Fundamental Kinetics of Supercritical Coal Liquefaction: Effect of Catalysts and Hydrogen-Donor Solvents

FINAL REPORT

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Abstract

This report outlines a distribution kinetics approach to macromolecular reactions that has been applied to several processes. The objective was to develop an understanding of high-temperature, dense-phase thermolytic processes for complex macromolecular systems, such as coal. Experiments and theory are described for chemical models that simulate depolymerization of coal. The approach has been exceptionally successful for the model macromolecular systems. Development of a novel chemical reaction engineering analysis, based on distribution kinetics, was a major accomplishment of the current research.

1. Executive Summary

The objective of this research was to develop an understanding of high-temperature, dense-phase thermolytic processes for complex macromolecular systems, such as coal. This final report shows progress toward the overall objective to understand supercritical fluid extraction of hydrocarbons from coal. Our strategy was to simulate coal as a high molecular-weight polymeric material, and to study the degradation of such polymers under various conditions. The hypothesis was that degradation of such macromolecules is applicable to the decomposition (depolymerization) of the coal network. The work had the added benefit of contributing to the important problems of polymer degradation and plastics recycling. The particular macromolecules studied experimentally were polystyrene, polyethylene, poly(α -methylstyrene), poly(methyl methacrylate), and poly(styrene allyl alcohol).

The theory of macromolecular decomposition (Chapter 3) is basic to understanding and characterizing polymeric materials, including complex networked systems such as coal. Development of a novel chemical reaction engineering analysis for macromolecular reactions, based on distribution kinetics, was a major accomplishment of the research. This approach, successful in quantitatively describing a range of experiments on several different macromolecules, has broad applicability. The theoretical work involved distribution kinetics to develop chemical reaction models for macromolecular reactions. Experimentally, thermolytic degradation (liquefaction) of polymers was investigated with different solvents, including hydrogen-donor and nondonor solvents. Model macromolecular compounds provided a means to study the reaction kinetics of polymers undergoing molecular cracking to fuel and feedstock materials. Molecular-weight distributions (MWDs) and their moments were measured by HPLC gel permeation chromatography (GPC). Experimental data were interpreted with population-balance equations based on continuous-distribution kinetics. Rate coefficients were determined for chain-end and random scission degradation processes.

In Chapter 4 we hypothesize that coal liquefaction is similar to thermal depolymerization of a macromolecular network by random and chain-end scission events. In a batch reactor, coal particles in a heated solvent are considered to undergo degradation by molecular cleavage to form macromolecules that are soluble in the solvent. The solubility is supposed to decrease with increasing MW according to a polynomial expression for the solubility parameter $K(x)$. Population mass balances for the MW distributions of molecules in solid and liquid are formulated with a mass transfer term to allow solubilization. The two integrodifferential equations are transformed to ordinary differential equations by forming MW moments. These equations can be solved for moments, with which the MWDs can be represented, for example, as gamma distributions.

In Chapter 5 we report on thermal degradation of polystyrene dissolved in mineral oil. Samples were analyzed by HPLC-GPC to obtain the dependence of polymer MWDs on reaction

time for the batch reaction. Experimental data indicated that polystyrene degrades both by random chain scission and chain-end scission. The existence of weak links was evident, as indicated by rapid chain scission during an initial time period. The experimental MWDs were analyzed with a continuous-distribution kinetics model to obtain separate rate coefficients for weak-link and strong-link scission. Rate coefficients were also obtained for the chain-end degradation of polystyrene to specific monomers and oligomers. Activation energies of the weak-link and strong-link and of chain-end scission rate coefficients were determined from data at different temperatures.

Thermal degradation of solubilized poly(methyl methacrylate) (PMMA) in toluene in a steady-state, tubular-flow reactor was studied by measuring MWDs at various residence times and temperatures (Chapter 6). A model based on continuous-distribution kinetics was employed to analyze the data. Chain-end degradation was first order in polymer concentration with an activation energy of 8.4 kcal/mol. There was no evidence of random-chain scission.

Depending on the particular polymer, hydrogen (H-)donors can increase, decrease, or have no effect on degradation rate (Chapter 7). We experimentally investigated the effect of H-donor 6-hydroxy tetralin on polystyrene degradation, and found that the rate decreases with increasing H-donor concentration. Mathematical expressions for the degradation rate parameters were obtained by applying continuous-distribution kinetics to the MWD of the reacting polymer. A model was developed for radical mechanisms based on the chain-reaction concept with elementary steps of initiation, depropagation, H-abstraction and termination. The model accounted for the different effects of the H-donor on polymer degradation.

Degradation kinetics of solubilized binary polymer mixtures were investigated by examining the time evolution of MWDs (Chapter 8). Because the reaction mechanism for polymer degradation involves radicals, we developed an approach that accounts for the elementary reactions of initiation, termination, H-abstraction, and chain scission. Experimentally, we determined the concentration effect of poly(α -methyl styrene) (PAMS) on the random-chain degradation of polystyrene dissolved in mineral oil at 275 °C in a batch reactor by evaluating the time evolution of the MWDs. Molecular-weight moments yielded expressions for the number- and weight-average MW and degradation rate coefficients. The experimental data indicated that the interaction of mixed radicals with polymer by H-abstraction caused the random-chain scission degradation rate of polystyrene to decrease with increasing PAMS concentration.

Papers published in scientific journals and oral presentations given at professional meetings as a result of the FETC-sponsored work are listed in Appendix 1.

2. Introduction

Direct liquefaction of coal (Lumpkin, 1988), which typically occurs with coal particles immersed in a solvent, involves thermal cracking by breaking chemical bonds within the coal macromolecular network. At elevated temperature and pressure, the solvent enhances heat and mass transfer and, if the coal is slurried, provides a convenient transportation medium. The free-radical products of coal thermolysis must be capped (stabilized) to prevent retrograde, repolymerization reactions. Such undesirable reactions form coke and other refractory products. Donor solvents can be added to the solvent mixture to provide hydrogen to cap the radicals. The donor solvent is regenerated, sometimes catalytically with iron- or molybdenum-based catalysts, by hydrogenation with dissolved hydrogen gas (Lumpkin, 1988).

Research on coprocessing of plastics and coal has recently been reported (Luo and Curtis, 1996a,b; Joo and Curtis, 1996). These initial studies indicate the promise of such coprocessing. The approach developed in our laboratory has potential to deepen understanding of the fundamental chemical reaction kinetics needed to design and scale up such processes.

The experience gained from coal and petroleum residuum coprocessing provides useful, guiding information that will carry over to coal-plastics coprocessing. Resid cracking is known to be improved by coprocessing with coal, which simultaneously converts both the coal and resid oil to liquid fuel. In addition to this synergistic reactive interaction, resid-coal coprocessing provides feedstock flexibility for petroleum and coal processing. Coal is a solid containing aromatic species and having a H/C atomic ratio of 0.6-0.8, whereas a plastic such as polyethylene (PE) with H/C ratio of ~2.0 melts at temperatures near 100 °C. The PE can serve as a solvent and source of hydrogen atoms, thus replacing donor solvent in direct liquefaction. Another advantage of coprocessing is that coal and PE at $T > 100$ °C form a slurry that can be pumped into a high-pressure flow reactor, rather than entering through mechanical locks. Ceylan and Stock (1991) hypothesized reaction pathways for resid-coal coprocessing at mild temperature conditions ($T < 400$ °C). They inferred that hydrogen transfer and bond scission were key steps in the radical mechanism for the chemical process. Aliphatics (such as PE) contribute stabilizing hydrogen atoms and combine with coal aromatic species. Miller et al. (1989) focused on moderate temperatures and pressures to lower operating costs and to reduce gas production, and confirmed that coke forms during coal-resid coprocessing at 450 °C due to retrogressive (repolymerization) reactions. These results suggest that coal-plastics coprocessing at mild temperatures ($T < 400$ °C) would be advantageous.

A high-temperature dense-phase process can be either supercritical or subcritical, depending on the properties of the fluid. Cost effectiveness requires that the temperature and pressure of the process should be minimized to reduce energy and materials costs. Pyrolysis processes usually involve high temperatures with solid, liquid, and gas phases interacting in complex and sometimes detrimental ways. The UC Davis work focused, therefore, on developing the necessary engineering data for processes that would meet the economic requirements by minimizing temperature, pressure, and number of interacting phases.

For process design, development, and evaluation, a complete quantitative description would entail mathematical modeling of the composition of the reaction mixture during thermolysis. An accurate representation of decomposition rates would be needed. Typical methods for rate measurements are thermogravimetric analysis (TGA), melt index determination, light-scattering, viscosity analysis, and HPLC-GPC. The TGA analysis provides polymer degradation data for the apparent relation between rate of volatile-component loss during pyrolysis and change in number-average molecular-weight M_n . Viscosity of remaining polymer gives the weight-average molecular-weight M_w for polymer degradation in solution. In the present work, HPLC-GPC was introduced to measure MWD, and the relation between GPC chromatogram data and properties of polymer, such as number- and weight-average MW (M_n , M_w) and variance of MWD of the polymer (McCoy and Madras, 1997). This approach uses continuous-distribution kinetics and time-dependent moments to describe the dynamics of polymer degradation and polymerization.

Generally, chain scission of polymer (or polyolefin) can be explained by random-chain scission, chain-end scission, and mid-chain scission. Radical formation on the main chain is essential for these decomposition reactions whether the chain scission is thermal or chemical. We developed a continuous-distribution approach for random-chain and chain-end scission and repolymerization based upon radical mechanisms (Kodera and McCoy, 1997). The important concept behind the continuous-distribution approach is that the MWD of the mixture can be represented as a continuous function. The MWD then serves as a density function or frequency distribution that can be integrated to determine averages. Such integrations allow representation of chain scission (degradation) and addition (polymerization) reactions.

We have applied these ideas to macromolecular thermolysis, which gives both random and specific products due to random-chain scission and chain-end scission, respectively. Distribution balance equations for MWDs of random and specific products are proposed to account for initiation-termination and propagation-depropagation reactions, such as H-abstraction, chain cleavage, recombination, disproportionation, and coupling of polymer and the corresponding radical. The present theory is introduced by assuming the rate coefficients are independent of MW x , which is valid if the change in average MW of the polymer mixture is not too great (Madras et al., 1997a). The integro-differential governing equations are solved in terms of molecular-weight moments. The moments form a hierarchy of ordinary differential equations, which can be solved to the desired order, usually up to second moments. In the present treatment we invoke two common approximations and solve analytically for algebraic moment expressions. The long-chain approximation (LCA) (Gavalas, 1966; Nigam et al., 1994) maintains that initiation and termination reaction events are infrequent and therefore their rates are negligible relative to hydrogen abstraction and propagation-depropagation chain reaction rates. The second approximation is the quasi-stationary-state approximation (QSSA), which is valid when the concentration of free radicals is extremely small, so that their rate of change with time is negligible compared to other rates. For either chain-end or random-chain scission, the reversible processes reduce to irreversible decomposition reactions when the addition (repolymerization) rate coefficients are relatively small. Previously derived and experimentally verified expressions for macromolecular degradation are thus recovered from the general theory.

3. Fundamental Theory

We consider that macromolecules can react in three ways: by transforming without change in molecular-weight, by undergoing chain scission, and by combining to form higher molecular-weight compounds. We indicate the chemical species with the capital letters, $P(x)$, $Q(x)$, $R(x)$, where x represents the molecular-weight (MW). The MWDs of these species are $p(x,t)$, $q(x,t)$, and $r(x,t)$, respectively, where at time t , for example, $p(x,t)dx$ is the molar concentration (mol/volume) of species P having values of x in the range x to $x+dx$. The primary reaction types that represent the elementary steps in a reaction mechanism are provided in Table 3.1.

Transformation: A transformation without change in chain length or with negligible change in MW, e.g., from a radical to a stable polymer, can be written as

Then the rates of change of the two species are

$$\partial p / \partial t = - \partial r / \partial t = k r(x,t) \quad (3.1)$$

Chain scission: When a chain is cleaved by bond scission, the two products have MWs, x and $x' - x$, that add to the reactant MW, x' ,

The rates of change of the three species are

$$\partial p / \partial t = - k p(x,t) \quad (3.2)$$

Table 3.1. Distribution Kinetics of Primary Reactions.Stoichiometric kernels: $\Omega(x, x') = 1/x'$, $\Omega(x_s, x') = \delta(x - x_s)$, $\Omega(x - x_s, x') = \delta[x - (x' - x_s)]$

Reaction Type	Primary Reaction	Rate Expressions	Moment Expressions (k is independent of MW)
Trans-formation	$R(x) \rightarrow P(x)$	$\partial p/\partial t = -\partial r/\partial t = k r(x, t)$	$dp^{(n)}/dt = -dr^{(n)}/dt = k r^{(n)}(t)$
Random-chain scission	$P(x') \rightarrow Q(x) + R(x' - x)$	$\partial p/\partial t = -k p(x, t)$ $\partial q/\partial t = k \int_x^\infty p(x', t) \Omega(x, x') dx' = \partial r/\partial t$	$dp^{(n)}/dt = -k p^{(n)}(t)$ $dq^{(n)}/dt = k p^{(n)}(t)/(n+1) = dr^{(n)}/dt$
Chain-end scission	$P(x') \rightarrow Q(x_s) + R(x' - x_s)$ x_s is the MW of the specific product	$\partial p/\partial t = -k p(x', t)$ $\partial q/\partial t = k \int_x^\infty p(x', t) \Omega(x_s, x') dx'$ $\partial r/\partial t = k \int_x^\infty p(x', t) \Omega(x - x_s, x') dx'$	$dp^{(n)}/dt = -k p^{(n)}(t)$ $dq^{(n)}/dt = -k x_s^n p^{(0)}(t)$ $dr^{(n)}/dt = k \sum_{j=0}^n \binom{n}{j} x_s^j (-1)^j p^{(n-j)}(t)$
Addition reaction	$P(x') + Q(x - x') \rightarrow R(x)$	$\partial p/\partial t = -k p(x, t) \int_0^x q(x', t) dx'$ $\partial q/\partial t = -k q(x, t) \int_0^x p(x', t) dx'$ $\partial r/\partial t = k \int_0^x p(x', t) q(x - x', t) dx'$	$dp^{(n)}/dt = -k p^{(n)}(t) q^{(0)}(t)$ $dq^{(n)}/dt = -k q^{(n)}(t) p^{(0)}(t)$ $dr^{(n)}/dt = k \sum_{j=0}^n \binom{n}{j} p^{(j)}(t) q^{(n-j)}(t)$

$$\partial q/\partial t = \partial r/\partial t = k \int_x^\infty \Omega(x, x') p(x', t) dx' \quad (3.3)$$

The rates for q and r have equivalent forms because the scission stoichiometric coefficient, or kernel, is symmetric (Aris and Gavalas, 1966), $\Omega(x, x') = \Omega(x' - x, x')$. The kernel represents a reaction in which a molecule cleaves into two product molecules whose sizes, x and $x' - x$, sum to the reactant size, $x' \geq x$.

A general, normalized expression for the stoichiometric coefficient reduces to the cases of random-chain scission (McCoy and Madras, 1997), i.e., $\Omega(x, x') = 1/x'$ (Aris and Gavalas, 1966), and scission at the chain midpoint, $\Omega(x, x') = \delta(x - x'/2)$. For chain-end scission when a specific product of fixed MW x_s and a chain of MW $x' - x_s$ are formed, the stoichiometric kernels are $\delta(x - x_s)$ and $\delta(x - (x' - x_s))$, respectively.

Addition reaction: Two macromolecules of MW x' and $x - x'$ can join together by bimolecular chain addition or cross-linking to form a product of MW x ,

The rates depend on concentrations of both reactants and hence are second-order,

$$\partial p/\partial t = -k p(x) \int_0^x q(x') dx' \quad (3.4)$$

$$\partial q/\partial t = -k q(x) \int_0^{\infty} p(x') dx' \quad (3.5)$$

$$\partial r/\partial t = k \int_0^x p(x') q(x-x') dx' \quad (3.6)$$

Moment solution: The integral forms of the above rate expressions lend themselves to moment calculations. The moments of the MWDs are defined as the integrals over the MW x ; for example,

$$p^{(n)}(t) = \int_0^{\infty} p(x, t) x^n dx \quad (3.7)$$

The zeroth moment ($n = 0$) is the time-dependent total molar concentration (mol/volume) of the macromolecule. The first moment, $p^{(1)}(t)$, is the mass concentration (mass/volume). The normalized first moment (average MW) and second central moment (variance of the MWD) are given, respectively, by $p^{avg} = p^{(1)}/p^{(0)}$ and $p^{var} = p^{(2)}/p^{(0)} - [p^{avg}]^2$. The three moments, $p^{(0)}$, p^{avg} ($= M_n$), and p^{var} , provide the shape characteristics of the MWD, and can be used to construct the MWD. When the initial MWD is $p(x, t=0) = p_0(x)$, its moments are $p^{(n)}(t=0) = p_0^{(n)}$. The Γ distribution function (e.g., Wang et al., 1994; 1995) can be constructed from the zeroth, first, and second moments.

Model for Macromolecular Thermolysis

The purpose of this section is to identify the important elementary reactions and incorporate them in a mathematical model based on continuous-distribution kinetics. We will consider that branched and linear polyethylene undergoes homolytic chain cleavage, coupling and disproportionation of radical, chain cleavage of radical, and intramolecular and intermolecular hydrogen abstraction. Addition reactions between radicals and olefins are also considered. We adopt the notation in Table 1 for the general model of the radical mechanism for thermal treatment of polymer.

Table 3.2. Species symbol and MWD notation for macromolecule and radical reactions.

Species	MWD	Definition
$P(x)$	$p(x, t)$	n -alkane or <i>iso</i> -alkane polymer
$Q(x)$	$q(x, t)$	polymer with at least one unsaturated C-C bond (alkene)
$Q_s(x)$	$q_s(x, t)$	monomer or oligomer of MW x_s , e.g., an alkane or alkene specific product of chain-end scission
$R_c^*(x)$	$r_c(x, t)$	radical with an unpaired electron at the chain-end
$R_r^*(x)$	$r_r(x, t)$	radical with unpaired electron at a random position on a main chain carbon
$R_s^*(x)$	$r_s(x, t)$	radical formed by intramolecular isomerization (back-biting reaction) of R_c^*
$R_{es}^*(x)$	$r_{es}(x, t)$	end-radical given by fragmentation of R_s^*

The reversible initiation-termination reaction provides the end-radicals:

The LCA indicates a negligible contribution of initiation and termination steps (Reaction D) to overall rate of the degradation (changes in moments in the function of time), although they are important steps in the mechanism

The end-radicals are converted into the other species in several ways:

(i) Reactions between radicals: The reverse reaction of Reaction D shows coupling of end-radicals. Disproportionation of radicals giving both paraffin and olefin, coupling between random-radicals (cross-linking), and coupling between random-radical and end-radical giving branched polymer all can be treated as special cases of the termination reaction.

(ii) Radical-promoted intermolecular hydrogen abstraction of polymer: The end-radical given by the initiation reaction D provides both the random (mid-chain) radical and end-radical by intermolecular hydrogen-abstraction of a hydrogen atom from a polymer. This bimolecular process is expressed as pseudo-first-order reactions (Reactions E and F) as discussed by Kodera and McCoy (1997):

The reverse reactions represent pseudo-first-order transformations of radicals into the corresponding polymer in the presence of excess polymer as a source of hydrogen. Intermolecular hydrogen abstraction applies to thermal cracking of hydrocarbons at a high pressure. When oxygen is involved, the reactions E and F can be major initiation steps for the degradation.

(iii) Fragmentation of the random-radical by β -scission: This is random-chain scission, an essential step in random degradation (Reaction G). The resulting 1-alkene Q (x') has a random distribution in MW,

(iv) Recombination of alkene: Reverse reaction of random-chain scission is recombination, which gives a branched radical expressed here as a random-radical (Reaction G). Recombination of random-radicals with alkene also gives the corresponding branched radicals (Reaction H).

Recombination is an important step for some conditions such as polymer-melt pyrolysis and high pressure thermolysis (e.g., Song et al., 1994; Khorasheh and Gray, 1993) as well as intermolecular hydrogen abstraction.

(v) Intramolecular hydrogen abstraction of end-radicals: The formation of specific products, e.g., styrene and allyl alcohol-styrene fragments from poly(styrene-allyl alcohol) degradation (Wang et al., 1995), is considered as intramolecular hydrogen abstraction of an end-radical (Reaction I) followed by fragmentation of the resulting specific radical (Reactions J and K).

The driving force for the reaction I is the gain of stability of primary end-radicals relative to secondary radicals, or secondary end-radicals relative to tertiary radicals (each stabilization is about 4 kcal/mol for low MW hydrocarbons (Reaction I). The Rice-Kossiakoff mechanism suggests the formation of specific products from bond scission of the main chain of polymer. Depending on the chemical structure of the polymer, 1,4-radical shift or 1,5-radical shift or other shifts would be possible.

Fragmentation of the specific radical gives specific products as both alkene (Reaction J) and alkane (Reactions K and L).

The alkyl radical $R_{es}^*(x_s)$ is converted into the corresponding alkane as a specific product via hydrogen abstraction from the polymer. Recombination of alkene as a specific product with a random-radical gives a branched radical (reaction M).

Alkenes given in reaction G also undergo chain scission and hydrogen abstraction, especially for degradation at high conversion. One cannot distinguish alkenes from alkanes in a reaction mixture by GPC analysis, so we simplify these schemes by using $P(x)$ to designate both alkane and alkene. Coking is excluded from the present schemes because none occurred in our experiments. Coking would be observed when alkenes undergo oligomerization (McCoy, 1993) by radical addition followed by cyclization, and aromatization by hydrogen abstraction at higher reaction temperatures. Aromatic coke can deposit by a reversible adsorption-desorption process (McCoy and Subramaniam, 1995).

Simplified Model for Polymer Thermolysis

The following reaction scheme describes simultaneous random-chain scission and chain-end scission, where $P(x)$ represents *n*- and *iso*-alkane and alkene, $R^*(x)$ is the corresponding radical in the forms of both end and random-radicals, and $R_s^*(x)$ represents a precursor for a specific product $Q_s(x_s)$ of alkane and alkene. For intermolecular hydrogen abstraction of R_e^* and R_r^* , we assume $k_{he} \approx k_{hr} \equiv k_h$. For mathematical simplicity, a single specific product is assumed to form via Reaction 4.J. We assume that initiation and termination do not contribute appreciably to the overall rate (LCA). Four reactions constitute the model:

- (i) intermolecular hydrogen abstraction,

- (ii) propagation-depropagation for random-chain scission,

- (iii) intramolecular hydrogen abstraction in chain-end scission,

- (iv) propagation-depropagation for chain-end scission,

The distribution balance equations for $p(x,t)$, for radical $r(x,t)$ and $r_s(x,t)$, and for a specific product $q_s(x_s,t)$ follow from Eqs 4.1 - 6:

$$\partial p / \partial t = -k_h p(x) + k_H r(x) + k_b \int_x^\infty r(x') \Omega(x, x') dx' - k_a p(x) \int_0^\infty r(x') dx' \quad (3.8)$$

$$\partial q_s / \partial t = k_{bs} \int_{x_s}^\infty r_s(x') \delta(x' - x_s) dx' - k_{as} q_s(x') \int_0^\infty r(x') dx' \quad (3.9)$$

$$\begin{aligned} \partial r / \partial t = & k_h p(x) - k_H r(x) - k_b r(x) + k_a \int_0^x r(x-x') p(x') dx' + k_b \int_x^\infty r(x') \Omega(x, x') dx' \\ & - k_a r(x) \int_0^\infty p(x') dx' - k_{ih} r(x) + k_{iH} r_s(x) + k_{bs} \int_{x_s}^\infty r_s(x') \delta[x - (x' - x_s)] dx' \end{aligned}$$

$$+ k_{as} r(x) \int_0^{\infty} q_s(x') dx' \quad (3.10)$$

$$\partial r_s / \partial t = k_{ih} r(x) - k_{iH} r_s(x) - k_{bs} r_s(x) + k_{as} \int_0^x q_s(x') r(x - x') dx' \quad (3.11)$$

The initial conditions are $p(x, t=0) = p_0(x)$ and $q_s(x_s, t=0) = 0$. Applying the moment operation

(McCoy, 1993; McCoy and Wang, 1994), $\int_0^{\infty} [] x^n dx$, to the integro-differential equations yields

$$dp^{(n)} / dt = -k_{hp}^{(n)} + k_{iH} r^{(n)} + k_b Z_{n0} r^{(n)} - k_a p^{(n)} r^{(0)} \quad (3.12)$$

$$dq_s^{(n)} / dt = k_{bs} x_s^n r_s^{(0)} - k_{as} q_s^{(n)} r^{(0)} \quad (3.13)$$

$$dr^{(n)} / dt = k_h p^{(n)} - k_{iH} r^{(n)} - k_b r^{(n)} + k_a \sum_{j=0}^n \binom{n}{j} r^{(j)} p^{(n-j)} + k_b Z_{n0} r^{(n)} - k_a r^{(n)} p^{(0)} \\ - k_{ih} r^{(n)} + k_{iH} r_s^{(n)} + k_{bs} \sum_{j=0}^n \binom{n}{j} (x_s)^j (-1)^j r_s^{(n-j)} + k_{as} r^{(n)} q_s^{(0)} \quad (3.14)$$

$$dr_s^{(n)} / dt = k_{ih} r^{(n)} - k_{iH} r_s^{(n)} - k_{bs} r_s^{(n)} + k_{as} \sum_{j=0}^n \binom{n}{j} q_s^{(j)} r^{(n-j)} \quad (3.15)$$

where $Z_{n0} = 1, 1/2$, or $1/3$ for $n = 0, 1$, or 2 (McCoy and Wang, 1994).

The specific product has the unique MW x_s , so that $q_s(x, t) = q_s^{(0)}(t) \delta(x - x_s)$, and therefore $q_s^{(n)} = x_s^n q_s^{(0)}$. For the specific product we need to solve only for the zeroth moment. When several specific compounds are present, they are summed over s in the balance equations and the complete MWD is semi-continuous (Cotterman et al., 1985).

Zeroth moments ($n=0$) are governed by the following differential equations, where QSSA for radical species has been applied:

$$dp^{(0)} / dt = -k_{hp}^{(0)} + k_{iH} r^{(0)} + k_b r^{(0)} - k_a p^{(0)} r^{(0)} \quad (3.16)$$

$$dq_s^{(0)} / dt = k_{bs} r_s^{(0)} - k_{as} q_s^{(0)} r^{(0)} \quad (3.17)$$

$$dr^{(0)} / dt = k_h p^{(0)} - k_{iH} r^{(0)} - k_{ih} r^{(0)} + k_{iH} r_s^{(0)} + k_{bs} r_s^{(0)} + k_{as} r^{(0)} q_s^{(0)} = 0 \quad (3.18)$$

$$dr_s^{(0)} / dt = k_{ih} r^{(0)} - k_{iH} r_s^{(0)} - k_{bs} r_s^{(0)} + k_{as} q_s^{(0)} r^{(0)} = 0 \quad (3.19)$$

Summing Eqs 18 and 19 yields

$$r^{(0)} = (k_{ih} / k_{iH}) p^{(0)} \quad (3.20)$$

Applying Eq 20 to 16 followed by integration with $p^{(0)}(t) = p_0^{(0)}$ gives

$$p^{(0)}(t) = \exp(k_d t) / [\exp(k_d t) - 1] k_a / k_b + 1 / p_0^{(0)} \quad (3.21)$$

where $k_d = k_b k_{ih} / k_{iH}$. Applying Eq 20 to 19 gives

$$r_s^{(0)} = r^{(0)} (k_{ih} + k_{as} q_s^{(0)}) / (k_{bs} + k_{iH}) \quad (3.22)$$

Then,

$$dq_s^{(0)} / dt = k_{bs} r_s^{(0)} - k_{as} q_s^{(0)} r^{(0)} \\ = [k_{bs} (k_{ih} + k_{as} q_s^{(0)}) / (k_{bs} + k_{iH}) - k_{as} q_s^{(0)}] (k_{ih} / k_{iH}) p^{(0)} \quad (3.23)$$

Integration of Eq 23 with initial condition $q_s^{(0)}(t=0) = 0$ gives

$$q_s^{(0)}(t) = (k_{bs} k_{ih} / k_{as} k_{iH}) \{ 1 - [k_b / [k_b + k_a p_0^{(0)} (\exp(k_d t) - 1)]]^{(k_{as} k_{iH} / k_a (k_{bs} + k_{iH}))} \} \quad (3.24)$$

Figure 4.1.

A. Schematic drawing of the experimental apparatus: (1) nitrogen cylinder, (2) valve, (3) rotameter, (4) heater, (5) stirrer, (6) reactor, (7) thermocouples, (8) molten-salt bath, (9) ice bath, (10) soap-bubble meter, (11) controllers, (12) digital thermometer readout.

B. Sketch of the apparatus for the mathematical model showing the notation for volumes, molar MWDs, and flow rate.

Experiments. Coal liquefaction experiments in a solvent of polymer melt could be carried out under nitrogen gas at several temperatures in the range 350-450 °C. The experimental apparatus would be similar to that of our study of polyethylene (HDPE) pyrolysis. Our prior publications (Wang et al., 1993, 1994; Zhang et al., 1993; McCoy et al., 1994) describe how coal particles are handled and prepared for thermal depolymerization. Whereas experiments can be conducted at high pressure if the reactor is closed, here we discuss flow experiments at atmospheric pressure. Figure 1 shows polymer melt, containing suspended coal particles, in the heated reactor (immersed in a molten-salt bath), and vapor carried to the condenser vessel (immersed in an ice bath) by flow of nitrogen sweep gas. The gas flows through 1/16 in. stainless-steel tubing, 3.4 m of which is coiled and immersed in the molten salt so that gas temperature reaches the bath temperature. Nitrogen enters at the reactor base through a half-inch diameter, 316 stainless-steel frit (Supelco) with 2 μm pores, which disperse the gas but prevent backflow of polymer melt. Connecting tubes are 10.5 mm internal diameter stainless-steel tubing. Exit gas flow rate ($0.25 \text{ cm}^3/\text{s}$), measured by water displacement from an inverted graduated cylinder, is not affected by small amounts of gaseous products and is thus constant during the experiment. Observations made in the HDPE work by looking down into the open reactor during a preliminary pyrolysis experiment confirm that the HDPE melt is well-mixed by approximately 1 mm gas bubbles rising through the melt. This eliminates the potential problem of uneven heating that can occur in unstirred liquefaction systems. The molten-salt bath is a mixture of potassium nitrate, sodium nitrite, and sodium nitrate in molar ratio 7:7:1, stirred by an agitator (Fisher Scientific StedFast stirrer model SL 600) and heated by a 3 kW element (Omega TBL-A-131/240V). The bath temperature is measured with a Type J thermocouple (Omega) and controlled to ± 1 °C by a temperature controller. The stainless-steel reactor of internal volume 10 cm^3 is fitted into a steel protective sleeve lined with steel shot (3.4 mm diameter) to improve heat transfer. The volume available to condensable vapor, $V_v = 64 \text{ cm}^3$, includes reactor and condenser vapor spaces and connecting tube. The volume available to noncondensable gas, $V_g = 324 \text{ cm}^3$, includes V_v and the tube leading away from the condenser. The flow experiments are performed as described in Sezgi et al. (1998), a paper that describes polyethylene pyrolysis.

In the HDPE study, cooled pyrolysis products at the end of an experiment are solidified polymer remaining in the reactor, semi-solid condensate in the condenser vessel, and gas. Gas product was collected at 20 min intervals during the experiment and analyzed by GC (Perkin-Elmer model 8500; J&W Scientific capillary alumina column, 30 m $\times$ 0.53 mm). Reactor and condenser vessels were separately weighed before and after each experiment to determine final polymer and condensate mass. Each product was dissolved at 90 °C in 100 ml of HPLC reagent-grade 1,2,4-trichlorobenzene (TCB, Fisher Scientific) and analyzed by HPLC-GPC. A mixture of dissolved polymer melt and condensate was prepared by mixing 10 ml of each solution. Before GPC analysis, all samples were again diluted 5- to 30-fold to maximize sensitivity. The HPLC system (Hewlett-Packard 1050) consists of a 100 μL sample loop, a precision pump, and a refractive-index detector (Hewlett-Packard 1047A). Two GPC columns (Waters 10674, 300mm $\times$ 7.5mm) packed with cross-linked styrene divinylbenzene copolymer beads (10 μm diameter) were used in series. The eluent TCB was pumped at a constant flow rate of precisely 1.00 mL/min. Column and detector temperatures were maintained at 50.0 °C.

Distribution-Kinetics Model. To illustrate how distribution kinetics can be applied to coal liquefaction, we examine a simplified process in a two-phase batch reactor containing a solvent (polymer melt) with suspended coal particles. As the coal network is disassembled by molecular cleavage, the macromolecular reaction products are solubilized in the solvent. The subscripts s and f denote coal (solid) and liquefied (fluid) molecules, respectively.

MWDs (mol/(vol·MW)) are defined (Wang et al., 1995; McCoy and Madras, 1997) so that at time t , $p(x,t)dx$ is the molar concentration (mol/volume) of macromolecules having values of MW x in the range x to $x+dx$. Moments of MWDs are defined as integrals over x .

$$p^{(n)}(t) = \int_0^{\infty} p(x, t) x^n dx \quad (4.1)$$

The zeroth, first, and second moments have been defined in Chapter 3.

Population balances (Madras et al., 1997) for the MWDs are based on mass balances. Both random and chain-end scission can occur. A chain-end scission reaction yields two molecular products, one a small, soluble molecule cleaved from the chain end, and the other a relatively insoluble, large-MW macromolecule. The mass-transfer rate from coal particles to solvent can be described (Sezgi et al., 1998) by an overall mass transfer coefficient,

$$K(x) = K_0 - K_1 x,$$

which is assumed to decrease linearly with MW to account for lower mass-transfer rates of higher-MW components. The interphase mass-transfer driving force is given by $(p_s - Kp_f)$, where p_s , p_f , and K are all functions of x so that the driving force depends on the particular component being liquefied. The solubility (equilibrium) constant for the macromolecules is assumed to increase with MW according to the polynomial,

$$K(x) = \sum_{j=1} K_j x^j \quad (4.2)$$

Such expressions for $\kappa(x)$ and $K(x)$ would permit mathematical solutions to the mass balance equations through MW moments.

The random-scission reaction can be written as

equations by forming n th moments. These equations can be solved for moments, which allow the MWDs to be represented as gamma distributions. Of course, the moments are the key quantities for relating the mathematical model to actual measurements.

Results of polyethylene pyrolysis in our laboratory (Sezgi et al., 1998) suggest an approach to a fundamental kinetics investigation of *coprocessing* of plastics and coal. The molecular cracking of coal-polymer mixtures to fuel and feedstock materials promises significant environmental and energy benefits. Our laboratory has developed methods and published results for thermolytic degradation of coal (Zhang et al., 1993; McCoy et al., 1994; Wang et al., 1993; 1994) and of plastics (Sezgi et al., 1998) *separately*. These techniques could be combined for the efficient and economical production of fuel and specialty chemicals by coprocessing waste plastics and coal *together*. The heart of such a study would be the experimental thermolysis apparatus and the new theory of distribution chemical reaction kinetics that we have developed to acquire and interpret experimental data for macromolecular reactions. High-temperature experiments can readily be adapted to coprocessing by mixing coal particles into the polymer melt, which is stirred by inert gas bubbles. The gas also serves to sweep the volatile reaction products from the reactor. Solid catalysts, hydrogen donors, and other beneficial agents could be added. This reactor not only provides more detailed experimental details than most research reactors, but also represents a promising basic design for a commercial process. We provide here a discussion of experiments and theory for coprocessing.

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Such expressions for $\kappa(x)$ and $K(x)$ would permit mathematical solutions to the mass balance equations through MW moments.

The random-scission reaction can be written as

and chain-end scission as

where $Q(x_m)$ is a monomer or oligomer of mass x_m . The rate expressions for reactions A and B have been related to radical mechanisms (Kodera and McCoy, 1997). The random-scission rate should increase with the number of bonds that can be cleaved. Hence, k_r should generally increase with x , but in this introductory treatment we consider k_r is constant with x . The chain-end scission rate is essentially proportional to the number of chain-ends and is thus independent of the chain length and of x , the MW of a macromolecule. The stoichiometric kernels are $1/x'$ for random scission, and $\delta[x-(x'-x_m)]$ and $\delta(x-x_m)$ for the two products of chain-end scission (Wang et al., 1995). Rate expressions for reactions A and B have been applied previously in our work on polymer degradation and plastics pyrolysis.

If composition is assumed uniform at any time throughout the coal particles and the liquid, the mass balance for *coal particles* is

$$\begin{aligned} \partial p_s / \partial t = & - \kappa (p_s - Kp_f) - k_r p_s(x) + 2 k_r \int_x^{\infty} p_s(x') (1/x') dx' \\ & - k_e p_s(x) + k_e \int_x^{\infty} p_s(x') \delta[x-(x'-x_m)] dx' \end{aligned} \quad (4.3)$$

and for the *liquid*,

$$\partial p_f / \partial t = + \kappa (p_s - Kp_f) + k_e \int_x^{\infty} p_s(x') \delta(x - x_m) dx' \quad (4.4)$$

We have assumed that once macromolecules are solubilized, they do not undergo further degradation. It is not difficult to go beyond this assumption by applying distribution kinetics to chain scission of the solubilized molecules.

Applying the moment operation, $\int_0^\infty [...]x^n dx$, to each equation yields the following differential equations:

for coal particles,

$$\begin{aligned} dp_s^{(n)}/dt = & -\kappa_o [p_s^{(n)} - \sum_{j=1}^n K_j p_f^{(n+j)}] - \kappa_l [p_s^{(n+1)} - \sum_{j=1}^n K_j p_f^{(n+j+1)}] \\ & - k_r p_s^{(n)}(n-1)/(n+1) - k_e p_s^{(n)} + k_e \sum_{j=0}^n \binom{n}{j} (-x_m)^j p_s^{(n-j)} \end{aligned} \quad (4.5)$$

for liquid,

$$dp_f^{(n)}/dt = +\kappa_o [p_s^{(n)} - \sum_{j=1}^n K_j p_f^{(n+j)}] + \kappa_l [p_s^{(n+1)} - \sum_{j=1}^n K_j p_f^{(n+j+1)}] + k_e x_m^n p_s^{(0)} \quad (4.6)$$

For $n = 0$ the differential equations are molar balances:

for coal particles,

$$dp_s^{(0)}/dt = -\kappa_o [p_s^{(0)} - \sum_{j=1} K_j p_f^{(j)}] - \kappa_l [p_s^{(1)} - \sum_{j=1} K_j p_f^{(j+1)}] + k_r p_s^{(0)} \quad (4.7)$$

for liquid,

$$dp_f^{(0)}/dt = +\kappa_o [p_s^{(0)} - \sum_{j=1} K_j p_f^{(j)}] + \kappa_l [p_s^{(1)} - \sum_{j=1} K_j p_f^{(j+1)}] + k_e p_s^{(0)} \quad (4.8)$$

Adding together molar balances for solid and fluid shows that chain scission increases the number of molecules,

$$d(p_s^{(0)} + p_f^{(0)})/dt = (k_r + k_e) p_s^{(0)} \quad (4.9)$$

As the mass transfer terms cancel by addition, Eq 4.9 is valid for any mass transfer expression that permits the moment operation.

For $n = 1$ the differential equations are mass balances:

for coal particles,

$$dp_s^{(1)}/dt = -\kappa_o [p_s^{(1)} - \sum_{j=1} K_j p_f^{(j+1)}] - \kappa_l [p_s^{(2)} - \sum_{j=1} K_j p_f^{(j+2)}] - k_e x_m p_s^{(0)} \quad (4.10)$$

for liquid,

$$dp_f^{(1)}/dt = +\kappa_o [p_s^{(1)} - \sum_{j=1} K_j p_f^{(j+1)}] - \kappa_l [p_s^{(2)} - \sum_{j=1} K_j p_f^{(j+2)}] + k_e x_m p_s^{(0)} \quad (4.11)$$

When the two mass balance equations are added, terms cancel so that the rate of change of total mass is zero in the batch reactor, $dp_s^{(1)}/dt + dp_f^{(1)}/dt = 0$.

Initial conditions for coal and liquid MWDs are $p_s(x, t=0) = p_{so}(x)$ and $p_f(x, t=0) = 0$, and for moments, $p_s^{(n)}(t=0) = p_{so}^{(n)}$ and $p_f^{(n)}(t=0) = 0$.

Truncation of the solubility polynomial is necessary to solve the equations. When this is done, the resulting linear, simultaneous, ordinary differential equations are readily solved by established methods.

The next two chapters describe how we treated the thermal degradation of polystyrene dissolved in mineral oil and poly(methyl methacrylate) in toluene at various temperatures. Samples were analyzed by gel permeation chromatography to obtain the dependence of polymer molecular weight distributions (MWDs) on reaction time.

5. Polystyrene

Experimental data for polystyrene at 240-300 °C indicated degradation both by random chain scission and specific chain-end scission. The existence of weak links was evident, as indicated by rapid chain scission during an initial time period. The MWDs were analyzed with a continuous-mixture kinetics model to obtain separate rate coefficients for weak-link and strong-link scission. Rate coefficients for the specific chain-end degradation of polystyrene to monomers and oligomers were also obtained. Activation energies of the weak-link and strong-link rate coefficients were 2.5 and 7.5 kcal/mol, and chain-end scission activation energies were 0.6 and 0.3 kcal/mol for monomer and oligomer production, respectively.

Introduction. Polystyrene degradation was reviewed by Cameron and MacCallum (1967) and updated by Jellinek (1983). Though thermal degradation of polystyrene has been extensively investigated by pyrolysis experiments, the degradation kinetics and mechanism remain subjects of inquiry and discussion (McNeill et al., 1990). The existence of weak links in polystyrene was initially proposed by Jellinek (1949). Grassie and Kerr (1957) and also Cameron and Kerr (1968) applied this concept to explain the rapid drop of polystyrene molecular weight at low reaction times. Chiantore et al. (1981) provided further evidence of weak-link scission by degrading polystyrene at 200-300 °C by pyrolysis and measuring the molecular weight distribution (MWD) by gel permeation chromatography. They also measured the rate coefficient and the energy of activation for the degradation at long times. They did not, however, measure rate coefficients for weak-link chain scission, which occurs in the first few minutes of degradation.

Commercial application of polystyrene recycling by pyrolysis has been hindered by the high viscosity and uneven heat transfer rates for melting polymer, and by dependence of reaction rates on reactor geometry and mixing. To avoid these problems, degradation of the polymer in solution is proposed. Sato et al. (1990) and Murakata et al. (1991) investigated degradation of poly(α -methyl styrene), poly(p-methyl styrene) and polystyrene in solution, but did not report rate coefficients or energies of activation.

The objective was to study degradation of polystyrene in solution at various temperatures, confirm the presence of weak links, and identify specific products of degradation. Rate coefficients for weak- and strong-link scission and for chain-end scission are obtained by applying the moment theory based on continuous-mixture kinetics to the MWD of the polymer. Activation energies are obtained from the temperature dependence of the rate coefficients.

Experiments: Pretreatment of Polystyrene. The MWD of the raw polymer was determined by dissolving 0.200 g of polystyrene (Polysciences, Inc.) in 100 mL of tetrahydrofuran (THF) (Fisher Scientific) and analyzing 100 μ L of this sample by gel permeation chromatography (GPC). This procedure gives the mass MWD, which can be converted to molar MWD by dividing by MW. The mass MWD (Figure 5.1) indicates a number average MW of 45,000 and a weight average MW of 200,000. The many peaks in the lower MW range (Figure 5.1) would interfere with analysis of the degradation products. To eliminate these low MW peaks, the polymer was fractionated (Kamide and Matsuda, 1989) by partially dissolving 50 grams of polymer in 500 mL of toluene. The solution was continuously stirred with a magnetic stirrer and 750 mL of the precipitating agent, 1-butanol, was slowly added until 70% of the polymer was precipitated. The precipitate was dried to constant weight at 110 °C, and stored under nitrogen. The MWD of the treated polymer, with number average MW of 95,000 and weight average MW of 190,000, is shown in

Figure 5.1. The values $M_w = 2M_n$ indicate that the initial molar MWD is approximately exponential (Madras and McCoy, 1997).

Figure 5.1. Mass MWD (normalized by dividing by mass concentration) of untreated polystyrene (solid line) and pretreated feed polystyrene (dashed line).

The MWD of the mineral oil (Fisher Scientific) was obtained by GPC with a refractive index detector because the mineral oil is UV-invisible. Number- and weight-average molecular weights of mineral oil were 364 and 397, respectively.

Degradation of Polystyrene. Degradation of the treated polymer in mineral oil was conducted in a heated flask equipped with a reflux condenser. Mineral oil was heated to the desired temperature and 20 g/L of the treated polystyrene added to the solution. The temperature was measured using a Type K thermocouple (Fisher Chemicals) and controlled with a Thermolyne 45500 power controller. Samples of 1.0 mL were taken at 2-3 minute intervals for the first 30 minutes, and at 30 minute intervals up to 3 hours, for GPC analysis. Because polystyrene does not completely dissolve in mineral oil at room conditions, the sample was immediately dissolved in 1.0 mL of THF before precipitation and 100 μ L of this solution was injected into the HPLC-GPC.

The mineral oil without polymer was heated at 300 $^{\circ}$ C for 3 hours to test for solvent degradation. No change in the MWD was observed, indicating that the solvent is stable at temperatures of the reaction experiments.

Analysis of Degradation Products. The HPLC (Hewlett-Packard 1050) system consists of a sample loop of 100 μ L, a gradient pump that pumps THF at a constant flow rate of 1.0 mL/min, and an on-line UV detector. The GPC system contains three serial 300 mm x 7.5 mm PLgel columns (Polymer Lab Inc.) of cross-linked poly(styrene-divinyl benzene) with pore sizes of 100, 500, and 10^4 $\text{\AA}$. The chromatograph of the sample injected in the HPLC-GPC provides the MWD

of the polymer. A calibration curve of retention time versus MW for polystyrene was obtained by using polystyrene MW standards (Polymer Lab Inc. and Aldrich Chemicals) in the MW range 162 to 0.93 million.

Distribution-Kinetics Model. In continuous-kinetics models, the polymer is considered to be a mixture with a large number of different size molecules, so that MW is a continuous variable. The molar concentration of polymer in the MW range $(x, x + dx)$ is $p(x,t) dx$. GPC gives the mass MWD, $x p(x,t)$, which can be converted to molar MWD, $p(x,t)$, by dividing by MW, x . The MW moments of the molar MWD, $p(x,t)$, are defined by

$$p^{(n)}(t) = \int_0^{\infty} x^n p(x,t) dx \quad (5.1)$$

Thus $p^{(0)}$ is the molar concentration of the polymer (mol/L) and $p^{(1)}$ is the mass concentration (g/L). First and second moments are determined from experimental measurements of the number- and weight-average MWs defined as

$$M_n = p^{(1)}/p^{(0)} \text{ and } M_w = p^{(2)}/p^{(1)} \quad (5.2)$$

A continuous mixture can undergo an infinite number of consecutive reactions to yield a wide range of products. The polymer decomposition can be written as a combination of random degradation,

and chain-end degradation,

where x_i is the molecular weight of the specific product formed by chain-end scission. We have previously developed continuous kinetics models for various types of polymer degradation, e.g., by combined random-chain scission and chain-end scission (Wang et al., 1995), and by chain-end scission only (Madras et al. 1995b). However, thermal degradation of polystyrene is more complicated due to the presence of weak links, which rupture at a higher rate than other links in the polystyrene chain. The weak (w) and strong (s) links can be represented as the sum of independent distributions,

$$p(x,t) = p_w(x,t) + p_s(x,t) \quad (5.3)$$

Thus, at any time t , the molar concentration of the polymer is the addition of the molar concentrations of the weak and strong links,

$$p^{(0)}(t) = p_w^{(0)}(t) + p_s^{(0)}(t) \quad (5.4)$$

For a first-order degradation in a stirred-batch reactor, the rate expressions for random scission of weak and strong links have the respective forms,

$$\partial p_w / \partial t |_{\text{random}} = -k_w(x) p_w(x,t) + 2 \int_x^{\infty} k_w(x') p_w(x',t) \Omega(x,x') dx' \quad (5.5)$$

$$\partial p_s / \partial t |_{\text{random}} = -k_s(x) p_s(x,t) + 2 \int_x^{\infty} k_s(x') p_s(x',t) \Omega(x,x') dx' \quad (5.6)$$

Because the amount of specific products formed is small, it is reasonable to assume that all specific products arise only from chain-end scission of strong links,

$$\partial p / \partial t |_{\text{specific}} = -k_i(x) p_s(x,t) + \int_x^{\infty} k_i(x') p_s(x',t) \Omega(x-x_i, x') dx' \quad \text{for } A(x'-x_i) \quad (5.7)$$

and

$$\partial q_i / \partial t = \int_x^{\infty} k_i(x') p_s(x',t) \Omega(x_i, x') dx' \quad \text{for } A(x_i) \quad (5.8)$$

where q_i is the MWD of the specific product. The MWDs of the polymer and the products are determined by using suitable expressions for rate coefficients and stoichiometric kernels. The experimental data indicate that the degradation is small ($p^{(0)}/p_0^{(0)} < 2$). As the dependence of the

rate coefficient on molecular weight is not significant for a small extent of reaction, we can assume the rate coefficients to be independent of the molecular weight.

$$k_w(x) = k_w \quad (5.9)$$

$$k_s(x) = k_s \quad (5.10)$$

$$k_i(x) = k_i \quad (5.11)$$

The stoichiometric kernel $\Omega(x, x')$ is defined to satisfy the normalization and symmetry conditions. For polymer degradation, the following stoichiometric kernels for random scission and specific scission are employed:

$$\Omega(x, x') = 1/x' \quad (\text{for random distribution of degradation products}) \quad (5.12)$$

$$\Omega(x - x_i, x') = \delta(x - x' + x_i) \quad (5.13)$$

$$\Omega(x_i, x') = \delta(x - x_i) \quad (5.14)$$

Equations 13 and 14 are stoichiometric kernels, represented by Dirac delta functions, for two products having molecular weights, $x - x_i$ and x_i , resulting from the chain-end scission of reactant with MW x' .

For the specific products (monomer, $i=1$; oligomers, $i=2$), the mass balance equation for a batch reactor is

$$\partial q_i / \partial t = k_i \int_x^\infty p_s(x', t) \delta(x - x_i) dx' \quad (5.15)$$

with the initial condition, $q_i(x, t=0) = 0$. For the reaction mixture, the rates of random and chain-end scission degradation are combined,

$$\begin{aligned} \partial p_s(x, t) / \partial t = & -k_s p_s(x, t) + 2 k_s \int_x^\infty p_s(x', t) \Omega(x, x') dx' \\ & - \sum_{i=1}^2 [k_i p_s(x, t) - k_i \int_x^\infty p_s(x', t) \Omega(x - x_i, x') dx'] \end{aligned} \quad (5.16)$$

$$\partial p_w(x, t) / \partial t = -k_w p_w(x, t) + 2 k_w \int_x^\infty p_w(x', t) \Omega(x, x') dx' \quad (5.17)$$

with the initial condition $p_w(x, t=0) = p_{w0}(x)$ and $p_s(x, t=0) = p_{s0}(x)$. The subscript 0 denotes the initial condition.

Moment equations, defined in equation 1, can be obtained by applying the moment operation, $\int_0^\infty x^n [] dx$, to the equations 15-17 to yield

$$dq_i^{(n)} / dt = k_i x_i^{(n)} p^{(0)}(t) \quad (5.18)$$

for specific scission products. For the polymer, we have separate equations for strong and weak links,

$$\begin{aligned} dp_s^{(n)} / dt = & -(n-1)k_s p_s^{(n)} / (n+1) \\ & - (k_1 + k_2) p_s^{(n)} + \sum_{j=0}^n \binom{n}{j} p_s^{(n-j)} (-1)^j (k_1 x_1^j + k_2 x_2^j) \end{aligned} \quad (5.19)$$

$$dp_w^{(n)} / dt = -(n-1)k_w p_w^{(n)} / (n+1) \quad (5.20)$$

where $\binom{n}{j}$ is the binomial expression.

Then the zeroth moment expressions for the polymer mixture are obtained by solving equations 19 and 20,

$$p_w^{(0)}(t) = p_{w0}^{(0)} \exp(k_w t) \quad (5.21)$$

$$p_s^{(0)}(t) = p_{s0}^{(0)} \exp(k_s t) \quad (5.22)$$

The zeroth moment for specific products of chain-end scission is obtained by solving equation 18,

$$q_i^{(0)}(t) = k_i p_{s0}^{(0)} [\exp(k_s t) - 1] / k_s \quad (5.22)$$

When $k_s t \ll 1$, the zeroth moment for specific products can be approximated as

$$q_i^{(0)}(t) = k_i p_{s0}^{(0)} t \quad (5.24)$$

The weak link concentration is much smaller than that of strong links. Thus, we consider that all the fast-reacting weak links have been consumed by the time t_f , so that the concentration of weak-link scission products remains constant for $t \geq t_f$. The concentration of random scission products is the sum of weak- and strong-link scission products,

$$p^{(0)}(t \leq t_f) = p_{w0}^{(0)} \exp(k_w t) + p_{s0}^{(0)} \exp(k_s t) \quad (5.25)$$

$$p^{(0)}(t \geq t_f) = p_{w0}^{(0)} \exp(k_w t_f) + p_{s0}^{(0)} \exp(k_s t) \quad (5.26)$$

Results and Discussion

Both random and specific scission was observed for the degradation of polystyrene at 240-300 °C. The experimental MWD (Figure 5.2) shows the shift of the polymer MWD due to random scission, and two distinguishable peaks for specific products. The first peak is the monomer at MW = 162 and the second is a combination of oligomers of MW = 250-2500. No evidence for repolymerization or crosslinking, which would be indicated by high MW products in the MWD, was observed.

Figure 5.2 Normalized mass MWD of polystyrene reacted (solid line) at 260 °C for 180 minutes and pretreated feed polystyrene (dashed line).

The rate coefficients of random scission degradation are obtained when $\ln [p^{(0)}/p_0^{(0)}]$ is plotted as a function of time, where $p_0^{(0)}$ is initial molar concentration of the polymer (mol/L). Figure 5.3 shows at early times a rapid increase in the zeroth moment (decrease in average

molecular weight) indicating the presence of weak links. The error bars of 2% are based on the error computed from multiple experiments.

Figure 5.3. Plot of $\ln[p(0)/p_0(0)]$ versus time to determine random-scission rate coefficients: ● 300 °C, ◆ 280 °C, ■ 260 °C, □ 260 °C (second experiment), and ▲ 240 °C.

Table 5.1. Rate parameters determined from experiments at four temperatures.

Temperature, °C	t_f , min	k_s , min ⁻¹	k_w , min ⁻¹	k_1 , min ⁻¹	k_2 , min ⁻¹
240	35	0.0021	0.054	0.00172	0.0142
260	31	0.0029	0.060	0.00180	0.0146
280	28	0.0037	0.065	0.00186	0.0148
300	25	0.0045	0.070	0.00192	0.0151

Several explanations have been forwarded for the presence of weak links in polystyrene (Grassie and Kerr, 1957; Jellinek, 1983; Richards and Salter, 1967). Usually attributed to an abnormal addition step during polymerization, weak links are expected to be randomly distributed along the polymer chain so that their scission is random (Chiantore et al., 1981). Because the polystyrene is manufactured with the catalyst butyl lithium, two types of configuration of the phenyl group in the polystyrene chain are possible,

The latter is formed in the addition step of polymerization due to the anti-Markownikoff rule (Allen and Patrick, 1974) and is weak (easily degradable) compared to the normal (first) structure.

The equations derived from continuous-kinetics theory (Eqs 25-26) are used to determine the parameters t_f , k_s , and k_w (Table 5.1) by fitting the experimental data with the Marquardt-Levenburgh method (Press et al., 1993). The initial molar concentrations of the weak and strong links were also determined to be $p_{w0}^{(0)} = 2.36 \times 10^{-7}$ mol/L and $p_{s0}^{(0)} = 1.1 \times 10^{-5}$ mol/L. The nonlinear parameter estimation was facilitated by having good first approximations for the parameters, e.g., $p_{s0}^{(0)} \approx p_0^{(0)} \gg p_{w0}^{(0)}$, $t_f \approx 30$ min, and $k_s \approx$ slope of the long-time asymptote (Figure 5.3). The rate coefficients for strong links, 0.002 - 0.0045 min $^{-1}$, compare well with the values (0.003 - 0.008 min $^{-1}$) reported by Chiantore et al. (1981). The activation energies, determined from the temperature dependence of the rate coefficients, were 2.5 and 7.5 kcal/mol for the random scission of weak links and strong links, respectively. This is close to the value, 6.9 kcal/mol, reported by Chiantore et al. (1981). These activation energies are much smaller than those previously observed for random scission (30 - 40 kcal/mol) of poly (styrene-allyl alcohol). A possible explanation for the low activation energy is that the hydrogen-abstraction step is rate-controlling. Chiantore et al. (1981) suggest that the low values for the energies of activation indicate the mechanism of scission is complex and may involve more than one-rate controlling step.

According to our model, irreversible chain scission of strong links can continue until all polymer is degraded to monomer. The time when the reaction would cease can be estimated from Eq 22, which relates initial and final moles of molecules with strong links. We estimate that more than two days is required for the reaction to go to theoretical completion. The time for our experiments, 3 h or less, is relatively short, thus justifying the assumption that rate coefficients are independent of MW for low extent of reaction.

The rate coefficients of the specific scission of polystyrene were determined by examining the formation of the monomer and oligomers. The monomer was identified by GC-MS to be 2,2 dimethyl 4-phenyl butane (styrene with a butyl group attached to the end) with the following structure

The monomer is not styrene because the polystyrene is manufactured by the polymerization of styrene with the catalyst butyl lithium. A large number of oligomers are formed due to specific scission and these are lumped together for the following analysis.

Rate coefficients, k_1 and k_2 , for the specific scission of polystyrene to monomer ($i=1$) and oligomers ($i=2$), are determined by equation 23. The slope of a plot of specific product concentration divided by initial strong-link concentration versus $\tau = [\exp(k_s t) - 1]/k_s$ should be a straight line with slope equal to the rate coefficient. The approximate equation 24 was not used because $k_s t$ was 0.8 at the highest temperature. The area of a distribution is determined by numerical integration and corresponds to the zeroth moment. The slopes of the lines determined by linear regression give the specific rate coefficients, k_1 and k_2 . The small values of the intercepts are caused by weak-link chain-end scission, an effect we otherwise ignore. The energies of activation obtained from Arrhenius plots are very small, 0.6 and 0.3 kcal/mol, for monomer and oligomers, respectively.

6. Poly(methyl methacrylate)

The rate of degradation of poly(methyl methacrylate) (PMMA) to methyl methacrylate (MMA) was investigated in the liquid phase with toluene as the solvent. The degradation experiments were carried out in a tubular flow reactor at 1000 psig (6.8 MPa) and at four different temperatures (200, 225, 275, and 300 °C). Polymer concentration was varied from 1 to 4 g/L. A discrete model for the first-order rate of polymer degradation was derived and compared to the continuous kinetics approach. Both models lead to the same expression for the monomer concentration to increase linearly with time. Rate constants were evaluated using the moments of the molecular weight distributions of the reacted and unreacted polymer. The rate was first-order in polymer concentration and the activation energy was 8.4 kcal/mol (34.2 kJ/mol). This activation energy suggests that the rate controlling step for the thermal degradation of PMMA is the depropagation process.

Introduction. Our research group has investigated the degradation of poly(styrene-allyl alcohol) (Wang et al., 1995; Madras et al., 1995a), poly(α -methylstyrene) (Madras et al., 1995b) in solution, and determined rate parameters as well as the dependence of the rate constants on polymer concentration and temperature. The steady-state tubular-reactor has several advantages. Since the reactions occur in the liquid phase, the reactant and all the products have the same reactor residence time, which is directly controlled by the flow rate through the system. Since the temperature is uniform for all fluid elements, the temperature dependence is accurately determined. The same technique was used to determine the rate constants for the degradation of poly(methyl methacrylate) (PMMA) to methyl methacrylate (MMA) in toluene solution. Experiments were conducted at 1000 psig (6.8 MPa), temperatures from 200-300 °C, and polymer concentrations from 1-4 g/L. Rate constants were determined by analyzing the MWDs of the reactor effluent at various residence times. Reaction order was determined from the dependence of the rate constants

on polymer concentration, and the energy of activation from the dependence of rate constants on temperature. Also, a mechanism for the degradation and a framework for the kinetics were proposed.

Experiments:

Pretreatment of PMMA. PMMA was obtained from Aldrich Chemical Company, Inc. The MWD of PMMA was determined by dissolving 0.200 g of PMMA in 100 mL of tetrahydrofuran (THF) (Fisher Scientific) and analyzing this sample by gel permeation chromatography (GPC). Mass MWDs, which can be converted to molar MWDs by dividing by MWs, conveniently display the peaks. The mass MWD indicates a number average MW of 300 and a weight average MW of 11,900. The graph shows many peaks in the lower MW range of raw PMMA that would interfere with product(s) of degradation. To eliminate these low MW peaks, the polymer was fractionated (Kamide and Matsuda, 1989) by partially dissolving 50 grams of polymer in 500 mL of toluene at 30 °C. This solution was continuously stirred with a magnetic stirrer and 750 mL of the precipitating agent, n-butanol, slowly added. Precipitated polymer was dried to constant weight in an oven maintained at 110 °C and stored under nitrogen in a sealed bottle. The number average MW of the treated polymer increased to 6,850.

Degradation of PMMA. The steady-state tubular-flow reactor was 0.45 m length with 0.028 m internal diameter. Detailed descriptions of apparatus and experimental procedure are provided elsewhere (Zhang et al., 1992; Wang et al., 1993). Treated PMMA was dissolved in toluene to the desired concentration (1 - 4 g/L) at 35 °C and passed through the reactor maintained at constant pressure, 6.8 MPa, and at the desired temperature. The solution was cooled by a water cooled heat-exchanger, and flowed through a pressure-reduction valve. The flow rate was controlled by a rotameter placed after the pressure-reduction valve. Thermal degradation experiments at each temperature and polymer concentration were performed at four different flow rates (6, 9, 12, 20 mL/min at STP conditions). At each condition, two effluent samples of 10 mL were taken for GPC analysis. Residence time in the reactor was determined by calculating the density of solvent at reactor conditions (Lee and Kesler, 1975).

Analysis of Degradation Products. Samples were analyzed with HPLC-GPC. The HPLC (Hewlett-Packard 1050) system consists of a sample loop of 100 μ L, a gradient pump that pumps THF at a constant flow rate of 1.0 mL/min, and an on-line UV detector. The GPC system consists of three PLgel columns (Polymer Lab Inc.) of 300 mm $\times$ 7.5 mm. The three columns of cross-linked poly(styrene-divinyl benzene) had pore sizes of 100, 500, and 10^4 Å and were used in series for efficient separation and resolution of peaks.

Various wavelengths were investigated in the range of 200-330 nm, and 205 nm was chosen because of the separation of the MMA and toluene peaks. The first sample of 10 mL is concentrated to 2 mL by evaporating toluene (Fisher Scientific) at 70 °C under vacuum. This is dissolved in THF (Fisher Scientific) and a sample of 100 μ L is injected into the HPLC-GPC. Since MMA is evaporated during the concentration of the sample, the chromatograph of this sample provides only the polymer portion of the reacted polymer. To evaluate the concentration of MMA in the sample, the second sample of 10 mL is dissolved in THF, injected into the GPC system, and the concentration calculated from the area of the peak.

A calibration curve (retention time versus MW) was constructed by using polystyrene standards (MW ranging from 162 to 1.5 million) obtained from Polymer Lab Inc. Styrene and α -methylstyrene were dissolved in THF, and analyzed in the GPC. The calibration was extended to the lower MW range. The monomer peak was also calibrated quantitatively by injecting known amounts of MMA in the GPC. The standard deviation between the peak area and the known amount of MMA was 3.5%.

Mechanism. Thermal degradation mechanisms for polymers depend on molecular structure and experimental conditions. As mentioned earlier, two extremes are possible, pure random degradation and pure depolymerization. Random degradation of a polymer occurs by bond scission at any position along the chain backbone. Depolymerization occurs by scission at the chain-end, which for homopolymers yields monomers.

The reacted polymer has three distinct peaks in the MWD below 1000. To identify these peaks, the effluent from the GPC was separated based on retention time, and the samples were analyzed by GC-MS. The GC-MS analysis confirmed that the peak at MW = 100 was MMA. The peak at MW = 380 is an oligomer of THF, formed by the exposure of the GPC eluent, THF, to air. The peak at MW = 1000 was identified as methyl silicones in the MW range 900-1100. Used as additives to increase the thermal stability of the polymer (Reich and Stivala, 1971), methyl silicones are non-degradation products that are inert in these experiments. Because they detach from the polymer only at high temperatures, methyl silicones are not removed during the pretreatment of the polymer.

The degradation of PMMA is a radical chain reaction that occurs in three steps (Grassie and Scott, 1985; Reich and Stivala, 1971). During initiation the polymer degrades randomly into two radicals by breakage of the bond in the β position (indicated by the vertical arrow):

The depropagation step, reverse of the propagation step in the polymerization process, consists of the production of the monomer from the newly created radicals:

The termination occurs by interaction of the pair of radicals to re-form a polymer:

This model, with the stationary-state assumption for all radical concentrations, leads to a rate equation that is first-order in polymer concentration.

Theoretical Model. The combined mass of monomer and polymer at any time is constant and equals the initial polymer mass,

$$p^{(1)} + q_s^{(1)} = p_o^{(1)} \quad (6.1)$$

confirming the conservation of polymer mass. This follows from Eq 4.28,

$$d[p^{(1)} + q_s^{(1)}]/dt = 0 \quad (6.2)$$

and the initial conditions, $p^{(1)}(t=0) = p_o^{(1)}$ and $q_s^{(1)}(t=0) = 0$. For chain-end scission only (no random scission), the polymer molar concentration, $p^{(0)}$, is constant. Also, because the rate equation for molar concentration of monomer is

$$dq_s^{(0)}/dt = k p^{(0)} \quad (6.3)$$

we have the linear increase of monomer with time,

$$q_s^{(0)} = k t p_o^{(0)} \quad (6.4)$$

Because $q_s^{(n)} = x_s^n q_s^{(0)}$, the mass concentration of monomer is $q_s^{(1)} = x_s q_s^{(0)}$. When all polymer has been converted to monomer, the final value of the monomer mass concentration is

$$q_s^{(1)}(t_{\max}) = N x_s p_o^{(1)} \quad (6.5)$$

where N is the number of monomer units in the initial polymer. The molar concentration of the monomer is obtained by dividing the mass concentration of the monomer by its molecular weight.

Results and Discussion. The degradation rate constants at four temperatures were obtained by analyzing the MWDs for three polymer concentrations at various residence times. The rate constant is calculated from equation 6.4, where $p_o^{(0)}$ is the molar feed concentration (mol/L), t is the residence time, and $q_s^{(0)}$ is the molar concentration of the MMA (mol/L). Molar concentration is the zeroth moment (mol/L) of the mass MWD (g/(L MW)) divided by the MW. The area of the MMA peak (which corresponds to the zeroth moment) is determined by numerical integration.

The plots of t versus $R = q_s^{(0)}/p_o^{(0)}$ confirm the linear relationship for the experimental conditions. The slope of the line gives the rate constant, k . The line passes through the origin confirming that there is no overlap of the toluene peak in the first half of the MMA peak. The rate constant dependence on temperature yields an activation energy of 8.4 ± 0.4 kcal/mol for the degradation of PMMA to MMA. This relatively small value is consistent with results for the degradation of poly(styrene-allyl alcohol) to four specific products: styrene, oligomer of allyl alcohol and styrene (SA), oligomer of two allyl alcohols and styrene (ASA), and a trimer of SA.

The activation energies for these products were 7.4, 7.5, 5.2, 4.4 kcal/mol, respectively (Wang et al., 1995; Madras et al., 1995a). The activation energy is 16 kcal/mol for the degradation of poly(α -methylstyrene) to α -methylstyrene (Madras et al., 1995b).

As already described, the chain-end scission of PMMA to MMA may occur in three steps: random initiation, depropagation, and termination. The activation energies for these steps are 34 kcal/mol, 13 kcal/mol, and 3 kcal/mol, respectively (Jellinek, 1955). The initiation step is a random scission of a bond along the polymer backbone and has a large activation energy. The termination step combines two radicals and has a very small activation energy. The activation energies for depolymerization are similar to those for polymerization for which the activation energies for initiation, propagation, and termination lie between 30 to 60 kcal/mol, 4 to 9 kcal/mol, and 0 to 5 kcal/mol, respectively (Uglea and Negulescu, 1991).

The activation energy suggests that depropagation step may be the rate controlling step for the degradation of PMMA to MMA in solution. This is in contrast to gas-phase pyrolysis where the activation energy is in the range 31-42 kcal/mol (Jellinek, 1955). Thus the initiation reaction may be the controlling step in pyrolysis degradation whereas the depropagation step could be controlling in solution degradation. Pyrolysis usually occurs in the range 300-500 °C while liquid-phase degradation occurs in the lower temperature range of 150-300 °C. This may be due to factors such as differences in density, thermal conductivity, viscosity, or heat capacity for the solids, liquids, and gases involved in the two processes.

Summary. Thermal degradation of solubilized PMMA (in toluene) in a steady-state, tubular-flow reactor was studied by measuring MWDs at various residence times. A discrete model, consistent with continuous mixture kinetics, was employed to analyze the experimental data. The degradation was found to be first-order in polymer concentration with an activation energy of 8.4 kcal/mol. This low activation energy suggests that the depropagation step may be controlling the liquid-phase chain-end scission of PMMA to MMA at the conditions investigated. There was no evidence of random chain scission.

7. Hydrogen Donor Effect

An important effect in the degradation of solubilized polymers is the influence of the solvent on the rate. Depending on the particular polymer, hydrogen (H-)donors can increase, decrease, or have no effect on degradation rate. We experimentally investigated the effect of H-donor 6-hydroxy tetralin on polystyrene degradation, and found that the rate decreases with increasing H-donor concentration. Mathematical expressions for the degradation rate parameters were obtained by applying continuous-distribution kinetics to the MWD of the reacting polymer. A model was developed for radical mechanisms based on the chain-reaction concept with elementary steps of initiation, depropagation, H-abstraction and termination. The model accounted for the different effects of the H-donor.

Introduction. The solvent effect for polystyrene thermal degradation was investigated by Sato et al. (1990). The conversion of polystyrene to low-MW products decreased with the increase of the H-donating ability of the solvents. The study, however, did not determine degradation rate coefficients. Madras et al. (1995) found that tetralin enhanced the rate of degradation of poly(styrene-allyl alcohol). Rate coefficients were determined as a function of tetralin concentration and temperature. Madras et al. (1996a) found that tetralin had no effect on the degradation of poly(α -methyl styrene). These studies indicate the varied effect of the H-donor. Though there have been several experimental studies on H-donor solvents, an overall theory for the mechanism is not available.

Experiments. The HPLC (Hewlett-Packard 1050) system consists of a 100 mL sample loop, a gradient pump, and an on-line variable wavelength ultraviolet (UV) detector. Three PLgel columns (Polymer Lab Inc.) (300 mm x 7.5 mm) packed with cross-linked poly(styrene-divinyl benzene) with pore sizes of 100, 500, and 10^4 Å are used in series. Tetrahydrofuran (HPLC grade, Fisher

Chemicals) was pumped at a constant flow rate of 1.00 mL/min. Narrow MW polystyrene standards of MW 162 to 0.93 million (Polymer Lab and Aldrich Chemicals) provided the calibration curve of retention time versus MW.

The thermal decomposition in mineral oil was conducted in a 100 mL flask equipped with a reflux condenser to ensure the condensation and retention of volatiles. A 60 mL volume of mineral oil (Fisher Chemicals) was heated to 275 °C, and various amounts (0 - 0.60 g) of the H-donor, 6-hydroxy tetralin (Aldrich Chemicals), and 0.12 g of monodisperse polystyrene (MW = 110,000) (Aldrich Chemicals) were added. The temperature of the solution was measured with a Type K thermocouple (Fisher Chemicals) and controlled within ± 3 °C using a Thermolyne 45500 power controller. Samples of 1.0 mL were taken at 15 minute intervals and dissolved in 1.0 mL of tetrahydrofuran (HPLC grade, Fisher Chemicals). An aliquot (100 μ L) of this solution was injected into the HPLC-GPC system to obtain the chromatograph, which was converted to MWD with the calibration curve. Because the mineral oil is UV invisible, its MWD was determined by a refractive index (RI) detector. No change in the MWD of mineral oil was observed when the oil was heated for 3 hours at 275 °C without polystyrene.

Mathematical Model. According to the Rice-Herzfeld mechanism, polymers can react by transforming their structure without change in MW, e.g., by H-abstraction or isomerization. They can also undergo chain scission to form lower MW products, or undergo addition reactions yielding higher MW products. Chain scission can occur either at the chain-end yielding a specific product, or at a random position along the chain yielding a range of lower MW products. The radicals formed by H-abstraction or chain scission are usually influenced by the presence of the H-donor.

We proposed continuous-distribution mass (population) balances for the various steps involved in the radical mechanism. The rate coefficients are assumed to be independent of MW, a reasonable assumption at low conversions (Madras et al., 1997). As before, the solution procedure involved the LCA and QSSA.

Polymer degradation in some circumstances can occur solely by random chain scission. We represent the chemical species of the reacting polymer, and the radicals as $P(x)$ and $R^*(x)$ and their MWDs as $p(x,t)$ and $r(x,t)$, respectively, where x represents the continuous variable, MW. Since the polymer reactants and random scission products are not distinguished in the continuous distribution model, a single MWD, $p(x,t)$, represents the polymer mixture at any time, t . The initiation-termination reactions are ignored, according to the LCA. The reversible H-abstraction process is simplified to

The random-scission chain reaction is

The reversible H-donor reactions are

where D and D^{*} represent H-donor and its dehydrogenated form, respectively. Because the MW of P(x) and R^{*}(x) differ only by the atomic weight of hydrogen, we consider their MWs are the same.

Population balance equations for the polymer MWD, p(x,t), and for the radical MWD, r(x,t), are formulated and solved by the moment method (McCoy and Madras, 1997). Both LCA and the QSSA are applied to obtain the zeroth moment expression for the initial condition, p⁽⁰⁾(t=0) = p₀⁽⁰⁾,

$$p^{(0)}(t) = p_0^{(0)} \exp(k_r t) \quad (7.4)$$

and a plot of $\ln(p^{(0)}/p_0^{(0)})$ should be linear in time with slope k_r,

$$k_r = k_b (k_h + k_d C)/(k_H + k_D C) \quad (7.5)$$

This equation, showing how the degradation rate coefficient depends on H-donor concentration, C, is plotted in Figure 7.1 for several special cases.

Polymers like poly(α-methyl styrene) undergo degradation by chain-end scission yielding monomers and other low-MW specific products, Q_s(x_s). The chain-end scission reaction is

H-abstraction by the chain-end radical is considered reversible,

The chain-end radical, R_e^{*}(x), can also undergo radical isomerization to form a specific radical, R_s^{*}(x), via a cyclic transition state,

The reversible, propagation-depropagation reactions whereby a specific radical yields a specific product and a chain-end radical is

Figure 7.1. Plot of the rate coefficient of random chain scission, k_r , versus H-donor concentration, C , to show the different effects of the H-donor concentration and rate parameters (Eq 7.5).

The reactions of the H-donor expressed in terms of D , the hydrogenated and D^* , the dehydrogenated forms of the donor, are

Applying the LCA and QSSA to the population balance equations yields for the specific product,

$$q_s^{(0)}(t) = k_s p_0^{(0)} t \quad (7.11)$$

where

$$k_s = (k_{he} + k_{de}C) k_{bs} k_{ih} / ((k_{bs} + k_{ih})(k_{Hc} + k_{De}C)) \quad (7.12)$$

This is a key result for chain-end scission influenced by H-donor concentration, C , and is similar to Eq 7.5 for random chain scission. A plot of $q_s^{(0)}(t)/p_0^{(0)}$ versus time would be linear with a slope k_s , which depends on C .

Discussion. As usual the random-scission degradation rate coefficient, k_r , was determined from the experimental data by analyzing the time dependence of the polystyrene MWDs. The graphs of

$p_{\text{tot}}^{(0)}/p_{\text{tot}}^{(0)}$ versus time for various H-donor concentrations were linear after 45 minutes. For times less than 45 minutes, scission of weak links causes a rapid increase in the molar concentration (Stivala et al., 1983; Madras et al., 1997; Chiantore et al., 1981). The initial molar concentration of the strong links in polystyrene, $p_0^{(0)}$, was determined from the intercept of the regressed line of the $p_{\text{tot}}^{(0)}/p_{\text{tot}}^{(0)}$ data for $t \geq 45$ minutes. The slopes, corresponding to the rate coefficient for random scission, k_r , are determined from the plot of $\ln(p^{(0)}/p_0^{(0)})$ versus time. The rate coefficient decreases with increasing H-donor (6-hydroxy tetralin) concentration (Figure 7.2). This behavior is consistent with Eq 7.5 when $k_h \gg k_d C$ (Figure 7.1). This behavior is also observed for the polystyrene degradation in the presence of tetralin (Sato et al., 1990).

Figure 7.2. Effect of hydrogen donor (6-hydroxy tetralin) mass concentration, C_m , on the rate coefficient of random chain scission, k_r , of polystyrene at 275 C.

When $k_h \ll k_d C$, the rate coefficient has a first-order dependence at low H-donor concentrations and a zero-order dependence at high H-donor concentrations. This has been experimentally observed for poly(styrene-allyl alcohol) degradation in the presence of tetralin at 150 °C (Madras et al., 1995). When $k_d C \ll k_h$ and $k_D C \ll k_H$, the rate coefficient is independent of the H-donor concentration. This is consistent with poly(α -methyl styrene) degradation in the presence of H-donor solvents.

For chain-end scission, the effect of H-donor concentration is qualitatively similar to that in Figure 1. For chain-end scission rates for degradation of poly(styrene allyl-alcohol) in presence of

tetralin at 150 °C (Madras et al., 1995), specific product molar concentrations are linear in time, as predicted by Eq 7.11. The rate coefficient for chain-end scission, k_s , can be obtained from the slope of the molar concentration of the specific product versus time. The dependence is consistent with Eq 7.12 when $k_{he} \ll k_{de} C$, which relates the chain-end scission rate coefficient to the H-donor concentration. The prediction of the continuous-kinetics model are thus consistent with the different observations of the H-donor effect.

8. Polymer Mixtures

Waste streams usually contain mixtures of polymers and it may be costly to separate them prior to degradation. Most basic research on degradation, however, is for single polymers. Degradation rates depend on the mixture type, and adding another polymer can increase, decrease, or leave unchanged the rate of the first polymer. Determining the decomposition mechanisms for polymer mixtures is of interest for polymer recycling. In this study, we presented techniques to determine the degradation kinetics of solubilized binary polymer mixtures by examining the time evolution of MWDs. Because the reaction mechanism for polymer degradation involves radicals, we have developed an approach that accounts for the elementary reactions of initiation, termination, hydrogen abstraction, and chain scission. Experimentally, we determined the concentration effect of poly(α -methyl styrene) (PAMS) on the random-chain degradation of polystyrene dissolved in mineral oil at 275 °C in a batch reactor by evaluating the time evolution of the MWDs. Molecular-weight moments yielded expressions for the number- and weight-average MW and degradation rate coefficients. The experimental data indicated that the interaction of mixed radicals with polymer by hydrogen abstraction caused the random-chain scission degradation rate of polystyrene to decrease with increasing PAMS concentration.

Introduction. The rate of polymer degradation can be modified by the addition of conventional free-radical initiators, oxidizers or hydrogen donors, but it might be easier to alter the degradation rate by blending two polymers (Gardner et al., 1993). Studies by pyrolysis of polymer mixtures have reported varied results. For example, some reports indicated a significant interaction between polystyrene and polyethylene (Koo and Kim, 1993; Koo et al., 1991; McCaffrey et al., 1996), while others observed no interaction between these polymers (Roy et al., 1978; Wu et al., 1993). The pyrolytic polystyrene degradation rate was significantly enhanced in the presence of poly(methyl acrylate) and poly(butyl acrylate) at 430 °C (Gardner et al., 1993). Richards and Salter (1964), on the other hand, observed that the rate of polystyrene degradation decreased with increasing molecular weight (MW) of added PAMS. These reports suggest the need for an analysis of the underlying reaction mechanisms.

Degradation of polymers in solution has been proposed to ameliorate problems encountered in commercial applications (Sato et al., 1990), and several studies have been reported (Murakata et al., 1993; Madras et al., 1996c; Wang et al., 1995; Madras et al., 1996a; Madras et al., 1996b). No studies on the degradation of polymer mixtures in solution, however, have been published.

Experiments. The HPLC (Hewlett-Packard 1050) system consists of a 100 μ L sample loop, a gradient pump, and an on-line variable wavelength ultraviolet (UV) detector. Three PLgel columns (Polymer Lab Inc.) (300 mm x 7.5 mm) packed with cross-linked poly(styrene-divinyl benzene) with pore sizes of 100, 500, and 10,000 Å are used in series. Tetrahydrofuran (HPLC grade, Fisher Chemicals) was pumped at a constant flow rate of 1.00 mL/min. Narrow MW polystyrene standards of MW 162 to 0.93 million (Polymer Lab and Aldrich Chemicals) were used to obtain the calibration curve of retention time versus MW, which was stable during the period of the experiments. The calibration curve, modeled as a second-order polynomial, indicates a higher accuracy in the measurement of lower MW polymers.

The thermal decomposition of polystyrene in mineral oil was conducted in a 100 mL flask equipped with a reflux condenser to ensure the condensation and retention of volatiles. To observe

a significant effect of PAMS on the conversion, polystyrene of high MW was chosen. 60 mL of mineral oil (Fisher Chemicals) was heated to 275 °C, and various amounts (0 - 0.60 g) of monodisperse PAMS (MW = 11,000, Scientific Polymer Products), and 0.12 g of monodisperse polystyrene (MW = 330,000, Aldrich Chemicals) were added. The temperature of the solution was measured with a Type K thermocouple (Fisher Chemicals) and controlled within ± 1 °C by a Omega CN-2042 temperature controller. Samples of 1.0 mL were taken at 15 minute intervals and dissolved in 1.0 mL of tetrahydrofuran (HPLC grade, Fisher Chemicals). The chromatograph obtained by injecting 100 μ L of this solution into the HPLC-GPC system was converted to MWD. The peaks of the reacted polystyrene, PAMS, and the oligomers were distinct, so that moments could be calculated by numerical integration. Because the solvent mineral oil is UV invisible, its MWD was determined with a refractive index (RI) detector. No change in the MWD of mineral oil was observed when the oil was heated for 3 hours at 275 °C without polystyrene.

Model. The proposed scheme, based on the Rice-Herzfeld concept (Nigam et al., 1994) of chain reactions, includes the important elementary steps involving radicals. The degradation rate of polymer A undergoing random-chain scission is influenced by polymer B undergoing chain-end scission. We represent the reacting polymer A and its radicals as $P_A(x)$ and $R^*(x)$ and their MWDs as $p_A(x,t)$ and $r(x,t)$, respectively, where x represents the continuous variable, MW. As the polymer reactants and random scission products are not distinguished in the distribution kinetics model, a single MWD, $p_A(x,t)$, represents the polymer in the mixture at any time, t . The initiation-termination reactions are represented as

where $\rightleftharpoons$ represents a reversible reaction. The reversible hydrogen abstraction process is

The depropagation chain reaction is

The polymer B, the chain-end radical, the specific radical, and the specific product are represented as $P_B(x)$, $R_e^*(x)$, $R_s^*(x)$, $Q_s(x_s)$, respectively, and their corresponding MWDs as $p_B(x,t)$, $r_e(x,t)$, $r_s(x,t)$ and $q_s(x_s,t)$. The formation of chain-end radicals by a reversible random-scission initiation-termination reaction is

Hydrogen abstraction by the chain-end radical is considered reversible,

The chain-end radical can undergo radical isomerization via a cyclic transition state to form a specific radical,

The depropagation reaction yields the specific product and a chain-end radical from a specific radical,

where x_s is the MW of the specific product.

The interaction of the two degrading polymers is through hydrogen abstraction (McCaffrey et al., 1996) represented as a reversible disproportionation reaction. The end radical of polymer B combines with polymer A to form an intermediate radical complex that undergoes transformation to polymer B and a radical of polymer A.

Including the intermediate complex, R_i^* , facilitates the formulation of the population balance equations for the reversible disproportionation. If R_i^* is ignored in equation 1.8, the forward and reverse rate coefficients would be k_d and k_D , respectively.

With the aid of Table 1, the rate expressions and moments can be formulated. Based on LCA, k_f , k_{fs} , k_t and k_{ts} are set to zero. The zeroth moments for the polymer, radicals and the monomer, $p^{(0)}$, $r^{(0)}$, $q^{(0)}$ are defined as

$$p^{(0)}(t) = \int_0^\infty p(x,t) dx \quad (8.9)$$

$$r^{(0)}(t) = \int_0^\infty r(x,t) dx \quad (8.10)$$

$$q^{(0)}(t) = \int_0^\infty q(x,t) dx \quad (8.11)$$

The initial conditions for moments are

$$P_B^{(0)}(t=0) = P_{B0}^{(0)}, P_A^{(0)}(t=0) = P_{A0}^{(0)} \text{ and } r^{(0)}(t=0) = 0 \quad (8.12)$$

When QSSA holds,

$$dr^{(0)}/dt = dr_s^{(0)}/dt = dr_e^{(0)}/dt = dr_i^{(0)}/dt = 0 \quad (8.13)$$

Algebraic manipulations yield

$$P_A^{(0)}(t) = P_{A0}^{(0)} \exp(k_r t) \quad (8.14)$$

and a plot of $\ln(p^{(0)}/p_0^{(0)})$ is linear in time with slope k_r ,

$$k_r = (2 k_b k_h / (k_d p_{B0}^{(0)})) + k_b (k_{he} + k_h) / k_H \quad (8.15)$$

The molar concentration is related to the mass concentration, $p^{(1)} = M_n p^{(0)}$, by the average MW, M_n .

The proposed mechanism represents the interaction of radicals of two reacting polymers and shows how the polymer undergoing chain-end scission affects the degradation rate of the polymer undergoing random-chain scission. The degradation rate coefficient is a function of the added polymer concentration, and also depends on the temperature and pressure. This can explain the varied results found in experiments for degradation rates in polymer mixtures.

Results. We have measured the influence of PAMS mass concentration on polystyrene degradation at 275 °C. Because polystyrene degrades by random-chain scission and PAMS degrades by chain-end scission, the polystyrene degradation rate is given by Eqs 8.14 and 8.15. The random-scission degradation rate coefficient, k_r , was determined from the experimental data by analyzing the time dependence of the polymer-mixture MWDs. Because the mass of specific products formed by polystyrene chain-end scission at 275 °C for 10 hours is less than 2% (Madras et al., 1996c), we considered that polystyrene degrades solely by random-chain scission.

Polystyrene degrades rapidly at low reaction times due to weak links in the polymer chain caused by side-group asymmetry or chain-branching (Chiantore et al., 1981; Madras et al., 1996c). As our earlier work demonstrated, the weak and strong links in polystyrene can be represented by additive distributions, so that the total molar concentration, $p_{A_{tot}}^{(0)}$, of the polymer is the sum of the molar concentrations of the weak, $p_{Aw}^{(0)}$, and strong links, $p_A^{(0)}$ (Madras et al., 1996c). As the weak link concentration is approximately two orders of magnitude smaller than the strong link concentration, only the random rate coefficients of strong links are examined in this study. The initial molar concentration of the strong links in polystyrene, $p_{A0}^{(0)}$, is determined from the intercept of the regressed line of the $p_{A_{tot}}^{(0)}/p_{A_{tot}0}^{(0)}$ data for $t \geq 45$ minutes. The slopes, corresponding to the rate coefficient for random scission, k_r , are determined from the plot of $\ln(p_A^{(0)}/p_{A0}^{(0)})$ versus time, as given by Eq 8.14. Madras et al. (1997) show how data are analyzed when the polystyrene degradation rate coefficient is a function of MW, i.e., $k_r(x)$. Equation 8.15 explains how the polystyrene degradation rate coefficient depends on PAMS concentration. The polystyrene degradation rate coefficient, k_r , decreases with increasing PAMS mass (or molar) concentration. This is consistent with the experimental data.

The hypothesized interaction of the degrading polymers is through the free radicals and their rates of hydrogen abstraction. When $k_d = k_D = 0$, the two polymers react independently and the moment equations are identical to those derived for a single polymer undergoing chain-end scission or random-chain scission (Madras and McCoy, 1997). The rate coefficient for random-chain scission of polystyrene is a function of the PAMS mixture concentration through the fundamental radical rate parameters, k_b , k_h , k_{he} , k_d , k_H , and the initial number-average molecular weight of PAMS (Eq 8.15). The addition of PAMS inhibits the random-chain scission of polystyrene, similar to the effect on hydrogen-donors on the degradation of polystyrene (Madras and McCoy, 1997).

Experimental results reported here and in the literature, as well as model predictions in the current study, suggest that mixtures of different materials can have a range of effects on polymer degradation. One infers that "dirty" plastics will react in different ways depending on the particular impurity mix. It is possible some metallic additives will have a catalytic (or possibly a catalytic deactivating) influence. Many biomass additives will be stable at temperatures in our experiments.

The present results for solvent and polymer additives illustrate the range of behavior that should be expected.

9. Concluding Remarks

This report outlines a distribution kinetics approach to macromolecular reactions that has been applied to several processes. The broad applicability is based on the range of phenomena that can be represented and interpreted:

- random scission (or scission biased toward midchain scission) and/or addition (step polymerization and crosslinking),
- single monomer scission (i.e., chain-end scission) and/or addition (chain-end polymerization),
- reversible scission kinetics and in general the approach to equilibrium,
- radical (or catalyzed ion) reaction mechanisms,
- multiphase behavior, including liquid-vapor and solid-liquid mass transfer.

We have described experiments for chemical models that simulate depolymerization of coal. Although the approach has been exceptionally successful for the model macromolecular systems, a similar treatment to explicate coal liquefaction will require more investigation. Development of a novel chemical reaction engineering analysis, based on distribution kinetics, was a major accomplishment of the current research. This approach, was successful in quantitatively describing experiments on several different polymers. The theoretical work involved distribution kinetics to develop chemical reaction models for macromolecular reactions. Experimentally, thermolytic degradation (liquefaction) of macromolecular compounds was investigated with different solvents, including hydrogen-donor and nondonor solvents. Model macromolecular compounds provided a means to study the reaction kinetics of complex materials undergoing molecular cracking for fuel and feedstock processing. Molecular-weight distributions (MWDs) and their moments were measured by HPLC-GPC. Experimental data were interpreted with population-balance equations based on continuous-distribution kinetics, and rate coefficients were determined for chain-end and random scission degradation processes. Accompanied by this mathematical analysis, the experimental studies have revealed essential features of polymer chain-scission kinetics.

Macromolecular systems, either in solution or solid form (e.g., coal), typically contain a large number of homologous molecules spanning a MW range. The methods of MW determination and of polymer synthesis and purification usually provide MWDs, such as determined by GPC, that are relatively smooth functions of MW. Integrals over MW are well-defined for such MWDs, so that MW moments can be readily calculated. Polymer MWDs determined by GPC are typically accurate at high MW, ensuring that higher moments are reliable. This contrasts to dynamic response experiments, where temporal moments can be compromised by long tail effects. In the event that low MW monomers or oligomers are present, the MWD can be represented as a semi-continuous function. This is the case when chain-end scission yields specific products.

Continuous-distribution kinetics provides the basis for interpretation of the experimental observations. As the reactions for polymer degradation are chain-scission events, the stoichiometry can be represented in terms of integrals over the polymer MWD. For batch reactions, the population balance equations are integrodifferential equations that can be solved by a moment procedure. Ordinary differential equations for the moments are readily solved for the products of random and chain-end scission. To determine rate coefficients, only zeroth moments are required.

10. References Cited

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The activation energies for these products were 7.4, 7.5, 5.2, 4.4 kcal/mol, respectively (Wang et al., 1995; Madras et al., 1995a). The activation energy is 16 kcal/mol for the degradation of poly(α -methylstyrene) to α -methylstyrene (Madras et al., 1995b).

As already described, the chain-end scission of PMMA to MMA may occur in three steps: random initiation, depropagation, and termination. The activation energies for these steps are 34 kcal/mol, 13 kcal/mol, and 3 kcal/mol, respectively (Jellinek, 1955). The initiation step is a random scission of a bond along the polymer backbone and has a large activation energy. The termination step combines two radicals and has a very small activation energy. The activation energies for depolymerization are similar to those for polymerization for which the activation energies for initiation, propagation, and termination lie between 30 to 60 kcal/mol, 4 to 9 kcal/mol, and 0 to 5 kcal/mol, respectively (Uglea and Negulescu, 1991).

The activation energy suggests that depropagation step may be the rate controlling step for the degradation of PMMA to MMA in solution. This is in contrast to gas-phase pyrolysis where the activation energy is in the range 31-42 kcal/mol (Jellinek, 1955). Thus the initiation reaction may be the controlling step in pyrolysis degradation whereas the depropagation step could be controlling in solution degradation. Pyrolysis usually occurs in the range 300-500 °C while liquid-phase degradation occurs in the lower temperature range of 150-300 °C. This may be due to factors such as differences in density, thermal conductivity, viscosity, or heat capacity for the solids, liquids, and gases involved in the two processes.

Summary. Thermal degradation of solubilized PMMA (in toluene) in a steady-state, tubular-flow reactor was studied by measuring MWDs at various residence times. A discrete model, consistent with continuous mixture kinetics, was employed to analyze the experimental data. The degradation was found to be first-order in polymer concentration with an activation energy of 8.4 kcal/mol. This low activation energy suggests that the depropagation step may be controlling the liquid-phase chain-end scission of PMMA to MMA at the conditions investigated. There was no evidence of random chain scission.

7. Hydrogen Donor Effect

An important effect in the degradation of solubilized polymers is the influence of the solvent on the rate. Depending on the particular polymer, hydrogen (H)-donors can increase, decrease, or have no effect on degradation rate. We experimentally investigated the effect of H-donor 6-hydroxy tetralin on polystyrene degradation, and found that the rate decreases with increasing H-donor concentration. Mathematical expressions for the degradation rate parameters were obtained by applying continuous-distribution kinetics to the MWD of the reacting polymer. A model was developed for radical mechanisms based on the chain-reaction concept with elementary steps of initiation, depropagation, H-abstraction and termination. The model accounted for the different effects of the H-donor.

Introduction. The solvent effect for polystyrene thermal degradation was investigated by Sato et al. (1990). The conversion of polystyrene to low-MW products decreased with the increase of the H-donating ability of the solvents. The study, however, did not determine degradation rate coefficients. Madras et al. (1995) found that tetralin enhanced the rate of degradation of poly(styrene-allyl alcohol). Rate coefficients were determined as a function of tetralin concentration and temperature. Madras et al. (1996a) found that tetralin had no effect on the degradation of poly(α -methyl styrene). These studies indicate the varied effect of the H-donor. Though there have been several experimental studies on H-donor solvents, an overall theory for the mechanism is not available.

Experiments. The HPLC (Hewlett-Packard 1050) system consists of a 100 mL sample loop, a gradient pump, and an on-line variable wavelength ultraviolet (UV) detector. Three PLgel columns (Polymer Lab Inc.) (300 mm x 7.5 mm) packed with cross-linked poly(styrene-divinyl benzene) with pore sizes of 100, 500, and 10^4 Å are used in series. Tetrahydrofuran (HPLC grade, Fisher

Chemicals) was pumped at a constant flow rate of 1.00 mL/min. Narrow MW polystyrene standards of MW 162 to 0.93 million (Polymer Lab and Aldrich Chemicals) provided the calibration curve of retention time versus MW.

The thermal decomposition in mineral oil was conducted in a 100 mL flask equipped with a reflux condenser to ensure the condensation and retention of volatiles. A 60 mL volume of mineral oil (Fisher Chemicals) was heated to 275 °C, and various amounts (0 - 0.60 g) of the H-donor, 6-hydroxy tetralin (Aldrich Chemicals), and 0.12 g of monodisperse polystyrene (MW = 110,000) (Aldrich Chemicals) were added. The temperature of the solution was measured with a Type K thermocouple (Fisher Chemicals) and controlled within ± 3 °C using a Thermolyne 45500 power controller. Samples of 1.0 mL were taken at 15 minute intervals and dissolved in 1.0 mL of tetrahydrofuran (HPLC grade, Fisher Chemicals). An aliquot (100 μ L) of this solution was injected into the HPLC-GPC system to obtain the chromatograph, which was converted to MWD with the calibration curve. Because the mineral oil is UV invisible, its MWD was determined by a refractive index (RI) detector. No change in the MWD of mineral oil was observed when the oil was heated for 3 hours at 275 °C without polystyrene.

Mathematical Model. According to the Rice-Herzfeld mechanism, polymers can react by transforming their structure without change in MW, e.g., by H-abstraction or isomerization. They can also undergo chain scission to form lower MW products, or undergo addition reactions yielding higher MW products. Chain scission can occur either at the chain-end yielding a specific product, or at a random position along the chain yielding a range of lower MW products. The radicals formed by H-abstraction or chain scission are usually influenced by the presence of the H-donor.

We proposed continuous-distribution mass (population) balances for the various steps involved in the radical mechanism. The rate coefficients are assumed to be independent of MW, a reasonable assumption at low conversions (Madras et al., 1997). As before, the solution procedure involved the LCA and QSSA.

Polymer degradation in some circumstances can occur solely by random chain scission. We represent the chemical species of the reacting polymer, and the radicals as $P(x)$ and $R^*(x)$ and their MWDs as $p(x,t)$ and $r(x,t)$, respectively, where x represents the continuous variable, MW. Since the polymer reactants and random scission products are not distinguished in the continuous distribution model, a single MWD, $p(x,t)$, represents the polymer mixture at any time, t . The initiation-termination reactions are ignored, according to the LCA. The reversible H-abstraction process is simplified to

The random-scission chain reaction is

The reversible H-donor reactions are

where D and D^{*} represent H-donor and its dehydrogenated form, respectively. Because the MW of P(x) and R^{*}(x) differ only by the atomic weight of hydrogen, we consider their MWs are the same.

Population balance equations for the polymer MWD, p(x,t), and for the radical MWD, r(x,t), are formulated and solved by the moment method (McCoy and Madras, 1997). Both LCA and the QSSA are applied to obtain the zeroth moment expression for the initial condition, p⁽⁰⁾(t=0) = p₀⁽⁰⁾,

$$p^{(0)}(t) = p_0^{(0)} \exp(k_r t) \quad (7.4)$$

and a plot of $\ln(p^{(0)}/p_0^{(0)})$ should be linear in time with slope k_r,

$$k_r = k_b (k_h + k_d C)/(k_H + k_D C) \quad (7.5)$$

This equation, showing how the degradation rate coefficient depends on H-donor concentration, C, is plotted in Figure 7.1 for several special cases.

Polymers like poly(α-methyl styrene) undergo degradation by chain-end scission yielding monomers and other low-MW specific products, Q_s(x_s). The chain-end scission reaction is

k_{fs}

H-abstraction by the chain-end radical is considered reversible,

k_{he}

The chain-end radical, R_e^{*}(x), can also undergo radical isomerization to form a specific radical,

R_s^{*}(x), via a cyclic transition state,

k_{ih}

The reversible, propagation-depropagation reactions whereby a specific radical yields a specific product and a chain-end radical is

k_{bs}

Figure 7.1. Plot of the rate coefficient of random chain scission, k_r , versus H-donor concentration, C , to show the different effects of the H-donor concentration and rate parameters (Eq 7.5).

The reactions of the H-donor expressed in terms of D , the hydrogenated and D^* , the dehydrogenated forms of the donor, are

Applying the LCA and QSSA to the population balance equations yields for the specific product,

$$q_s^{(0)}(t) = k_s P_0^{(0)} t \quad (7.11)$$

where

$$k_s = (k_{He} + k_{De}C) k_{bs} k_{ih} / ((k_{bs} + k_{ih})(k_{He} + k_{De}C)) \quad (7.12)$$

This is a key result for chain-end scission influenced by H-donor concentration, C , and is similar to Eq 7.5 for random chain scission. A plot of $q_s^{(0)}(t)/P_0^{(0)}$ versus time would be linear with a slope k_s , which depends on C .

Discussion. As usual the random-scission degradation rate coefficient, k_r , was determined from the experimental data by analyzing the time dependence of the polystyrene MWDs. The graphs of

$p_{\text{tot}}^{(0)}/p_{\text{tot}0}^{(0)}$ versus time for various H-donor concentrations were linear after 45 minutes. For times less than 45 minutes, scission of weak links causes a rapid increase in the molar concentration (Stivala et al., 1983; Madras et al., 1997; Chiantore et al., 1981). The initial molar concentration of the strong links in polystyrene, $p_0^{(0)}$, was determined from the intercept of the regressed line of the $p_{\text{tot}}^{(0)}/p_{\text{tot}0}^{(0)}$ data for $t \geq 45$ minutes. The slopes, corresponding to the rate coefficient for random scission, k_r , are determined from the plot of $\ln(p^{(0)}/p_0^{(0)})$ versus time. The rate coefficient decreases with increasing H-donor (6-hydroxy tetralin) concentration (Figure 7.2). This behavior is consistent with Eq 7.5 when $k_h \gg k_d C$ (Figure 7.1). This behavior is also observed for the polystyrene degradation in the presence of tetralin (Sato et al., 1990).

Figure 7.2. Effect of hydrogen donor (6-hydroxy tetralin) mass concentration, C_m , on the rate coefficient of random chain scission, k_r , of polystyrene at 275 C.

When $k_h \ll k_d C$, the rate coefficient has a first-order dependence at low H-donor concentrations and a zero-order dependence at high H-donor concentrations. This has been experimentally observed for poly(styrene-allyl alcohol) degradation in the presence of tetralin at 150 °C (Madras et al., 1995). When $k_d C \ll k_h$ and $k_D C \ll k_H$, the rate coefficient is independent of the H-donor concentration. This is consistent with poly(α -methyl styrene) degradation in the presence of H-donor solvents.

For chain-end scission, the effect of H-donor concentration is qualitatively similar to that in Figure 1. For chain-end scission rates for degradation of poly(styrene allyl-alcohol) in presence of

tetralin at 150 °C (Madras et al., 1995), specific product molar concentrations are linear in time, as predicted by Eq 7.11. The rate coefficient for chain-end scission, k_s , can be obtained from the slope of the molar concentration of the specific product versus time. The dependence is consistent with Eq 7.12 when $k_{he} \ll k_{de} C$, which relates the chain-end scission rate coefficient to the H-donor concentration. The prediction of the continuous-kinetics model are thus consistent with the different observations of the H-donor effect.

8. Polymer Mixtures

Waste streams usually contain mixtures of polymers and it may be costly to separate them prior to degradation. Most basic research on degradation, however, is for single polymers. Degradation rates depend on the mixture type, and adding another polymer can increase, decrease, or leave unchanged the rate of the first polymer. Determining the decomposition mechanisms for polymer mixtures is of interest for polymer recycling. In this study, we presented techniques to determine the degradation kinetics of solubilized binary polymer mixtures by examining the time evolution of MWDs. Because the reaction mechanism for polymer degradation involves radicals, we have developed an approach that accounts for the elementary reactions of initiation, termination, hydrogen abstraction, and chain scission. Experimentally, we determined the concentration effect of poly(α -methyl styrene) (PAMS) on the random-chain degradation of polystyrene dissolved in mineral oil at 275 °C in a batch reactor by evaluating the time evolution of the MWDs. Molecular-weight moments yielded expressions for the number- and weight-average MW and degradation rate coefficients. The experimental data indicated that the interaction of mixed radicals with polymer by hydrogen abstraction caused the random-chain scission degradation rate of polystyrene to decrease with increasing PAMS concentration.

Introduction. The rate of polymer degradation can be modified by the addition of conventional free-radical initiators, oxidizers or hydrogen donors, but it might be easier to alter the degradation rate by blending two polymers (Gardner et al., 1993). Studies by pyrolysis of polymer mixtures have reported varied results. For example, some reports indicated a significant interaction between polystyrene and polyethylene (Koo and Kim, 1993; Koo et al., 1991; McCaffrey et al., 1996), while others observed no interaction between these polymers (Roy et al., 1978; Wu et al., 1993). The pyrolytic polystyrene degradation rate was significantly enhanced in the presence of poly(methyl acrylate) and poly(butyl acrylate) at 430 °C (Gardner et al., 1993). Richards and Salter (1964), on the other hand, observed that the rate of polystyrene degradation decreased with increasing molecular weight (MW) of added PAMS. These reports suggest the need for an analysis of the underlying reaction mechanisms.

Degradation of polymers in solution has been proposed to ameliorate problems encountered in commercial applications (Sato et al., 1990), and several studies have been reported (Murakata et al., 1993; Madras et al., 1996c; Wang et al., 1995; Madras et al., 1996a; Madras et al., 1996b). No studies on the degradation of polymer mixtures in solution, however, have been published.

Experiments. The HPLC (Hewlett-Packard 1050) system consists of a 100 μ L sample loop, a gradient pump, and an on-line variable wavelength ultraviolet (UV) detector. Three PLgel columns (Polymer Lab Inc.) (300 mm x 7.5 mm) packed with cross-linked poly(styrene-divinyl benzene) with pore sizes of 100, 500, and 10,000 Å are used in series. Tetrahydrofuran (HPLC grade, Fisher Chemicals) was pumped at a constant flow rate of 1.00 mL/min. Narrow MW polystyrene standards of MW 162 to 0.93 million (Polymer Lab and Aldrich Chemicals) were used to obtain the calibration curve of retention time versus MW, which was stable during the period of the experiments. The calibration curve, modeled as a second-order polynomial, indicates a higher accuracy in the measurement of lower MW polymers.

The thermal decomposition of polystyrene in mineral oil was conducted in a 100 mL flask equipped with a reflux condenser to ensure the condensation and retention of volatiles. To observe

a significant effect of PAMS on the conversion, polystyrene of high MW was chosen. 60 mL of mineral oil (Fisher Chemicals) was heated to 275 °C, and various amounts (0 - 0.60 g) of monodisperse PAMS (MW = 11,000, Scientific Polymer Products), and 0.12 g of monodisperse polystyrene (MW = 330,000, Aldrich Chemicals) were added. The temperature of the solution was measured with a Type K thermocouple (Fisher Chemicals) and controlled within ± 1 °C by a Omega CN-2042 temperature controller. Samples of 1.0 mL were taken at 15 minute intervals and dissolved in 1.0 mL of tetrahydrofuran (HPLC grade, Fisher Chemicals). The chromatograph obtained by injecting 100 μ L of this solution into the HPLC-GPC system was converted to MWD. The peaks of the reacted polystyrene, PAMS, and the oligomers were distinct, so that moments could be calculated by numerical integration. Because the solvent mineral oil is UV invisible, its MWD was determined with a refractive index (RI) detector. No change in the MWD of mineral oil was observed when the oil was heated for 3 hours at 275 °C without polystyrene.

Model. The proposed scheme, based on the Rice-Herzfeld concept (Nigam et al., 1994) of chain reactions, includes the important elementary steps involving radicals. The degradation rate of polymer A undergoing random-chain scission is influenced by polymer B undergoing chain-end scission. We represent the reacting polymer A and its radicals as $P_A(x)$ and $R^*(x)$ and their MWDs as $p_A(x,t)$ and $r(x,t)$, respectively, where x represents the continuous variable, MW. As the polymer reactants and random scission products are not distinguished in the distribution kinetics model, a single MWD, $p_A(x,t)$, represents the polymer in the mixture at any time, t . The initiation-termination reactions are represented as

where $\rightleftharpoons$ represents a reversible reaction. The reversible hydrogen abstraction process is

The depropagation chain reaction is

The polymer B, the chain-end radical, the specific radical, and the specific product are represented as $P_B(x)$, $R_c^*(x)$, $R_s^*(x)$, $Q_s(x_s)$, respectively, and their corresponding MWDs as $p_B(x,t)$, $r_c(x,t)$, $r_s(x,t)$ and $q_s(x_s,t)$. The formation of chain-end radicals by a reversible random-scission initiation-termination reaction is

Hydrogen abstraction by the chain-end radical is considered reversible.

The chain-end radical can undergo radical isomerization via a cyclic transition state to form a specific radical,

The depropagation reaction yields the specific product and a chain-end radical from a specific radical,

where x_s is the MW of the specific product.

The interaction of the two degrading polymers is through hydrogen abstraction (McCaffrey et al., 1996) represented as a reversible disproportionation reaction. The end radical of polymer B combines with polymer A to form an intermediate radical complex that undergoes transformation to polymer B and a radical of polymer A,

Including the intermediate complex, R_i^* , facilitates the formulation of the population balance

equations for the reversible disproportionation. If R_i^* is ignored in equation 1.8, the forward and reverse rate coefficients would be k_d and k_D , respectively.

With the aid of Table 1, the rate expressions and moments can be formulated. Based on LCA, k_f , k_{fs} , k_t and k_{ts} are set to zero. The zeroth moments for the polymer, radicals and the monomer, $p^{(0)}$, $r^{(0)}$, $q^{(0)}$ are defined as

$$p^{(0)}(t) = \int_0^\infty p(x,t) dx \quad (8.9)$$

$$r^{(0)}(t) = \int_0^\infty r(x,t) dx \quad (8.10)$$

$$q^{(0)}(t) = \int_0^\infty q(x,t) dx \quad (8.11)$$

The initial conditions for moments are

$$P_B^{(0)}(t=0) = P_{B0}^{(0)}, P_A^{(0)}(t=0) = P_{A0}^{(0)} \text{ and } r^{(0)}(t=0) = 0 \quad (8.12)$$

When QSSA holds,

$$dr^{(0)}/dt = dr_s^{(0)}/dt = dr_c^{(0)}/dt = dr_i^{(0)}/dt = 0 \quad (8.13)$$

Algebraic manipulations yield

$$P_A^{(0)}(t) = P_{A0}^{(0)} \exp(k_r t) \quad (8.14)$$

and a plot of $\ln(p^{(0)}/p_0^{(0)})$ is linear in time with slope k_r ,

$$k_r = (2 k_b k_h / (k_d p_{B0}^{(0)})) + k_b (k_{he} + k_h) / k_H \quad (8.15)$$

The molar concentration is related to the mass concentration, $p^{(1)} = M_n p^{(0)}$, by the average MW, M_n .

The proposed mechanism represents the interaction of radicals of two reacting polymers and shows how the polymer undergoing chain-end scission affects the degradation rate of the polymer undergoing random-chain scission. The degradation rate coefficient is a function of the added polymer concentration, and also depends on the temperature and pressure. This can explain the varied results found in experiments for degradation rates in polymer mixtures.

Results. We have measured the influence of PAMS mass concentration on polystyrene degradation at 275 °C. Because polystyrene degrades by random-chain scission and PAMS degrades by chain-end scission, the polystyrene degradation rate is given by Eqs 8.14 and 8.15. The random-scission degradation rate coefficient, k_r , was determined from the experimental data by analyzing the time dependence of the polymer-mixture MWDs. Because the mass of specific products formed by polystyrene chain-end scission at 275 °C for 10 hours is less than 2% (Madras et al., 1996c), we considered that polystyrene degrades solely by random-chain scission.

Polystyrene degrades rapidly at low reaction times due to weak links in the polymer chain caused by side-group asymmetry or chain-branching (Chiantore et al., 1981; Madras et al., 1996c). As our earlier work demonstrated, the weak and strong links in polystyrene can be represented by additive distributions, so that the total molar concentration, $p_{A_{tot}}^{(0)}$, of the polymer is the sum of the molar concentrations of the weak, $p_{A_w}^{(0)}$, and strong links, $p_A^{(0)}$ (Madras et al., 1996c). As the weak link concentration is approximately two orders of magnitude smaller than the strong link concentration, only the random rate coefficients of strong links are examined in this study. The initial molar concentration of the strong links in polystyrene, $p_{A0}^{(0)}$, is determined from the intercept of the regressed line of the $p_{A_{tot}}^{(0)}/p_{A_{tot}0}^{(0)}$ data for $t \geq 45$ minutes. The slopes, corresponding to the rate coefficient for random scission, k_r , are determined from the plot of $\ln(p_A^{(0)}/p_{A0}^{(0)})$ versus time, as given by Eq 8.14. Madras et al. (1997) show how data are analyzed when the polystyrene degradation rate coefficient is a function of MW, i.e., $k_r(x)$. Equation 8.15 explains how the polystyrene degradation rate coefficient depends on PAMS concentration. The polystyrene degradation rate coefficient, k_r , decreases with increasing PAMS mass (or molar) concentration. This is consistent with the experimental data.

The hypothesized interaction of the degrading polymers is through the free radicals and their rates of hydrogen abstraction. When $k_d = k_D = 0$, the two polymers react independently and the moment equations are identical to those derived for a single polymer undergoing chain-end scission or random-chain scission (Madras and McCoy, 1997). The rate coefficient for random-chain scission of polystyrene is a function of the PAMS mixture concentration through the fundamental radical rate parameters, k_b , k_h , k_{he} , k_d , k_H , and the initial number-average molecular weight of PAMS (Eq 8.15). The addition of PAMS inhibits the random-chain scission of polystyrene, similar to the effect on hydrogen-donors on the degradation of polystyrene (Madras and McCoy, 1997).

Experimental results reported here and in the literature, as well as model predictions in the current study, suggest that mixtures of different materials can have a range of effects on polymer degradation. One infers that "dirty" plastics will react in different ways depending on the particular impurity mix. It is possible some metallic additives will have a catalytic (or possibly a catalytic deactivating) influence. Many biomass additives will be stable at temperatures in our experiments.

The present results for solvent and polymer additives illustrate the range of behavior that should be expected.

9. Concluding Remarks

This report outlines a distribution kinetics approach to macromolecular reactions that has been applied to several processes. The broad applicability is based on the range of phenomena that can be represented and interpreted:

- random scission (or scission biased toward midchain scission) and/or addition (step polymerization and crosslinking),
- single monomer scission (i.e., chain-end scission) and/or addition (chain-end polymerization),
- reversible scission kinetics and in general the approach to equilibrium,
- radical (or catalyzed ion) reaction mechanisms,
- multiphase behavior, including liquid-vapor and solid-liquid mass transfer.

We have described experiments for chemical models that simulate depolymerization of coal. Although the approach has been exceptionally successful for the model macromolecular systems, a similar treatment to explicate coal liquefaction will require more investigation. Development of a novel chemical reaction engineering analysis, based on distribution kinetics, was a major accomplishment of the current research. This approach, was successful in quantitatively describing experiments on several different polymers. The theoretical work involved distribution kinetics to develop chemical reaction models for macromolecular reactions. Experimentally, thermolytic degradation (liquefaction) of macromolecular compounds was investigated with different solvents, including hydrogen-donor and nondonor solvents. Model macromolecular compounds provided a means to study the reaction kinetics of complex materials undergoing molecular cracking for fuel and feedstock processing. Molecular-weight distributions (MWDs) and their moments were measured by HPLC-GPC. Experimental data were interpreted with population-balance equations based on continuous-distribution kinetics, and rate coefficients were determined for chain-end and random scission degradation processes. Accompanied by this mathematical analysis, the experimental studies have revealed essential features of polymer chain-scission kinetics.

Macromolecular systems, either in solution or solid form (e.g., coal), typically contain a large number of homologous molecules spanning a MW range. The methods of MW determination and of polymer synthesis and purification usually provide MWDs, such as determined by GPC, that are relatively smooth functions of MW. Integrals over MW are well-defined for such MWDs, so that MW moments can be readily calculated. Polymer MWDs determined by GPC are typically accurate at high MW, ensuring that higher moments are reliable. This contrasts to dynamic response experiments, where temporal moments can be compromised by long tail effects. In the event that low MW monomers or oligomers are present, the MWD can be represented as a semi-continuous function. This is the case when chain-end scission yields specific products.

Continuous-distribution kinetics provides the basis for interpretation of the experimental observations. As the reactions for polymer degradation are chain-scission events, the stoichiometry can be represented in terms of integrals over the polymer MWD. For batch reactions, the population balance equations are integrodifferential equations that can be solved by a moment procedure. Ordinary differential equations for the moments are readily solved for the products of random and chain-end scission. To determine rate coefficients, only zeroth moments are required.

10. References Cited

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