

[Review Paper]**Distribution Kinetics of Plastics Decomposition**Yoichi KODERA^{†1)} and Benjamin J. McCOY^{†2)*}^{†1)} National Institute of Advanced Industrial Science and Technology, AIST West, 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, JAPAN^{†2)} Dept. of Chemical Engineering, Louisiana State University, Baton Rouge, LA 70803, USA

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Distribution kinetics is a method to analyze polymer reactions kinetically in terms of the molecular-weight (or chain-length) distributions (MWDs) of components in a macromolecular mixture. Governing equations for temporal and spatial dependence of the MWDs are based on population balance equations (PBEs) for the distinguishable species. Moments of the MWDs are related to observable properties, such as average MW and polydispersity, and can be measured for polymeric systems by procedures such as size-exclusion chromatography. The moments are related mathematically to rate parameters in the PBEs. The distribution kinetics approach is thus a method for interpreting experimental observations of MWD dynamics in terms of chemical reaction mechanisms.

Keywords

Polymer degradation, Pyrolysis, Reaction mechanism, Radical reaction

1. Introduction

Thermal processing of macromolecular substances such as plastics and biomass is important for the effective utilization of unused organic resources. In several countries such as Japan and Germany, liquefaction and gasification of post-consumer plastics or industrial plastic wastes have attracted considerable attention. Problems still hinder the design and efficient processes, for example, reducing coke and char formation, removing chlorine and other unwanted by-products, and improving the final product quality. Due to the nature of waste treatment, demanding conditions of energy input and product control are required for economically-feasible plastics conversions into a source of fuel or chemicals. For designing a reactor and planning an industrial process, kinetic data play an essential role. Suitable reactors must be designed, constructed, and operated based on reliable knowledge of how plastics decompose. Estimations of raw-material treatment capacity, production rate of products, and equipment specifications are directly linked to economic feasibility of treatment processes for plastic wastes¹⁾. Many previous studies of plastics decomposition focused on the low-molecular weight products of pyrolysis, for example, liquid distillate or volatile product formation rates during pyrolysis^{2)~5)}. Such liquid or gas products are relatively easy to integrate into existing chemical plant operations. Other design issues for macro-

molecular conversion are heat consumption and reactor residence time. Many reports on polymer decomposition omit quantitative discussion, and focus mainly on qualitative issues, such as chemical analysis of products. The kinetic analysis and simulation of plastics decomposition are still challenging tasks due to the limited methods of monitoring the conversion and of interpreting the experimental data.

Polymer decomposition aims for MW reduction. Distribution kinetics describes the principal features of polymer decomposition and thus assists in the quantitative understanding^{6)~9)} of these complex processes. Time-dependent changes of MWDs reflect the progress of decomposition. Due to practical problems such as low heat transfer and viscosity, the important and energy-consuming processes of the conversion lay in the change of polymer solid or melt to waxy products rather than volatiles formation from liquid components. Size-exclusion chromatography (SEC) is an effective and often-reported method to monitor the MWD shifts of reaction mixtures during polymer decomposition^{10),11)}. However, SEC has not always appeared in kinetic investigations because of the lack of a kinetic model relating the apparent changes in MWDs of polymer to the progress of polymer degradation.

In this article, we review kinetic modeling for thermal decomposition of plastics. This article includes general reactions of polymer cracking, a general model for radical reactions and its application, and distribution kinetics for thermogravimetric analysis. Firstly, polyolefin-cracking is discussed as a general model of polymer decomposition. For the production of fuel and

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chemicals, polymer decomposition has been examined under various conditions of thermal decomposition such as pyrolysis and solvolysis. Despite the many organic reactions, the decomposition can be sorted into three categories, MW increase, decrease, and negligible change in MW. Depending on the chemical structure or economic feasibility, catalytic or non-catalytic cracking, or solvolysis is used to produce the target products. The distribution kinetics can be applied to the kinetic evaluation of various types of macromolecular conversion. The difficulty lies in the chemical processing of high-MW feedstocks, which usually have a wide distribution in the MWs. The main theme of this review is the distribution kinetics for cracking of polyolefins, which are the major polymers in post-consumer plastics. Secondly, typical kinetic models based on radical reactions were discussed. For known mechanisms of radical-chain reactions in hydrocarbon cracking, simplified reactions of reversible chain scission and recombination are explained to construct distribution kinetics models. With some alterations, the procedure for kinetic study used here can be applied to other types of plastics and processing, such as oxidative degradation and solvolysis. Thirdly, we introduce the distribution kinetics for thermogravimetric analysis (TGA). The rate of volatilization based on mass loss in TGA was interpreted through the combined equations of mass and molar amount of a polymer for a model of reversible random degradation and specific degradation.

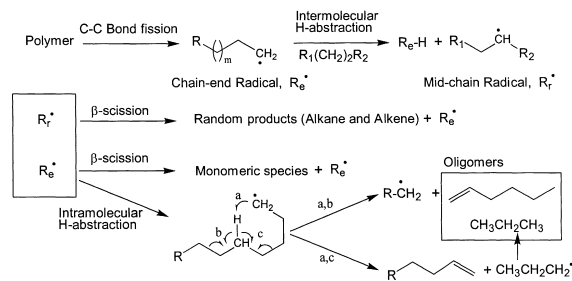
2. General Models of Polymer Decomposition

The primary objective of polymer decomposition is to reduce MWs of macromolecules, and thus the kinetics should describe the overall dynamics of decomposing polymer in terms of MWs. Conventional distribution-kinetics models for polymer degradation described random chain scission^(6),12),13). Among the various reactions during polymer decomposition, we consider three types of polymer transformation; reactions with MW reduction such as chain scission, MW increase such as recombination, and negligible MW change such as isomerization. Typical reactions shown in **Fig. 1** are described according to the notation for the distribution kinetics. PBEs of chemical species are obtained and converted into moments, which can represent MWDs of those species.

2.1. Typical Reaction Models

2.1.1. Transformation with Negligible MW Change

Some types of transformation such as isomerization and radical stabilization of macromolecules with high MWs give negligible MW change. For two types of macromolecular species A and B, one can write the reaction of A converting into B with a constant MW of x as



Recombination is allowed in some reactions. Aromatization becomes important under some conditions. Decomposition of alkenes is also important for a long duration.

Fig. 1 General Mechanisms of Polymer Pyrolysis



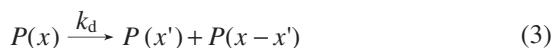
When k is the rate coefficient for this transformation, the rates of changes of two species are

$$-\frac{\partial a(x, t)}{\partial t} = ka(x, t) = \frac{\partial b(x, t)}{\partial t} \quad (2)$$

The MWD is defined as $a(x, t)dx$, the molar concentration (mol/volume) of A in the MW range of x to $x + dx$. The rate coefficient, k , will in general depend upon MW⁽⁴⁾, and can be determined by kinetic analysis. When MW-dependence of k is known, one can substitute $k(x)$ for simulation.

2.1.2. Random Degradation

During thermal decomposition of polymers, apparent events are typically bond scission in the main chain and branched moiety. Random degradation is the degradation by apparent scission of polymer backbone at a random position giving randomly distributed MWs. Despite the number of underlying reactions, random degradation of a macromolecule, P , of molecular weight of x is simply depicted as



in terms of the rate constant k_d . This scheme denotes that a macromolecule P with MW of x decomposes at a random position along the main chain to yield the products with MWs of x' and $x - x'$. Since radical stabilization or transfer of hydrogen is negligible in MW change for large MWs of macromolecules, we simply use the notation of $P(x)$ giving $P(x')$ and $P(x - x')$. One may treat the product $P(x')$ as the other species if the products is distinguishable from the feed $P(x)$. When a main chain is cleaved by random C-C bond scission (Eq. (3)) with a rate coefficient k_d , the rate of change of P is

$$\frac{\partial p}{\partial t} = -k_d p(x) + 2k_d \int_x^\infty p(x') \Omega(x, x') dx' \quad (4)$$

The term, $\Omega(x, x')$, is a stoichiometric kernel^(15),16) given by $1/x'$ for random scission. According to Eq. (4), one mole of macromolecule undergoing random scission gives two moles of random scission products.

Table 1 Typical Moment Expressions Generated from Rate Expressions

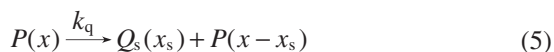
Overall reaction	Rate expression	Moment expression
Random degradation $P(x) \longrightarrow Q(x') + R(x-x')$	$\partial p/\partial t = -k_p p(x)$ $\partial q/\partial t = \partial r/\partial t$ $= k_d \int_x^\infty p(x') \Omega(x, x') dx'$	$dp^{(n)}/dt = -k_p p^{(n)}$ $dq^{(n)}/dt = dr^{(n)}/dt$ $= k_d Z_{n0} p^{(n)}$
Specific degradation $P(x) \longrightarrow Q_s(x_s) + R(x-x_s)$	$\partial p/\partial t = -k_q p(x)$ $\partial q_s/\partial t = k_q \int_x^\infty p(x') \Omega(x_s, x') dx'$ $\partial r/\partial t = k_q \int_x^\infty p(x') \Omega(x-x_s, x') dx'$	$dp^{(n)}/dt = -k_q p^{(n)}$ $dq_s^{(n)}/dt = k_q x_s^n p^{(0)}$ $dr^{(n)}/dt = k_q \sum_{j=0}^n \binom{n}{j} x_s^j (-1)^j r^{(n-j)}$
Recombination $P(x-x') + Q(x') \longrightarrow R(x)$	$\partial p/\partial t = -k_a p(x) \int_0^x q(x') dx'$ $\partial q/\partial t = -k_a q(x) \int_0^x p(x') dx'$ $\partial r/\partial t = k_a \int_0^x p(x') q(x-x') dx'$	$dp^{(n)}/dt = -k_a p^{(n)} q^{(0)}$ $dq^{(n)}/dt = -k_a q^{(n)} p^{(0)}$ $dr^{(n)}/dt = k_a \sum_{j=0}^n \binom{n}{j} p^{(j)} q^{(n-j)}$

Stoichiometric kernels: $\Omega(x, x') = 1/x'$ (random degradation)¹³, $\Omega(x_s, x') = \delta(x-x_s)$ and $\Omega(x-x_s, x') = \delta[x-(x'-x_s)]$ (specific degradation)^{15,17}. The value of Z_{n0} is defined as $1/(n+1)^{15}$.

2.1.3. Specific Degradation

In poly(styrene-allyl alcohol) (PSA) decomposition¹⁷, two types of products were observed by SEC. One is a broad peak slowly shifting to the lower MW and the other is a group of spiked peaks increasing their intensities at fixed MWs. Apparently, the components widely distributed in the broad peak are the products of random chain scission. A few spiked peaks of oligomers increase with faster rate of formation and are thus distinct from random scission products. Based on the kinetic behaviors, these products were categorized into two types of degradation, random degradation and specific degradation, which were treated in a kinetic model to obtain each kinetic parameter.

A kinetic model was derived to determine the kinetic parameters for the simultaneous degradation by random and specific scission. The notation of the overall scheme for specific degradation is



The specific products, Q_s , can be one or more species such as monomer, dimer, and trimer in polystyrene and similar polymers. As found in a typical SEC of PS copolymer¹⁷, the monomer and oligomers form rapidly by specific degradation products rather than random degradation, which gives broad continuous MWDs.

For simultaneous degradation by random and specific scission (Eqs. (3) and (5)), balance equations of P and Q_s are

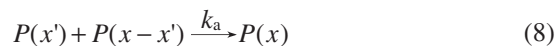
$$\begin{aligned} \partial p/\partial t &= -k_d p(x) + 2k_d \int_x^\infty p(x') \Omega(x, x') dx' \\ &\quad - k_q p(x) + k_q \int_x^\infty \delta[x-(x'-x_s)] p(x') dx' \quad (6) \end{aligned}$$

$$\partial q_s/\partial t = k_q \int_x^\infty \delta(x'-x_s) p(x') dx' \quad (7)$$

The term, $\delta(x'-x_s)$, is a stoichiometric kernel for specific scission¹⁷.

2.1.4. Recombination

Under some reaction conditions, recombination as radical addition or condensation can be an important reaction. Equation (8) with rate constant k_a designates the recombination between two macromolecules of MW x' and $x-x'$ forming an addition product.



When macromolecules sustain recombination (Eq. (8)) with random chain scission (Eq. (3)), the balance equation of P is

$$\begin{aligned} \partial p/\partial t &= -k_d p(x) + 2k_d \int_x^\infty p(x') \Omega(x, x') dx' \\ &\quad - 2k_a p(x) \int_0^x p(x') dx' + k_a \int_0^x p(x-x') p(x') dx' \quad (9) \end{aligned}$$

Considering recombination of monomers and macromolecular species, the distribution kinetics can be applied to polymerization^{18,19}.

2.2. Moment Solutions

With the moment operation, PBEs are converted into moment equations of macromolecular species changing with time. Moments are often used to characterize a continuous distribution in statistics, and express important features of MWDs. Applying the moment generation function $\int_0^\infty [] x^n dx$ to a PBE yields the n -th moment of the MWD²⁰. Typical moment expressions derived from rate expressions are summarized in **Table 1**^{9,19}. For example, applying the moment operation to Eq. (4) yields

$$p^{(n)}(t)/dt = -k_d p^{(n)} + 2k_d Z_{n0} p^{(n)} \quad (10)$$

where $Z_{n0} = 1, 1/2,$ and $2/3$ when $n = 0, 1,$ and $2,$ respectively.

The zeroth moment (molar concentration) of P is

$$p^{(0)}(t)/dt = -k_d p^{(0)} + 2k_d p^{(0)} = k_d p^{(0)}$$

The solution to this ordinary differential equation is

$$p^{(0)}(t) = p_0^{(0)} \exp(k_d t) \quad (11)$$

where $p_o^{(0)}$ is the initial value of zeroth moment. Equation (11) shows the molar concentration of P increasing exponentially with time. The linear relationship of $\ln[p^{(0)}(t)/p_o^{(0)}]$ with reaction time is generally found in random degradation of a typical polyolefin, and since the random bond scission generally occurs in plastics degradation, a similar relationship was observed for substrates other than polyolefins^{21)~23)}.

The first moment (mass concentration) of P is

$$p^{(1)}(t)/dt = 0 \quad (12)$$

which confirms the constant mass concentration of P when all components remain in the reaction system. The second moment of P according to Eq. (10) is

$$p^{(2)}(t)/dt = p_o^{(0)} \exp[-(k_d/3)t] \quad (13)$$

These moments provide the shape characteristics of the MWD, and can be used to construct the MWD. The number-average MW, M_n , the weight-average MW, M_w , of polymer, and variance of the MWDs, p^{var} , are defined by the equations $M_n(t) = p^{(1)}(t)/p^{(0)}(t)$, $M_w(t) = p^{(2)}(t)/p^{(1)}(t)$, and $p^{var} = p^{(2)}(t)/p^{(0)}(t) - [p^{(1)}(t)/p^{(0)}(t)]^2$. The Gamma distribution is an example of a versatile representation of distributions²⁴⁾ that can be constructed from the moments.

The moment-generating function was applied to Eqs. (6) and (7) to yield equations for the n -th moments of the species P and Q_s during simultaneous conversion by random and specific degradation,

$$dp^{(n)}/dt = -k_d p^{(n)} + 2k_d Z_{n0} p^{(n)} - k_q p^{(n)} + k_q \sum_{j=0}^n \binom{n}{j} (-1)^j x_s^j p^{(n-j)} \quad (14)$$

$$dq_s^{(n)}/dt = k_q x_s^n p^{(0)} \quad (15)$$

The zeroth moments of P and Q_s ($n = 0$ in Eqs. (14) and (15)) are thus

$$p^{(0)}(t) = p_o^{(0)} \exp(k_d t) \quad (16)$$

$$q_s^{(0)}(t) = (p_o^{(0)} k_q / k_d) [\exp(k_d t) - 1] \quad (17)$$

where $p_o^{(0)}$ is the initial molar concentration of P . These results simulate the formation of P and Q_s in the competitive degradation by random and specific scission in terms of the molar concentrations under the condition that no components leave the reaction system. The molar concentrations of degradation products are obtained by the simple calculation of MWDs of reaction mixtures changing with time. Equation (16) shows the theoretical value of $p^{(0)}(t)/p_o^{(0)}$ changing with time, and Eq. (17) also shows the increase of a specific product, Q_s . Because typical values of k_d and k_q are much smaller than 1, the experimental results usually give a linear relationship for Q_s , which follows from Eq. (17) with $\exp(k t) \approx 1 + k t$ when $k \ll 1$. Equation (17) is thus simplified to $q_s^{(0)}(t) = p_o^{(0)} k_q t$, so that the rate coefficient, k_q , can be determined from the data of the molar concentration of Q_s . The rate constant, k_d , is obtained from the slope of $\ln[p^{(0)}(t)/p_o^{(0)}]$ versus time.

By application of moment expressions evaluated from the PBE, the observed shifting MWDs allow evaluation of kinetic parameters. Although plastics ultimately consist of discrete components of macromolecules, the continuous-distribution approach adopted here readily simulates the dynamics of macromolecular reactions in terms of MWD with time. Compared to discrete models, the continuous-distribution approach provides a simple and straightforward tool for describing macromolecular conversions for kinetic analysis of experimental data as well as simulation by computation.

3. Kinetic Modeling Based on Radical Chain Reactions

3.1. Typical Radical Reactions in Polymer Decomposition

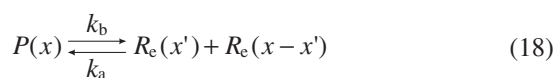
In the previous section, we obtained kinetic models of random/specific degradation and recombination. Kinetic parameters of each type of overall transformation can be obtained by comparing kinetic equations with experimental data of MWDs of polymers. The method simplifies the many types of radical reactions that occur during polymer pyrolysis. The question is what the obtained parameter means and how the underlying reactions contribute to the fate of polymer components. Random and specific degradation involve competitive pathways for realistic radical mechanisms. The radical mechanisms underlie the apparent MWD data shift with time and the kinetic relationship between feed and products. There have been reported quite a few studies on the degradation behavior of polymers, but we still have limited knowledge of the reactions and physical properties of each polymer. However, distribution kinetics based on typical radical mechanisms will explain and simulate the fates of polymer and its product.

A number of papers have appeared on cracking mechanisms of light naphtha distillates in petrochemical processing. Radical chain reactions similar to the Rice-Herzfeld mechanism²⁵⁾ have often been cited in the papers in polymer degradation. Due to the similarity of polyolefin chemical structures, such a reaction mechanism should explain random degradation of a polymer. Oligomer formation *via* the back-biting reaction is known in polymer chemistry, and corresponds to the Rice-Kossiakoff mechanism²⁶⁾ in hydrocarbon cracking. We introduce such radical mechanisms into distribution kinetics in order to construct kinetic models of polymers and their products¹⁹⁾. Typical radical reactions are chosen as major elementary reactions to describe the fate of a polymer upon pyrolysis. Based on the elementary reactions, PBEs of polymer and radicals were derived to construct the distribution kinetic model for polymer pyrolysis. The

typical radical reactions are summarized as follows.

3. 1. 1. Initiation and Termination of Radical Chain Reactions

In polyolefin pyrolysis, the radical initiation step (Eq. (14)) is usually explained as homolytic C–C bond fission at a random position along the backbone of a polymer (P). This step gives chain-end radicals, R_e , which have an unpaired electron at the chain end. The radical can be primary, secondary, or tertiary, and each radical is in a different energetic level to act in subsequent reactions. Compared with other polyolefins, polyvinyl chloride sustains side-chain scission preferentially to evolve hydrogen chloride prior to main-chain scission. The reverse reaction is termination of the chain reaction by recombination of two radicals, which is assumed to occur *via* recombination. The ratio of recombination/disproportionation is stated as about 2-10^(27),28).



The rate expressions for this reaction are

$$\frac{\partial p}{\partial t} = -k_b p(x) + k_a \int_0^x r(x') r(x-x') dx' \quad (19)$$

$$\frac{\partial r_e}{\partial t} = 2k_b \int_x^\infty p(x') \Omega(x, x') dx' - 2k_a r(x) \int_0^\infty r(x') dx' \quad (20)$$

The moment-generating function was applied to yield the n -th moments of the species P and R_e , as in Eqs. (21) and (22).

$$\frac{dp^{(n)}}{dt} = k_b p^{(n)} + k_a \sum_{j=0}^n \binom{n}{j} r^{(j)} r^{(n-j)} \quad (21)$$

$$\frac{dr_e^{(n)}}{dt} = 2k_b Z_{n0} p^{(n)} + 2k_a r^{(n)} r^{(0)} \quad (22)$$

When a linear polymer is considered, the C–C bond scission is assumed to occur equally at a random position along the main chain. As in light hydrocarbons, the rate of the initiation step would vary with the chain length. The initiation step, however, has a large activation energy and is relatively improbable compared to other reaction steps. In the kinetic derivation, the rate coefficient, therefore, can be safely assumed independent of chain length or MW for each overall scheme.

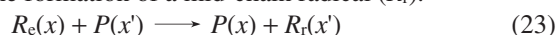
Jellinek stated the weak-link hypothesis in polystyrene pyrolysis that explains the two-stage rates of degradation in polystyrene decomposition⁽²⁹⁾. Although there is no direct observation of the irregularity of main chain such as by nuclear magnetic resonance (NMR) and other spectroscopic methods, the accelerated degradation was confirmed by experimental evidence^(30,31). In the decomposition of “aged plastics,” an oxidized moiety in a polymer may play a role as a weak link thus accelerating the rate of decomposition.

In the presence of air, the chain reaction will start by oxygen-promoted hydrogen abstraction at a random position along a polymer main-chain. An oxidizing

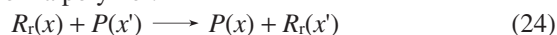
reagent also can promote radical formation^(32),33). Air contamination and the starting polymer structure will change the initiation step, which may lead to different rates of the overall course of decomposition. It should be noted that heat transfer and melting are also important for initiating plastic conversion^(34),35).

3. 1. 2. Intermolecular Hydrogen-abstraction

Radicals form in various elementary reactions in radical chain reactions, for example, a chain-end radical (R_e) abstracts hydrogen of neutral polymer. The H-abstraction is typically assumed to occur at a random position along a main chain of a polymer, resulting in the formation of a mid-chain radical (R_r).



A mid-chain radical also can abstract a hydrogen atom from a polymer.

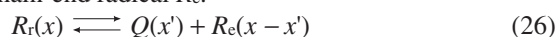


An unstable primary radical would promote intermolecular hydrogen-abstraction from polymer, resulting in the formation of a mid-chain radical (R_r) of secondary or tertiary structure. The bimolecular process of polymer radicals, R , interacting with a large excess of polymer, P , can be considered as the pseudo-first order transformation as in Eq. (25).



3. 1. 3. Fragmentation of Mid-chain Radical and Radical Addition

A mid-chain radical can undergo several types of reactions, including fragmentation by β -scission. This step contributes to MW reduction because β -scission allows radical species to decompose faster than neutral polymer. The products are an α -alkene Q and a chain-end radical R_e .



The reverse reaction is radical addition to alkene. In light hydrocarbon cracking, addition products are observed by GC upon liquid-phase cracking rather than gas-phase cracking⁽³⁶⁾. Radical addition of polymer will yield MWDs shifted to higher MWs. Such a shift to higher MWs was reported for the polymer of a reactor in distillative pyrolysis of polyethylene melt⁽³⁷⁾.

3. 1. 4. Intramolecular Hydrogen-abstraction of Chain-end Radical

A 1,5-radical shift is a typical intramolecular-hydrogen abstraction of a chain-end radical, although a 1,4- or 1,6-shift is possible depending on the chemical structure. The radical-shift reaction is written as

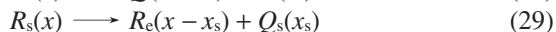
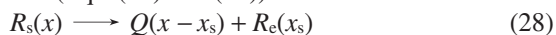


and is known as the Rice–Kossiakoff mechanism in light hydrocarbons. In polymer chemistry, Eq. (27) is also referred to as a back-biting reaction. Since typical paraffin compounds decompose in this manner, similar reactions of linear polyethylene and decomposed fragments would also occur. The decomposition pathway of the radical-shift reaction followed by β -scission is important because this step leads to the

formation of oligomers of dimer and trimer, which are the typical volatile components during polymer decomposition.

3.1.5. Fragmentation of Specific Radical

We called the radicals formed by intramolecular hydrogen-abstraction of chain-end radicals as specific radicals. The important reaction for specific radicals is β -scission to form oligomers and radicals, which correspond to low-MW components such as dimer and trimer (Eqs. (28) and (29)).



The chain-end radical, R_e , can be quenched to give aliphatic product $P(x_s)$.

3.1.6. Fragmentation of Chain-end Radical and Radical Addition

Monomer formation in poly(methyl methacrylate) and poly(α -methylstyrene) decomposition is typically explained by β -scission of chain-end radicals (depolymerization),



This depolymerization step gives little effect on MW reduction of polymer comparing with the fragmentation of mid-chain radicals³⁸. The reverse reaction is radical addition, or chain polymerization. It is well known that polymerization and depolymerization are in equilibrium at a high temperature³⁹. Above this ceiling temperature, depolymerization proceeds dominantly over polymerization.

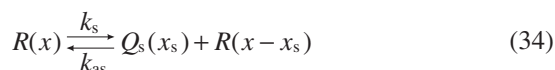
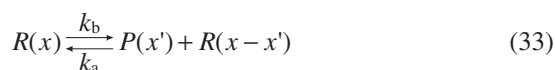
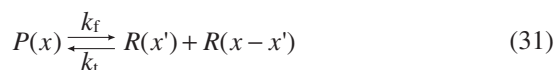
Concentration of α -olefin increases with decomposition progress, and will affect recombination. In some cases, recombination gives branched products. Decomposition of α -olefin and formation of branched species will lead to different chemical properties from paraffins in their reactions. When one needs to focus on these processes, kinetic models including those species will be needed.

3.2. Kinetic Models Considering Radical Reactions

Typically, polystyrene pyrolysis is examined with a kinetic model based on radical mechanisms. PS pyrolysis has been well studied in product analysis and kinetics because PS and its copolymers are the abundant plastic wastes. PS also suggests potential versatility for producing fuel oil and chemicals, such as styrene and the other derivatives. Conventional kinetics is based on rate of volatilization, as observed in thermogravimetric analysis. The distribution kinetics approach provides the clearer kinetic interpretation based on typical radical reactions, PBEs, and moment solutions. Then, we compare the kinetic model with experimental data to obtain the kinetic parameters for polystyrene pyrolysis.

The mechanism was simplified in view of reversible random degradation and chain-end degradation, and the major reactions are depicted as Eqs. (31) through (34).

In these schemes, P , R , and Q_s designate polystyrene, polymer radical, and specific products. Specific products are volatile components among the pyrolysis products, which are a mixture of monomer and dimer, experimentally. For mathematical simplicity, this mixture is treated as one component and has a mean MW of monomer and dimer. The following schemes are a simplified mechanism for PS pyrolysis: initiation and termination of radical chain reaction (Eq. (31)), intermolecular H-abstraction (Eq. (32)), fragmentation of mid-chain radicals and its reverse reaction (Eq. (33)), and specific product formation (Eq. (34)). Depending on the purpose and necessity, one can consider more detailed chemical species or radical reactions. In the first, the kinetic model for reversible transformation in Eqs. (31) through (34) is examined. Then, non-reversible cases are examined in this section.



The PBEs for P , R , and Q_s are

$$\begin{aligned} \partial p/\partial t = & -k_f p(x) + k_t \int_0^x r(x') r(x-x') dx' \\ & -k_h p(x) + k_H r(x) + k_b \int_x^\infty r(x') \Omega(x, x') dx' \\ & -k_a p(x) \int_0^\infty r(x') dx' \end{aligned} \quad (35)$$

$$\begin{aligned} \partial r/\partial t = & 2k_f \int_0^\infty p(x') \Omega(x, x') dx' - 2k_t r(x) \int_0^\infty r(x') dx' \\ & + k_h p(x) - k_H r(x) - k_b r(x) + k_b \int_x^\infty r(x') \Omega(x, x') dx' \\ & + k_a \int_0^x p(x') r(x-x') dx' - k_a r(x) \int_0^\infty p(x') dx' \\ & - k_s r(x) + k_s \int_x^\infty r(x') \delta[x - (x' - x_s)] dx' \\ & + k_{as} \int_0^x q_s(x_s) r(x' - x_s) dx' - k_{as} r(x) \int_0^\infty q_s(x_s) dx' \end{aligned} \quad (36)$$

$$\partial q_s/\partial t = k_s \int_x^\infty r(x') \delta(x' - x_s) dx' - k_{as} q_s(x_s) \int_0^\infty r(x') dx' \quad (37)$$

The long-chain approximation (LCA) suggests a negligible effect of initiation and termination reactions compared with the predominant influence of the chain reactions, H-abstraction and radical fragmentation, often cited as propagation-depropagation. The LCA is applied to the balance equations. With the initial conditions, $p(x, t=0) = p_0$ and $q_s(x_s, t=0) = 0$, the n -th moment are given as follows.

$$dp^{(n)}/dt = -k_h p^{(n)} + k_H r^{(n)} + k_b Z_{n0} r^{(n)} - k_a p^{(n)} r^{(0)} \quad (38)$$

$$\begin{aligned} dr^{(n)}/dt &= k_h p^{(n)} - k_H r^{(n)} - k_b r^{(n)} + k_b Z_{n0} r^{(n)} \\ &+ k_a \sum_{j=0}^n \binom{n}{j} r^{(j)} p^{(n-j)} - k_a r^{(n)} p^{(0)} \\ &- k_s r^{(n)} + k_s \sum_{j=0}^n \binom{n}{j} x_s^j (-1)^j r^{(n-j)} \\ &+ k_{as} \sum_{j=0}^n \binom{n}{j} r^{(j)} q_s^{(n-j)} - k_{as} r^{(n)} q_s^{(0)} \quad (39) \end{aligned}$$

$$dq_s^{(n)}/dt = k_s x_s^n r^{(0)} - k_{as} q_s^{(n)} r^{(0)} \quad (40)$$

When the quasi-steady-state approximation (QSSA) is applied to radicals, zeroth moments ($n = 0$) give the molar concentration of P and Q ,

$$p^{(0)}(t) = k_b / [k_a + (k_b/p_o^{(0)} - k_a) \exp(-K t)] \quad (41)$$

$$q_s^{(0)}(t) = (k_s/k_{as}) \left\{ 1 - k_b^{(k_{as}/k_a)} \left[k_b + (\exp(-K t) - 1) k_a p_o^{(0)} \right]^{(-k_{as}/k_a)} \right\} \quad (42)$$

where $K = k_b k_b / k_H$. The mathematical results in Eqs. (41) and (42) show that the molar concentration of P and Q_s approaches k_b/k_a and k_s/k_{as} , respectively, at time going to infinity.

Considering non-reversible case of Eqs. (33) and (34), a similar mathematical procedure gives the following equations,

$$dp^{(n)}/dt = -k_h p^{(n)} + k_H r^{(n)} + k_b Z_{n0} r^{(n)} \quad (43)$$

$$\begin{aligned} dr^{(n)}/dt &= k_h p^{(n)} - k_H r^{(n)} - k_b r^{(n)} + k_b Z_{n0} r^{(n)} \\ &- k_s r^{(n)} + k_s \sum_{j=0}^n \binom{n}{j} x_s^j (-1)^j r^{(n-j)} \quad (44) \end{aligned}$$

$$dq_s^{(n)}/dt = k_s x_s^n r^{(0)} \quad (45)$$

Applying QSSA to radicals, the zeroth moments of P and Q_s are given as

$$p^{(0)}(t) = p_o^{(0)} \exp(-K t) \quad (46)$$

$$q_s^{(0)}(t) = (p_o^{(0)} k_s / k_b) [\exp(K t) - 1] \quad (47)$$

where $K = k_b k_b / k_H$. These results are identical to distribution kinetics without consideration of radical in Eqs. (16) and (17). The rate k_d in the overall kinetics corresponds to the term $k_b k_b / k_H$, and the overall formation rate, k_q , of specific products corresponds to radical fragmentation rate, k_s , in the radical mechanism.

Thermal decomposition of polymer involves many types of radical reactions of macromolecules with wide MWDs. It is not easy to describe every macromolecular reaction in a kinetic model, and, to be more difficult, some reactions may be affected by physical conditions such as viscosity or unknown underlying reactions. However, the distribution kinetics handles influential factors in the mechanism as an overall kinetic parameter for a defined reaction.

The distribution-kinetics method based on radical

mechanisms provides an effective tool for the investigation of various reaction conditions. It is necessary to consider radical mechanisms for understanding various aspects of plastics decomposition. Hydrogen donor addition, for example, is sometimes effective for promoting plastics decomposition⁴⁰. The interaction between polymer radicals and a hydrogen donor was theoretically and experimentally examined by McCoy and coworkers^{41,42}. It is noteworthy that similar and simple kinetic modeling can apply to solvolysis due to the random nature of main-chain scission and availability of degradation rates obtained with SEC data. In practical examples of plastics waste treatment, pure or mixed plastics display different reactivities. Distribution kinetics based on radical mechanisms is useful to understand the kinetics by relating the reactivity of each plastic component to the MWDs with time^{43,44}.

4. Distribution Kinetics for Thermogravimetric Analysis

MWDs changing with time represent basic behavior during polymer pyrolysis, with gas, liquid, and coke increasing. Most kinetic studies are based on rates of formation of each fraction by determining their boiling temperature ranges. Typically, the release rate of volatile products is the rate of decomposition^{45,46}. Thermogravimetric analysis (TGA) has been used for examining decomposition of various materials and determining decomposition rate and kinetic parameters in the pyrolysis of both inorganic and organic substances^{47,48}. TG curves provide valuable information such as decomposition temperature and rate of volatilization. Different from ordinary mole-based kinetics of the reactions of simple components, the kinetic data by TGA are weight losses of volatile matter. In kinetic modeling by global kinetics, the rate of volatilization has been interpreted as decomposition rate. An empirical equation including a power term of a weight fraction is generally used to obtain decomposition rates by fitting it to the weight loss data. For simple decomposition it is relatively easy to correlate the rate of weight loss to the rate of reaction. However, TGA is often used for determination of kinetic parameters for the thermal decomposition of complex organic substances including coal, biomass, and plastics. Even plastics with simple chemical structures sustain complex radical reactions at TG pyrolysis. It is a challenging task to integrate weight-loss data of volatile-product evaporation, and ultimately, to an overall decomposition rate of combined macromolecular reactions. Some efforts have been reported by relating TG data to computer-assisted simulation with detailed mechanisms⁴⁹ and reaction models with distributed activation energies for coal conversion⁵⁰.

Plastics decomposition is essentially MW reduction by chain scission with radical addition influencing it under some conditions. The apparent shift in MWD is the overall result of various radical reactions, which can be categorized as chain scission, addition, and isomerization, corresponding to fragmentation, agglomeration, and other transformation. We can simplify those reactions into three types of overall reactions: random degradation, chain-end degradation and recombination. Each overall reaction theoretically relates to MW-reduction, volatiles formation, and MW-enhancement, respectively. Polyethylene pyrolysis was performed in a thermobalance with forced evacuation of volatile products by nitrogen-gas flow³⁷, and the distribution kinetics was linked with rate of volatilization. A thermobalance is designed to perform pyrolysis with minimum mass transfer resistance and sufficient heat transfer so that the reactions of chain scission and recombination mainly control the TG data. A kinetic model describing formation of volatile products in TG pyrolysis with negligible mass transfer resistance was derived from the distribution kinetics, and the kinetic parameters of chain-end degradation were determined⁵¹. In this section, distribution kinetics is developed to interpret TG data in terms of random/specific degradation and recombination. As a typical example, PS pyrolysis with a thermobalance was analyzed to determine the kinetic parameters.

4.1. Theory

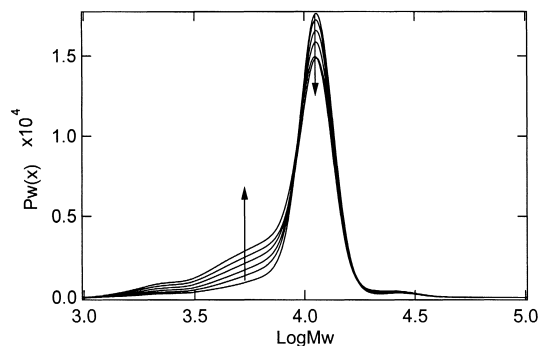
The purpose of the kinetic model in this section is to relate the weight loss of TG sample to the three major reactions of random and chain-end degradation, and recombination. The Sestak-Berggren equation in Eq. (48) is a typical kinetic model based on mass for TGA.

$$dy/dt = ky^v(1 - qy)^\mu \quad (48)$$

where y is mass fraction (m/m_0) at time, t , and q , v , and μ are adjusting parameters. The rate coefficient, k , is usually expressed by the Arrhenius equation with the pre-exponential or frequency factor, A , and the activation energy, E .

$$k = A \exp(-E/RT) \quad (49)$$

where R is the gas constant, and T is the absolute temperature. The distribution kinetics method is mole-based kinetics combining defined reactions with the aim to relate the apparent observation of volatilization to polymer decomposition reactions. As general reactions for TG pyrolysis, random/specific degradation and recombination (Eqs. (3), (5), and (8)) are used to construct a kinetic model. The mechanistic definition of specific degradation in the reaction mechanism involves two cases. One is depolymerization of chain-end radical as in poly(methyl methacrylate) and poly(α -methylstyrene) decomposition. The other is an overall reaction of intramolecular radical shift of chain-end radicals followed by radical fragmentation to yield oligomers. The resulting oligomers may decom-



In the direction of the arrows, isothermal periods of 0, 10, 20, 35, 50, and 65 min. MW standard sample of PS (40 mg, Polymer Laboratories, Mp 13100) was pyrolyzed with a thermobalance. The residual sample in tetrahydrofuran was analyzed by GPC.

Fig. 2 MWDs of PS Melt (normalized mass distribution, $P_w(x)$ vs. $\log M_w$) in TG Pyrolysis at 350°C

pose further to monomer. The balance equations and moment operation yield moles and mass of polymer melt, n and m , of a TG sample as shown in Eqs. (50) and (51)⁵².

$$dn/dt = k_d n - k_a \rho_m n^2 / m \quad (50)$$

$$dm/dt = -k_q x_s n \quad (51)$$

where k_d , k_q , and k_a are the rate coefficients of random degradation, specific degradation, and recombination. The density of polymer melt is ρ_m , and x_s is an average molecular weight of volatile products. As derived in the previous chapter, those rate coefficients are the overall form of the combined rates of underlying radical reactions.

The material balance equations, Eqs. (50) and (51), show moles of polymer increase by first-order random degradation and decrease by second-order recombination. The mass of polymer decreases with the evaporation of volatile products by specific degradation.

4.2. Data Analysis of PS Pyrolysis with a Distribution-kinetics Model

Polystyrene pyrolysis with TGA data was evaluated with the distribution kinetics presented in the previous section. During isothermal heating, weight and MWD of polystyrene change with time. The MWDs of PS were analyzed by SEC with reaction times. Weight and MWD data were examined with Eqs. (50) and (51) to obtain the rate coefficients. **Figure 2** shows the MWDs of PS degradation at 350°C under helium flow of 40 ml/min. A peak top of the broad peak gradually declined and the peak shoulder in the lower MW region to the peak top became higher. As shown in **Fig. 3**, the higher MW region at $\log M_w = 4.4$ also increased its height especially at the time 0-50 min. The apparent increase of the mass distribution in the high MW region suggests recombination of macromolecular components. A similar increase of high MW components of

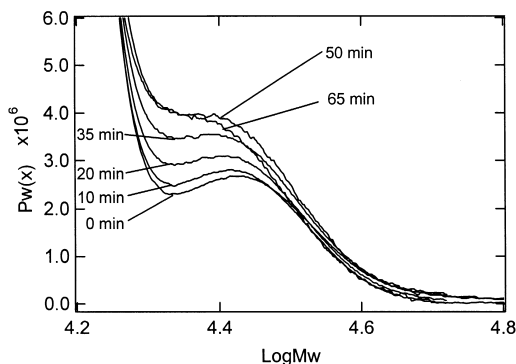


Fig. 3 MW Enlargement with Isothermal Periods in the Expanded Figure of the High-MW Region of Fig. 2

polymer melt was observed in distillative pyrolysis of PE³⁷). **Figure 4** shows that moles and mass of PS decreased linearly with time in the pyrolysis conditions. With moles of PS and the slope of dm/dt , Eq. (51) gave k_q increasing from 0.6 to 1.1 min^{-1} . Equation (50) gives the numerical relationship of PS moles to k_d and k_a , and it is difficult to obtain each rate coefficient separately. Thus, a computer-assisted fitting procedure was designed to obtain each kinetic parameter.

The rate coefficients are defined for random degradation, recombination, and specific degradation by the Arrhenius equation in Eqs. (52), (53), and (54), respectively.

$$k_d = A_d \exp(-E_d/RT) \quad (52)$$

$$k_a = A_a \exp(-E_a/RT) \quad (53)$$

$$k_q = A_s \exp(-E_s/RT) \quad (54)$$

where A is a pre-exponential value and E is an activation energy for the overall reaction.

For nonisothermal TGA, Eq. (55) defines a constant heating rate,

$$dT/dt = \beta \quad (55)$$

To obtain the kinetic parameters, the experimental data were fit to Eqs. (50) through (55) by error minimization. The pre-exponentials, A_d , A_a , and A_s were set to estimated values, 6×10^{12} , 6×10^9 , and $6 \times 10^{12} \text{ min}^{-1}$, respectively, and the three unknown activation energies, E_d , E_a , and E_s , were obtained by the non-linear fitting procedure. We reported the results of the activation energies for PS pyrolysis by isothermal TGA at 335-355°C, and E_d , E_a , and E_s were given at 170.1-176.0, 77.3-86.9, and 142.1-151.7 kJ/mol, respectively⁵¹). Nonisothermal TGA gives results over wider ranges possibly due to various underlying reactions during the pyrolysis at wide-ranging temperatures⁵³).

4.3. TG Curve Properties

A TG curve gives important information, for example, the temperature at which volatilization begins is considered as the decomposition temperature, and a slope of the curve is considered as a decomposition rate. In this section, the slope of a TG curve, especial-

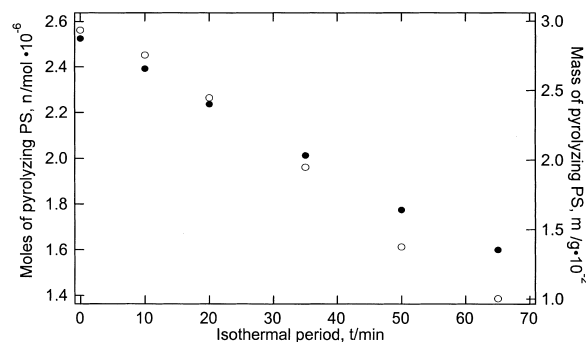


Fig. 4 Moles (circles) and Mass (dots) of Pyrolyzing PS with Isothermal Periods at 350°C

ly at the inflection point, is theoretically examined in terms of the rates of degradation and recombination. Isothermal and nonisothermal (constant heating rate) conditions are typical operations in TGA, and the TG curves have different shapes. The second differential of Eq. (50) gives

$$d^2m^2/dt^2 = -(dk_q/dt)x_s n - k_q x_s (dn/dt) \quad (56)$$

At the inflection point, $d^2m^2/dt^2 = 0$.

$$(dk_q/dt)x_s n = -k_q x_s (dn/dt) \quad (57)$$

Applying Eq. (50) to Eq. (57) gives

$$dk_q/dt = k_q(-k_d + k_a \rho_m n/m) \quad (58)$$

From Eq. (51),

$$n = -(1/k_q x_s)(dm/dt) \quad (59)$$

Eliminating n in Eq. (58) by Eq. (59) and using weight fraction $y (= m/m_0)$ gives

$$d \ln y/dt = -(d \ln k_q/dt + k_d)(k_q x_s/k_a \rho_m) \quad (60)$$

From $k_q = A_s \exp(-E_s/RT)$,

$$\ln k_q/dt = \ln A_s - E_s/RT \quad (61)$$

Applying heating rate $\beta = dT/dt$ to Eq. (61),

$$d \ln k_q/dt = (-E_s/RT^2)\beta \quad (62)$$

Equations (60) and (62) yield

$$d \ln y/dt = (E_s \beta/RT^2 - k_d)(k_q x_s/k_a \rho_m) \quad (63)$$

For isothermal TGA ($\beta = 0$), Eq. (63) at the inflection point gives

$$dy/dt = -y(k_d k_q x_s)/(k_a \rho_m) \quad (64)$$

Equation (56) with $d^2m^2/dt^2 = 0$ gives $dn/dt = 0$, which means that the moles of the polymer reach a maximum value at the inflection point.

For nonisothermal TGA ($\beta > 0$), the second derivative of Eq. (51) at the inflection point gives

$$d^2m^2/dt^2 = -d(k_q x_s n)/dt = 0 \quad (65)$$

Applying $dT/dt = \beta$ to Eq. (65) gives

$$d(k_q x_s n)/dt = (x_s/\beta)d(k_q n)dT = 0 \quad (66)$$

Equation (66) shows $k_q n$ reaches the maximum value at the inflection point.

Equation (63) shows that larger β gives the steeper slope at a fixed y value if $E_s \beta/RT^2 \gg k_d$. We have negligible difference of the slopes in nonisothermal TGA of poly(ether-ether-ketone)⁵¹). Then, the similar slope is supported by Eq. (63) at $E_s \beta/RT^2 \ll k_d$, which yields

$$d \ln y/dt = -k_d k_q x_s / k_a \rho_m \quad (67)$$

The term $k_d k_q / k_a$ appears in both isothermal and non-isothermal TGA, and this motivated us to derive the computer-assisted fitting procedure in determining the kinetic parameters of the overall reactions of degradation and recombination.

5. Conclusions

Chemistry and engineering—combining fundamental and applied knowledge—are crucial in macromolecular processing for polymer recycling. Plastics decomposition for an optimized and economically-feasible recycling process requires an appropriate reaction theory and an evaluation method based on it. The chemical and physical behaviors of reacting macromolecules will vary with the progress of decomposition. It is very difficult to trace how every macromolecular species participates in the elementary reactions under the different physical conditions of the varieties of viscosity of liquid and polymer melts, temperature gradients, and so on. We have focused on the main events of molecular-weight reduction to simplify the various elementary radical-chain reactions. By introducing radical mechanisms into distribution kinetics, one can understand the relationship between the apparent observation of MWDs shifting with time and the underlying radical reactions. The distribution kinetics approach provides a solution for quantitative understanding of plastics pyrolysis, and assists in the study of more complex reaction systems, such as polymer mixtures or hydrogen donor addition. Furthermore, the distribution kinetic model was applied to TGA to derive relationships to reversible random degradation and volatilization of specific scission products. Under some assumptions and approximations, the changes in MWDs and volatilization were interpreted to provide the kinetic parameters of random degradation, recombination, and specific degradation. The distribution kinetics relates those apparent data to the underlying reactions, and contributes to the design and improvement of reactors and processes.

Nomenclatures

A	: pre-exponential factor in Arrhenius expression	[min ⁻¹]
E	: activation energy	[kJ/mol]
k	: rate coefficient	[min ⁻¹]
m	: $p^{(1)}(t)$, mass of pyrolyzing polymer	[g]
n	: $p^{(0)}(t)$, moles of pyrolyzing polymer	[mol]
$p^{(n)}(t)$: $\int_0^\infty p(x, t) x^n dx$, n -th-order moment of the molecular-weight distribution	[—]
$p(x, t)$: molecular-weight distribution of the polymer	[—]
R	: gas constant	[0.008314 kJ/mol·K]
T	: temperature	[K]
t	: time	[min]
x	: molecular weight	[g/mol]
y	: m/m_0 , mass fraction of polymer remaining	[—]

<Greeks>

β	: temperature increase rate	[K/min]
ρ_m	: mass density of polymer melt	[g/ml]
<Subscripts>		
a	: addition (recombination)	
d	: dissociation (random degradation)	
q, s	: specific scission (specific degradation)	
f	: bond fission	
t	: termination	
h, H	: hydrogen abstraction	
b	: β -scission	
as	: addition of specific products	

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要 旨

プラスチック分解の連続分布速度論

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連続分布速度論はマクロ分子混合物成分の分子量分布（または主鎖長）を基にした高分子反応の速度論的解析の方法である。個々の化合物として分離検出が不可能な混合成分に対して分子量分布関数を考え、その増減の収支方程式を立てる。収支方程式からはモーメント値が得られる。高分子の分子量分布の特徴を表すモーメント値は、それぞれの成分のモル濃度や重量濃度などを与える。モーメント値は平均分子量や分布の分散と関連づけられる。成分の分解反応を表す収支方程式の速度係数項と

モーメント値は速度式上で関連している。反応機構を基にした速度式から得られるモーメントの理論的経時変化とサイズ排除クロマトグラフィーで得られる分子量分布から算出されるモーメントの実測値を比較することで速度係数を求めることが可能である。連続分布速度論を用いればプラスチックの分子量分布の経時変化を分解機構を考慮して、シミュレートしたり、速度係数を算出することが可能となる。