July 26, 1996

file: 94204T07.PDF

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

Quarterly Report 7 .

Reporting Period: April-June, 1996

Principal Investigators: Ben J. McCoy, J.M. Smith

Students: Giridhar Madras, Yoichi Kodera

July 26, 1996

GRANT NO. DOE DE-FG22-94PC94204

**Department of Chemical Engineering and Materials Science
University of California, Davis, CA 95616. (916) 752-1435**

PERIOD OF GRANT AWARD: August, 1994 - August, 1997

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DTIC QUALITY INSPECTED 4

19980313 126

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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

Quarterly Report 7

Reporting Period: April-June, 1996

Principal Investigators: Ben J. McCoy, J.M. Smith

Students: Giridhar Madras, Yoichi Kodera

July 26, 1996

GRANT NO. DOE DE-FG22-94PC94204

**Department of Chemical Engineering and Materials Science
University of California, Davis, CA 95616. (916) 752-1435**

PERIOD OF GRANT AWARD: August, 1994 - August, 1997

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

96 SEP - 1 AM 10:50

DOE/PC94204

Executive Summary

This quarterly report relates our recent progress toward the overall objective of understanding the supercritical fluid extraction of hydrocarbons from coal. Our approach is to simulate coal as a high molecular-weight polymeric material and study the degradation of polymers under various conditions, including temperature, pressure, and solvent. The degradation of such macromolecules is applicable to the decomposition (depolymerization) of the coal network. Another potential application of this research is to the recycling of plastics.

Our recent research involved the study of the oxidative degradation of polystyrene in trichlorobenzene using *tert*-butyl peroxide. A continuous-mixture kinetics model for the rate of polymer degradation and peroxide consumption was developed to describe the temporal behavior of the molecular-weight distributions and its various moments. Based on this work, a research paper entitled "Oxidative Degradation Kinetics of Polystyrene in Solution," will be submitted to the journal, *Chemical Engineering Science*. A draft copy is attached as Appendix A.

Polyethylene pyrolysis and a new approach to its kinetics and mechanism have been examined. Linear polyethylene was thermally treated in a batch reactor at 390–450 °C for 0.5–4 h under a nitrogen atmosphere at 1 atm. The reaction product was a mixture of gas, liquid, and wax, which were analyzed by GC and HPLC-GPC to obtain the time dependence of the molecular-weight distributions of the reactant polymer and its products. A new method of kinetic analysis of pyrolysis based on continuous-kinetics theory is being developed for the evaluation of optimum reaction conditions for polyethylene conversion. This model is different from the conventional discrete or lumped kinetics models, because it provides for a more detailed mechanism of polymer decomposition involving (1) degradation by random scission, specific scission, chain-end scission, and mid-chain scission, (2) chain growth by radical addition to an olefin and by radical coupling, (3) isomerization by disproportionation of two radicals. We formulate each polymer decomposition process into moment equations derived from population balance equations. These equations predict fates of various species such as alkanes, alkenes, and radicals. Based on this work, a research paper is currently under preparation. An abstract of the manuscript is attached as Appendix B.

Our presentation for the Fifth World Congress of Chemical Engineering entitled, "Polymer Thermolysis for Plastics Recycling," was given on July 17. The extended abstract that was published in the Proceedings is attached (Appendix C).

Appendix A.**OXIDATIVE DEGRADATION KINETICS
OF POLYSTYRENE IN SOLUTION*****DRAFT Manuscript******Giridhar Madras and Benjamin J. McCoy***

Department of Chemical Engineering and Materials Science
University of California, Davis, CA 95616
Phone: (916) 752-1435 Fax: (916) 752-1031
bjmccoy@ucdavis.edu.

Abstract

Polymer degradation is an example of fragmentation of macromolecules of distributed molecular weight (MW). The kinetics of polystyrene (PS) degradation by di-tert-butyl peroxide was investigated in the stirred liquid phase at 428 K in presence of oxygen with trichlorobenzene as the solvent. Peroxide was consumed by the PS decomposition reaction and by an independent reaction with dissolved oxygen. Gel permeation chromatography (GPC) showed that the initial PS molar molecular weight distribution (MWD) was exponential in MW. After the peroxide was depleted (in less than 15 min), GPC analysis of polymer samples showed that the final MWD was also exponential in MW for all experimental conditions. The initial peroxide concentration, 5 to 40 g/L, and polymer concentration, 12.5 to 50 g/L, affected the reaction rates and hence the final MWDs. A continuous-kinetics model for polymer fragmentation and simultaneous peroxide reaction can describe the temporal behavior of the MWD and its moments. To be consistent with the experimental data, the model incorporates purely random chain scission and a scission rate constant that increases linearly with MW. Moment analysis provides estimates of the rate constants for the consumption of peroxide and for decomposition of the polymer.

Introduction

Decomposition of large molecules is an important practical topic in polymer science (Cameron and MacCallum, 1967; Reich and Stivala, 1971; Jellinek, 1983 or 55?), and is also applicable to basic phenomena in coal or biomass liquefaction, gasification, and combustion. Polymer degradation can be used in conjunction with gas chromatography to characterize polymeric structure (Flynn and Florin, 1985), and has also been proposed for large-scale plastics recycling (Miller, 1994). Degrading polymer by adding peroxide is a common manufacturing technique (Curry and Jackson, 1988). For example, the controlled addition of peroxide to polypropylene yields a higher melt flow index and superior processing properties (Bourland, 1987) as a result of chain scission leading to a narrower molecular weight distribution (Green and Prieski, 1964). Rocha et al. (1995) measured the effect of peroxide concentration on properties of degraded polypropylene. Kamiya and Niki (1978), in a review of oxidative degradation, commented that kinetics and mechanism are complex and results have been contradictory. Reich and Stivala (1971) discussed various schemes to interpret the complexities. Most investigations of polymer degradation have focused on analysis of experimental data by lumped, or MW-averaged, kinetics. Experimental data and mathematical models for chain scission kinetics and MWD dynamics are needed for a more complete understanding of this important fragmentation process. A promising approach is continuous-mixture kinetics, which can provide a detailed, quantitative description of polymeric processes.

The polymer degradation mechanism depends on molecular structure and experimental conditions. Two extremes of chain backbone scission are possible, pure random scission and pure depolymerization. Random-scission degradation of a polymer occurs by bond scission at any position along the chain backbone. Midpoint chain scission, observed in ultrasonic degradation of polymers (Price and Smith, 1991, 1993), divides the chain into two equal length segments. Depolymerization of homopolymers by scission at the chain end yields monomers. Investigations by Montgomery and Winkler (1950) on the oxidative degradation of polystyrene (PS) in solution by benozyl peroxide showed that degradation proceeded by random scission of polymer chains.

Spodheim et al. (1948) observed that the relationship between viscosity and average molecular weight remained the same during the degradation, indicating that neither repolymerization nor cross-linking took place during the degradation. Unlike other polymer degradation processes that may involve chain-end scission or repolymerization, oxidative degradation is particularly interesting as a fragmentation process subject solely to random chain scission.

Jellinek (1955) proposed that oxidative degradation of PS occurs in four steps. Reaction A is an initiation process transforming peroxide into radicals, B is a propagation step combining polymer and radicals, C is the chain scission, and D is a termination step that neutralizes peroxide radicals with oxygen. Reactions A and B are considered to be rapid and thus do not influence the overall rate of degradation (Griffiths and Phillips, 1994; Seres et al., 1994). Both reactions C and D consume peroxide and occur in parallel with rate constants k_1 and k_2 , respectively. As shown below, the experimental observations are explained by a model with first-order random chain scission and a (Langmuir-type) rate expression for peroxide loss that is first-order at low and zero-order at high peroxide concentrations.

Polymer chain degradation can be interpreted as a fragmentation process (Ballauff and Wolf, 1981; Ziff and McGrady, 1986; McCoy and Wang, 1995) with temporal-spatial dynamics governed by a population balance equation for the (discrete or continuous) MWD. Products of binary fragmentation are distributed according to a stoichiometric coefficient (fragmentation kernel). This coefficient has been formulated for continuous-kinetics chain scission occurring randomly along the chain, at the chain midpoint, and for the range of intermediate scission events (McCoy and Wang, 1995). The fragmentation kernel for specific scission products (chain-end scission to produce monomers, dimers, trimers, and other oligomers) is closely related to the expression for midpoint scission. Ternary and higher-order fragmentation processes can be represented as sequences of binary scissions (Wang and McCoy, 1995). We have previously developed continuous-kinetics interpretations for experimental studies of degradation by simultaneous midchain scission and chain-end scission for poly(styrene allyl alcohol) (Wang et al., 1995; Madras et al., 1995) and by chain-end scission for poly(methyl methacrylate) (Madras et al.,

1996b) and for poly(α -methyl styrene) (Madras et al., 1996). GPC analysis shows these polymers are mixtures of large numbers of different sized molecules, so that the MW can be considered a continuous variable, x , along with time, t , in the molar MWD, $p(x,t)$. The polymer MWDs were reasonably well represented as gamma distributions (Madras et al., 1995b). Continuous-mixture models have also been applied to the kinetics of coal liquefaction (Wang et al., 1994), catalyst deactivation (Subramaniam and McCoy, 1994), pyrolysis (McCoy (1996), and reversible oligomerization (McCoy, 1993). The capability of continuous-kinetics models to explain solubilized polymer degradation kinetics motivated us to reconsider oxidative thermolysis phenomena.

The objective of the present paper is to study the oxidative degradation of PS in trichlorobenzene solution at 428 K at various concentrations of polymer and of di-tert-butyl peroxide. Experimental data indicate that the peroxide is consumed by a Langmuir-type reaction in parallel with the polymer chain scission. We propose a continuous-kinetics model for the degradation of PS that satisfactorily accounts for the experimental observations. The MWDs are analyzed with the model to obtain fundamental rate data. The continuous-kinetics concept provides an effective and straightforward procedure to describe or predict the change in MWDs for degradation of a polymer containing molecules of different MWs.

Experimental Procedure

The untreated polymer MWD was determined by dissolving 0.200 g of PS (Polysciences, Inc.) in 100 mL of tetrahydrofuran (THF) (Fisher Scientific) and analyzing 100 μ L of this sample by 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 in-series columns of cross-linked poly(styrene-divinyl benzene) with pore sizes of 100, 500, and 10^4 Å provided efficient separation and resolution of the peaks. Various wavelengths were investigated in the range of 200-330 nm, and 254 nm was chosen for maximum absorbance by PS. A calibration curve of retention time versus MW was constructed with PS

standards (Polymer Lab Inc and Aldrich Chemicals) of MW ranging from 162 to 1.5 million and styrene dissolved in THF.

As in earlier degradation experiments (Wang et al., 1995; Madras et al., 1996a) it is necessary to pretreat the polymer to provide a well-characterized initial MWD. The mass MWD of the raw PS indicates a number-average MW of 45,000 and a weight-average MW of 200,000. The peaks in the lower MW range, which would interfere with the determination of degradation products, were eliminated by fractionation (Kamide and Matsuda, 1989). During continuous stirring, 50 g of raw PS was partially dissolved in 500 mL of toluene at 303 K, and 750 mL of the precipitating agent, n-butanol, slowly added until 70% of the polymer was precipitated. The precipitated polymer was dried to constant weight in a 383 K oven, dissolved in trichlorobenzene (Fisher Chemicals), and stored under nitrogen in a sealed bottle. The MWD of the pretreated PS shows a single peak. The MWDs for reacted polymer were shifted strongly to lower MWs for reaction times of 15 min or less.

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 molar concentration of polymer in the MW range $(x, x + dx)$ is $p(x,t)dx$. Molar MWDs for the reaction conditions were calculated from the mass MWDs and plotted as $\ln(\text{MWD})$ vs MW for the pretreated and reacted polymer. The straight lines on the semilog plots indicate that all the MWDs are exponential, i.e., the special case of the gamma MWD when $\alpha = 1$ and $p(x=0) = 0$ (Wang et al., 1995). For the initial pretreated PS MWD, we can write

$$p_o(x) = [p_o^{(0)}/\beta_o] \exp(-x/\beta_o) \quad (1)$$

where the subscript o indicates the initial value. The MW moments of the molar MWD, $p(x,t)$, are defined by $p^{(n)}(t) = \int_0^\infty x^n p(x,t) dx$, and 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 the number- and weight-average MWs defined as

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

For exponential MWDs, $M_n = \beta$ and $M_w = 2\beta$, thus, for the MWD of the pretreated polymer, $M_{no} = 95,000$ and $M_{wo} = 190,000$. Exponential MWDs are characterized by a polydispersity equal to

two, $D = p^{(2)}p^{(0)}/[p^{(1)}]^2 = M_w/M_n = 2$.

The degradation of the treated PS (12.5-50 g/L, Table 1) dissolved in trichlorobenzene was conducted in an open flask. A known amount (5-40 g/L, Table 1) of di-tert-butyl peroxide (Aldrich Chemicals) was added to this solution at 428 K, and 1 mL samples were taken for GPC analysis every 15 minutes. In the absence of peroxide no PS degradation occurred at this temperature. Reaction mixture samples of 100 μ L were each dissolved in 1 ml of THF (Fisher Scientific) and 100 μ L of this solution was injected into the HPLC-GPC. MWD results showed no evidence of repolymerizing or cross-linking reactions, which would be indicated by broadening of the MWD due to formation of high MW compounds. Specific products from chain-end scission (depolymerization), which would be indicated by separate low-MW peaks, were not observed. We did not attempt to quench the reaction before peroxide was depleted to determine the time-dependence of the MWD evolution. The final MWD, when peroxide is totally consumed, is sufficient to evaluate rate constants. If values of the rate constants are known, the fragmentation model can then be used to predict the MWD evolution in time.

Results

MWDs of the reacted polymer are exponential distributions that shift to lower MW. All the MWD data collapse approximately (within experimental error) onto a single line when $\ln[p(x)\beta/p^{(0)}]$ is plotted versus x/β . Data scatter is higher at the high MW range of the MWD. Calculations for molar MWDs show that the first moment of the degraded polymer (the zero moment of the mass MWD determined by numerical integration) is the same as that of the unreacted polymer, confirming the mass balance. The GPC provides, in addition to the MWD, values of M_n and M_w , defined in Eq. 2. Knowing that the initial mass concentration of PS is constant with time, $p_0^{(1)} = p^{(1)}(t)$, allows calculation of the zero and second moments, $p^{(0)}(t)$ and $p^{(2)}(t)$.

A mathematical description of the dynamics of the reacting system must account (i) for the decrease of the peroxide concentration, $c(t)$, with time due to consumption by reaction with oxygen and by reaction with the polymer, and (ii) for the PS decomposition that shifts the polymer MWD,

$p(x,t)$. The population balance equation governing the time evolution of the MWD in the batch reactor is expressed (Aris and Gavalas, 1966; Wang et al., 1995) in terms of a stoichiometric coefficient, $\Omega(x,x')$, for the fragmentation $x' \rightarrow x + (x' - x)$,

$$\partial p(x,t)/\partial t = -k_1(x) c(t) p(x,t) + 2 c(t) \int_x^\infty k_1(x') \Omega(x,x') p(x',t) dx' \quad (3)$$

Various reaction rate expressions were tried for the peroxide deactivation by combination with oxygen. A Langmuir-type rate expression was consistent with the dependence on the peroxide concentration. This type of rate expression (first-order in oxygen at low concentrations and zero-order at high concentrations) was used successfully to model the photo-oxidation of polyolefins in presence of oxygen (de Bruin, 1996; Jansen, 1994). The mass balance for the peroxide is thus

$$dc(t)/dt = -k_2 c(t)/[K + c(t)] - c(t) \int_0^\infty k_1(x') p(x',t) dx' \quad (4)$$

where the integration ensures that a polymer of *any* MW can undergo chain scission and thus consume peroxide. The expressions that represent the experimental results are a purely random (independent of x) fragmentation kernel (McCoy and Wang, 1994; Aris and Gavalas, 1966) and a scission rate constant linear in MW,

$$\Omega(x,x') = 1/x' \text{ and } k_1(x) = \kappa x \quad (5)$$

Other forms for $k_1(x)$ lead to results that do not quantitatively simulate the observations. The peroxide concentration thus obeys the differential equation,

$$dc/dt = -c [k_2/(K + c) + \kappa p^{(1)}] \quad (6)$$

whose solution with the initial condition for peroxide concentration, $c(t=0) = c_0$, is

$$\exp(-bk_2t) = (c/c_0)^{bK/(1+bK)} [(1 + bK + bc)/(1 + bK + bc_0)]^{1/(1+bK)} \quad (7)$$

where $b = \kappa p^{(1)}/k_2$ is invariant by virtue of the constant mass concentration, $p^{(1)} = p_0^{(1)}$.

Obviously, Eq 6 can be altered to accommodate other rate expressions for the peroxide deactivation, and then integrated to get an equation replacing Eq 7 for $c(t)$.

A mathematical solution for Eq. (3) is facilitated by defining a new variable, θ , to replace time:

$$d\theta = \kappa c dt \quad (8)$$

This expression can be integrated by parts with the initial condition $\theta(t=0) = 0$ and the final value

$$\theta(t \rightarrow \infty) = \theta_m,$$

$$\theta_m = \kappa \int_0^{c_0} t \, dc = c_0/p^{(1)} - [k_2 / (\kappa p_0^{(1)2})] \ln B \quad (9)$$

where $B = (1 + bK + bc_0)/(1 + bK)$. Other forms for the peroxide deactivation rate expression, easily integrated by computer algebra software, lead to relations for θ_m different from Eq 9.

Next, the differential $d\theta$ can be substituted to simplify Eq. (3),

$$dp/d\theta = -x p(x, \theta) + 2 \int_x^\infty p(x', \theta) \, dx' \quad (10)$$

Differentiating Eq. (10) with respect to x and applying Laplace transformation (Aris and Gavalas, 1966) defined by

$$p(x) = \int_0^\infty \exp(-s\theta) p(x, \theta) \, d\theta \quad (11)$$

yield

$$(s + x) dp/dx + 3p = dp_0/dx \quad (12)$$

In terms of the integrating factor $\phi(x) = (s + x)^3$ the solution is

$$p = (1/\phi) \int_x^\infty dx' (dp_0/dx') \phi(x') / (s + x') \quad (13)$$

After integration and inversion of the Laplace transform, the MWD is found to be

$$p(x, t) = [p^{(0)} / \beta] \exp(-x/\beta) \quad (14)$$

where $\beta = M_n$ is given by

$$\beta = \beta_0 / (1 + \beta_0 \theta) \quad (15)$$

If $p^{(0)}(t)$ and $\beta(t)$ are substituted with their values at $t = 0$, the MWD is identical to the initial MWD, Eq. (1). This demonstrates that the MWD evolves in time (i.e., θ) as a self-similar exponential distribution in the scaled dimensionless variable, x/β . The first few MW moments are given by

$$p^{(0)} = p_0^{(0)} (1 + \beta_0 \theta) \quad (16)$$

$$p^{(1)} = p_0^{(1)} \quad (17)$$

$$p^{(2)} = 2 p^{(0)} \beta^2 \quad (18)$$

or in general,

$$p^{(n)}(t) = n! p^{(0)}(t) \beta^n \quad (19)$$

For all values of time, the number- and weight-MW averages are related by $M_n = M_w/2$, as experimentally observed for the initial and final exponential MWDs. The mass MWD, $x p(x,t)$, evolves from its initial value to the final value when $\theta = \theta_m$. Of course, the functional form of θ_m is influenced by the peroxide deactivation rate expression.

Because a moment solution of the governing integro-differential equation suffices to interpret our experiments, we next develop moment expressions directly by operating on Eq. (10) with $\int_0^\infty x^n [] dx$ to derive the governing equation for the moments,

$$dp^{(n)} / d\theta = - p^{(n+1)} (n - 1)/(n + 1) \quad (20)$$

The first moment ($n = 1$), or mass concentration, is obviously constant with θ , but the time derivative of the second moment depends on the third moment, indicating a closure problem. A solution to Eq. (20) can be found, however, to be

$$p^{(n)} = n! p^{(1)} \beta^{n-1} \quad (21)$$

where β satisfies $d\beta/\beta^2 = - d\theta$ and thus has the form of Eq. (15). The resulting moment expressions are identical to those, Eq. (19), derived for $p(x,t)$.

In the absence of oxidizer, polymers may undergo chain scission if the temperature is high enough (greater than the temperature of the present experiments). For the special case of nonoxidative thermolytic degradation by random chain scission (no chain-end scission) and with rate coefficient κx , the variable θ is simply κt , and an initial exponential MWD would proceed via exponential MWDs to a delta function at $x = 0$ in the $t \rightarrow \infty$ limit. For PS, however, the thermolysis is not so simple, as chain-end depolymerization to specific products (e.g., styrene) occurs in addition to random scission.

The reaction ends when peroxide is depleted, $c(t \rightarrow \infty) = 0$, and according to Eq. 15, θ becomes

$$\theta_m = 1/\beta_m - 1/\beta_o \quad (22)$$

where β_o and β_m are the initial and final values of M_n . The dependence of θ_m on c_o is a nonlinear increasing function. The effect of initial polymer mass concentration, $p_o^{(1)}$, is conveniently plotted as $1/\theta_m$ versus $p_o^{(1)}$. The experimental error, estimated as the standard deviation for triplicate

runs, was 5 percent. The values of the three parameters, determined by the Marquardt-Levenburg method (Press et al., 1988), that provide the best fit to the data will be reported later. These values determined by the nonlinear curve-fit minimize the average squared deviation between predicted and experimental points.

To illustrate the evolution of a MWD we evaluated β as a function of time (Eqs. 15 and 8) by numerical integration of Eq. 7, and substituted into the mass distribution based on Eq. 14,

$$xp(x,t) = p^{(0)} e^{-x/\beta} x/\beta \quad (23)$$

The initial values chosen were $c_0 = 0.272$ mol/L and $p_0^{(1)} = 12.5$ g/L, and rate parameter values were those listed above. The MWD changes until all peroxide is consumed and the final mass distribution is reached. Despite the complexities of the reaction mechanism, the model thus allows prediction of the MWD evolution.

Discussion and Concluding Remarks

The oxidative thermolysis of polystyrene manifests interesting and unusual behavior compared to other polymer degradation processes. The outstanding features of the experimental results are as follows: (i) MWDs are exponential in MW before and after oxidative degradation, and thus the polydispersity is always two, (ii) the effect of initial peroxide concentration on average MW (M_n) is nonlinear with decreasing slope, (iii) the effect of initial polymer mass concentration on M_n is nonlinear with increasing slope.

The proposed continuous-kinetics model can be solved to yield easily computed equations that successfully explain the experimental results. The governing population balance equation for the MWD provides differential equations for the moment dynamics. By accounting for the shape characteristics of the MWD, the MW moments allow a more thorough understanding than is possible by conventional lumped kinetics. The deactivation of peroxide by oxygen requires a Langmuir-type rate expression to interpret quantitatively the effect of the initial peroxide concentration. Such rate expressions can be derived for a mechanism in which the reactants (peroxide and oxygen) form an intermediate complex by an equilibrated reversible addition reaction. The complex subsequently reacts irreversibly to form final products,

The thermal decomposition of hydroperoxide, for example, proceeds by a hydrogen-bonded transition state (Kamiya and Niki, 1978). Polymer decomposition is first-order in polymer concentration and in peroxide concentration (i.e., second-order overall).

The data are interpreted by assuming that the rate coefficient for polymer chain scission increases linearly with MW. This form of the rate coefficient, $k(x) = \kappa x$, leads directly to the self-similar exponential MWDs observed in the oxidative thermolysis experiments. Oxidative degradation of polymer drives the reaction to proceed much faster than our earlier experiments with purely thermal degradation, which were satisfactorily explained with rate coefficients independent of MW. The strong shift of MWD caused by a higher reactivity made necessary the more detailed MW dependence of the rate coefficient. Previously, an average rate coefficient was sufficient to describe the small shifts of MWD by midchain scission and production of low MW products by chain-end scission.

Assuming that chain scission occurs randomly along the PS backbone, and thus $\Omega(x, x') = 1/x'$, was also justified by the experimental observations. Thermal degradation at higher temperatures may involve not only random chain scission, but also chain-end scission, hydrogen abstraction to quench free radicals, radical addition to polymer chains, and other complexities. Such involved mechanistic steps are most straightforwardly described by average rate coefficients independent of MW, although it is conceivable that a judicious experimental plan may be possible that will untangle these complications. Oxidative thermolysis, occurring at substantially lower temperatures than thermal degradation, apparently follows a simpler mechanism, thus allowing a model based on purely random chain scission and a k_x rate coefficient to describe the observations.

Nomenclature

b = $\kappa p_0^{(1)}/k_2$ parameter, L/mol

c oxidizer concentration, mol/L

K		coefficient in oxidizer-loss rate expression, mol/L
k_1	$= \kappa x,$	rate coefficient for polymer chain scission, L/mol.min
k_2		rate coefficient in oxidizer-loss rate expression, mol/L.min
M_n	$= p^{(1)}/p^{(0)}$	number-average molecular weight, g/mol
M_w	$= p^{(2)}/p^{(1)}$	weight-average molecular weight, g/mol
p		polymer molecular-weight distribution, (mol/L)/(g/mol)
$p^{(n)}$		nth polymer molecular-weight moment, (mol/L)(g/mol) ⁿ
$p^{(1)}$	$= p_o^{(1)}$	polymer mass concentration, g/L
β	$= M_n$	parameter in the exponential MWD, g/mol
θ		substitute variable for time ($d\theta = \kappa c dt$), mol/g
κ		rate coefficient for chain scission, L/g.min

Subscripts

o	initial value
m	final value (when oxidizer is totally consumed)

Table 1. Results for MWDs determined by GPC analysis of oxidatively degraded PS in solution at 428 K: c_0 is initial molar concentration of peroxide, $p^{(1)}$ is constant mass concentration of PS, M_n is number-average MW of degraded PS, and M_w is weight-average MW of PS.

c_0 , mol/L	$p^{(1)}$, g/L	M_n , g/mol	M_w , g/mol
0	12.5	95,000	190,000
0.0068	12.5	78,000	156,000
0.034	12.5	61,000	122,000
0.068	12.5	50,000	100,000
0.136	12.5	25,000	50,000
0.205	12.5	14,000	28,000
0.272	12.5	6,500	13,000
0.342	12.5	4,500	9,000
0.272	0	0	0
0.272	12.5	6,500	13,000
0.272	25	18,000	36,000
0.272	50	36,000	72,000
0.272	100	39,500?	78,000?

Literature Cited

- Aris, R., G.R. Gavalas, "On the Theory of Reactions in Continuous Mixtures," *Phil. Trans. R. Soc. London A* **260**, 351 (1966).
- Ballauff, M., B.A. Wolf, "Degradation of Chain Molecules. 1. Exact Solution of the Kinetic Equations," *Macromolecules*, **14**, 654 (1981).
- Bourland, L., "Low MW polypropylenes: Homogenous Flow Modifiers for Conventional PP," *Polymer Preprints*, **28**, 189 (1987).
- Cameron, G.G., J.R. MacCallum, J. Macromol. Sci., Rev. Macromol. Chem., C1(2) 327 (1967).
- Curry, J., S. Jackson, "Free Radical Degradation of Polypropylene," *Chemical Engineering Progress*, **84**, 43 (1988).
- de Bruijn, J.C.M., " Degradation Profiles of Thick High-Density Polyethylene Samples after Outdoor and Artificial Weathering, " In *Polymer Durability*; Clough, R.L., Billingham, N.C., Gillen, K.T., eds; American Chemical Society, Washington D.C , 1996; pp 599-620.
- Flynn, J.H., R.E. Florin, "Degradation and Pyrolysis Mechanisms," In *Pyrolysis and GC in Polymer Analysis*; Leibman, S.A., Levy, E.S., eds; Marcel Dekker Inc., New York, 1985; pp 149-208.
- Green, R.G., E.T. Preiski, Process for degrading stereoregular polymers. U.S. Patent No.3, 144, 436 (1964).
- Griffiths, J.F., C.H. Phillips, "Experimental and Numerical Studies of the Combustion of Ditertiary Butyl Peroxide in the Presence of Oxygen in the Presence of Oxygen at Low Pressure in a Mechanically Stirred Closed Vessel," *Combustion and Flame*, **81**, 304 (1990).
- Jansen, K.M.B., "Analytical Approximation of Degradation Profiles in Polymer Products," *Poly. Eng. Sci.* **34**, 1610 (1994).
- Jellinek, H.H.G., *Degradation of Vinyl Polymers*, Academic Press, NY (1955).
- Kamide, K., Matsuda, S., In *Determination of Molecular Weight*, Cooper, A.R., Ed.; John Wiley & Sons, New York, 1989, p. 201.

- Kamiya, Y., Niki, E., "Oxidative Degradation," *In Aspects of Degradation and Stabilization of Polymers*, Jellinek, H.H.G., Ed.; Elsevier, New York, 1978.
- Madras, G., J.M. Smith, B.J. McCoy, "Effect of Tetralin on the Degradation of Polymer in Solution," *I&EC Research*. **34**, 4222 (1995).
- Madras, G., J.M. Smith, B.J. McCoy, "Thermal Degradation of Poly(α -Methylstyrene) in Solution," *Polymer Degradation and Stability*. (1996a); In Press.
- Madras, G., J.M. Smith, B.J. McCoy, "Degradation of Poly(Methyl Methacrylate) in Solution," *I&EC Research*. **35**, 1795 (1996b).
- McCoy, B.J., G. Madras, "Degradation Kinetics of Macromolecules in Solution : Dynamics of Molecular Weight Distributions," submitted (1996c).
- McCoy, B.J., "Continuous-Mixture Kinetics and Equilibrium for Reversible Oligomerization Reactions," *AIChE J.* **39**, 1827 (1993).
- McCoy, B.J., "Continuous Kinetics of Cracking Reactions: Thermolysis and Pyrolysis," *Chem. Eng. Sci.* **51**, 2903 (1996).
- McCoy, B.J., M. Wang, "Continuous-mixture fragmentation kinetics: Particle size reduction and molecular cracking," *Chem. Eng. Sci.* **49**, 3773 (1994).
- Miller, A. "Industry invests in reusing plastics," *Env. Sci. Tech.*, **28**, 16A (1994).
- Montgomery, D.S., C.A. Winkler, "The Degradation of Polystyrene," *Can. J. Research*, **B24**, 179 (1946).
- Price, G.J., P.F. Smith, "Ultrasonic Degradation of Polymer Solutions. 1. Polystyrene Revisited," *Polymer International* **24**, 159 (1991).
- Price, G.J., P.F. Smith, "Ultrasonic Degradation of Polymer Solutions: 2. The Effect of Temperature, Ultrasound Intensity and Dissolved Gases on Polystyrene in Toluene," *Polymer* **34**, 4111 (1993).
- Press, W.H., Flannery, B.P., Teukolsky, S.A., W.T. Vetterling *In Numerical Recipes in C, The Art of Scientific Computing*. Cambridge University Press, New York (1988).
- Reich, L.; Stivala, S.S. *Elements of Polymer Degradation*, McGraw-Hill, New York,

1971, p. 164.

Rocha, M.C.G., F.M.B. Coutinho, S.T. Balke, "A Study of Polypropylene Peroxide Promoted Degradation," *Polymer Testing*, **14**, 369 (1995).

Seres, L., Nacsa, A., N.L. Arthur, "Thermal Decomposition of Di-t-Butyl Peroxide in the Presence of $(\text{CH}_3)_2\text{C}=\text{CH}_2$," *Int. J. Chemical Kinetics.*, **26**, 227 (1994).

Spodheim, H.W., Bladgley, W.J., R.B. Mesrobian, "Polymerization-Degradation of Styrene in Solution," *J. Poly. Sci.* **3**, 410 (1948).

Subramaniam, B.; B.J. McCoy, "Catalyst Activity Maintenance or Decay--A Model for Formation and Desorption of Coke," *Ind. Eng. Chem. Res.*, **33**, 504 (1994).

Wang, M., C. Zhang, J.M. Smith, B.J. McCoy, "Continuous-Mixture Kinetics of Thermolytic Extraction of Coal in Supercritical Fluid," *AIChE J.* **40**, 131 (1994).

Wang, M., J.M. Smith, B.J. McCoy, "Continuous Kinetics for Thermal Degradation of Polymer in Solution," *AIChE J.* **41**, 1521 (1995).

Ziff, R.M., E.D. McGrady, "Kinetics of Polymer Degradation," *Macromolecules* **19**, 2513 (1986).

Acknowledgment

The financial support of Pittsburgh Energy Technology Center Grant No. DOE DE-FG22-94PC94204 and EPA Grant No. CR 822990-01-0 is gratefully acknowledged. Discussions with Professor J.M. Smith are appreciated.

Appendix B

Polymer Decomposition for Plastics Recycling

Yoichi Kodera, J. M. Smith, B. J. McCoy

Abstract

A potential method for plastics recycling is by polymer degradation to lower molecular-weight products that can serve as fuel or feedstock. We will describe experiments for the thermolytic decomposition of solubilized polyethylene with and without catalysis. Batch and flow reactors, designed to provide well-defined residence times, yield results for dense-phase (sub- or supercritical) decomposition reactions. HPLC gel permeation chromatography of the reactor effluent gives polymer molecular-weight distributions. These distributions are the basis for continuous-kinetics analysis of the fragmentation phenomena, which are random and chain-end scission events. Free-radical mechanisms for chain scission and addition reactions yield governing equations for the molecular-weight distributions that are solved by molecular-weight moment analysis.

Appendix C

Fifth World Congress of Chemical Engineering

July 26, 1996

Polymer Thermolysis for Plastics Recycling

Giridhar Madras, J.M. Smith, and Ben J. McCoy

Department of Chemical Engineering and Materials Science
University of California, Davis, CA 95616 Tel. (916) 752-6923
bjmccoy@ucdavis.edu

ABSTRACT

One approach to plastics recycling is the thermolytic degradation of polymer in solution to simpler molecules. We have investigated fundamental aspects of polymer thermolysis in a steady-state flow reactor operated at low temperatures (relative to pyrolysis) and at pressures high enough to maintain a liquid solution. The molecular-weight distributions (MWDs) of the feed and effluent at each condition were examined by gel permeation chromatography (GPC) as a function of residence time. In general the polymers are degraded by either random chain scission, and/or by depolymerization to specific low molecular-weight compounds (e.g., monomers, dimers, ...). The experimental data for MWDs were interpreted with rate expressions based on continuous kinetics, and rate coefficients and activation energies were determined for the specific and random degradation processes. Experimental results are described for poly(styrene-allyl alcohol), poly(α -methyl styrene), and poly(methyl methacrylate).

Disposal of plastic wastes has become a worldwide problem with the current costs of dumping these wastes in landfills as high as \$150 per ton. With increasing governmental regulations and increasing consumption of plastics, the cost of conventional disposal is likely to increase. These economic factors, coupled with increasing environmental concerns, have prompted researchers to investigate plastics recycling by degradation as an alternative. Most investigations of polymer degradation have centered on determining the yield of monomer and rate of change of average molecular weight. Rate equations were typically based on free-radical mechanisms. A need exists to develop a knowledge base of fundamental kinetics for designing such chemical recycle methods.

High-pressure, dense-phase thermolysis of polymers is a process with advantages over pyrolysis, which is a high

temperature, low pressure process. Because the solvent is dense compared with ambient-pressure vapor at the same temperature, the solvent properties are superior. The continuously-flowing, high-pressure solvent solubilizes and sweeps away the products of thermolytic decomposition. Pyrolysis, on the other hand, usually leads to gaseous products and high MW repolymerized fractions and char. We use continuous-mixture kinetics based on molecular-weight distributions (MWDs) governed by population balance equations [1-4] to interpret the experimental data for degradation of three polymers. The aim of this presentation is to provide an integrated description of the research done at UC Davis on polymer thermolysis for plastics recycling [5-8].

CONTINUOUS KINETICS THEORY

The continuous-mixture concept provides an effective procedure to analyze the change of MWDs for polymer degradation to molecules of different molecular weights. Continuous-mixture models have been used previously by our group to determine the kinetics for the liquefaction of coal [9] and for catalyst deactivation [10]. The approach is based on fragmentation physics described by population balance equations.

Polymer degradation occurs when polymer chains are broken under the influence of thermal, mechanical, or chemical energy. Chain-end depolymerization and random- and midpoint-chain scission are mechanisms that have been observed in liquid-phase polymer degradation. Mathematical models, unified by continuous-mixture kinetics, can show how these different mechanisms affect polymer degradation in solution. The governing integro-differential equations can be solved analytically for realistic conditions, and rate expressions for the polymer fragmentation govern the evolution of the MWDs. Moment analysis for first-order continuous kinetics shows the temporal behavior of MWDs. Chain-end depolymerization yields monomer product and polymer molecular-weight moments that vary linearly with time. In contrast, random- and midpoint-chain scission models display exponential time behavior. The mathematical results reasonably portray experimental observations for polymer degradation. This approach, based on the time evolution of continuous distributions of chain length or molecular weight, provides a framework for interpreting several types of polymer degradation processes.

EXPERIMENTS

MWDs of reacted and unreacted polymer mixtures were determined by HPLC-GPC and independently confirmed by GC-MS. All

polymers tested were purchased from commercial chemical companies, and contained low MW polymers and oligomers that would interfere with GPC analysis of thermolysis products. To eliminate these low MW peaks, the polymer was fractionated by dissolving the polymer in organic solvent (e.g., toluene). Then a precipitating agent (e.g., butanol) was slowly added to this solution with continuously stirring. High molecular weight polymer precipitated and was dried in an oven to constant weight. The MWD of the treated polymer in all cases could be described mathematically by a gamma distribution. The thermal degradation of the treated polymer in solution was conducted in a steady-state tubular-flow reactor at temperatures in the range 100-300°C and high pressure, 6.8 MPa = 1000 psig. Detailed descriptions of apparatus and experimental procedure are provided in our earlier papers [5-8]. All the experiments were conducted in the liquid phase so that the reaction products remain in solution. The relatively low temperatures ensured negligible repolymerization.

Poly(Styrene-Allyl Alcohol)

Early studies were conducted for thermal degradation of poly(styrene-allyl alcohol). In the presence of t-butanol solvent, both random and specific scission of the polymer occurred at 130-200°C and 1000 psig [5]. However, when 1-butanol was used as the solvent, no degradation of the polymer was observed at these conditions in the absence of tetralin [6]. This suggests that t-butanol acted as a mild hydrogen-donor. Activation energies were in the range of 5-10 kcal/mol for specific degradation and 33 kcal/mol for the random degradation process. The effect of a hydrogen-donor solvent (tetralin) on the thermal degradation of poly(styrene-allyl alcohol) in liquid solution was investigated at various tetralin concentrations, polymer concentrations, and temperatures (130-200°C). A plot of rate coefficients versus tetralin concentration indicated a first-order rate at low tetralin concentrations and a zero-order dependence at high tetralin concentrations [6].

Poly(α -Methylstyrene)

The thermal degradation of poly(α -methylstyrene) (PAMS) in solution was investigated at various temperatures (150-225°C) and polymer concentrations (2.00-20.0 g/L) [7]. The molecular weight distributions (MWDs) of the reacted polymer at these conditions were examined at four different residence times. Experimental

data indicated that the polymer degraded to its monomer, α -methylstyrene. No other degradation products were observed. Continuous-mixture ideas were used to examine the MWDs and to obtain the rate coefficient for degradation and its activation energy. The rate was first-order in polymer concentration with a rate constant at 225°C of 0.01 min⁻¹ and an activation energy of 16.0 kcal/mol (66.5 kJ/mol). The maximum conversion observed at 275°C was 1.2 %. Hydrogen-donor solvent, tetralin, had no effect on the degradation.

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 [8]. The degradation experiments were carried out 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 led to the same expression for monomer concentration increasing 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 kJ/mol). This activation energy suggests that the rate controlling step for the thermal degradation of PMMA is the depropagation process.

CONCLUDING REMARKS

Our studies with solubilized polymer have yielded encouraging results, both for the experimental technique and the theoretical interpretation of the thermolytic kinetics. Polymer thermolysis yields mixtures of products with a distribution of MWs, which we have described by continuous MWDs. The MWDs of the polymer were determined by HPLC-GPC. The resulting MWDs measured at different residence times allowed the quantitative determination of the rates of reaction. The experimental data was interpreted by continuous-mixture kinetics, an approach that provides an accurate, fundamental, and quantitative description of polymer degradation in solution. An important potential application of the concepts is the recycling of plastics.

ACKNOWLEDGEMENT

The financial support of Pittsburgh Energy Technology Center

Grant No. DOE DE-FG22-94PC94204 and EPA Grant No. CR 822990-01-0 is gratefully acknowledged.

LITERATURE CITED

1. Aris, R., G.R. Gavalas, *Phil. Trans. R. Soc. London* **A260**, 351 (1966).
2. McCoy, B.J., *AIChE J.* **39**, 1827 (1993).
3. McCoy, B.J., M. Wang, *Chem. Eng. Sci.* **49**, 3773 (1994).
4. McCoy, B.J., *Chem. Eng. Sci.* **51**, 2903 (1996).
5. Wang, M., J.M. Smith, B.J. McCoy, *AIChE J.* **41**, 1521 (1995).
6. Madras, G., J.M. Smith, B.J. McCoy, *I&EC Research* **34**, 4222 (1995).
7. Madras, G., J.M. Smith, B.J. McCoy, "Thermal Degradation of Poly(α -Methylstyrene) in Solution," *Polymer Degradation and Stability*. (1996); In Press.
8. Madras, G., J.M. Smith, B.J. McCoy, "Degradation of PMMA in Solution," *I&EC Research* (1996); In Press.
9. Wang, M., C. Zhang, J.M. Smith, B.J. McCoy, *AIChE J.* **40**, 131 (1994).
10. Subramaniam, B., B.J. McCoy, *I&EC Research* **33**, 504 (1994).

M97054569

Report Number (14) DOE/PC/94204--T10

Publ. Date (11) 19960726

Sponsor Code (18) DOE/FE, XF

JC Category (19) UC-101, DOE/ER

DOE