

# Continuous Kinetics for Thermal Degradation of Polymer in Solution

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*Continuous kinetics of thermal degradation of poly(styrene-allyl alcohol) (PSA) in solution are explored theoretically and experimentally. Thermal degradation experiments for PSA of number-average molecular weight 1,640 in *t*-butanol solution were conducted in a steady-state flow reactor at 6.8 MPa and 403–473 K. The molecular-weight distributions (MWDs) of the original polymer and its reaction products were measured as a function of residence time by gel permeation chromatography. The MWD of the initial PSA is described by a gamma distribution function. Experimental data indicated that the polymer cracks to specific, low-molecular-weight (MW) products and degrades by random chain scission. Results are interpreted by a mathematical model based on the continuous kinetics for specific and random degradation processes. Rate coefficients are determined separately from the dynamic data of the MW moments for the specific products and the MWDs for the reacting polymer. Activation energies obtained are 5.9–7.4 kcal/mol for specific degradation processes and 35 kcal/mol for the random degradation process. The detailed MWDs are related to conventional lumped (number-average molecular-weight) data.*

## Introduction

The degradation and stabilization of polymers are of considerable importance from both practical and theoretical points of views (Allen and Edge, 1992). Degradation is significant for several reasons: (1) the degradation of polymers in different environments is a major limiting factor in their applications (Hawkins, 1984); (2) thermal degradation by pyrolysis coupled with gas chromatography is an important analytical procedure for identifying polymeric structure (Flynn and Florin, 1985); and (3) induced degradation can potentially be used in recycling waste plastics (Powell, 1990; Miller, 1994). Thermal degradation of polymers is similar in some respects to other thermal decomposition processes, for example, petroleum cracking and coal thermolysis.

Early work on polymer degradation was reviewed by Simha and Wall (1958) and Jellinek (1955). Degradation by thermal-, radiation- and oxygen-induced processes were considered by Simha and Wall. Primary measurements were (1) yield of monomer, (2) rate of decrease of average molecular weight, and (3) rate of volatilization. Rate equations were developed for free-radical mechanisms, which included both random-bond breakage within the chain and specific, or preferential, breakage of terminal bonds. The International Symposium,

Brussels (Gevakens, 1975), reviewed trends in degradation research, including experimental methods and kinetics. Madorski (1964) reviewed data on rates, activation energies, and experimental methods for thermal degradation of a variety of polymers. Two other books edited by Jellinek (1978, 1983) contain much fundamental information. For example, Chapter 10 in Jellinek (1983) critiques thermal-gravimetric-analysis (TGA) methods for measuring degradation rates. A handbook of degradation has also recently been published (Hamid et al., 1992). These sources contain considerable information on kinetics and mechanisms of degradation.

A few studies combine experimental and theoretical investigations to address quantitatively the kinetics and mechanisms of polymer degradation (Reich and Stivala, 1971; Hawkins, 1984; Kehlen et al., 1988). These studies involve the determination of a number of factors, not all of which are easy to obtain experimentally: for example, identification of intermediate and final products, and analysis of dynamic data for molecular-weight distribution (MWD) or average MW. Mechanisms have been proposed and the kinetic rate equations for each mechanism formulated (Jellinek, 1983; Ziff and McGrady, 1985, 1986). For each kinetic scheme, the depen-

dence of polymer properties, whose dynamic behavior can be obtained experimentally, is predicted from the kinetic rate equations. These predictions are compared with the experimental dynamic data to evaluate the models. Two general approaches were used in the early studies to treat the general set of equations for initiation, propagation, transfer, and termination reactions:

(1) Starting with a monodisperse sample (a single MW) all reactions that form all species of intermediates and products are enumerated based on statistical theory of random breaking of links (Simha and Wall, 1958; Wall, 1962; Jellinek, 1978). The mathematical problem was treated in two different ways: either the desired functions were obtained by probability considerations, or these functions were derived from differential rate equations. Jellinek (1955) also developed a theory for random scission modified by randomly distributed weak bonds. A disadvantage of these theories is that they are not readily applied to degradation of polydisperse polymers.

(2) Pyrolytic thermal degradation (occurring in gas or vacuum) is typically a two-phase process, with higher MW species remaining in the condensed phase and lower MW products evaporating. Starting with a polydisperse sample and removing the produced monomer by evaporation, Gordon (1961) and Boyd (1970) showed that the form of MWD for the polymer remains unaltered through a mild degradation but shifts to lower MW values.

Since degradation follows complex kinetic schemes, satisfactory solutions are often difficult to obtain for comparison with experimental data by the preceding approaches. With the advance of instrumentation, dynamic MWD data can be obtained during degradation processes by gel permeation chromatography, field-flow fractionation, or mass spectrometry (Cooper, 1989). Monitoring the temporal change of the MWD caused by degradation offers an opportunity to test kinetic models. Degradation is a chemical fragmentation process generally occurring in a polydisperse mixture. For systems with many species or size classifications the continuous-mixture concept is applicable, providing a mathematical tool to deal with the kinetics of polymer degradation. Continuous-mixture mathematics is based on mass or population balance equations that govern the temporal-spatial behavior of a frequency distribution function (Aris and Gavalas, 1966; Cheng and Redner, 1990). Ziff and McGrady (1985, 1986) and Kehlen et al. (1988) theoretically investigated the continuous kinetics of degradation. Based on the early work of Aris and Gavalas (1966), Syamlal and Wittmann (1985) and Prasad et al. (1986) presented a continuous-mixture model for liquefaction of coal, which can be considered a complex, high-MW, polymerlike solid. The application of continuous kinetics to coal thermolysis (Wang et al., 1994) also showed how experimental MWDs of thermal decomposition products can be described by mass-balance equations. McCoy (1993) provided a framework for the continuous kinetics of addition (fusion) and cracking (fission) processes in reversible oligomerization. Random and proportioned stoichiometric coefficients yielded different limiting distributions of oligomers for batch equilibrium processes. McCoy and Wang (1994) further extended the theory of cracking (size reduction) kinetics by showing that the stoichiometric coefficients for the product distribution can be written in a general form that allows random and specific products as special cases.

Vigil et al. (1988) discussed a discrete model of coagulation with single-particle breakoff.

The objective of this study is to apply concepts of continuous kinetics to the thermal degradation of poly(styrene-allyl alcohol) (PSA) in *t*-butanol solution. The experimental technique introduces a novel approach by employing a steady-state flow reactor and measuring the initial (inlet) and product MWDs by gel permeation chromatography (GPC). The reactor is operated at high pressure so that the thermal decomposition reactions occur in the liquid phase, ensuring that all components are solubilized during their residence time. MWD data for different residence times and temperatures provide the basis for developing and evaluating the model. A gamma distribution represents the initial MWD. Both random and specific degradation are included in the kinetic model. Mathematical solutions are developed by applying moment theory to solve the governing integrodifferential equations.

## Experiments

### Pretreatment of PSA samples

PSA of number-average molecular weight 1,100 (Polysciences, Inc.) has the chemical formula,  $(C_8H_8 \cdot C_3H_6O)_n$ , indicating a straight chain of  $n$  units. The MWD of the PSA sample obtained by GPC measurements is shown in Figure 1. The distribution is not smooth, indicating some component peaks in the lower molecular-weight range. To remove the low MW peaks, the original samples were pretreated by fractional precipitation (Rafikov et al., 1964; Kamide and Matsuda, 1989).

To fractionate the PSA, a 50-g sample was dissolved in 500-mL *t*-butanol in a 2,000-mL flask. A precipitating agent, distilled water, is slowly added to stirred polymer solution at 35°C. After 50-mL water is added, some precipitate starts to settle as a swollen phase. This fraction, containing the macromolecules of highest molecular weight, can be separated by decantation or centrifugation if the method is used to determine MWDs of polymers. Since in our case the goal is to separate out and remove the small MW fractions, 1,250 mL of water is continuously added to the solution. Then, the pre-

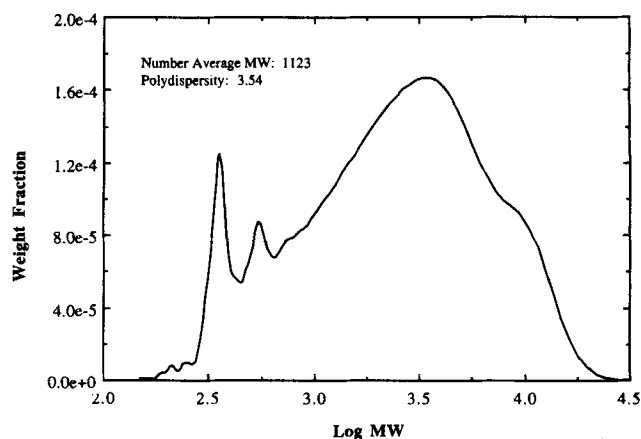
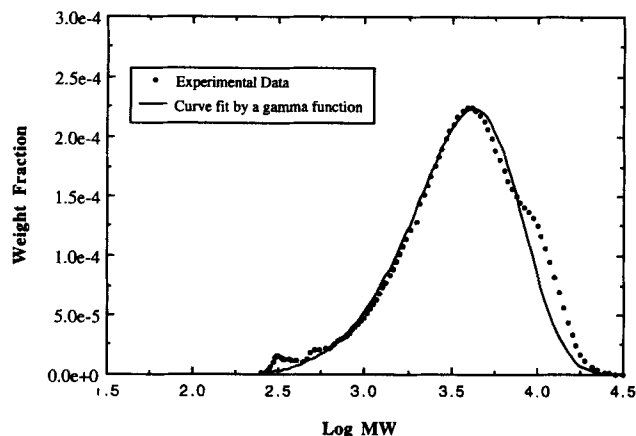


Figure 1. GPC measurement of MWD for original PSA samples.



**Figure 2.** MWD with a gamma distribution fit for pretreated PSA samples fed to the reactor for thermal degradation.

precipitate (large molecular weight fraction of PSA) and the liquid phase are separated by centrifugation. The precipitate is dried in an oven at 60°C until constant weight. The yield of the large MW fraction is 60–70%. This pretreated sample is stored in a closed container under nitrogen for the thermal degradation experiments. The MWD of the pretreated PSA sample is shown in Figure 2, which indicates a smooth MWD and number-average MW of 1,640.

### Thermal degradation experiments for PSA

Thermal degradation experiments with PSA solution were conducted in a steady-state flow reactor through which the solution flows continuously. Although the present experiments are at subcritical temperatures, the detailed apparatus and the operation procedure are described in the reports of supercritical processes (Zhang et al., 1992; Wang et al., 1993). The apparatus consists of four sections: (1) feed and pressurizing section; (2) extraction section; (3) temperature-control section; (4) flow-rate-control and sample-collection section. The experiments were done at high pressure, 6.8 MPa (1,000 psig), to prevent vaporization of the solvent or solutes at high temperatures. Two parallel piston-type accumulators with a maximum volumetric capacity of 8 liters were pressurized with compressed nitrogen. The stainless-steel reactor is 0.45 m long and 0.029-m ID with 0.0048-m wall thickness. A preheater coil is wound around the reactor. The preheater-reactor assembly is placed in an electric furnace of 1.4-kW maximum power. A J-type thermocouple with the junction enclosed in a 1.6-mm-ID stainless-steel sheath is inserted from the bottom of the reactor. Pressure is measured with an Ashcroft gauge having a pressure range of 0–5,000 psig (0–34 MPa). The temperature is controlled by a proportional-integral-derivative (PID) controller (Omega Model-2,000) and continuously recorded by a Varian Model 9176 recorder. The PSA solution flows downward in the flow reactor, through a Nupro 60-micron stainless-steel filter, a pressure-reduction valve, and a water-cooled heat exchanger. Finally, the effluent flows through a rotameter. Effluent samples of 25 mL were collected for GPC analysis.

PSA, pretreated as described, was dissolved in *t*-butanol to a concentration of 2 g/L. The thermal degradation experi-

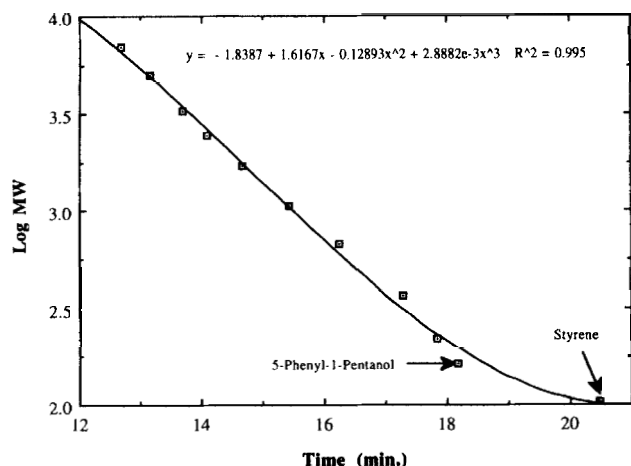
ments were carried out at constant pressure, 6.8 MPa (1,000 psig). As the decomposition reactions occur in the liquid phase, all reactant and product elements have the same residence time, unlike pyrolysis of a condensed phase in gas or under vacuum. The temperature was continuously increased at a heating rate of 0.14 K/s to the desired temperature and then held constant until the end of a run. A time of 10–20 min was required to reach the desired temperature levels (403–473 K). Thermal degradation experiments at four residence times (14, 23, 46 and 122 min) were performed at each temperature. After reaching steady state, two 25-mL samples of the reaction mixture were taken from the exit of the reactor. All of the experiments were conducted at liquid-phase reaction conditions and mild temperatures, which eliminates repolymerization and carbonization reactions and limits the amount of random chain scission.

### Analysis of polymer degradation products with GPC

The MWDs of the effluent samples were determined by GPC using PLgel columns coupled with a Hewlett-Packard 1050 HPLC. Two PLgel columns (Polymer Lab), 0.30 m × 0.0075 m, of 100 and 500 Å pore size, respectively, packed with 5-μm cross-linked poly(styrene-divinylbenzene) copolymer, were used in series. The HPLC reagent-grade tetrahydrofuran (THF, Baker Analyzed) was continuously pumped through the columns at a flow rate of 1.0 mL/min. The injected sample volume was 100 μL at a concentration about 2 g/L. A variable-wavelength spectrophotometric detector with a wide wavelength range (190–700 nm) was used to examine the wavelengths of 235, 254 and 280 nm in preliminary experiments. The wavelength 254 nm was chosen since it gives the maximum absorbance for the effluent samples. A refractive index detector was used to confirm the MWDs indicated by the UV detector.

Effluent samples were collected at four temperatures and four residence times. Ten mL of each sample were concentrated to about 2 mL by evaporating excess *t*-butanol solvent under vacuum at 323 K. Prior to this procedure it was established that boiling the feed-polymer solution for 2 h does not cause degradation or alter the MWD. Each concentrated sample was dissolved in THF, a satisfactory solvent for the PSA. The samples completely dissolved in THF, and no segregation of components was observed during GPC analysis. In the preliminary experiments, the injection-volume range (20–100 μL) of the sample and the velocity range (0.5–4 mL/min) were tested and no effects on retention time or shape of MWD were observed. This indicates that there were no significant effects of association in solution nor of column adsorption (Yau et al., 1979). GPC measurements with pyridine as mobile phase yielded chromatograms closely similar to those with THF, indicating that the results were not solvent-specific.

Narrow molecular-weight range poly(styrene) standards (MW = 162–20,000) from Polymer Lab were dissolved in THF for peak-position calibration (Yau et al., 1979). Styrene and 5-phenyl-1-pentanol in THF were used to extend the calibration to lower MW. Figure 3 shows the calibration curve of MW vs. retention time, which is satisfactorily fitted by a cubic polynomial. The number-average MW of the untreated PSA was measured with the GPC method as 1123, in agreement

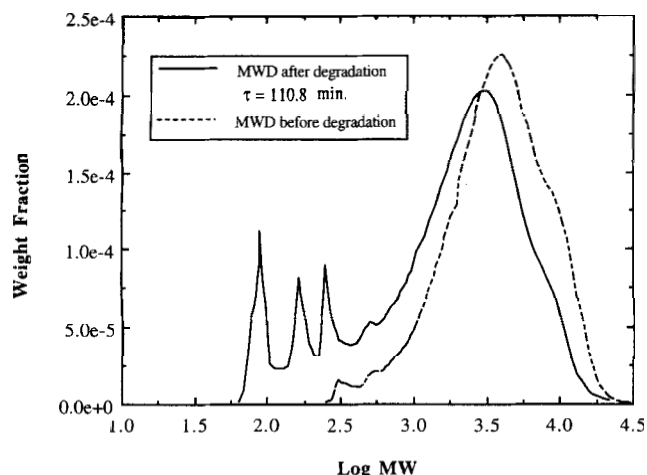


**Figure 3. Calibration curve for GPC with poly(styrene) standards, 5-phenyl-1-pentanol, and styrene.**

with the value supplied by the manufacturer, 1100. Based on the assessment that such calibration standards are satisfactory for the purposes and conditions of thermal degradation experiments, the MWDs were determined with a data acquisition system (Chem Station) and GPC software incorporating the poly(styrene) calibration data. One of the experimental MWDs at 433 K is presented in Figure 4 and is compared with the feed MWD. Detailed experimental MWD results and model simulations are discussed below.

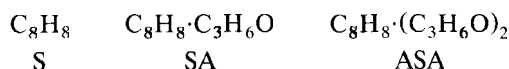
### Mechanism

The degradation paths for polymer molecules that are decomposed by heat in the absence of oxygen depends on molecular structure and experimental conditions. One extreme is pure random degradation, represented by binary scission of bonds at any position along the chain. The other extreme is pure depolymerization for homopolymers, which usually refers to the release of a monomeric species by scission at the chain end. Thermal degradation of PSA displays degradation behavior consistent with both of these two basic

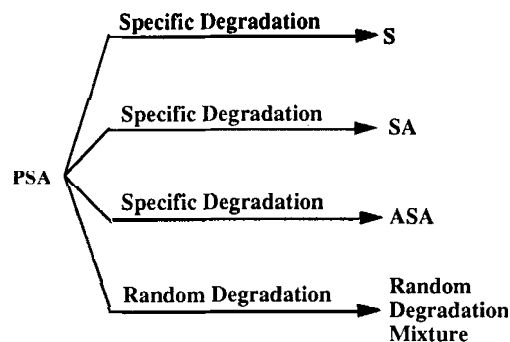


**Figure 4. MWD before (---) and after (—) thermal degradation at 423 K and 6.8 MPa.**

mechanisms. In Figure 4, the GPC chromatogram of the reaction mixture shows a region with  $MW < 500$  where three distinct peaks are observed, and a region with  $MW > 500$  where the chromatogram shifts toward lower MW relative to the feed polymer. Figure 4 suggests that one or two very small peaks are superimposed on the MWD at MWs higher than the three obvious peaks. Although they could become significant at higher temperatures, these small peaks are ignored in the current analysis. By comparing the GPC chromatograms for the reaction mixtures with those for pure styrene (S) and 5-phenyl-1-pentanol, the two lowest MW-specific products are identified as styrene and the oligomer (SA) of an allyl alcohol and a styrene molecule. We infer, based on its MW, that the third specific product is an oligomer of two allyl alcohols and one styrene (that is, ASA). The very small peak at  $MW = 497$  is possibly  $(SA)_3$ . Any allyl alcohol (A) produced during degradation would evaporate during sample preparation for GPC. The chemical formulas of S, SA, and ASA are

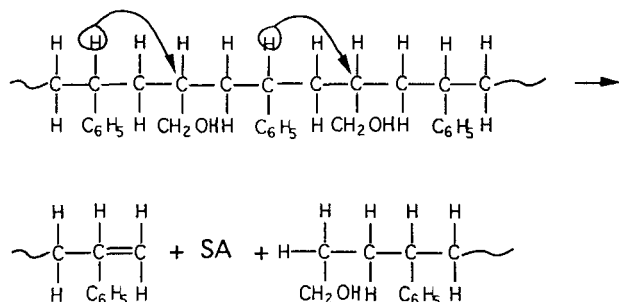


The experimental results suggest that PSA, which can be written as the regular copolymer,  $\cdots -SASASA-\cdots$ , degrades through a combination of random and specific degradation processes. Random degradation causes the main chain to break down randomly to form smooth product MWDs that cover a wide range of MW. Specific chain scissions are responsible for forming three specific products, S, SA, and ASA. The large MW fragments can further degrade by either specific or random processes. Both processes are important for PSA at our experimental conditions, and are treated as parallel reactions according to the following diagram:



Flynn and Florin (1985) pointed out that thermal degradation of some styrene copolymers, such as that of styrene and dimethyl fumarate, can form specific products other than monomers. Intramolecular transfer offers an effective way of producing molecules in the dimer and trimer range, as described by Madorsky (1964) for degradation of poly(styrene). When poly(styrene) was pyrolyzed in nitrogen the products consisted of, in addition to monomer, a mixture of saturated and unsaturated compounds, but mostly of dimers and trimers. A mechanism of chain scissions was proposed to explain the formation of the monomers, dimers, and trimers. The C—C bonds in  $\beta$ -position to double bonds are considered weaker than ordinary C—C bonds. Bonds between hydrogen and a tertiary carbon are weaker than those between

hydrogen and a secondary carbon. This suggests that the formation of S, SA, and ASA in our experiments can take place according to the following process, illustrated by the formation of SA:



Similar reactions are involved in the formation of S and ASA. Although Madorsky (1964) suggested that the two H-transfer steps can possibly occur simultaneously, it is more likely the steps occur consecutively. This two-step scission can thus be considered equivalent to a random chain scission followed by a specific depolymerization at a chain end.

## Theoretical Model

### Initial MWDs for polymers

To represent the MWD of the feed polymer we employ a gamma distribution, which reduces to the Gaussian or Poisson distribution as special cases (Abramowitz and Stegun, 1968). The molar fraction gamma distribution is defined for  $y = (x - x_s)/\beta$  as

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

and for  $y \leq 0$ ,  $p(x) = 0$ . The weight fraction gamma distribution is

$$p_w(x) = xp(x). \quad (2)$$

The average position,  $x^{\text{avg}}$ , and width of a peak,  $\sigma$ , which are related to the first and second moments of the gamma distribution, are given by Abramowitz and Stegun (1968) as

$$x^{\text{avg}} = x_s + \alpha\beta \quad (3)$$

and

$$\sigma^2 = \alpha\beta^2. \quad (4)$$

The zero moment,  $m_0$ , is the total molar concentration of the polymer mixture. The position of the peak maximum,  $x_p$ , is determined by  $dp(x)/dx = 0$ , which yields

$$x_p = x_s + (\alpha - 1)\beta. \quad (5)$$

Mathematica software was employed to fit the experimental MWD data for the pretreated PSA to Eqs. 1 and 2. Figure 2 shows that the gamma distribution and experimental data agree reasonably well. The parameters obtained for the

feed-polymer MWD based on molar fraction are  $\alpha = 1.7$ ,  $\beta = 850$ , and  $x_s = 190$ . This gamma distribution is used as the initial MWD in the kinetics model.

### Concepts of continuous kinetics for polymer degradation

A mixture with a very large number of different-size polymer molecules approaches the condition of a continuous mixture, whose distribution is not distinguished by a discrete index but by a continuous variable such as MW. A continuous mixture is capable of undergoing an infinite number of reactions, in the current case irreversible dissociations of continuously distributed molecules. Following the notation of Aris and Gavalas (1966), we define  $A(x)$  to be a polymer molecule with molecular weight  $x$ . Polymer degradation can be written as a combination of

$$\text{random degradation: } A(x') \rightarrow A(x) + A(x' - x) \quad (6)$$

and

$$\text{specific degradation: } A(x') \rightarrow A(x_i) + A(x' - x_i) \quad (7)$$

where  $x_i$  is the molecular weight of the specific unit that is detached from a polymer molecule. The term specific degradation is used here to describe the elimination of a low-MW fragment from a polymer chain to form a specific product. We define the time-dependent MWD of  $A(x)$ , based on molar concentration, by  $p(x, t)$ . Let the rate coefficient for degradation of  $A(x)$  be  $k(x)$  and define  $v(x, x')$  as the fraction of  $A(x')$  that cracks to  $A(x)$ . The parallel reactions for degradation of  $A(x)$  are assumed first order. The general rate equation for random degradation can be written as follows (Aris and Gavalas, 1966; McCoy and Wang, 1994; Wang et al., 1994):

$$\frac{dp(x, t)}{dt} = -k(x)p(x, t) + 2 \int_x^\infty k(x')p(x', t)v(x, x')dx'. \quad (8)$$

For specific degradation two rate equations are required to describe  $A(x_i)$  and  $A(x' - x_i)$ ,

$$\begin{aligned} \text{for } A(x' - x_i): \quad \frac{dp(x, t)}{dt} = & -k(x)p(x, t) \\ & + \int_x^\infty k(x')p(x', t)v(x - x_i, x')dx' \end{aligned} \quad (9)$$

$$\text{for } A(x_i): \quad \frac{dq_i(x_i, t)}{dt} = \int_x^\infty k(x')p(x', t)v(x_i, x')dx' \quad (10)$$

where  $q_i(x_i, t)$  is the MWD of the specific product  $i$ . On the right sides of Eqs. 8 and 9, the first term accounts for the loss of the reactant  $A(x)$  due to its degradation, and the second term accounts for the gain of  $A(x)$  resulting from the degradation of polymer molecules with MWs larger than  $x$ . For the specific product  $A(x_i)$  there is no loss due to degrada-

tion, and only one term appears on the right side of Eq. 10. A product molecule is represented by *each* integral term in Eqs. 9 and 10; hence, the factor of 2 required in Eq. 8 does not appear in either Eq. 9 or 10.

The MWDs that result from Eqs. 8, 9 and 10 are determined by the forms of rate coefficients and stoichiometric kernels. The rate coefficients,  $k(x)$ , are generally dependent on  $x$  for both random and specific degradation. One possible form is given by

$$k(x) = k_b x^b \quad (11)$$

where  $b$  is a parameter representing the degree of dependence of  $k(x)$  on molecular weight  $x$ . McCoy (1993) used the expression with  $b = 0$  for reversible oligomerization, and Wang et al. (1994) used  $b = 1$  so that larger coal components were more easily degraded. In the present work, since the MW of reactants is not large, the choice  $b = 0$  proves adequate to describe the experimental data.

The stoichiometric kernel  $v(x, x')$  is defined to satisfy normalization and symmetry conditions (Aris and Gavalas, 1966),

$$\int_0^{x'} v(x, x') dx = 1 \quad (12)$$

and

$$v(x, x') = v(x' - x, x'). \quad (13)$$

These concepts were applied to model the thermal decomposition of coal (Prasad et al., 1986; Wang et al., 1994). McCoy (1993) utilized Dirac delta functions to describe fission that yields fragments that are precisely proportioned; for example, for an oligomer that cracks to products of MW ratio (1/4):(3/4), the expressions are  $\delta(x - x'/4)$  and  $\delta(x - 3x'/4)$ . McCoy and Wang (1994) recently proposed a general fragmentation kernel that includes both random fragmentation and specific fragmentation processes. For polymer degradation the following stoichiometric fraction kernels can be employed:

$$\text{random degradation: } v(x, x') = B[x(x' - x)]^d \quad (14)$$

$$\text{specific degradation: } v(x' - x_i, x') = \delta[x - (x' - x_i)] \quad (15)$$

$$v(x_i, x') = \delta(x - x_i) \quad (16)$$

where  $B$  is a constant determined by the normalization condition (Eq. 13),  $d \geq 0$  is a parameter, and  $x_i$  is the MW for a specific product. The *totally* random degradation kernel, with  $d = 0$ , is chosen for the current model. Equations 15 and 16, respectively, are for the two products having molecular weights of  $x' - x_i$  and  $x_i$  resulting from specific degradation of reactant with molecular weight  $x'$ .

### Model formulation

We make the following assumptions:

1. The reactions for both specific and random degradation are first order and all rate coefficients are independent of the MW.

2. The MWDs of the reaction mixtures can be described by a gamma distribution whose parameters depend on residence time, and therefore are different from those for the feed polymer. These parameters can be determined by moment methods. In general, any realistic continuous form of the MWD can be used in the theory.

3. All products from the binary degradation processes are dissolved in solution, and no cross-link or repolymerization reactions occur in our experiments.

4. The flow reactor can be treated as a steady-state plug-flow reactor.

**Reactor Equations.** Based on the mechanism and assumptions just discussed, the following governing equations can be written for our experiments in the steady-state plug-flow reactor. For the specific products (S, SA, and ASA) represented by the three peaks in Figure 4:

$$\frac{dq_i(x, \tau)}{d\tau} = \int_x^\infty k_i p(x', \tau) \delta(x - x_i) dx' \quad i = 1, 2, 3. \quad (17)$$

Here, the residence time is  $\tau = z/v$ ,  $q_i(x_i, \tau)$  are MWDs for the specific products, and  $i = 1, 2$ , and 3 represents S, SA, and ASA, respectively. The initial conditions are

$$q_i(x, \tau = 0) = 0 \quad i = 1, 2, 3. \quad (18)$$

For the reaction mixture we include effects of random degradation *and* the large MW products of specific degradation:

$$\begin{aligned} \frac{dp(x, \tau)}{d\tau} = & -k_r p(x, \tau) + 2 \int_x^\infty k_r p(x', \tau) v(x, x') dx' \\ & - \sum_{i=1}^3 \left\{ k_i p(x, \tau) - \int_x^\infty k_i p(x', \tau) v(x - x_i, x') dx' \right\}. \end{aligned} \quad (19)$$

The initial condition for this differential equation is

$$p(x, \tau = 0) = p_0(x) \quad (20)$$

where the MWD for the feed polymer is  $p_0(x)$ , a gamma distribution given by Eq. 1.

Although the preceding equations could be solved numerically, a straightforward moment method is adequate because the mild conditions ensured a small conversion. The MWDs of the reaction mixtures for different experiments are thus expected to be gamma distributions that are slightly, but measurably, different from the initial MWD. Moment methods are applied to determine the parameters for these gamma distributions. From the preceding governing equations we formulate moment equations by operating on them with  $\int_x^\infty x^j [\dots] dx$ . The MW moments are defined as

$$q^{(j)}(\tau) = \int_0^\infty x^j q(x, \tau) dx \quad (21)$$

where the superscript  $j$  indicates the order of the moment.

**Moment Operations for Specific Products.** The moment operation, applied to Eq. 17, is interchanged with the time derivative, yielding ordinary differential equations for moments:

$$\frac{dq_i^{(j)}(\tau)}{d\tau} = k_i x_i^j p^{(0)}(\tau) \quad i = 1, 2, 3. \quad (22)$$

As shown below,  $p^{(0)}(\tau) = p_o^{(0)} \exp(k_r \tau)$ , and for special cases  $j = 0, 1, 2$ , solving Eq. 22 leads to the following results:

$$j = 0 \quad q_i^{(0)}(\tau) = \frac{k_i}{k_r} p^{(0)}(0) (\exp(k_r \tau) - 1) \quad i = 1, 2, 3 \quad (23)$$

$$j = 1 \quad q_i^{(1)}(\tau) = \frac{k_i}{k_r} x_i p^{(0)}(0) (\exp(k_r \tau) - 1) \quad i = 1, 2, 3 \quad (24)$$

$$j = 2 \quad q_i^{(2)}(\tau) = \frac{k_i}{k_r} x_i^2 p^{(0)}(0) (\exp(k_r \tau) - 1) \quad i = 1, 2, 3. \quad (25)$$

The zero moments,  $q_i^{(0)}(\tau)$ , represent the molar concentrations of specific products, S, SA, and ASA. Equation 23 indicates that molar concentrations for specific products increase with time. The first and second moments can be used to describe the average MW and variance (Abramowitz and Stegun, 1968),

$$x_i^{\text{avg}}(\tau) = \frac{q_i^{(1)}(\tau)}{q_i^{(0)}(\tau)} = x_i \quad i = 1, 2, 3 \quad (26)$$

$$\sigma_i^2 = \frac{q_i^{(2)}(\tau)}{q_i^{(0)}(\tau)} - (x_i^{\text{avg}})^2 = x_i^2 - x_i^2 = 0 \quad i = 1, 2, 3. \quad (27)$$

Equations 26 and 27 confirm that MWDs for the specific products are delta functions, which represent pure compounds. This indicates that continuous kinetics includes the traditional kinetics based on a discrete index.

**Moment Operations for the Reaction Mixture.** Applying the moment operation to the governing equation for the reaction mixture (Eq. 19) yields

$$\begin{aligned} \frac{dp^{(j)}(\tau)}{d\tau} = & -(k_r + k_1 + k_2 + k_3) p^{(j)}(\tau) \\ & + 2 \int_0^\infty x^j dx \int_x^\infty k_r p(x', \tau) v(x, x') dx' \\ & + \sum_{i=1}^3 \int_0^\infty x^j dx \int_x^\infty k_i p(x', \tau) v(x' - x_i, x') dx'. \end{aligned} \quad (28)$$

In Eq. 14, choosing  $d = 0$  gives

$$v(x, x') = \frac{1}{x'}, \quad (29)$$

which yields a totally random distribution of degradation products. Equations 15 and 29 are substituted into Eq. 28. The resulting moment equation is an ordinary differential equation

$$\begin{aligned} \frac{dp^{(j)}(\tau)}{d\tau} = & -(k_r + k_1 + k_2 + k_3) p^{(j)}(\tau) + 2k_r Z_{j0} p^{(j)}(\tau) \\ & + \sum_{i=0}^j \binom{j}{i} p^{(j-i)}(\tau) (-1)^i [k_1 x_1^i + k_2 x_2^i + k_3 x_3^i] \end{aligned} \quad (30)$$

where  $\binom{j}{i}$  is the binomial expansion coefficient, and  $Z_{j0}$  is a special case of  $Z_{j\infty}$  discussed in detail by McCoy and Wang (1994). For  $j = 0, 1$ , and  $2$ ,  $Z_{j0}$  is equal to  $1, 1/2$ , and  $1/3$ , respectively. The initial condition is

$$p^{(j)}(0) = \int_0^\infty x^j p_o(x) dx. \quad (31)$$

For  $j = 0$ , Eqs. 30 and 31 are simplified to

$$\frac{dp^{(0)}(\tau)}{d\tau} = k_r p^{(0)}(\tau) \quad (32)$$

with

$$p^{(0)}(\tau = 0) = p_o^{(0)}. \quad (33)$$

Solving Eq. 32 yields

$$p^{(0)}(\tau) = p_o^{(0)} \exp(k_r \tau). \quad (34)$$

For  $j = 1$ , simplifying Eqs. 30 and 31 leads to

$$\frac{dp^{(1)}(\tau)}{d\tau} = -(k_1 x_1 + k_2 x_2 + k_3 x_3) p^{(0)}(\tau) \quad (35)$$

and

$$p^{(1)}(\tau = 0) = p_o^{(1)}. \quad (36)$$

Solving Eq. 35 gives

$$p^{(1)}(\tau) = p_o^{(1)} - \frac{k_1 x_1 + k_2 x_2 + k_3 x_3}{k_r} (\exp(k_r \tau) - 1). \quad (37)$$

For  $j = 2$ , Eq. 30 leads to

$$\frac{dp^{(2)}(\tau)}{d\tau} + \frac{1}{3} k_r p^{(2)}(\tau) = k_{x^2} p^{(0)}(\tau) - 2k_x p^{(1)}(\tau) \quad (38)$$

where

$$k_x = k_1 x_1 + k_2 x_2 + k_3 x_3 \quad (39)$$

and

$$k_{x^2} = k_1 x_1^2 + k_2 x_2^2 + k_3 x_3^2. \quad (40)$$

Substituting Eqs. 34 and 37 into Eq. 38 gives a first-order linear nonhomogeneous differential equation,

$$\frac{dp^{(2)}(\tau)}{d\tau} + \frac{1}{3}k_r p^{(2)}(\tau) = f(\tau) \quad (41)$$

where

$$f(\tau) = k_x^2 p_o^{(0)} \exp(k_r \tau) - 2k_x \left[ p_o^{(1)} - \frac{k_x}{k_r} p_o^{(0)} (\exp(k_r \tau) - 1) \right] \quad (42)$$

and the initial condition is

$$p^{(2)}(\tau = 0) = p_o^{(2)}. \quad (43)$$

Solving the differential equation gives

$$\begin{aligned} p^{(2)}(\tau) = & p_o^{(2)} \exp[-(1/3)k_r \tau] \\ & + \frac{3}{4} p_o^{(0)} \left\{ \frac{k_x^2}{k_r} + 2 \left( \frac{k_x}{k_r} \right)^2 \right\} \{ \exp(k_r \tau) - \exp[-(1/3)k_r \tau] \} \\ & - 6 \left( \frac{k_x}{k_r} \right) \left\{ p_o^{(1)} + p_o^{(0)} \left( \frac{k_x}{k_r} \right) \right\} \{ 1 - \exp[-(1/3)k_r \tau] \}. \end{aligned} \quad (44)$$

The average MW and the variance for the reaction mixtures can be obtained from  $p^{(0)}(\tau)$ ,  $p^{(1)}(\tau)$ , and  $p^{(2)}(\tau)$ . The results will depend on temperature and  $\tau$ :

$$x^{\text{avg}}(\tau) = x_o^{\text{avg}} \exp(-k_r \tau) - \frac{k_x}{k_r} (1 - \exp(-k_r \tau)) \quad (45)$$

$$\begin{aligned} \sigma^2(\tau) = & \sigma_o^2 \exp[-(4/3)k_r \tau] + (x_o^{\text{avg}})^2 \exp[-(4/3)k_r \tau] \\ & + \frac{3}{4} \left\{ \frac{k_x^2}{k_r} + 2 \left( \frac{k_x}{k_r} \right)^2 \right\} \{ 1 - \exp[-(4/3)k_r \tau] \} \\ & - 6 \left( \frac{k_x}{k_r} \right) \left\{ x_o^{\text{avg}} + \left( \frac{k_x}{k_r} \right) \right\} \{ \exp(-k_r \tau) - \exp[-(4/3)k_r \tau] \} \\ & - \{ x^{\text{avg}}(\tau) \}^2. \end{aligned} \quad (46)$$

**MWDs for the Reaction Mixtures.** Since we have assumed that MWDs for the reaction mixtures can be described as gamma distributions, the change of MWDs during degradation is represented by the change of the distribution parameters, for example,  $x_s$ ,  $\alpha$ , and  $\beta$ . We denote  $\alpha$  and  $\beta$  for the reaction mixtures as functions of residence time, thus,  $\alpha(\tau)$  and  $\beta(\tau)$ . According to Eqs. 3 and 4, when  $x_s \ll x^{\text{avg}}$ , the following equations relate  $\alpha(\tau)$  and  $\beta(\tau)$  to the average MW and variance:

$$\beta(\tau) = \frac{\sigma^2(\tau)}{x^{\text{avg}}(\tau)} \quad (47)$$

$$\alpha(\tau) = \frac{[x^{\text{avg}}(\tau)]^2}{\sigma^2(\tau)} \quad (48)$$

where  $x^{\text{avg}}(\tau)$  and  $\sigma^2(\tau)$  are obtained from Eqs. 45 and 46.

**Table 1. Gamma Distribution Parameters for the Reaction Mixtures\***

$T(K)$	403	423	443	473
$\alpha(\tau)$	1.70	1.67	1.63	1.58
	1.69	1.65	1.60	1.54
	1.67	1.62	1.57	1.51
	1.63	1.58	1.52	1.46
$\beta(\tau)$	865	875	885	904
	878	901	915	963
	891	921	937	1,001
	913	944	962	1,036

\*The four entries at each temperature are for residence times  $\tau \approx 14, 23, 46$ , and 111 minutes. The initial values are  $\alpha = 1.70$  and  $\beta = 847$ .

Table 1 shows values of  $\alpha$  and  $\beta$  for the four temperatures and four residence times. The MWDs for the reaction mixtures are

$$p(x, \tau) = p^{(0)}(\tau) y^{[\alpha(\tau)-1]} \exp(-y) / \{ \beta(\tau) \Gamma[\alpha(\tau)] \} \quad (49)$$

and

$$p_w(x, \tau) = x p(x, \tau) \quad (50)$$

where  $y = (x - x_s)/\beta(\tau)$ .

## Results and Discussion

The experimental MWD results and model simulations for the four temperatures are presented in Figures 5 to 8. In these figures only, the noted residence times are based on a velocity (density) at 1 atm and 298 K. The three distinguishable peaks in the range  $MW \leq 500$  represent three specific products: S, SA, and ASA. The other distinct feature is the shift of the MWD toward the low MW range, caused mainly by random degradation. This shift is similar to that observed by Iring et al. (1976) for the thermal oxidation of polyolefins. No cross-linking or polymerization processes, which would yield high MW species, were observed under our experimental conditions.

Two types of parameters appear in the model: those in the gamma distribution describing the feed-polymer MWD, and the rate coefficients for specific and random degradation. As mentioned, the parameters in the initial gamma distribution were obtained by fitting the MWD data for the feed polymer.

The rate coefficients for specific degradation were determined by the zero moments for specific products at different residence times. Since our experiments occurred at mild conditions and relatively short residence times,  $k_r \tau$  is small. By substitution of the approximation

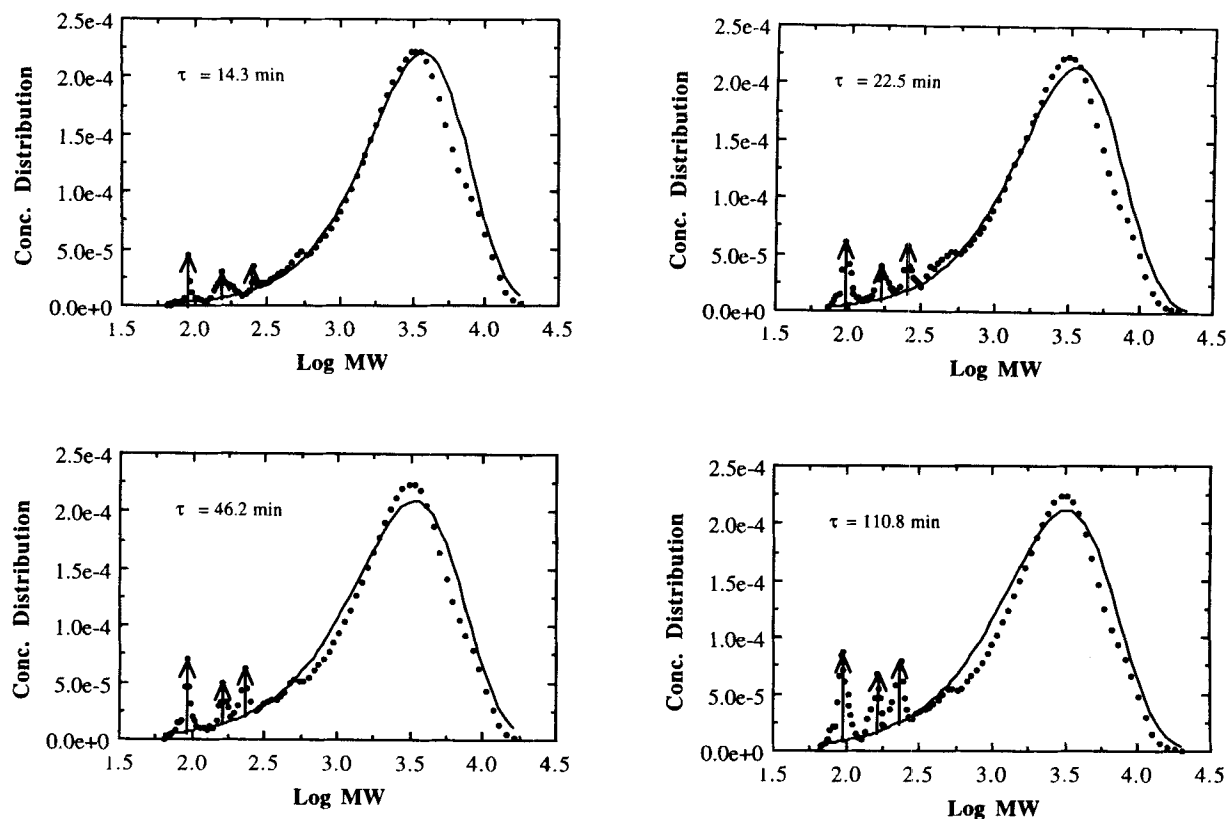
$$\exp(k_r \tau) \approx 1 + k_r \tau. \quad (51)$$

Equation 23 yields

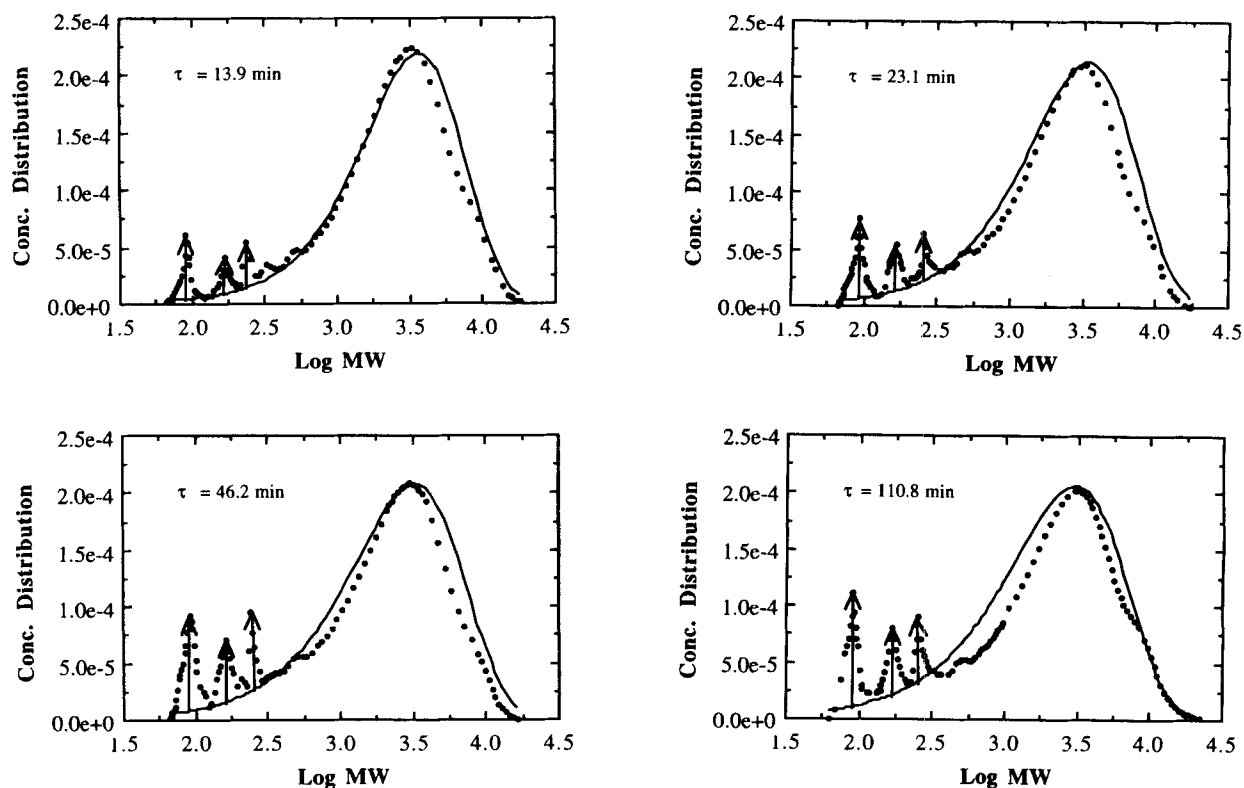
$$q_i^{(0)}(\tau) = k_i p_o^{(0)} \tau \quad i = 1, 2, 3, \quad (52)$$

which gives a linear relationship between the zero moment and residence time. The zero moment of each specific prod-

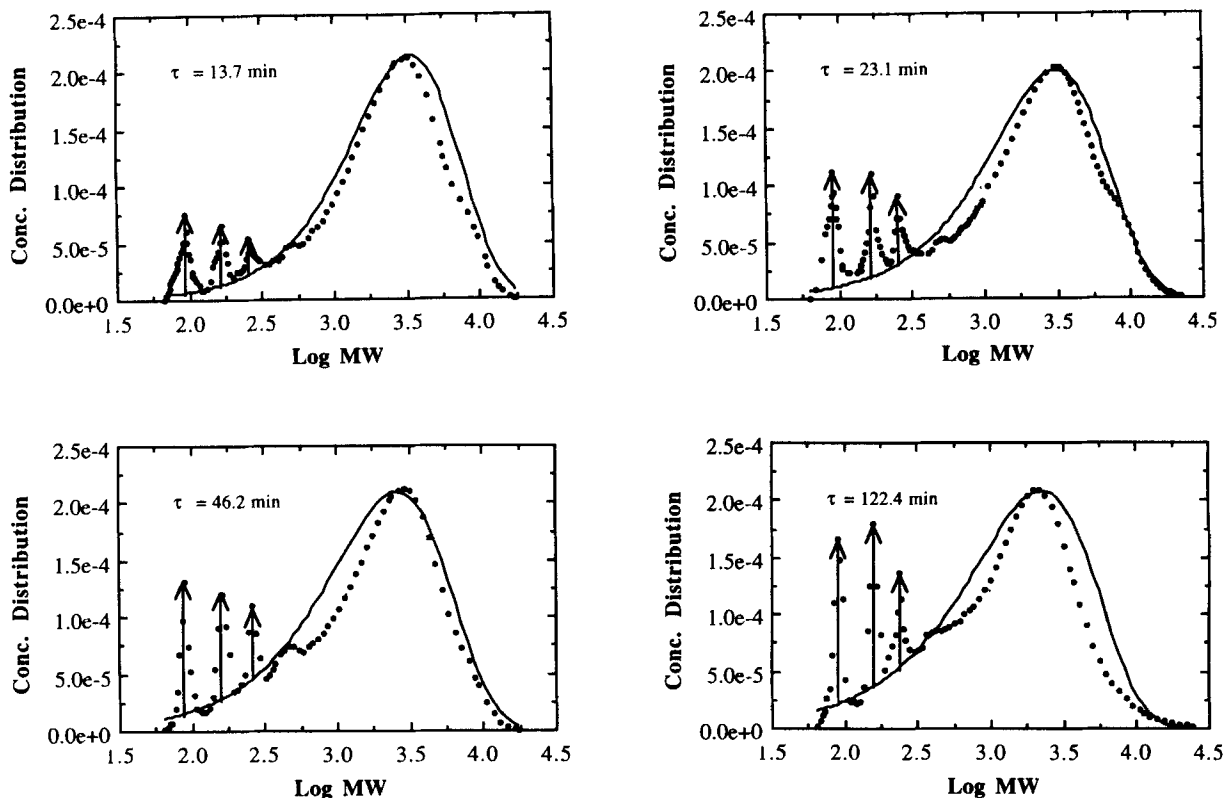




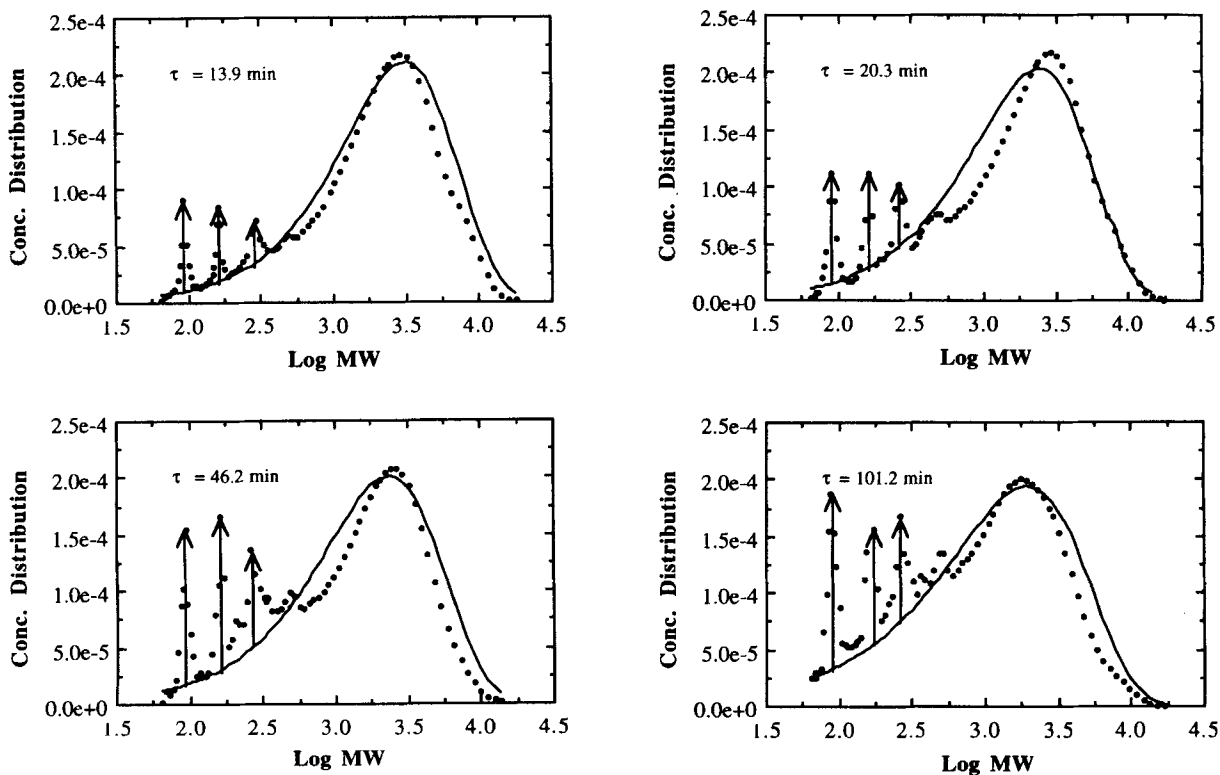
**Figure 5. Experimental results of MWD vs. model simulations based on continuous kinetics at 403 K and 6.8 MPa.**  
Experimental results, line; model simulation, arrow; Dirac delta function for specific products.



**Figure 6. Experimental results of MWD vs. model simulations based on continuous kinetics at 423 K and 6.8 MPa.**  
Experimental results, line; model simulation, arrow; Dirac delta function for specific products.



**Figure 7. Experimental results of MWD vs. model simulations based on continuous kinetics at 443 K and 6.8 MPa.**  
Experimental results, line; model simulation, arrow; Dirac delta function for specific products.



**Figure 8. Experimental results of MWD vs. model simulations based on continuous kinetics at 473 K and 6.8 MPa.**  
Experimental results, line; model simulation, arrow; Dirac delta function for specific products.

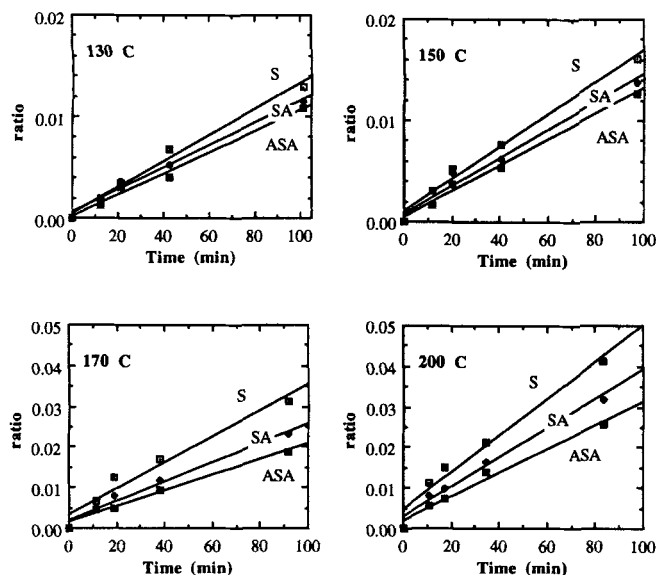


Figure 9. Ratio  $q_i^{(0)}(\tau)/p_o^{(0)}$  for the three specific products: temperatures vs. residence time.

uct peak was taken to be the area above the gamma distribution function for the reaction mixture. The obtained values were divided by the feed moment,  $p_o^{(0)}$ , and plotted as a function of residence time. The least-squares-fitted results (Figure 9) are in approximate agreement with the linear relationship of Eq. 52. The slope for each line in Figure 9 gives the rate coefficient  $k_i$  for a specific degradation. The peaks for specific products are represented as Dirac delta functions with heights equivalent to the highest measured concentrations of S, SA, or ASA. The actual peaks have a nonzero width (or variance) due to isomers of the specific products, or more probably, dispersion in GPC measurements.

Based on the experimental MWDs for the reaction mixtures at the four temperatures (Figures 5 to 8), the average MW and variance were calculated by Eqs. 45 and 46. To calculate  $\alpha(\tau)$  and  $\beta(\tau)$ , Eqs. 47 and 48 were applied. Since the experimental MWDs for the reaction mixtures were based on weight fraction, Eq. 50 was used to convert MWDs based on molar fraction into MWDs based on weight fraction. By fitting the model with the experimental results, the rate coefficient  $k_r$  was determined. The experimental results and model simulations, presented in Figures 5 to 8, show that the experimental MWDs are reasonably well simulated.

The Arrhenius plots of the rate coefficients for both specific and random degradation are presented in Figures 10 and 11 and correspond to the following activation energies:

$$\begin{aligned} \text{random degradation} & E_r = 35 \text{ kcal/mol} \\ \text{specific degradation} & E_1 = 7.4 \text{ kcal/mol for S} \\ & E_2 = 6.8 \text{ kcal/mol for SA} \\ & E_3 = 5.9 \text{ kcal/mol for ASA} \end{aligned} \quad (53)$$

The values for specific degradation are lower than that for random degradation, and decrease as the MW of the product increases. Thus, random degradation processes require higher energy, which supports the conclusion that random degrada-

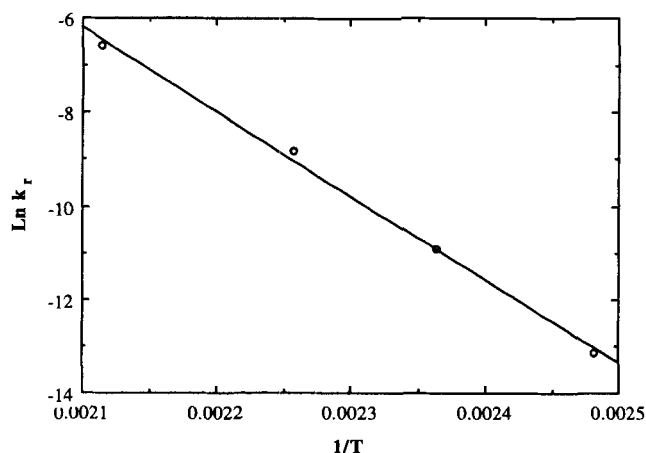


Figure 10. Arrhenius plot for the random degradation rate constant,  $k_r$ .

tion involves main-chain scission and specific degradation involves intramolecular transfer. The activation energy for the pyrolytic degradation of poly(styrene) is in the range 44–55 kcal/mol (Sawada, 1976; Flynn and Florin, 1985), and is affected by purity, method of preparation, and initial MWD for the feed polymer. Furthermore, the values depend on the range of conversion chosen for determination. Our lower activation energies indicate that poly(styrene) is more stable than PSA.

It is commonly observed that the average MW of the residual polymer decreases during the course of degradation. With continuous kinetics the variation of average MW for the reaction mixture can be obtained from Eq. 45. The experimental results from GPC and theoretical calculations are presented in Figure 12, and show fair agreement. Figure 12 indicates a linear relationship for the average MW vs. residence time due to mild conditions and short residence times.

## Conclusions

The thermal degradation of solubilized PSA in a steady-state flow reactor has provided fundamental information on

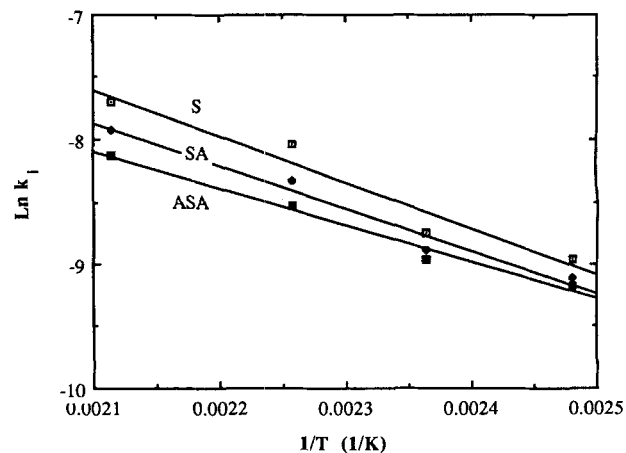
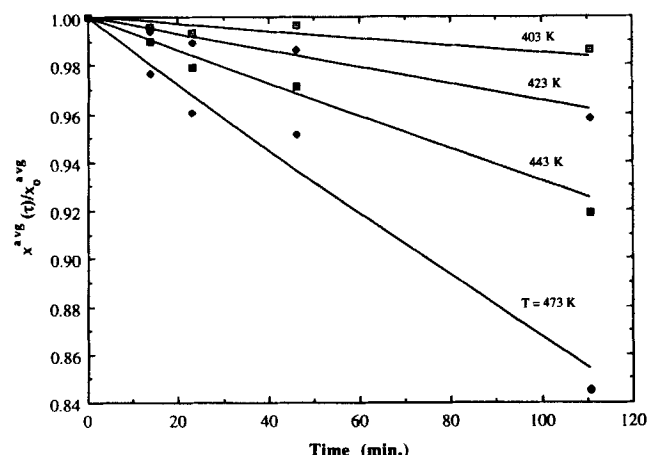


Figure 11. Arrhenius plot for the specific degradation rate constants,  $k_i$ ,  $i = 1, 2, 3$ .



**Figure 12. Model calculations vs. experimental data for number-average molecular weight at different temperatures.**

Experimental data, line; model calculations.

the kinetics and mechanism of a class of polymer reactions. A novel feature of the experiments, in comparison to pyrolysis, is that the reaction occurs in liquid phase, which facilitates the analysis of *all* reaction products. The monitoring of MWDs with GPC at different residence times shows that there are three specific products, S, SA, and ASA at MW < 500 and that the MWDs for the reaction mixture shift toward lower MWs. This is evidence that both specific- and random-degradation reactions occur. A continuous kinetics model, including both specific and random degradation, has been developed and solved using MW moment theory. The model satisfactorily describes the experimental MWD results for four temperatures in the range 403–473 K. The parameters, resulting from a fit of the model to experimental results, are in general agreement with existing information about polymer degradation.

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## Notation

- $B$  = coefficient in the stoichiometric kernel
- $k_b$  = proportional constant in the rate coefficient expression
- $p(x, \tau)$  = MWDs of the reaction mixtures based on molar fraction
- $q^{(j)}$  =  $j$ th order MW moments
- $v$  = velocity in the plug-flow reactor
- $x_s$  = lowest molecular weight for a gamma distribution
- $x^{avg}(\tau)$  = number-average molecular weight for the reaction mixtures
- $x_0^{avg}$  = number-average molecular weight for the feed polymer
- $y$  = dimensionless molecular weight
- $z$  = length of reactor
- $\sigma^2(\tau)$  = variance
- $\delta(x)$  = Dirac delta function of  $x$
- $\Gamma$  = gamma function

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