Kinetic Study on Continuous Flow Reactor for Thermal Degradation of Polymer

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Abstract
Previous works on the kinetics of the thermal degradation of polymer are entirely concerned with the reaction resulted in batch-wise operation. In this study, the kinetics for the thermal degradation of polymer was extended to the kinetics of continuous flow operation. Then the kinetic equation derived for continuous flow operation was compared with the observed result obtained by continuous operation to discuss about the validity.

For several mechanistic cases of the thermal degradation of polymer the author derived equations for the chain length distribution, the average chain length and the average residence time of the reactor content staying in the reactor during continuous flow operation. For the monodispersed polymer degrading thermally with random depolymerization, the following kinetic equations were derived.

**Average chain length:** $\bar{DP}_n = 2L + 1 - L(L+1)/DP_0$

**Average residence time:** $i = (1/k_i)[(2L + 1)/L(L+1) - 1/DP_0]$

**Chain length distribution:** $w_{DP} = 1/[(DP^2 - 1)]/[((2L + 1)/L(L+1) - 1/DP_0)]$
1. Introduction

In this study the author will explain the kinetics in the thermal degradation of polymer by continuous flow operation. The kinetics for the thermal degradation of polymer is to derive the rate equation based on a reaction mechanism such as random scission or monomer scission, and solve it to obtain the weight loss rate, the molecular weight change of the original polymer and so on.

Previous works on the thermal degradation of polymer have already been compiled into several books [1, 2, 3]. In general, complicated mathematical expressions are developed because the thermal decomposition mechanism of the polymer is complicated and the reactants and products involved in the reaction are composed of a lot of components. All of works on the kinetics for the thermal degradation of polymer that have been previously carried out have been conducted exclusively for the thermal decomposition by batch operation. As a matter of course, the kinetic equations made for the thermal decomposition of batch operation cannot be applied to the plastic pyrolysis process of continuous flow operation as it is.

In this study the author first clarify the difference between the kinetics of batch operation and continuous flow operation, and then explain a series of basic formulas that link batch operation and continuous flow operation. Based on these basic formulas, the kinetic equations of batch operation were converted into the kinetic equations of continuous flow operation. In addition, the kinetically predicted chain length distribution of the reactor content staying in the reactor during continuous flow operation were compared with the experimentally obtained chain length distribution by continuous operation to discuss about the validity.
2. Kinetics of batch operation and continuous flow operation

Figure 1 shows a schematic diagram of the continuously operated reactor that is the subject of this study.

The batch operation is an unsteady operation. Therefore, the kinetic equations for batch operation represent the time change of such as residual quantity, product yield, intrinsic viscosity, molecular weight distribution, average molecular weight and so on, when the sample polymer is thermally decomposed. They are usually expressed using kinetic constants such as reaction rate constant, maximum degree of polymerization to be vaporized, initial polymerization degree and so on. By definition, components with a degree of polymerization less than the maximum degree of polymerization to be vaporized come out from the reactor and larger components remain in the reactor.

Generally, various quantities $X$ in the thermal decomposition of batch operation can be expressed by a function form as shown in Formula (a).

\[ X = f(t, k, L, DP_0) \]  \hspace{1cm} (a)

$t$ = time, $k$ = reaction rate constant, $L$ = maximum degree of polymerization to be vaporized, $DP_0$ = initial polymerization degree of raw polymer

The specification of Formula (a) is performed based on the thermal decomposition mechanism of the target polymer. If we know $k$, $L$ and $DP_0$ of the polymer, we can calculate the quantities $X$ on the thermal decomposition of batch operation at any time using the specified Formula (a).

On the other hand, the thermal decomposition performed in continuous operation as shown in Fig.1 is considered to be in a steady state. Therefore, the kinetic equations derived for the thermal decomposition by continuous operation express the various quantities $X$ of the reactor content staying in working reactor, such as the chain length distribution, the average chain length, the average residence time and so on using the kinetics constants. Naturally, the kinetics equations derived for the thermal decomposition by
continuous operation do not include time-dependent terms.

Eventually, the various quantities $X$ in the thermal decomposition of continuous operation can be expressed by a function form as shown in Formula (b). That is, the various quantities $X$ of the reactor content staying in working reactor can be calculated by applying $k$, $L$, $DP_0$ of the polymer to the kinetic formula of continuous operation.

$$X = F(k, L, DP_0)$$  \hspace{1cm} (b)

The conventional research on the kinetics of thermal degradation of polymer has been conducted exclusively on the batch-wise decomposition, and the kinetic formula of continuous operation applicable to recent waste plastic pyrolysis equipment is not known. In other words, the conventional research has been conducted for the purpose of realizing Formula (a), and has never been done for the purpose of realizing Formula (b).

In this study, first, the author will explain the basic equation that relates Formula (a) and Formula (b). Then, a procedure for converting the kinetic equation of batch operation to that of continuous operation will be described. Thereafter, the kinetic equations of continuous flow operation for several mechanistic cases of the thermal degradation of polymer are derived.

### 3. Basic formulas in order to relate batch and continuous flow operation

Most reactors, which have been used for the thermal degradation of waste plastics into liquid product in the industrial plant can be reduced to the same scheme as shown in Fig. 1. In the author's previous paper, it was referred to it as a ‘Degradation and Volatilization Reactor (DVR)’ [5]. The DVR is a continuous flow stirred tank reactor in which thermal degradation of polymers and volatilization of products simultaneously occur under a condition of steady state. In the DVR system, the input polymer is continuously melted into a viscous liquid while mixing with the reactor contents. At degradation temperature the reactor contents decompose into small molecules which are convertible to hydrocarbon vapor under reaction conditions and leave the reactor. Needless to say, all of the volatile products vaporize in the reactor before coming out as the output product of DVR. The volatile products consist of a lot of hydrocarbons, which enter into the condenser where they separate into the gaseous products and liquid products. Both the gaseous and liquid products consist of a series of hydrocarbons corresponding to the input polymer.
Here we define the unit "m.u.mole". The “m.u.mole” is an abbreviation for the monomeric unit mole. One mole of polymer with a degree of polymerization DP is defined as corresponding to DP [m.u.mole]. Furthermore, multiplying m.u.mole by the molecular weight “a” of the monomer gives the weight of polymer. That is, n [mole] of polymer having the degree of polymerization DP corresponds to nDP [m.u.mole] in m.u.mole unit and anDP [gram] in weight unit. In the following kinetic formula m.u.mole and mole are exclusively used. The reason is to generalize the kinetic formula so that it can be applied to polymers with different molecular weight monomers.

When 1 [m.u.mole] of polymer having an initial degree of polymerization DP₀ is decomposed (batch-wise), the number of moles of the degree of polymerization DP existing in the reactor after t hours is assumed to be nDP. Among Qdt [m.u.mole] of raw polymer supplied during the period from t to t + dt for DVR, the number of NDP [mole] and the amount of MDP [m.u.mole] of those having a polymerization degree DP existing in the reactor (continuous flow) are expressed by the following equations, respectively. “Q” is the feed rate of raw material polymer [m.u.mole/hour].

\[
N_{DP} = \int_{0}^{\infty} Qn_{DP}dt
\]

\[
M_{DP} = \int_{0}^{\infty} QDPn_{DP}dt
\]

Also, for DVR the polymer supplied during the period from t to t + dt currently exists Qdt(1-C) [m.u.mole] in the reactor. Here, “C” represents the fraction of weight reduction in the thermal decomposition of batch operation, therefore 1-C represents the residual fraction. Accordingly, the following relational expressions are established.

\[
\sum_{DP=L+1}^{DP_{0}} M_{DP} = \int_{0}^{\infty} Q(1-C)dt
\]

\[
\sum_{DP=L+1}^{DP_{0}} N_{DP} = \int_{0}^{\infty} Q \frac{1-C}{DP_{n,t}} dt
\]

\[
\overline{DP_{n}} = \frac{\sum_{DP=L+1}^{DP_{0}} M_{DP}}{\sum_{DP=L+1}^{DP_{0}} N_{DP}}
\]

\[
\dot{t} = \frac{1}{Q} \sum_{DP=L+1}^{DP_{0}} M_{DP} = \int_{0}^{\infty} (1-C)dt
\]

\[
V_{R} = v_{m} \dot{Q}t
\]

Here, it is assumed that the component having a chain length of L or less
due to decomposition should be quickly volatilized out of the reactor. Therefore, the left sides of the equations (3) and (4) represent the total amount of components [m.u.mole] and the total number of components [mole] staying in the reactor, respectively. In the above equation, the overline indicates the average value, and

\[ \text{DP}_{n,t} : \text{chain length at reaction time } t \text{ in batch reactor} \]
\[ \text{DP}_n : \text{chain length in continuous flow reactor} \]
\[ \tau : \text{average residence time [hour]} \]
\[ v_mQ : \text{volumetric feed rate [m}^3\text{/hour]} \]
\[ V_R : \text{reactor volume (}v_mQ\tau ) [m^3] \]
\[ C : \text{fraction of weight reduction in the thermal decomposition of batch operation} \]

By substituting the kinetic equation of batch operation into the equations (3) to (7), the equations representing various quantities X for continuous flow operation reactor (DVR) can be derived. They are specifically shown below.

4. Kinetic formula for monodisperse polymer in continuous flow operation

In general, the polymer consists of polydisperse polymer. But, in this study, we first start with the kinetic equation for the monodisperse polymer with a degree of polymerization DP_0 which is fed to the continuous flow reactor DVR, and then derive those for the polydisperse polymer.

4-1. Random degradation

We will derive the kinetic formula of the polymer that decomposes exclusively by random scission. When a monodisperse polymer 1 m.u.mole having an initial degree of polymerization DP_0 is decomposed by random scission, the equations showing the distribution of the degree of polymerization after time t are expressed as shown in equations (8) and (9). These expressions (for batch operation) were obtained by Jellinik [1].

When DP < DP_0

\[ n_{DP} = (1/DP_0)e^{-(DP_0-1)\tau}[(DP_0-\text{DP}-1)e^{-2\tau} - 2(DP_0-\text{DP})e^{-\tau}+(DP_0-\text{DP}+1)] \] (8)

When DP = DP_0

\[ n_{DP_0} = (1/DP_0)e^{-(DP_0-1)\tau} \] (9)

Here, \( \tau = k_{ir}t \) (\( k_{ir} \) : rate constant of random scission).
Substituting Eqs. (8), (9) into Eqs. (1), (2) and integrating, $N_{DP}$ and $M_{DP}$ are obtained as follows.

When $1 < DP < DP_0$,

$$N_{DP} = \frac{Q}{k_{ir}} \cdot \frac{2}{[DP_0 (DP_0^2 - 1)]}$$  \hspace{1cm} (10)

$$M_{DP} = \frac{Q}{k_{ir}} \cdot \frac{2}{(DP_0^2 - 1)}$$  \hspace{1cm} (11)

When $DP = DP_0$,

$$N_{DP_0} = \frac{Q}{k_{ir}} \cdot \frac{1}{[DP_0 (DP_0 - 1)]}$$  \hspace{1cm} (12)

$$M_{DP_0} = \frac{Q}{k_{ir}} \cdot \frac{1}{(DP_0 - 1)}$$  \hspace{1cm} (13)

The following two equations can be obtained from Eqs. (10) to (13).

$$\sum_{DP=L+1}^{DP_0} N_{DP} = \frac{Q}{k_{ir}} \cdot \frac{1}{L(L+1)}$$  \hspace{1cm} (14)

$$\sum_{DP=L+1}^{DP_0} M_{DP} = \frac{Q}{k_{ir}} \left[ \frac{2L+1}{L(L+1)} - \frac{1}{DP_0} \right]$$  \hspace{1cm} (15)

Furthermore, by substituting Eqs. (14) and (15) into Eqs. (5), (6), and (7), the average polymerization degree of reactor content, the average residence time, and the reactor volume in the case of continuous flow operation/random scission can be derived. They are shown by Eqs. (16), (17) and (18).

$$\overline{DP_n} = \frac{2L+1 - L(L+1)/DP_0}{DP_0}$$  \hspace{1cm} (16)

$$i = \frac{1}{k_{ir}} \left[ \frac{2L+1}{L(L+1)} - \frac{1}{DP_0} \right]$$  \hspace{1cm} (17)

$$V_R = \frac{v_m Q}{k_{ir}} \left[ \frac{2L+1}{L(L+1)} - \frac{1}{DP_0} \right]$$  \hspace{1cm} (18)

Moreover, the polymerization degree distribution of the reactor content is expressed by the following Eqs. (19) and (20).

When $DP_0 > DP \geq L+1$,

$$w_{DP} = \frac{2}{DP_0^2 - 1} \left[ \frac{2L+1}{L(L+1)} - \frac{1}{DP_0} \right]$$ \hspace{1cm} (19)

When $DP = DP_0$,

$$w_{DP_0} = \frac{1}{DP_0 - 1} \left[ \frac{2L+1}{L(L+1)} - \frac{1}{DP_0} \right]$$ \hspace{1cm} (20)

Here, in general, the initial degree of polymerization $DP_0$ of the polymer is very large compared to the distillation limit degree of
polymerization L, that is, \( \text{DP}_0 \gg L \). Therefore, terms containing \( \text{L} / \text{DP}_0 \) in Eqs.(16) to (20) are negligible compared to the other terms. For this reason, Eqs. (16) to (20) could be further simplified as shown below.

\[
\frac{\text{DP}_n}{2} = 2L + 1 \quad (16')
\]
\[
\iota = \left( \frac{1}{k_{ir}} \right) \cdot \frac{(2L + 1)/\{L(L + 1)\}}{\text{DP}_0} \quad (17')
\]
\[
V_R = \left( \frac{v_m Q}{k_{ir}} \right) \cdot \frac{(2L + 1)/\{L(L + 1)\}}{\text{DP}_0} \quad (18')
\]

When \( \text{DP}_0 > \text{DP} \geq L+1 \),

\[
\text{w}_{DP} = \left\{ \frac{2}{(\text{DP}_0^2 - 1)} \right\} \cdot \left\{ \frac{L(L + 1)/(2L + 1)}{\text{DP}_0} \right\} \quad (19')
\]

When \( \text{DP} = \text{DP}_0 \),

\[
\text{w}_{DP_0} = \left\{ \frac{1}{(\text{DP}_0 - 1)} \right\} \cdot \left\{ \frac{L(L + 1)/(2L + 1)}{\text{DP}_0} \right\} \quad (20')
\]

The followings can be said from the equations (16'), (17') and (18').

When the thermal decomposition proceeds by the random scission and the product having a polymerization degree of L or less is quickly volatilized out of the reactor, the average polymerization degree of the reactor content always becomes \( 2L + 1 \), regardless of the initial polymerization degree of the raw material and the decomposition rate constant. The average residence time is determined by giving the decomposition rate constant and the distillation limit polymerization degree L. Further, the reactor volume is obtained by multiplying the average residence time by \( v_m Q \) (volume flow rate of the raw material).

4.2 Random initiation, depropagation, and termination by disproportionation

Next, we will derive the kinetic equation when the polymer of such degradation mechanism is supplied to DVR. In the case of this degradation mechanism, it is necessary to consider two cases by comparing the average kinetic chain length \( \varepsilon \) and \( \text{DP}_0 \). The kinetic chain length is the number of times the degradation chain continues when decomposition begins.

a) \( \varepsilon \gg \text{DP}_0 \)

When \( \varepsilon \) is sufficiently larger than \( \text{DP}_0 \), once the decomposition starts, the decomposition continues until the molecule being disappears, so the degree of polymerization of the remaining polymer (the reactor content in this case) remains at \( \text{DP}_0 \). The fraction of weight reduction for batch
operation is given by the following equation \([1]\).

\[-\ln (1 - C) = (DP_0 - 1) k_{tr} t\]  

(21)

Substituting Eq. (21) into Eqs. (3) and (4) and integrating, the following two equations are obtained.

\[\sum_{DP=L+1}^{DP_0} N_{DP} = \frac{Q}{k_{tr}DP_0(DP_0 - 1)}\]  

(22)

\[\sum_{DP=L+1}^{DP_0} M_{DP} = \frac{Q}{k_{tr}(DP_0 - 1)}\]  

(23)

Substituting these two equations into Eqs. (5), (6), and (7), the following kinetic expressions are obtained.

\[\overline{DP_n} = DP_0\]  

(24)

\[t = 1/(k_{tr}(DP_0 - 1))\]  

(25)

\[V_R = v_m Q/(k_{tr}(DP_0 - 1))\]  

(26)

b) \(\varepsilon < DP_0\)

In this case, the fraction of weight reduction by decomposition and the average degree of polymerization are obtained as follows for the thermal decomposition in batch operation \([1]\).

\[-\ln (1 - C) = At\]  

(27)

\[\frac{1}{2L+1} \left[ \ln \left(1 - \frac{2L+1}{DP_0}\right) - \ln \left(1 - \frac{2L+1}{DP_n}\right) \right] = k_{tr} t\]  

(28)

Here, \(A = k_d \sqrt{2v_m k_{tr}/k_{td}}\)

And \(k_d\) and \(k_{td}\) express the rate constant of depopagation and termination by disproportionation, respectively.

Substituting Eqs. (27) and (28) into Eqs. (3) and (4) and integrating, the following two equations are obtained.

\[\sum_{DP=L+1}^{DP_0} M_{DP} = \frac{Q}{A}\]  

(29)

\[\sum_{DP=L+1}^{DP_0} N_{DP} = \frac{Q}{2L+1} \left[ \frac{1}{A} - \left( \frac{1 - \frac{2L+1}{DP_0}}{(2L+1)k_{tr} + A} \right) \right]\]  

(30)

Furthermore, the following relational expressions are obtained.
Thus, the result depends not only on the degradation mechanism but also on the magnitude relationship between $DP_0$ and $\varepsilon$. When $\varepsilon \gg DP_0$, the average polymerization degree remains unchanged at $DP_0$, and the average residence time is determined by $DP_0$ and the rate constant $k_{ir}$, regardless of the volatilization limit $L$. On the other hand, when $\varepsilon < DP_0$, the average degree of polymerization and the average residence time are almost independent of $DP_0$ and are determined by $L$ and $k_{ir}$.

4-3. Chain-end initiation, depropagation, and single molecule termination or termination by disproportionation

a) $\varepsilon \gg DP_0$

When $\varepsilon$ is sufficiently larger than $DP_0$, as described above, once the decomposition starts, the chain reaction continues until the molecule disappears, so the same result is obtained regardless of whether the single molecule termination or disproportionation. The degree of polymerization of the reactor content remains at $DP_0$. The fraction of weight reduction for batch operation is given by the following equation [1].

$$-\ln (1 - C) = 2k_{ie}t \quad (34)$$

Substituting Eq. (34) into Eqs. (3) and (4) and integrating, the following two equations are obtained.

$$\sum_{DP = L+1}^{DP_0} M_{DP} = \frac{Q}{2k_{ie}} \quad (35)$$

$$\sum_{DP = L+1}^{DP_0} N_{DP} = \frac{Q}{2k_{ie}DP_0} \quad (36)$$

Substituting these two equations into Eqs. (5), (6), and (7), the following kinetic expressions are obtained.
Unlike the case of random initiation, the average residence time in this case does not depend on the initial degree of polymerization.

\[ \overline{D}P_n = D P_0 \]
\[ \bar{t} = 1/2k_{ie} \]
\[ V_R = v_m Q / 2k_{ie} \]

b-1) $\varepsilon < D P_0$ with the single molecule termination

The average degree of polymerization and the fraction of weight reduction for batch operation are given by the following equations [1].

\[ (1-C)/(\overline{DP}_{n,t}) = 1/(DP_0) \]
\[ C = (2k_{ie}\varepsilon/(DP_0))t \]

In this case, since the residual ratio $1-C$ of the polymer decreases linearly with the elapse time, there is no polymer that exceeds the predetermined time $t_0$ (= $D P_0 / 2k_{ie}\varepsilon$). That is, there is no polymer with a residence time exceeding $t_0$ in the reactor. When the integration range in Eqs. (3) and (4) is set to 0 to $t_0$, the following results are obtained.

\[ \sum_{D P=L+1}^{D P_0} \frac{M_{DP}}{D P_0} = \frac{D P_0 Q}{4k_{ie}\varepsilon} \]
\[ \sum_{D P=L+1}^{D P_0} \frac{N_{DP}}{D P_0} = \frac{Q}{2k_{ie}\varepsilon} \]
\[ \overline{DP}_n = D P_0 / 2 \]
\[ \bar{t} = D P_0 / (4k_{ie}\varepsilon) \]
\[ V_R = v_m Q D P_0 / (4k_{ie}\varepsilon) \]

b-2) $\varepsilon < D P_0$ with the termination by disproportionation

The average degree of polymerization and the fraction of weight reduction for batch operation are given by the following equations [1].

\[ (1-C)/\overline{DP}_{n,t} = 1/D P_0 \]
\[ C = (k_d^2 k_{ie} v_m \sqrt{(k_{ie} D P_0)}/t^2) \]

When the equations (47) and (48) are applied to the equations (3) to (7), the following equations are obtained. Here, $A = k_d \times \text{square root}(k_{ie} v_m)$. 
This is the end of the explanation of the kinetic formula of the monodisperse polymer, and then the kinetic formula of the polydisperse polymer will be explained.

5. Kinetic formula for polydisperse polymer in continuous flow operation

For polydisperse polymers, the kinetic equation related to the continuous flow thermal decomposition of polymers can be derived in the same way as for monodisperse polymers. Here, as an example, the kinetic equation of the continuous flow operation will be derived for the case where a polymer whose initial degree of polymerization distribution is represented by the most provable distribution undergoes random scission.

The most provable distribution is expressed by the following formula.

$$\varphi(DP) = DPq^{n}e^{-qDP} \quad (54)$$

By definition,

$$\int_{0}^{\infty} \varphi(DP) dDP = 1 \quad (55)$$

Here, $q$ in Eq. (54) is the reciprocal of the average molecular weight of the polydisperse polymer after decomposition, and when $q_0$ is that for the raw material, the following equation is established with a good approximation in the case of random scission.

$$q - q_0 = k_{ir}t \quad (56)$$

When the polymerization degree distribution of a polydisperse polymer during thermal decomposition (batch operation) is expressed by $n_{DP*}$, the $n_{DP*}$ is expressed by the following formula from the $n_{DP}$ of a monodisperse polymer and the polymerization degree distribution of the raw material.
\[ n_{DP^*} = n_{DP_0^*} \varphi(DP_0) \bigg|_{DP_0=DP} + \int_{DP+1}^{\infty} n_{DP} \varphi(DP_0) dDP_0 \quad (57) \]

The first term on the right side of the above formula (57) represents the amount of raw material with a polymerization degree DP that remains as it is. And the second term represents the amount of polymerization degree DP obtained from molecules of polymerization degree DP+1, DP+2, DP+3 to DP, respectively. Substituting Eqs. (8), (9), and (54) into Eq. (64) to find \( n_{DP^*} \) and then using Eq. (56) to integrate the basic equations (1) and (2), we can obtain formulas expressing \( N_{DP^*} \) and \( M_{DP^*} \). \( N_{DP^*} \) and \( M_{DP^*} \) express the number of \( N_{DP} \) [mole] and the amount of \( M_{DP} \) [m.u.mole] of polydisperse polymer having a polymerization degree DP existing in the continuous flow reactor. The calculation results are shown below for the case where a polymer whose initial degree of polymerization distribution is represented by the most provable distribution undergoes random scission.

\[ N_{DP^*} = \frac{Q}{k_4} e^{-q_0^{DP^*}} \left[ \frac{q_0^2}{2DP - 1} + \frac{2q_0}{(2DP - 1)^2} + \frac{2}{(2DP - 1)^3} \right. \]
\[ + e^{-q_0} \left\{ \frac{q_0^2}{2DP - 2DP + 1} - \frac{2}{(2DP)^2} + \frac{2}{(2DP + 1)^2} \right\} \quad (58) \]

\[ M_{DP^*} = DPN_{DP^*} \quad (59) \]

**Table 1**  Predicted kinetic data by the random scission theory on polydispersed polymers

<table>
<thead>
<tr>
<th>( DP_0^* )</th>
<th>( \frac{k}{Q} )</th>
<th>( \sum_{DP=1}^{\infty} N_{DP^*} )</th>
<th>( \frac{k}{Q} )</th>
<th>( \sum_{DP=1}^{\infty} M_{DP^*} )</th>
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</table>

Table 1 shows the kinetic data calculated by computer according to Eqs.
Figure 2 shows the distribution of the degree of polymerization of the reactor content obtained from the data shown in Table 1 and Eqs. (58), (59), and the degree of polymerization of the raw material polymer expressed by Eq. (54).

![Figure 2 Chain length distribution of polydisperse polymer and its reactor content decomposing with random scission.](image)

- a: original polydisperse polymer having most probable distribution
- b: reactor content staying in the continuous flow reactor

The average molecular weight \( \overline{DP}_n^* \) of the reactor content is expressed by the following formula. The values of average \( \overline{DP}_n^* \) determined for various \( L \) and \( \overline{DP}_n^* \) are also shown in Table 1. The average \( \overline{DP}_n^* \) value indicates that it is close to \( 2L + 1 \), as in the case of the monodisperse polymer.

\[
\overline{DP}_n^* = \sum_{DP=L+1}^{\infty} M_{DP^*} / \left( \sum_{DP=L+1}^{\infty} N_{DP^*} \right) \quad (60)
\]

With respect to a polymer having a decomposition mechanism and/or a polymerization degree distribution other than the examples described above, kinetic equations relating to the thermal decomposition of the continuous flow operation can be derived by the similar method.

With respect to a polymer having a decomposition mechanism and/or a polymerization degree distribution other than the examples described above, corresponding kinetic equations relating to the thermal decomposition by continuous flow operation could be derived by a similar procedure.
6. Discussion

So far, we have derived equations representing the average degree of polymerization, distribution of polymerization degree, average residence time and so on in DVR for various decomposition mechanisms. In the following, we compare the kinetic equations derived for continuous flow operation with the observed result using DVR. At the same time, we will discuss about the validity of the derived kinetic equations.

For polyethylene  Fig. 3 shows the polymerization degree distribution of volatile product, reactor content and raw polymer when polyethylene (high density) is thermally decomposed with the continuous flow reactor \[4, 5\]. And Fig.4 shows the distribution of polymerization degree of each component predicted from the random scission theory.

According to the theory of random scission, each component of the volatile product is formed in the same ratio, so as shown in Fig.4, the chain degree distribution is represented by a straight line proportional to the polymerization degree. On the other hand, the distribution of the degree of polymerization of the reactor content is represented by Eqs. (19'), (20'). The distribution of the polymerization degree of the raw polymer is shown as a monodisperse polymer in Fig.4 for convenience, but since DP >> L in general, Eqs. (19'), (25') can be used. That is, even if a polydisperse polymer is used as a raw material, the same result as the monodisperse polymer is obtained in theory.
As is known in the general distillation operation, the distillation cannot separate the mixture clearly at a certain boiling point. That is, it does not occur such a simple separation that a component having a degree of polymerization of L or less is a volatile and a component having a degree of polymerization of L + 1 or more is a reactor content. Therefore, if the classification of the volatile and the reactor content is represented by an S-shaped separation curve, the predicted polymerization degree distribution of reactor content could be approximated to the polymerization degree distribution of the observed reactor content, as shown by dotted line.

The average molecular weight of the reactor content of polyethylene observed by the experiment at 410 °C under atmospheric pressure is 765 [4]. According to the kinetics, when L = 12.5 (C_{25} is the volatile chain length) is substituted into Eq. (16'), it is calculated as 728. Similarly, at the decomposition temperature 430°C, the average molecular weight of the reactor content is observed to be 985, and is calculated as 784 from the kinetics. It seems that the difference between the observed and the predicted value tends to increase as the decomposition temperature increases. However, the results derived from theoretical considerations could be in good agreement with the observed results. It considered that kinetic formulas derived from the theory of the random scission are sufficiently useful to understand the nature of reactor content for polymers, polyethylene, polypropylene, etc. where the random scission is predominant.

But, for volatile the agreement between the polymerization degree
distribution predicted from the theory and the observed polymerization degree distribution is not good. The center of the polymerization degree distribution of volatile is on the lower molecular weight side and is not uniform. The thermal degradation of polymers consists of two sorts of scission which simultaneously occur in a manner mentioned in the preceding paper [5, 6]. One is a random scission, and the other is a chain-end scission. The random scission of C–C links in polymers causes a molecular weight reduction of raw polymer increasing reactor contents, and the chain-end scission of C–C links causes a dissipation of reactor contents generating volatile products. The reason that the degree of polymerization distribution of volatile differs from the result expected from the random scission is supposed that the generation of volatile does not depend on the random scission but on the chain-end scission. In any case, conventional kinetics on the polymer decomposition have had little success with regard to the mechanism of volatile formation.

**For polystyrene**  Fig. 5 shows the polymerization degree distribution of volatile product, reactor content and raw polymer when polystyrene was thermally decomposed with the continuous flow reactor [5, 7].

The distribution of the polymerization degree of the reactor content of polystyrene differs from the result predicted by the theory of random scission, and is located on the higher molecular weight side. It is also clear that the distribution of volatile product is different from the distribution predicted.
from the random scission.

When polystyrene is thermally decomposed, its 50-60% becomes a monomer, and it is known as a polymer that is relatively easy to undergo the monomer scission. The random scission is also observed for polystyrene. Mlhotra et al. [8], based on the detail analysis by GPC, stated that polystyrene is reduced in molecular weight by the random scission, and its volatile product is generated by the scission from chain-end. As mentioned in the author’s previous paper [5], the thermal decomposition of polystyrene, like the thermal decomposition of polyethylene, is considered to be a parallel reaction of the random scission and the scission from chain-end. In the case of polystyrene, the rate of the scission from chain-end is relatively large, so the deviation from the result predicted from the theory of random scission may be large. In the thermal decomposition by the continuous flow operation, the distribution of polymerization degree of the reactor content of polystyrene reaches a dynamic equilibrium on the higher molecular weight side as compared with that of polyethylene. The reason is that the random scission of polystyrene does not stop there, but the chain-end scission is relatively fast, so that the reduction in molecular weight cannot catch up.

7. Conclusion

In this paper, basic formulas that link the kinetic equation of batch operation and the kinetic equation of flow operation in the thermal decomposition of polymer were presented. Based on the basic formula, kinetic equations for the thermal decomposition of various polymers in the continuous flow reactor, which are equations expressing the distribution of polymerization degree of the reactor content, the average degree of polymerization, the average residence time, etc., were derived. Then the kinetic equation derived for continuous flow operation was compared with the observed experimental result to discuss about the validity.

1) For the polymer, such as polyethylene, polypropylene that decomposes mainly by random scission, the results derived from theoretical considerations could be in good agreement with the observed results. The kinetic equations derived from the theory of the random scission are sufficiently useful to understand the nature of reactor content.

2) In the case of polystyrene, the rate of the scission from chain-end is relatively large, so the deviation from the result predicted from the theory
of random scission may be large. In the thermal degradation of polystyrene by the continuous flow operation, the distribution of polymerization degree of the reactor content reaches a dynamic equilibrium on the higher molecular weight side as compared with that of polyethylene. When the random scission and the chain-end scission are half-way like polystyrene, the kinetics of parallel reaction is required.

3) For the volatile product, the agreement between the polymerization degree distribution predicted from the theory and the observed result is not good. Conventional kinetics predicts the degree of polymerization of reactor content, but hardly explains the degree of polymerization of volatile products.

4) The kinetics of the continuous flow operation provides basic information for the pyrolysis process of waste plastics, such as the distribution of polymerization degree of the reactor content, the average residence time and so on.

References