# CONTINUOUS-DISTRIBUTION ANALYSIS FOR POLYETHYLENE DEGRADATION

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## INTRODUCTION

A potential method for plastics recycling is to decompose the polymer to lower molecular weight products that can serve as fuel or feedstock. A free-radical mechanism has been proposed to evaluate rate coefficients based upon continuous-distribution kinetics, which provides a simple and reliable method for examining the time-dependence of molecular-weight distributions (MWDs) of reaction products [1]. Population balance equations govern the MWD dynamics for the products. The balance equations are solved by a moment method, which allows the integro-differential equations to be transformed into ordinary differential equations that are readily solved to give the rate coefficient of polymer degradation.

The present objective is to apply these ideas to polyethylene pyrolysis, which gives both random and specific products due to random-chain scission and chain-end scission, respectively. The experimental results of polyethylene pyrolysis are interpreted by the mathematical model to obtain the overall *rate* of degradation and the activation energy. Distribution balance equations for MWDs of random and specific products are proposed to account for initiation-termination and propagation-depropagation reactions, such as hydrogen abstraction, chain cleavage, recombination, disproportionation, and coupling of polymer and the corresponding radical. We will develop the present theory by assuming the rate coefficient k is independent of MW x, which is valid if the change in average MW of the polymer mixture is not too great [2]. 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 numerically up to the desired moment 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) [3,4] 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 quasi-stationary-state approximation (QSSA) 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 very small. Previously derived and experimentally verified expressions for polymer degradation are thus recovered from the general theory.

## EXPERIMENTAL

Polyethylene (2 g, Polysciences, density 0.94 g/cm$^3$, MW 700) was heated with a molten-salt bath in a reactor (an open glass tube placed in a stainless steel vessel) equipped with a gas outlet. Pyrolysis conditions were 390-450 °C for 1-3 h under one atmosphere pressure of nitrogen. Solid and waxy products were recovered from the reactor and the gas outlet. A stainless steel tube at the reactor outlet allowed gaseous products to be collected by water displacement in an inverted graduated cylinder. Solid and waxy products dissolved in 1,2,4-trichlorobenzene were analyzed with a HPLC-GPC (Hewlett-Packard 1050 pump, HP RI detector 1047A) equipped with a 7.5 mm x 50 mm guard column and two 7.5 mm x 300 mm columns packed with PLgel 10 mm Mixed B (Polymer Laboratories). Peak-position calibration for the MWs of polyethylene degradation products was performed with *n*-hexane, triacontane (Aldrich), and narrow MW range polyethylene standards (MW = 170 and 540; Polymer Laboratories) dissolved in 1,2,4-trichlorobenzene. Gaseous products were analyzed by GC (50-m capillary alumina column using He as a carrier gas). The MWD of the initial polyethylene has the mean MWs, $M_n$ = 536 and $M_w$ = 609. The degradation results of MWDs on GPC chromatograms were interpreted as the changes in zero and first moments of the products in the reactor and the gas outlet as a function of time. The mass of volatile fractions was determined as the difference between the mass of the original polyethylene and total mass of reactor residue and gaseous products. The mass of gas was calculated based on the gas volume evolved in the pyrolysis and GC analysis of gaseous products. GPC data of the volatile fraction together with the weights gave the corresponding zeroth moment (molar concentration). The random product concentration was calculated as the sum of the reactor residue and volatile fraction concentrations.

## MODELING OF POLYETHYLENE DEGRADATION

The following simplified reaction scheme describes the important elementary reactions and incorporates them in a mathematical model based on continuous-distribution kinetics. We consider that polymer 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, 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 $R_s^{\bullet}(x)$ represents a precursor for a specific product $Q_s(x_s)$ of alkane and alkene. For mathematical simplicity, a single specific product is assumed. We assume that initiation and termination rates are nil because of the negligible contribution of initiation and termination to overall rate of the degradation (changes in moments in the function of time), although they are important steps in the complete Rice-Herzfeld mechanism [5]. Four reactions constitute the model:

(i) intermolecular hydrogen abstraction,

$$P(x) \underset{k_H}{\overset{k_h}{\rightleftharpoons}} R^{\bullet}(x) \qquad (A)$$

This bimolecular process is expressed as pseudo-first-order [1]. 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.

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

$$R^{\bullet}(x) \underset{k_a}{\overset{k_b}{\rightleftharpoons}} P(x') + R^{\bullet}(x-x') \qquad (B)$$

This random-chain scission is an essential step in random degradation. The resulting 1-alkene has a random distribution in MW. The reverse reaction (recombination) is an important step for some conditions, such as polymer-melt pyrolysis for a long period or high pressure thermolysis [6].

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

$$R^{\bullet}(x) \underset{k_{iH}}{\overset{k_{ih}}{\rightleftharpoons}} R_s^{\bullet}(x) \qquad (C)$$

The Rice-Kossiakoff mechanism [7] suggests the formation of specific products, $Q_s$, from the bond scission of the main chain of polymer via specific radical $R_s^{\bullet}$, where an end radical (unpaired electron at the chain-end) is converted into the corresponding specific radical. Depending on the chemical structure of polymer, 1,4-radical shift, or 1,5-radical shift via cyclic transition state, or other shifts would be possible. The driving force for the reaction C is the gain of stability of primary end-radical relative to secondary radical, or secondary end-radical relative to tertiary radical.

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

$$R_s^{\bullet}(x) \underset{k_{as}}{\overset{k_{bs}}{\rightleftharpoons}} Q_s(x_s) + R^{\bullet}(x-x_s) \qquad (D)$$

One can obtain the distribution balance equations for p(x,t), radical r(x,t), and $r_s(x,t)$, and for a specific product $q_s(x_s,t)$ followed by the moment operation to yield [1]:

$$dp^{(n)}/dt = -k_h p^{(n)} + k_H r^{(n)} + k_b Z_{n0} r^{(n)} - k_a p^{(n)} r^{(0)} \qquad (1)$$

$$dq_s^{(n)}/dt = k_{bs} x_s^n r_s^{(0)} - k_{as} q_s^{(n)} r^{(0)} \qquad (2)$$

$$dr^{(n)}/dt = k_h p^{(n)} - k_H r^{(n)} - k_b r^{(n)} + k_a \sum_{j=0}^{n} \binom{n}{j} r^{(j)} p^{(n-j)} + k_b Z_{n0} r^{(n)} - k_a r^{(n)} p^{(0)}$$
$$- k_{ih} r^{(n)} + k_{iH} r_s^{(n)} + k_{bs} \sum_{j=0}^{n} \binom{n}{j} (x_s)^j (-1)^j r_s^{(n-j)} + k_{as} r^{(n)} q_s^{(0)} \qquad (3)$$

$$dr_s^{(n)}/dt = k_{ih} r^{(n)} - k_{iH} r_s^{(n)} - k_{bs} r_s^{(n)} + k_{as} \sum_{j=0}^{n} \binom{n}{j} q_s^{(j)} r^{(n-j)} \qquad (4)$$

where $Z_{n0}$ = 1, 1/2, or 1/3 for n = 0, 1, or 2. 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 for the zeroth moment only. When several specific compounds are present, they are summed over s in the balance equations and the complete MWD is semi-continuous [8]. Zeroth moments (n=0; the time-dependent total molar concentration (mol/volume) of the macromolecule) are given as follows, where QSSA for radical species has been applied:

$$p^{(0)}(t) = \exp(k_d t)/[(\exp(k_d t) - 1)\, k_a/k_b + 1/p_o^{(0)}] \qquad (5)$$

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

$$= [k_{bs}(k_{ih} + k_{as} q_s^{(0)}) / (k_{bs} + k_{iH}) - k_{as} q_s^{(0)}] (k_h/k_H) p^{(0)} \quad (6)$$

$$q_s^{(0)}(t) = (k_{bs} k_{ih} / k_{as} k_{iH}) \{1 - [k_b / [k_b + k_a p_o^{(0)} (\exp(k_d t) - 1)]]^{(k_{as}k_{iH}/k_a(k_{bs}+k_{iH}))}\} \quad (7)$$

The equilibrium relations are found from the long time limit for the zeroth moments of the products due to random-chain scission and chain-end scission: $p^{(0)}(t \to \infty) = p_\infty^{(0)} = k_b/k_a$ and $q_s^{(0)}(t \to \infty) = q_{s\infty}^{(0)} = k_{bs} k_{ih} / k_{as} k_{iH}$. With QSSA, the summation of first moments (n = 1; the mass concentration (mass/volume)) for polymer and radicals (total mass concentration) gives $d[p^{(1)} + q_s^{(1)}]/dt = 0$ confirming the conservation of polymer mass. And $q_s^{(n)} = x_s^n q_s^{(0)}$ gives $dp^{(1)}/dt = - x_s dq_s^{(0)}/dt$. Then,

$$p^{(1)}(t) = p_o^{(0)} - x_s (k_{bs}k_{ih}/k_{as}k_{iH})\{1 - [k_b/[k_b + k_a p_o^{(0)}(\exp(k_d t) - 1)]]^{(k_{as}k_{iH}/k_a(k_{bs}+k_{iH}))}\} \quad (8)$$

$$q_s^{(1)}(t) = x_s (k_{bs}k_{ih}/k_{as}k_{iH})\{1 - [k_b/[k_b + k_a p_o^{(0)}(\exp(k_d t) - 1)]]^{(k_{as}k_{iH}/k_a(k_{bs}+k_{iH}))}\} \quad (9)$$

## RESULTS AND DISCUSSION

Polyethylene pyrolysis gave both random products and specific products due to random-chain scission and chain-end scission, respectively. The reaction products were recovered in three portions as a reactor residue, a volatile component from the tubing section of the reactor, and a gas product in the gas collector. The reactor residue and the volatile fraction are interpreted as random-chain scission products based on GPC analysis because they have the MWD of smooth curves on GPC chromatograms. No specific compounds with distinct peaks were observed in the reaction mixture. To interpret the data of polyethylene pyrolysis under our experimental conditions, the reactions A through D were further simplified to the *irreversible* reactions,

$$P(x) \xrightarrow{k_d} P(x') + P(x-x') \quad (E)$$

$$P(x) \xrightarrow{k_{ds}} Q_s(x_s) + P(x-x_s) \quad (F)$$

Recombination of olefinic polymer with radical can be ignored due to the low conversion and the low possibility of the bimolecular reaction. Also, recombination of alkene as specific products with radical (Reaction D) can be ignored due to the high volatility of the specific compounds and the normal pressure of the present experiment. Applying $k_a = k_{as} = 0$ to Eqs 5 and 7 gives the zeroth moments for random product P(x) and specific product $Q_s(x_s)$:

$$p^{(0)}(t) = p_o^{(0)} \exp(k_d t) \quad (10)$$

$$q_s^{(0)}(t) = (k_{ds}/k_d) p_o^{(0)} [\exp(k_d t) - 1] \quad (11)$$

where $k_{ds} = k_{bs}k_h k_{ih} / k_H (k_{bs}+k_{iH})$.

When $k_d t \ll 1$,

$$q_s^{(0)}(t) = k_{ds} p_o^{(0)} t \quad (12)$$

Typical MWD changes of random-chain scission products at 450 °C are shown in Figure 1. Figure 2 shows $\ln[p^{(0)}/p_o^{(0)}]$ versus reaction time, in which the slopes give the rate coefficients $k_d$ for random-chain scission at each reaction temperature. During the earliest period of the pyrolysis, the values of $\ln[p^{(0)}/p_o^{(0)}]$ increase rapidly especially at 410-450 °C. The enhanced rates for chain scission are explained as reactive C-C bonds (weak links) due to branching on the polyethylene main-chain. The calculated rate coefficients for random scission, $k_d$, are 0.507, 1.78, 3.14, and 5.11 ($\times 10^{-3}$ $min^{-1}$) at 390, 410, 430, and 450 °C, respectively, based on the reaction time 60-180 min. The activation energy, determined to be 36 kcal/mol by the Arrhenius plot, is reasonable compared with the expected value, from $k_d = k_b k_h / k_H$ in Eq 31, $E_d = E_b + E_h - E_H \approx 37$ kcal/mol ($E_b \approx 29$, $E_h \approx 8$, $E_H \approx 0$ kcal/mol). Figure 3 shows the volumetric amounts of gas evolution with reaction time. The rapid increases of the gas evolution during the first 60 min, consistent with the initial rates in Figure 2, are due to weak-link bond scission at short branches on the main chain. Volumetric amounts of the gas evolution were converted into total molar (ideal gas) concentrations of specific compounds. Eq 12 is applied to the molar concentrations of specific products of the gas evolution at the reaction time 120-180 min. The rate coefficients for chain-end scission, $k_{ds}$, are 4.83, 4.52, 9.12 and 11.2 ($\times 10^{-4}$ $min^{-1}$) at 390, 410, 430, and 450 °C, respectively, affording the activation energy for the chain-end scission as 15 kcal/mol. This activation energy is comparable to the expected value, $E_{ds} = E_h + E_{ih} - E_H \approx 8 + 8 - 0 = 16$ kcal/mol ($E_h \approx E_{ih} \approx 8$ kcal/mol; $E_H \approx 0$ kcal/mol), when $k_{bs} \gg k_{iH}$ in Eq 11, which gives $k_{ds} = k_{bs}k_h k_{ih}/k_H(k_{bs}+k_{iH}) \approx k_h k_{ih}/k_H$. The value is lower than for random-chain scission because of the dominant influence of hydrogen abstraction.

## CONCLUSIONS

The results of the continuous-distribution kinetics indicate that the degradation rate is expressed as the combination of the rate coefficients for radical fragmentation, hydrogen abstraction, and recombination of radical with alkene. These results provide an effective method to evaluate degradation processes and to obtain the properties of polymers and specific products during degradation. The proposed simplified model for polyethylene random-chain scission and chain-end scission describes the observations. The major features of the polyethylene pyrolysis are (1) the zeroth moment (molar concentration) of random products increases exponentially with time, affording rate coefficients with the activation energy 36 kcal/mol for random-chain scission, and (2) gas evolution provides molar concentration of specific products of chain-end scission, which allows the calculation of rate coefficients with the activation energy 15 kcal/mol.

## ACKNOWLEDGMENTS

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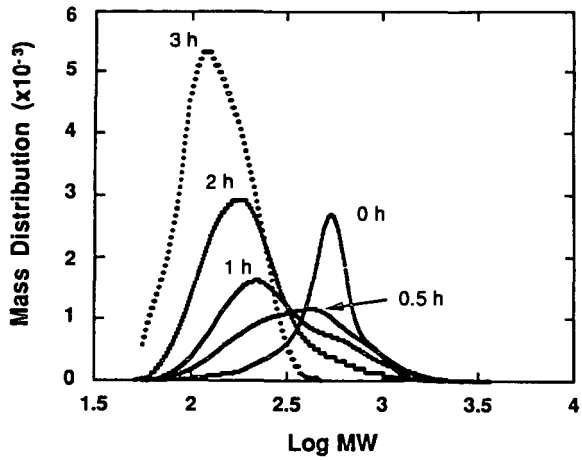


**Figure 1. Normalized mass MWDs of original polyethylene (0 h) and the random-chain scission products at 450 °C for 0.5 - 3 h.**

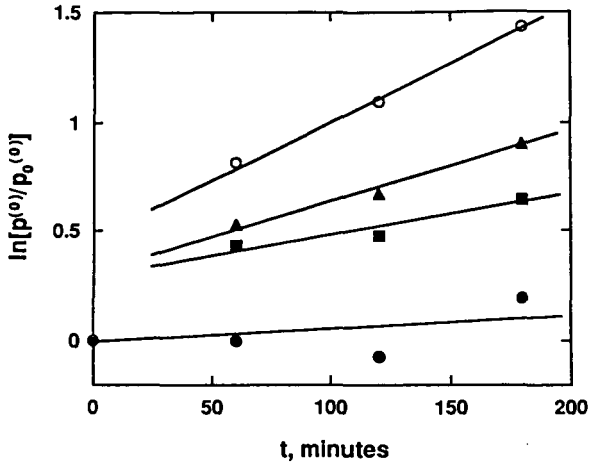


Figure 2. Plot of $\ln[p_o^{(0)}/ p^{(0)}]$ versus reaction time to determine the random-chain scission rate coefficient $k_d$..
● - 390 °C, ■ - 410 °C, ▲ - 430 °C, ○ - 450 °C

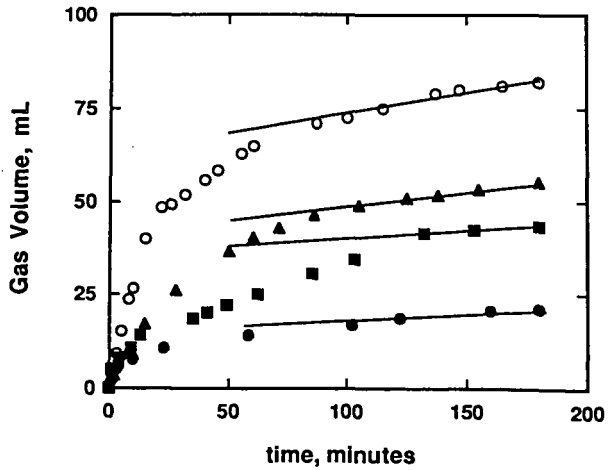


Figure 3. Volumetric amounts of gas evolved by the formation of specific products as a function of reaction time.
● - 390 °C, ■ - 410 °C, ▲ - 430 °C, ○ - 450 °C