods similar to those used in distribution kinetics of chemical reactions and described in this review can be applied in such cases. Continuous distribution kinetics has been applied to only a small fraction of appropriate reaction systems. We have discussed its application to thermolysis reactions, primarily involving synthetic polymers in organic solution. The straightforward method can, in principle, be applied to other reaction systems, including natural biopolymers. Particularly challenging problems include describing the time-evolution of multivariate distribution reactions such as branched macromolecules, applying the method to multiphase processes such as pyrolysis, and expanding the technique to manage complex polymer mixtures.

Summary

An approach to macromolecular reaction process analysis based on distribution kinetics and a free radical mechanism quantitatively describes experimental results for several different polymers. Applications discussed include analytical thermolysis or pyrolysis, polymer degradation for stability characterization or plastics recycling, and coal thermolysis to produce fuels and feedstocks. Distribution kinetics also has application in a broad range of other engineering applications, including particle dynamics, microbial growth processes, and aerosol science.

The theory shows how distribution kinetics can describe chemical-reaction models for macromolecular reactions. A fundamental model describes the radical mechanisms based on chain reactions with elementary steps of initiation, propagation−depropagation, hydrogen abstraction, and termination. MWDs and their moments can be measured by gel permeation chromatography (GPC) to show how the distributions and their moments vary as reactions progress. Experimental data are interpreted with PBEs to elucidate reaction mechanisms and to measure rate coefficients. Rate coefficients can depend on molecular characteristics such as MW, and activation energies for the reactions can be determined. Experiments have demonstrated the usefulness of these concepts for thermolytic degradation of coal and polymers with different solvents, including hydrogen-donor and nondonor solvents. Expected steady-state, long-time, or equilibrium conditions are revealed.

Continuous distribution kinetics provides a straightforward approach to reactions in macromolecular systems. The concepts apply in general to a range of binary scission and addition processes. Molecules can randomly combine and simultaneously break to smaller sizes that may be distributed randomly or nonrandomly. The type of reaction is governed by a stoichiometric coefficient that spans the range of molecular sizes. The distribution approaches similarity solutions for special cases of stoichiometry.

Acknowledgment

This work was supported in part by NSF Grant CTS-9810194.

Literature Cited

Abramowtiz, M., and I. A. Stegun, *Handbook of Mathematical Functions*, Chap. 26, National Bureau of Standards, Washington, DC (1968).

Amundson, N. R., *The Mathematical Understanding of Chemical Engineering Systems: Selected Works*, R. Aris and A. Varma, eds., Pergamon Press, New York, p. 400 (1980).

Aris, R., and G. R. Gavalas, “On the Theory of Reactions in Continuous Mixtures,” *Philos. Trans. R. Soc. London, Ser. A*, **260**, 351 (1966).

Astarita, G., and S. I. Sandler, eds., *Kinetic and Thermodynamic Lumping of Multicomponent Mixtures*, Elsevier, Amsterdam (1991).

Astarita, G., and R. Ocone, “Lumping Nonlinear Kinetics,” *AIChE J.*, **34**, 1299 (1988).

Briano, J. G., and E. D. Glandt, “Molecular Thermodynamics of Continuous Mixtures,” *Fluid Phase Equilib.*, **14**, 91 (1983).

Browarzik, D., “Continuous Kinetics of Dextran Degradation,” *J. Macromol. Sci. Pure Appl. Chem.*, **A34**, 397 (1997).

Browarzik, D., and H. Kehlen, “Hydrocracking Process of n-Alkanes by Continuous Kinetics,” *Chem. Eng. Sci.*, **49**, 923 (1994).

Browarzik, D., and H. Kehlen, “Continuous Kinetics of Reversible Reactions in Polydisperse Mixtures,” *Chem. Eng. Sci.*, **52**, 177 (1997).

Browarzik, D., and A. Koch, “Application of Continuous Kinetics to Polymer Degradation,” *J. Macro. Sci. Pure Appl. Chem.*, **A33**, 1633 (1996).

Burnham, A. K., “Application of the Sestak-Berggren Equation to Organic and Inorganic Materials of Practical Interest,” *J. Therm. Anal.*, **60**, 895 (2000).

Burnham, A. K., and R. L. Braun, “Global Kinetic Analysis of Complex Materials,” *Energy Fuels*, **13**, 1 (1999).

Choi, J. J., and Y. C. Bae, “Liquid-Liquid Equilibria of Polydisperse Polymer Systems: Applicability of Continuous Thermodynamics,” *Fluid Phase Equilib.*, **157**, 213 (1999).

Chu, K. J., J. B. P. Soares, and A. Penlidis, “Variation of Molecular Weight Distribution (MWD) and Short Chain Branching Distribution (SCBD) of Ethylene/1-Hexene Copolymers Produced with Different In-Situ Supported Metallocene Catalysts,” *Macromol. Chem. Phys.*, **201**, 340 (2000).

Cotterman, R. L., R. Bender, and J. M. Prausnitz, “Phase Equilibria for Mixtures Containing Very Many Components. Development and Application of Continuous Thermodynamics for Chemical Process Design,” *Ind. Eng. Chem. Proc. Des. Dev.*, **24**, 194 (1985).

Croxton, F. E., *Elementary Statistics*, Dover, New York (1953).

DeDonder, T., *L'Affinite*, Pt. 2, Gauthier-Villars, Paris (1931).

Dotson, N. A., R. Galvan, R. L. Laurence, and M. Tirrell, *Polymerization Process Modeling*, VCH Publishers, New York (1996).

Evans, R. M. L., D. J. Fairhurst, and W. C. K. Poon, "Universal Law of Fractionation for Slightly Polydisperse Systems," *Phys. Rev. Lett.*, **81**, 1326 (1998).

Flory, P. J., *Principles of Polymer Chemistry*, Cornell Univ. Press, Ithaca, NY (1953).

Gavalas, G. R., "The Long Chain Approximation in Free Radical Reaction Systems," *Chem. Eng. Sci.*, **21**, 133 (1966).

Gloor, P. E., Y. Tang, A. E. Kostanska, and A. E. Hamielec, "Chemical Modification of Polyolefins by Free Radical Mechanisms: A Modelling and Experimental Study of Simultaneous Random Scission, Branching and Crosslinking," *Polymer*, **35**, 1012 (1994).

Goto, M., and B. J. McCoy, "Inverse Size-Exclusion Chromatography for Distributed Pore and Solute Sizes," *Chem. Eng. Sci.*, **55**, 723 (2000).

Greenberg, M. D., *Foundations of Applied Mathematics*, Prentice-Hall, Englewood Cliffs, NJ (1978).

Gualtieri, J. A., J. M. Kincaid, and G. Morrison, "Phase Equilibria in Polydisperse Fluids," *J. Chem. Phys.*, **77**, 521 (1982).

Guy, L., and B. Fixari, "Waxy Polyethylenes from Solution Thermolysis of High Density Polyethylene: Inert and H-Donor Solvent Dilution Effect," *Polymer*, **40**, 2845 (1999).

Haberman, R., *Elementary Applied Partial Differential Equations*, Prentice-Hall, Upper Saddle River, NJ (1998).

Himmelblau, D. M., and K. B. Bischoff, *Process Analysis and Simulation—Deterministic Systems*, Wiley, New York, p. 192 (1968).

Ho, T. C., "A Simple Expression for the Collective Behavior of a Large Number of Reactions," *Chem Eng. Sci.*, **46**, 281 (1991).

Ho, T. C., and R. Aris, "On Apparent Second-Order Kinetics," *AIChE J.*, **33**, 1050 (1987).

Hulburt, H. M., and S. Katz, "Some Problems in Particle Technology—A Statistical Mechanical Formulation," *Chem. Eng. Sci.*, **19**, 555 (1964).

Jellinek, H. H. G., *Degradation of Vinyl Polymers*, Academic Press, New York (1955).

Karmore, V., and G. Madras, "Continuous Distribution Kinetics for the Degradation of Polystyrene in Supercritical Benzene," *Ind. Eng. Chem. Res.*, **39**, 4020 (2000).

Kehlen, H., M. T. Ratzsch, and J. Bergmann, "Continuous Kinetics of First Order Degradation Reactions in Polydisperse Mixtures," *Chem. Eng. Sci.*, **43**, 609 (1988).

Kim, Y.-C., and B. J. McCoy, "Degradation Kinetics Enhancement of Polystyrene by Peroxide Addition," *Ind. Eng. Chem. Res.*, **39**, 2811 (2000).

Kodera, Y., and B. J. McCoy, "Distribution Kinetics of Radical Mechanisms: Reversible Polymer Decomposition," *AIChE J.*, **43**, 3205 (1997).

Kodera, Y., T. Kondo, T. Saito, Y. Sato, and K. Ukegawa, "Continuous-Distribution Kinetic Analysis for Asphaltene Hydrocracking," *Energy Fuels*, **14**, 291 (2000).

Kossiakoff, A., and F. O. Rice, "Thermal Decomposition of Hydrocarbons, Resonance Stabilization and Isomerization of Free Radicals," *J. Amer. Chem. Soc.*, **65**, 590 (1943).

Krambeck, F. J., "Thermodynamics and Kinetics of Complex Mixtures," *Chem. Eng. Sci.*, **49**, 4179 (1994).

Kumar, G. S., V. R. Kumar, and G. Madras, "Continuous Distribution Kinetics for Thermal Degradation of LDPE in Solution," *J. Appl. Poly. Sci.*, (2001).

Laurence, R. L., R. Galvan, and M. V. Tirrell, "Mathematical Modeling of Polymerization Kinetics," *Polymer Reactor Engineering*, C. McGreavy, ed., VCH Publishers, New York (1994).

Madras, G., and V. Karmore, "Continuous Distribution Kinetics for Oxidative Degradation of PMMA in Solution," *Poly. Degr. Stab.*, **72**, 537 (2001).

Madras, G., and B. J. McCoy, "Effect of Hydrogen Donors on Polymer Degradation," *Catal. Today*, **40**, 321 (1998a).

Madras, G., and B. J. McCoy, "Time Evolution to Similarity Solutions for Polymer Degradation," *AIChE J.*, **44**, 647 (1998b).

Madras, G., and B. J. McCoy, "Oxidative Degradation Kinetics of Polystyrene in Solution," *Chem. Eng. Sci.*, **52**, 2707 (1997).

Madras, G., and B. J. McCoy, "Distribution Kinetics for Polymer Mixture Degradation," *Ind. Eng. Chem.. Res.*, **38**, 352 (1999).

Madras, G., and B. J. McCoy, "Time Evolution of Molecular Weight Distributions for Ultrasonic Degradation of Polymers," *AIChE J.*, (2001).

Madras, G., G. Y. Chung, J. M. Smith, and B. J. McCoy, "Molecular Weight Effect on the Dynamics of Polystyrene Degradation," *Ind. Eng. Chem. Res.*, **36**, 2019 (1997a).

Madras, G., J. M. Smith, and B. J. McCoy, "Thermal Degradation Kinetics of Polystyrene in Solution," *Polym. Degr. Stab.*, **58**, 131 (1997b).

Madras, G., S. Kumar, and S. Chattopadhyay, "Continuous Distribution Kinetics for Ultrasonic Degradation of Polymers," *Polym. Degr. Stab.*, **69**, 73 (2000).

Madras, G., J. M. Smith, and B. J. McCoy, "Degradation of Poly(methyl methacrylate) in Solution," *Ind. Eng. Chem. Res.*, **35**, 1795 (1996a).

Madras, G., J. M. Smith, and B. J. McCoy, "Thermal Degradation of Poly(α-Methylstyrene) in Solution," *Polym. Degr. Stab.*, **52**, 349 (1996b).

Madras, G., J. M. Smith, and B. J. McCoy, "Effect of Tetralin on the Degradation of Polymer in Solution," *Ind. Eng. Chem. Res.*, **34**, 4222 (1995).

McCaffrey, W. C., M. J. Brues, D. G. Cooper, and M. R. Kamal, "Thermolysis of Polyethylene/Polystyrene Mixtures," *J. Appl. Polym. Sci.*, **60**, 2133 (1996).

McCoy, B. J., "Continuous-Mixture Kinetics and Equilibrium for Reversible Oligomerization Reactions," *AIChE J.*, **39**, 1827 (1993).

McCoy, B. J., "Distribution Kinetics for Temperature-Programmed Pyrolysis," *Ind. Eng. Chem. Res.*, **38**, 4531 (1999a).

McCoy, B. J., "Hyperbranched Polymers and Aggregates: Distribution Kinetics of Dendrimer Growth," *J. Colloid Interf. Sci.*, **216**, 235 (1999b).

McCoy, B. J., "Polymer Thermogravimetric Analysis: Effects of Chain-End and Reversible Random Scission," *Chem. Eng. Sci.*, **56**, 1525 (2001).

McCoy, B. J., "Vapor Nucleation and Droplet Growth: Cluster Distribution Kinetics for Open and Closed Systems," *J. Colloid Interf. Sci.*, **228**, 64 (2000).

McCoy, B. J., and M. Goto, "Continuous-Mixture Model of Chromatographic Separations," *Chem. Eng. Sci.*, **49**, 2351 (1994).

McCoy, B. J., and G. Madras, "Degradation Kinetics of Polymers in Solution: Dynamics of Molecular Weight Distributions," *AIChE J.*, **43**, 802 (1997).

McCoy, B. J., and G. Madras, "Evolution to Similarity Solutions for Fragmentation and Aggregation," *J. Colloid Interf. Sci.*, **201**, 200 (1998).

McCoy, B. J., and G. Madras, "Discrete and Continuous Models for Polymerization and Depolymerization," *Chem. Eng. Sci.*, **56**, 2831 (2001).

McCoy, B. J., and M. Wang, "Continuous-Mixture Fragmentation Kinetics: Particle Size Reduction and Molecular Cracking," *Chem. Eng. Sci.*, **49**, 3773 (1994).

McCoy, B. J., and W. J. Sterling, "Phase-Equilibrium Fractionation of Continuous Distributions," *AIChE J.*, **46**, 751 (2000).

McGrady, E. D., and R. M. Ziff, "Analytical Solutions to Fragmentation Equations with Flow," *AIChE J.*, **34**, 2073 (1988).

Ng, S. H., H. Seod, M. Stanciulescu, and Y. Sugimoto, "Conversion of Polyethylene to Transportation Fuels through Pyrolysis and Catalytic Cracking," *Energy Fuels*, **9**, 735 (1995).

Nguyen, T. Q., Q. Z. Liang, and H.-H. Kausch, "Kinetics of Ultrasonic and Transient Elongational Flow Degradation: A Comparative Study," *Polymer*, **38**, 3783 (1997).

Nicmanis, M., and M. J. Hounslow, "Finite-Element Methods for Steady-State Population Balance Equations," *AIChE J.*, **44**, 2258 (1998).

Nigam, A., D. M. Fake, and M. T. Klein, "Simple Approximate Rate Law for Both Short- and Long-Chain Rice Herzfeld Kinetics," *AIChE J.*, **40**, 908 (1994).

Odian, G., *Principles of Polymerization*, Wiley-Interscience, New York (1991).

Prasad, G. N., C. V. Wittmann, J. B. Agnew, and T. Sridhar, "Modeling of Coal Liquefaction Kinetics Based on Reactions in Continuous Mixtures," *AIChE J.*, **32**, 1277 (1986).

Price, G. J., and P. F. Smith, "Ultrasonic Degradation of Polymer Solutions: 1. Polystyrene Revisited," *Polym. Int.*, **24**, 159 (1991).

Ramkrishna, D., “Solution of Population Balance Equations,” *Chem. Eng. Sci.*, **26**, 1134 (1971).
Ramkrishna, D., “The Status of Population Balances,” *Rev. Chem. Eng.*, **3**, 49 (1985).
Ramkrishna, D., *Population Balances: Theory and Applications to Particulate Systems in Engineering*, Academic Press, San Diego (2000).
Ratzsch, M. T., and H. Kehlen, “Continuous Thermodynamics of Complex Mixtures,” *Fluid Phase Equilib.*, **14**, 225 (1983).
Rice, F. O., and K. F. Herzfeld, “The Mechanism of Some Chain Reactions,” *J. Chem. Phys.*, **7**, 671 (1939).
Salacuse, J. J., and G. Stell, “Polydisperse Systems: Statistical Thermodynamics, with Applications to Several Models Including Hard and Permeable Spheres,” *J. Chem. Phys.*, **77**, 3714 (1982).
Segzi, N. A., W. S. Cha, J. M. Smith, and B. J. McCoy, “Polyethylene Pyrolysis: Theory and Experiments for Molecular-Weight-Distribution Kinetics,” *Ind. Eng. Chem. Res.*, **37**, 2582 (1998).
Solomons, T. W. G., *Fundamentals of Organic Chemistry*, Wiley, New York (1986).
Song, C., W.-C. Lai, and H. H. Schobert, “Condensed-Phase Pyrolysis of n-Tetradecane at Elevated Pressures for Long Duration. Product Distribution and Reaction Mechanisms,” *Ind. Eng. Chem. Res.*, **33**, 534 (1994).
Sterling, W. J., Y.-C. Kim, and B. J. McCoy, “Peroxide Enhancement of Poly(α-Methylstyrene) Thermal Degradation,” *Ind. Eng. Chem. Res.*, **40**, 1811 (2001a).
Sterling, W. J., K. S. Walline, and B. J. McCoy, “Experimental Study of Polystyrene Thermolysis to Moderate Conversion,” *Polym. Degr. Stab.*, (2001b).
Tobita, H., and K. Ito, “On the Calculation of Molecular Weight Distributions from the Moments Using Laguerre Polynomials,” *Polym. React. Eng.*, **1**, 407 (1992/1993).
Venkateshwaran, G., and A. Kumar, “Solution of Free Radical Polymerization,” *J. Appl. Polym. Sci.*, **45**, 187 (1992).
Wang, M., J. M. Smith, and B. J. McCoy, “Continuous Kinetics for Thermal Degradation of Polymer in Solution,” *AIChE J.*, **41**, 521 (1995).
Wang, M., J. M. Smith, and B. J. McCoy, “Kinetics of Coal Thermolysis with a Mixed Solvent of *t*-Butanol and Tetralin,” *Energy Fuel*, **7**, 78 (1993).
Wang, W. J., D. J. Yan, S. P. Zhu, and A. C. Hamielec, “Kinetics of Long Chain Branching in Continuous Solution Polymerization of Ethylene Using Constrained Geometry Metallocene,” *Macromolecules*, **31**, 8677 (1998).
Wang, W. J., D. J. Yan, S. P. Zhu, and A. C. Hamielec, “Long Chain Branching in Ethylene Polymerization Using Binary Homogeneous Metallocene Catalyst System,” *Poly. React. Eng.*, **7**, 327 (1999).
Wang, M., C. Zhang, J. M. Smith, and B. J. McCoy, “Continuous-Mixture Kinetics of Thermolytic Extraction of Coal in Supercritical Fluid,” *AIChE J.*, **40**, 131 (1994a).
Wang, M., C. Zhang, J. M. Smith, and B. J. McCoy, “Dynamics of the Extract Molecular Weight Distribution in Supercritical Extraction of Coal: Continuous-Mixture Kinetics,” *Energy Fuels*, **8**, 890 (1994b).
Woo, O. S., and L. J. Broadbelt, “Recovery of High-Valued Products from Styrene-Based Polymers Through Coprocessing: Experiments and Mechanistic Modeling,” *Catal. Today*, **40**, 121 (1998).
Yoon, J. S., I. J. Chin, M. N. Kim, and C. Kim, “Degradation of Microbial Polyesters—A Theoretical Prediction of Molecular Weight and Polydispersity,” *Macromolecules*, **29**, 3303 (1996).
Ziff, R. M., “New Solutions to the Fragmentation Equation,” *J. Phys. A: Math. Gen.*, **24**, 2821 (1991).
Ziff, R. M., and E. D. McGrady, “The Kinetics of Cluster Fragmentation and Depolymerisation,” *J. Phys. A: Math. Gen.*, **18**, 3027 (1985).
Ziff, R. M., and E. D. McGrady, “Kinetics of Polymer Degradation,” *Macromolecules*, **19**, 2513 (1986).

Appendix

Reversible rate expression development

A molecule can play four different roles in a reversible random scission reaction: scission parent, scission daughter, addition parent, and addition daughter. The rate expression will therefore be made up of four terms, and developing each is facilitated by writing the partial reaction equation for each role.

The reaction showing loss of an x by scission is

$$P(x)\xrightarrow{k_d}P(x')+P(x-x'). \tag{A1}$$

The reaction rate is first order,

$$\partial p/\partial t=-k_d p(x). \tag{A2}$$

The reaction showing the gain of an x by scission is

$$P(x')\xrightarrow{k_d}P(x)+P(x'-x), \tag{A3}$$

and the reaction rate is again first order. This reaction requires the production of a specified scission product from any of a range of macromolecules, so a reaction kernel is used:

$$\partial p/\partial t=2k_d\int_x^\infty p(x')\Omega(x,x')\,dx'. \tag{A4}$$

The integration is over any molecule larger than the specified product weight, x, because the scission parent must be larger than its progeny. The factor “2” is introduced because the $P(x)$ molecule could occupy two equivalent places in the reaction equation.

The loss of an x by addition is

$$P(x)+P(x'-x)\xrightarrow{k_a}P(x'). \tag{A5}$$

The reaction-rate expression is second order. $P(x)$ reacts with any other macromolecule,

$$\partial p/\partial t=-2k_a p(x)\int_0^\infty p(x')dx'. \tag{A6}$$

The gain of an x by addition is given by

$$P(x-x')+P(x')\xrightarrow{k_a}P(x). \tag{A7}$$

The rate is again second order, but the parent molecules both range in mass from the smallest up to x,

$$\partial p/\partial t=k_a\int_0^x p(x')p(x-x')\,dx'. \tag{A8}$$

The overall rate expression for reversible random scission is given by the sum of the four terms given earlier (Eq. 14). Rate expressions describing different mechanisms are derived in an analogous manner.

Stochiometric coefficient

The stoichiometric coefficient or reaction kernel, $\Omega(x,x')$, represents the probability that the scission of a molecule with MW x' will yield a molecule with MW x ($x'\geq x$). The kernel shows how the products of a scission reaction are distributed, and is defined to be symmetric, $\Omega(x,x') = \Omega(x'-x,x')$, and normalized $\int_0^{x'} \Omega(x,x')\,dx = 1$ (Aris and Gavalas, 1966). Chain-end scission requires that the product molecule be of a specified MW, so that the probability of obtaining a product molecule of any other weight is zero. The Dirac delta operator, defined such that $\delta(y) \to \infty$ for $y = 0$, and $\delta(y) = 0$ for $y \neq 0$, provides the necessary properties. For chain-end scission, where x_s is the specified product MW, the kernel is $\delta(x - x_s)$ for the end product and $\delta(x - (x' - x_s))$ for the resulting macromolecule (McCoy and Wang, 1994). The projection property of the Dirac delta operator is important,

$$\int_a^b p(x')\,\delta(x'-x)\,dx' = p(x),$$

where $a \leq x \leq b$. The required properties of symmetry and normalization are satisfied by the Dirac delta operator (Haberman, 1998).

Midpoint scission requires that the two product molecules be of the same weight, exactly one-half of the parent MW. Again the Dirac delta operator is convenient and the kernel is $\Omega(x,x') = \delta(x - x'/2)$ (Himmelblau and Bischoff, 1968). Midpoint scission is a special case of proportioned fragmentation, $\Omega(x,x') = \delta(x - bx')$, in which b describes the proportionality between the sizes of the product and parent molecules, and for midpoint scission $b = 1/2$ (McCoy, 1993).

Random-chain scission requires equal probability for the production of any mass daughter molecule, thus $\Omega(x,x') = c$, where c is a constant. Evaluating the normalization integral gives $c = 1/x'$ for random-chain scission (Aris and Gavalas, 1966).

A number of general forms for the reaction kernel have been developed (Ziff and McGrady, 1985, 1986; McGrady and Ziff, 1988; McCoy and Wang, 1994; Browarzik and Koch, 1996; Browarzik, 1997). McCoy and Wang (1994) proposed

$$\Omega(x,x') = Bx^m (x'-x)^m, \qquad 0 \leq m < \infty, \tag{A10a}$$

where the normalization property requires that

$$B = \Gamma(2m+2) / \left\{ \Gamma(m+1)^2 (x')^{2m+1} \right\}. \tag{A10b}$$

The generalized gamma function, $\Gamma(\alpha) = (\alpha - 1)\Gamma(\alpha - 1)$ for $\alpha > 1$ (Greenberg, 1978), allows for the possibility that m is not an integer (McCoy and Wang, 1994). For positive integers α, $\Gamma(\alpha) = (\alpha - 1)!$ (Greenberg, 1978). The limiting values of m yield the random scission kernel ($m = 0$, $\Omega(x,x') = 1/x'$) and the midpoint scission kernel ($m \to \infty$, $\Omega(x,x') = \delta(x - x'/2)$). A parabolic kernel used to model the thermal decomposition of coal (Prasad et al., 1986) and degradation of polymer (Ziff and McGrady, 1986) results when $m = 1$. For large m the kernel has a Gaussian form that becomes narrower and taller as m increases, leading to the limiting Dirac form as $m \to \infty$. As m varies between its limits, the general scission kernel expression represents a continuum of fission processes (McCoy and Madras, 1997), as shown in Figure A1 (McCoy and Wang, 1994). Although inclusion of the stoichometric kernel is essential to the model, the value of m has no effect on the time evolution of the zeroth and first moments of the distribution for reversible scission reactions, and only a small effect on the rate of change of the second moment (Madras and McCoy, 1998b).

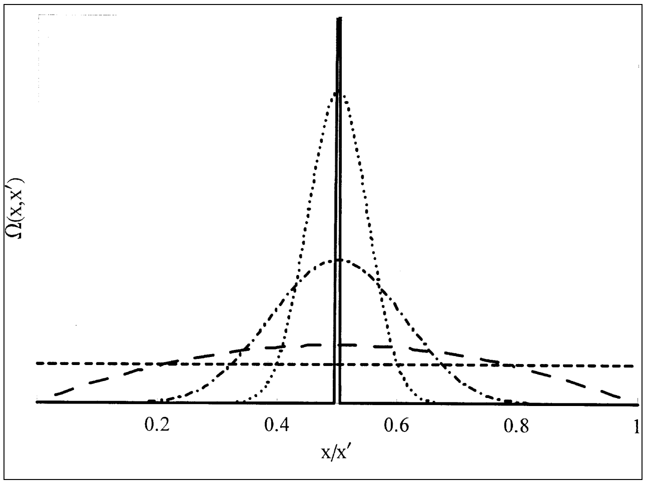

Figure A1. General stoichiometric coefficient as a function of MW (x) as given by Eq. 50.

– – – $m = 0$; — — $m = 1$; –·–·– $m = 10$; ··· $m = 50$; — $m = 100{,}000$ ($m \to \infty$).

Moment-rate expression

The moment-rate expression for reversible random scission can be developed from the reaction-rate expression (Eq. 14) by applying the moment operation (Eq. 20) to each term in the rate equation. The moment operation is linear, so term-by-term evaluation is appropriate. The necessary mathematical manipulations include changing the order of integration, changing variables, and introducing the binomial theorem (Himmelblau and Bischoff, 1968). In the first term, the derivative moves through the integral smoothly,

$$\int_0^\infty (\partial p/\partial t) x^n dx = \partial\left(p^{(n)}\right)/\partial t. \tag{A11}$$

The reaction-rate coefficients, k_a and k_d, are taken to be constants for this example, and therefore come out of the integrals. The first term on the righthand side (RHS) of the rate expression becomes, in moment form,

$$-k_d \int_0^\infty p(x) x^n\,dx = -k_d p^{(n)}. \tag{A12}$$

Simplification of the second term on the RHS for the random scission reaction kernel ($\Omega(x,x') = 1/x'$) requires changing the order of integration, evaluating the second integral, simplifying, and evaluating the first integral, respectively:

$$2k_d\int_0^\infty\left[\int_x^\infty p(x')(1/x')\,dx'\right]x^n\,dx$$

$$=2k_d\int_0^\infty (1/x')p(x')\left[\int_0^{x'} x^n\,dx\right]dx'$$

$$=\left[2k_d/(n+1)\right]\int_0^\infty (1/x')p(x')(x')^{n+1}\,dx'$$

$$=\left[2k_d/(n+1)\right]p^{(n)}. \tag{A13}$$

The third term in the moment-rate expression is obtained easily, as $p^{(0)}$ is a constant,

$$-2k_a\int_0^\infty x^n\left[p(x)\int_0^\infty p(x')\,dx'\right]dx=-2k_a\int_0^\infty x^n p(x)p^{(0)}\,dx$$

$$=-2k_a p^{(0)}p^{(n)}. \tag{A14}$$

Applying the moment operation to the final term requires changing the order of integration, followed by a change of variables ($y=x-x'$), evaluating the second integral via the binomial theorem, and finally evaluating the first integral,

$$k_a\int_0^\infty x^n\left\{\int_0^x p(x')p(x-x')\,dx'\right\}dx$$

$$=k_a\int_0^\infty p(x')\left\{\int_{x'}^\infty x^n p(x-x')\,dx\right\}dx'$$

$$=k_a\int_0^\infty p(x')\left\{\int_0^\infty (y+x')^n p(y)\,dy\right\}dx'$$

$$=k_a\Sigma_{j=0}^n\binom{n}{j}\int_0^\infty p(x')(x')^j\left[\int_0^\infty y^{n-j}p(y)\,dy\right]dx'$$

$$=k_a\Sigma_{j=0}^n\binom{n}{j}\int_0^\infty p(x')(x')^j p^{(n-j)}\,dx'$$

$$=k_a\Sigma_{j=0}^n\binom{n}{j}p^{(n-j)}p^{(j)}. \tag{A15}$$

The reaction-rate expression becomes the moment-rate expression for reversible random scission (Eq. 21) by collecting the preceding terms.

Manuscript received June 19, 2000, and revision received Apr. 27, 2001.