Degradation Kinetics of Polyethylene Terephthalate in Supercritical Methanol

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Degradation of polyethylene terephthalate (PET) in supercritical methanol was investigated to develop a chemical recycling process for waste plastics. Continuous kinetics analysis was applied to the experimental data. A batch reactor was used at 573 K under the estimated pressure of 20 MPa for a reaction time of 2−120 min. PET decomposed to its monomers, dimethyl terephthalate (DMT), and ethylene glycol (EG), by methanolysis in supercritical methanol. PET with a weight-average molecular weight of about 47,000 was converted to oligomer with that of 3,000 in 300 s and with that of 1,000 in 600 s. The largest yield of DMT was 80 mol % at 7,200 s and that of EG was 60 mol % at 3,600 s. Reaction products were analyzed with size exclusion chromatography, gas chromatography-mass spectrometry, and reversed phase liquid chromatography. The molecular-weight distribution (MWD) of the products was obtained as a function of reaction time. The yields of monomer components of the decomposition products, including byproducts, were measured. Continuous kinetics theory was developed to analyze the decomposition behavior. The theory includes MWD change of polymer by random and specific scissions and secondary reactions for monomer components. Change of MWD and monomers as a function of time was simulated by the continuous kinetics.

Introduction

Disposal and recycling of waste plastics have become a serious problem and it has become important to develop efficient treatment technology. The chemical recycling by depolymerization of polyethylene terephthalate (PET), which is a condensation polymer abundantly used, is necessary. Various chemical recycling methods for PET, such as methanolysis in liquid methanol (Grunschke et al., 1968), glycolysis in liquid ethylene glycol (Baliga and Wong, 1989), ester exchange (Delattre et al., 1979), and hydrolysis using an alkali (Datye and Vaidya, 1984), have been developed on commercial and pilot scales. These methods have problems, however, such as the use of catalyst and slow reaction. The reaction time for these methods are more than 5 h (Sako et al., 1998).

Supercritical fluids have been focused on for decomposition of plastics, because of the environmentally friendly nature of the fluids. Above its critical point, the supercritical fluid has large density like a liquid and high kinetic energy like a gas molecule, and the reaction rate is therefore expected to increase compared with the reaction under liquid conditions. Plastics are quickly decomposed in supercritical fluids by solvolysis (such as hydrolysis, alcoholysis) or pyrolysis. Condensation polymers with ether, ester, or acid amide linkages are easily decomposed to their monomers by solvolysis in supercritical water or supercritical methanol. Hydrolysis in supercritical water ($Tc = 647.3$ K, $Pc = 22.0$ MPa) (Yamamoto et al., 1996; Adschiri et al., 1997) or methanolysis in supercritical methanol ($Tc = 512.6$ K, $Pc = 8.09$ MPa) (Sako et al., 1997, 1998, 2000; Goto et al., 1998, 1999) has been studied for PET decomposition. In hydrolysis in supercritical water, the monomer products are terephthalic acid (TPA) and

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ethylene glycol (EG). Although TPA was recovered in a 90% yield, the yield of EG was only 10%, because of the secondary reaction catalyzed by reaction product TPA (Adschiri et al., 1997). Sako et al. (1997) reported that the methanolysis in supercritical methanol produced both monomers, dimethyl terephthalate (DMT), and EG with almost a 100% yield in 30 min without catalyst.

In this work, we investigated the depolymerization of PET to its monomers in supercritical methanol. From size exclusion chromatography (SEC), the evolution of the molecular weight-distribution (MWD) of polymer and oligomer was obtained. Concentrations of the monomers and byproducts produced in the reaction were measured as a function of reaction time.

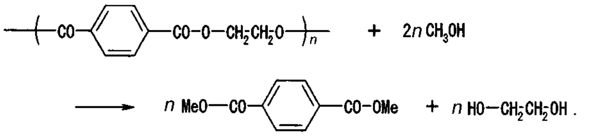
Distribution kinetics is a procedure for analyzing the dynamics of systems that are distributed in a property, such as MW. Polymer decomposition is such a dynamic system, as the molecular-weight distribution changes with time owing to chain cleavage. The governing equations for the MWD are population balance equations that can be solved by moment methods. Wang et al. (1995) studied polymer degradation by examining the random and the chain-end scission of poly(styrene-allyl alcohol) in solution. Rate parameters were determined from the polymer MWD, which was modeled as a continuous distribution evolving in time. Kodera and McCoy (1997) showed that radical mechanisms for polymer degradation could be interpreted by writing the population balance equations for the radical and nonradical species, and that overall rate coefficients were composites of rate coefficients in the detailed mechanism. Since then, several other polymer systems, including mixtures, have been investigated by the distribution kinetics approach. The effects of additives, such as hydrogen donors or strong oxidizers (peroxide), have also been studied.

PET methanolysis involves both random and chain-end scission, and is interesting from a theoretical point of view because of the secondary reactions of the chain-end scission products. A chemical reaction engineering theory combining continuous-distribution kinetics with specific-product chemical reactions has never been reported. In the current work, we present the population balance equation that governs the PET MWD, and solve with the moment method. Specific products of chain-end scission are governed by separate rate equations that are combined with secondary reaction kinetics of these specific species. The resulting system of ordinary differential equation for the batch reactor are solved and compared with experimental data to determine individual rate coefficients. The work demonstrates that conventional kinetics can be combined with distribution kinetics to analyze complex macromolecular reactions.

Mechanism

The reaction of PET in methanol at high temperature and high pressure involves degradation to oligomers and monomers by methanolysis and some secondary reactions. In the degradation of polymers, two reaction paths may represent the reactions to produce monomeric species from the polymer. One is pure random degradation, represented by binary scission of bonds at any position along the chain. The other extreme is specific reaction, which releases monomeric species of the polymer by scission at the chain end.

We have studied the degradation of PET in supercritical methanol in order to recover the monomers. The major reaction for the monomerization of PET in methanol is



(1)

Based on our experimental results, described later, the whole reaction can be represented by the reaction scheme shown in Figure 1. The reactions consist of the following

$$\mathrm{PET} + \mathrm{MeOH} \rightarrow \mathrm{Oligomer} \tag{2}$$

$$\mathrm{Oligomer} + \mathrm{MeOH} \rightarrow \mathrm{MHET} \tag{3}$$

$$\mathrm{Oligomer} + \mathrm{MeOH} \rightarrow \mathrm{DMT} + \mathrm{EG} \tag{4}$$

$$\mathrm{Oligomer} + \mathrm{H_2O} \rightarrow \mathrm{TAMME} + \mathrm{EG} \tag{5}$$

$$\mathrm{MHET} + \mathrm{MeOH} \rightarrow \mathrm{DMT} + \mathrm{EG} \tag{6}$$

$$\mathrm{MHET} + \mathrm{H_2O} \rightarrow \mathrm{TAMME} + \mathrm{EG} \tag{7}$$

$$\mathrm{EG} + \mathrm{MeOH} \rightarrow \mathrm{ME} + \mathrm{H_2O} \tag{8}$$

$$2\,\mathrm{EG} \rightarrow \mathrm{DEG} + \mathrm{H_2O}. \tag{9}$$

Here, MHET, DMT, EG, TAMME, ME, and DEG are methyl 2-hydroxyethyl terephthalate, dimethyl terephthalate, ethylene glycol, terephthalic acid monomethyl ester, 2-methoxyethanol, and diethylene glycol, respectively.

Theoretical Model

Continuous kinetics for polymer degradation

In the continuous-mixture model, the polymer, $A(x)$, is considered to be a mixture with a large number of different-size molecules, with MW or x, as a continuous variable. Polymer degradation can be written as a combination of random chain scission

$$A(x') \rightarrow A(x) + A(x'-x) \tag{10}$$

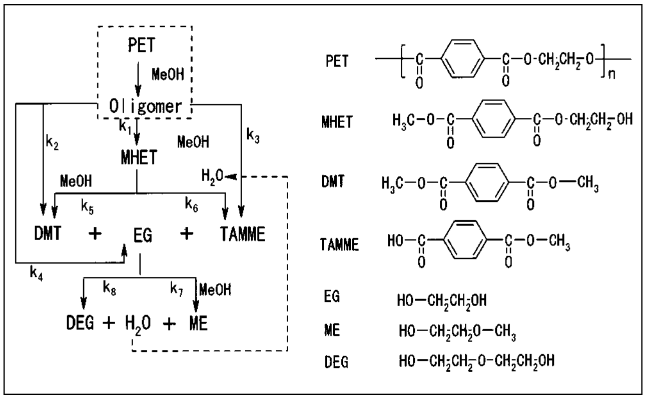


Figure 1. Reaction scheme for decomposition of PET in methanol.

and chain-end scission

$$A(x') \rightarrow A(x_i) + A(x' - x_i), \tag{11}$$

where x_i is the molecular weight of the specific product. The continuous kinetics has been developed (McCoy and Wang, 1994; Wang et al., 1994, 1995). The time-dependent MWD of $A(x)$ is defined based on molar concentration by $p(x,t)$. Let the rate coefficient for degradation of $A(x)$ be $k(x)$ and define $\Omega(x,\ x')$ as the fraction of $A(x')$ that cracks to $A(x)$. The parallel reactions for degradation of $A(x)$ are assumed to be first order. The general rate equation for random scission can be written as

$$\frac{dp(x,t)}{dt} = -k(x)p(x,t) + 2\int_x^\infty k(x')p(x',t)\Omega(x,x')\,dx'. \tag{12}$$

For specific scission, two rate equations are required to describe $A(x_i)$ and $A(x' - x_i)$. For $A(x' - x_i)$

$$\frac{dp(x,t)}{dt} = -k(x)p(x,t) + \int_x^\infty k(x')p(x',t)\Omega(x - x_i, x')\,dx'; \tag{13}$$

for $A(x_i)$

$$\frac{dq_i(x_i,t)}{dt} = \int_x^\infty k(x')p(x',t)\Omega(x_i,x')\,dx', \tag{14}$$

where $q_i(x_i,\ t)$ is the MWD of the specific product i. The stoichiometric term $\Omega(x,\ x')$ represents a reaction in which a molecule fragments into two product molecules whose sizes, x and $x' - x$, sum to the reactant size, $x' \geq x$. A detailed discussion for the stoichiometric term $\Omega(x,\ x')$ was given by Wang et al. (1995).

Model formulation

By applying continuous kinetics concepts to PET degradation, we make the following assumptions:

1. The reactions for both specific and random degradation are irreversible and all rate coefficients are independent of the MW. Reaction 1 was assumed to be a first-order reaction and Reaction 9 was assumed to be a second-order reaction. Although Reactions 2–8 are second-order reactions, they are described by first-order kinetics by assuming methanol and water are present in excess.
2. The MWDs of the reaction mixtures can be described by a gamma distribution whose parameters depend on residence time, and therefore are different from those for the feed polymer.
3. The reactant and products are dissolved in the solvent phase, which indicates no distinction between the polymer phase and the solvent phase under reacting conditions.
4. The reaction occurs in a well-mixed batch reactor.

The PET degradation and the secondary reaction are described in the following equations. Random scission

$$P(x') \xrightarrow{k_r} P(x) + P(x' - x). \tag{15}$$

Specific scission:

$$P(x') \xrightarrow{k_1} Q_1(x_1) + P(x' - x_1) \quad \text{production of MHET} \tag{16}$$

$$P(x') \xrightarrow{k_2} Q_2(x_2) + P(x' - x_2) \quad \text{production of DMT} \tag{17}$$

$$P(x') \xrightarrow{k_3} Q_3(x_3) + P(x' - x_3) \quad \text{production of TAMME} \tag{18}$$

$$P(x') \xrightarrow{k_4} Q_4(x_4) + P(x' - x_4) \quad \text{production of EG.} \tag{19}$$

Based on Reactions 2–5, the production of a molecule of DMT accompanies the production of a molecule of EG, and the production of a molecule of TAMME accompanies the production of a molecule of EG. Thus, $k_4 = k_2 + k_3$.

Secondary Reactions 6–9

$$Q_1(x_1) \xrightarrow{k_5} Q_2(x_2) + Q_4(x_4) \quad \text{production of DMT + EG} \tag{20}$$

$$Q_1(x_1) \xrightarrow{k_6} Q_3(x_3) + Q_4(x_4) \quad \text{production of TAMME + EG} \tag{21}$$

$$Q_4(x_4) \xrightarrow{k_7} Q_5(x_5) \quad \text{production of ME from EG} \tag{22}$$

$$2Q_4(x_4) \xrightarrow{k_8} (1/2)Q_6(x_6) \quad \text{dimerization of EG to DEG} \tag{23}$$

For these reactions, the following governing equations can be written based on the continuous kinetics. For the reaction mixture, we include effects of random degradation and specific degradation

$$\frac{dp(x,t)}{dt} = -k_r p(x,t) + 2\int_x^\infty k_r(x',t)p(x',t)\Omega(x,x')\,dx' - \sum_{i=1}^{4}\left[k_i p(x,t) - \int_x^\infty k_i p(x',t)\Omega(x - x_i, x')\,dx'\right]. \tag{24}$$

For the specific products

$$\frac{dq_i(x_i,t)}{dt} = \int_x^\infty k_i p(x',t)\,\Omega(x_i,x')\,dx' + R_i(t), \tag{25}$$

where $q_i(x_i,t)$ are MWDs for the specific products, and $i = 1$, 2, 3, and 4 represents MHET, DMT, TAMME, and EG, respectively. R_i is a monomer reaction term written as

$$R_1(t) = -(k_5 + k_6)q_1 \quad (26)$$

$$R_2(t) = k_5 q_1 \quad (27)$$

$$R_3(t) = k_6 q_1 \quad (28)$$

$$R_4(t) = (k_5 + k_6)q_1 - (k_7 + k_8)q_4 \quad (29)$$

The initial conditions are

$$p(x, t = 0) = p_0(x) \quad (30)$$

$$q_i(x_i, t = 0) = 0, \quad i = 1,2,3,4 \quad (31)$$

For the species produced by the secondary reaction,

$$\frac{dq_{s5}(t)}{dt} = k_7 q_4 \quad (32)$$

$$\frac{dq_{s6}(t)}{dt} = \frac{1}{2} k_8 q_4^2, \quad (33)$$

where subscripts 5 and 6 represent ME and DEG, respectively. The initial conditions are

$$q_{si}(x_i, t = 0) = 0, \qquad i = 5 \text{ and } 6. \quad (34)$$

Moment operations

The moments of the MWDs are defined as the integrals over the MW or x,

$$p^{(n)}(t) = \int_0^\infty x^n p(x,t)\,dx. \quad (35)$$

The zero moment, $p^{(0)}(t)$ is the time-dependent total molar concentration (mol/vol) of the polymer. The first moment, $p^{(1)}(t)$, is the mass concentration (mass/volume). The normalized first moment gives the average MW, $x^{\text{avg}} = p^{(1)}/p^{(0)}$, and the second central moment gives the variance of the MWD, $x^{\text{var}} = p^{(2)}/p^{(0)} - [x^{\text{avg}}]^2$. The three moments, $p^{(0)}$, x^{avg}, and x^{var}, provide the shape characteristics of the MWD. The polydispersity is defined as the ratio of the mass (or weight) average MW, $M_W = p^{(2)}/\ p^{(1)}$, to the molar (or number) average MW, $M_n = x^{\text{avg}}$, that is, $D = p^{(2)}p^{(0)}/[p^{(1)}]^2$.

The moment operation, applied to Eq. 24, is interchanged with the time derivative, yielding ordinary differential equations for moments

$$\frac{dp^{(n)}(t)}{dt} = -\left(k_r + \sum_{i=1}^{4} k_i\right) p^{(n)}(t) + 2\int_0^\infty x^n\,dx \int_x^\infty k_r p(x',t)\,\Omega(x,x')\,dx' + \sum_{i=1}^{4} \int_0^\infty x^n\,dx \int_x^\infty k_i p(x',t)\,\Omega(x - x_i, x')\,dx'. \quad (36)$$

For totally random distribution, $\Omega(x,x') = 1/x'$. For specific scission, $\Omega(x_i,x') = \delta(x - x_i)$. Substitution of these kernels into Eq. 36 yields the following ordinary differential equation

$$\frac{dp^{(n)}(t)}{dt} = -\left(k_r + \sum_{i=1}^{4} k_i\right) p^{(n)}(t) + 2k_r Z_{n0} p^{(n)}(t) + \sum_{j=0}^{n} \binom{n}{j} p^{(n-j)}(t)(-1)^j \sum_{i=1}^{4} k_i x_i^j, \quad (37)$$

where $\binom{n}{j} = n!/(n\text{-}j)!j!$ is the binomial expansion coefficient, and Z_{n0} is a special case of Z_{nm} discussed in detail by McCoy and Wang (1994). For n = 0, 1, and 2, Z_{n0} is equal to 1, 1/2, and 1/3, respectively. The initial condition is

$$p^{(n)}(0) = \int_0^\infty x^n p_0(x)\,dx. \quad (38)$$

For $n = 0$, Eqs. 37 and 38 are simplified to

$$\frac{dp^{(0)}(t)}{dt} = k_r p^{(0)}(t), \quad (39)$$

with

$$p^{(0)}(t = 0) = p_0^{(0)}. \quad (40)$$

Solving Eq. 39 yields

$$\frac{p^{(0)}(t)}{p_0^{(0)}} = \exp(k_r t). \quad (41)$$

For $n = 1$, simplifying Eqs. 37 and 38 leads to

$$\frac{dp^{(1)}(t)}{dt} = -\sum_{i=1}^{4} k_i x_i p^{(0)}(t), \quad (42)$$

and

$$p^{(1)}(t = 0) = p_0^{(1)}. \quad (43)$$

Solving Eq. 42 gives

$$p^{(1)}(t) = p_0^{(1)} - \frac{1}{k_r} \sum_{i=1}^{4} k_i x_i [\exp(k_r t) - 1] p_0^{(0)}. \quad (44)$$

For $n = 2$, Eqs. 37 and 39 lead to

$$\frac{dp^{(2)}(t)}{dt} = -\frac{1}{3} k_r p^{(2)}(t) - 2k_x p^{(1)}(t) + k_{x^2} p^{(0)}(t), \quad (45)$$

and

$$p^{(2)}(t = 0) = p_0^{(2)}, \quad (46)$$

where

$$k_x = \sum_{i=1}^{4} k_i x_i \tag{47}$$

and

$$k_{x^2} = \sum_{i=1}^{4} k_i x_i^2. \tag{48}$$

Substituting Eq. 41 and Eq. 44 into Eq. 45 gives a first-order linear nonhomogeneous differential equation

$$\frac{dp^{(2)}(t)}{dt} + \frac{1}{3} k_r p^{(2)}(t) = f(t), \tag{49}$$

where

$$f(t) = k_{x^2} p_0^{(0)} \exp(k_r t) - 2k_x \left[p_0^{(1)} - \frac{k_x}{k_r} p_0^{(0)} \{ \exp(k_r t) - 1 \} \right]. \tag{50}$$

Solving the differential equation gives

$$p^{(2)}(t) = p_0^{(2)} \exp\left\{ -\frac{1}{3} k_r t \right\} + \frac{3}{4} p_0^{(0)} \left\{ \frac{k_{x^2}}{k_r} + 2\left(\frac{k_x}{k_r} \right)^2 \right\} \left\{ \exp(k_r t) - \exp\left(-\frac{1}{3} k_r t \right) \right\} - 6 \frac{k_x}{k_r} \left(p_0^{(1)} + p_0^{(0)} \frac{k_x}{k_r} \right) \left\{ 1 - \exp\left(-\frac{1}{3} k_r t \right) \right\}. \tag{51}$$

The average MW and the variance for the reaction mixtures can be obtained from $p^{(0)}(t)$, $p^{(1)}(t)$, and $p^{(2)}(t)$. The results will depend on temperature and time

$$x^{\text{avg}}(t) = x_0^{\text{avg}} \exp(-k_r t) - \frac{k_x}{k_r} \{ 1 - \exp(-k_r t) \} \tag{52}$$

$$x^{\text{var}}(t) = x_0^{\text{var}} \exp\left(-\frac{4}{3} k_r t \right) + (x_0^{\text{avg}})^2 \exp\left(-\frac{4}{3} k_r t \right) + \frac{4}{3} \times \left\{ \frac{k_{x^2}}{k_r} + 2\left(\frac{k_x}{k_r} \right)^2 \right\} \left\{ 1 - \exp\left(-\frac{4}{3} k_r t \right) \right\} - 6\left(\frac{k_x}{k_r} \right) \left(x_0^{\text{avg}} + \frac{k_x}{k_r} \right) \left\{ \exp(-k_r t) - \exp\left(-\frac{4}{3} k_r t \right) \right\} - \{ x^{\text{avg}}(t) \}^2. \tag{53}$$

Moment equation for the specific degradation product is given by

$$\frac{dq_i^{(n)}(t)}{dt} = k_i x_i^n p^{(0)}(t) + x_i^n R_i^{(0)}(t), \quad i = 1,2,3,4 \tag{54}$$

where

$$R_1^{(0)}(t) = -(k_5 + k_6) q_1^{(0)}(t) \tag{55}$$

$$R_2^{(0)}(t) = k_5 q_1^{(0)}(t) \tag{56}$$

$$R_3^{(0)}(t) = k_6 q_1^{(0)}(t) \tag{57}$$

$$R_4^{(0)}(t) = (k_5 + k_6) q_1^{(0)}(t) - (k_7 + k_8) q_4^{(0)}(t). \tag{58}$$

For $n = 0$, substitution of Eq. 41 gives

$$\frac{dq_i^{(0)}(t)/p_0^{(0)}}{dt} + \frac{R_i^{(0)}(t)}{p_0^{(0)}} = k_i \exp(k_r t). \tag{59}$$

For the component of MHET, $i = 1$, the preceding equation is a linear differential equation, which gives the solution as

$$\frac{q_1^{(0)} t}{p_0^{(0)}} = \frac{k_1}{k_5 + k_6 + k_r} \{ -\exp[-(k_5 + k_6)t] + \exp(k_r t) \}. \tag{60}$$

For $n = 1$, the righthand side of Eq. 60 is multiplied by the monomer MW

$$\frac{q_1^{(1)}(t)}{p_0^{(0)}} = \frac{k_1 x_1}{k_5 + k_6 + k_r} \{ -\exp[-(k_5 + k_6)t] + \exp(k_r t) \}. \tag{61}$$

For $n = 2$, the solution is given by

$$\frac{q_1^{(2)}(t)}{p_0^{(0)}} = \frac{k_1 x_1^2}{k_5 + k_6 + k_r} \{ -\exp[-(k_5 + k_6)t] + \exp(k_r t) \}. \tag{62}$$

For the other components, differential equations, Eq. 59, have to be solved simultaneously. The zero moments, $q_i^{(0)}(t)$, represent the molar concentrations of specific products, MHET, DMT, TAMME, and EG.

For the species produced by the secondary reaction, ME and DEG, the molar concentrations are given by solving the following differential equations

$$\frac{dq_{s5}^{(0)}(t)}{dt} = k_7 q_4^{(0)}(t) \tag{63}$$

$$\frac{dq_{s6}^{(0)}(t)}{dt} = \frac{1}{2} k_8 q_4^{(0)}(t). \tag{64}$$

Final time conditions

In the degradation of polymer to convert to its monomer (Figure 1), the molecular weight of the polymer approaches the monomer molecular weight, x_{monomer}, after sufficient degradation, if there is no secondary reaction of the monomer.

We require that number-average MW must always be greater than monomer MW

$$M_n = \frac{p^{(1)}(t)}{p^{(0)}(t)} \geq x_{\text{monomer}}. \tag{65}$$

For methanolysis of PET, the monomer MHET subtracted by MeOH can be considered to be the monomeric unit of PET. Then, the polymerization degree is given by $p_0^{(1)}/(x_{\text{MHET}} - x_{\text{MeOH}})$ or $p_0^{(1)}/(x_{\text{DMT}} + x_{\text{EG}} - 2x_{\text{MEOH}})$. Thus, M_n must be greater than the MW of MHET minus the MW of MeOH, because in our continuous kinetics we neglect the contribution of MeOH. The final time, t_f, defined by the time when $M_n = x_s$, is then given by substituting Eqs. 41 and 44 into $M_n = x_s$

$$t_f = \frac{1}{k_r} \ln \frac{M_{no} + \Sigma k_i x_i / k_r}{x_1 + \Sigma k_i x_i / k_r}, \tag{66}$$

where $M_{n0} = p_0^{(1)}/p_0^{(0)}$.

MWDs for polymers

To represent the MWD of the feed polymer, we employ a gamma (Pearson type III) distribution, which is a versatile representation of the naturally distributed systems (Cotterman et al., 1985; Wang et al., 1994). The molar fraction gamma distribution is defined for $y = (x - x_s)/\beta$ as

$$p(x \geq x_s) = p^{(0)} \exp(-y) y^{\alpha-1} / [\beta \Gamma(\alpha)] \tag{67}$$

$$p(x \leq x_s) = 0. \tag{68}$$

The weight-fraction gamma distribution is

$$p_w(x) = x p(x). \tag{69}$$

The average position, x^{avg}, and width of a peak, x^{var}, which are related to the first and second moments of the gamma distribution, are given by Abramowitz and Stegun (1968) as

$$x^{\text{avg}} = x_s + \alpha\beta \tag{70}$$

and

$$x^{\text{var}} = \alpha\beta^2. \tag{71}$$

The zero moment, $p^{(0)}$, is the total molar concentration of the polymer mixture. The position of the peak maximum, x_p, is determined by $dp(x)/dx = 0$, which yields

$$x_p = x_s + (\alpha - 1)\beta. \tag{72}$$

The parameters in gamma distribution can be obtained by fitting the experimental MWD data.

Experiments

A batch reactor made of a stainless-steel tube sealed with Swagelok caps (about 5.4 cm^3 in volume) was used. PET of about 0.3 g and an adequate amount of methanol (0.98–1.41 g) to attain the desired pressure were charged into the reactor and the air in the reactor was replaced with N_2 gas. The amount of methanol charged was calculated by using the Peng-Robinson equation of state to get the desired pressure. The experiments were carried out at a reaction temperature of 573 K and an estimated pressure of 20 MPa for a reaction time of 2 to 120 min. The reaction was started by immersing the reactor in a molten salt bath that was preheated to the reaction temperature. After a certain time, the reactor was cooled quickly in a water bath to quench the reaction. The reaction products consisted of a liquid phase and a solid phase, and was analyzed by the following procedures. All the decomposition products were dissolved in hexafluoro isopropanol (HFIP) and analyzed by SEC (Tosoh, TSKgel Super HM-M) using HFIP as a mobile phase with a UV detector. Based on the SEC analysis, the evolution of MWD of polymers and oligomers was obtained. The yields of the components related with DMT were also obtained. GC-MS was used to identify and quantify low molecular-weight components. On the other hand, the decomposition products were filtered by adding water and then analyzed for EG related components by reversed-phase liquid chromatography (RPLC) (Waters, 5C18-MS) using water as the mobile phase with the RI detector.

The PET used was DIANITE PA-500 (Mitsubishi Rayon Co., Ltd., Japan) and its melting point (mp) was 528 K at atmospheric pressure, and its intrinsic viscosity was 0.76. Dehydrated methanol (Wako Pure Chemical Industries Ltd., Japan) with a purity higher than 99.8 % was used as a solvent.

Results and Discussion

The SEC elution curves of decomposition products at various reaction times were measured. The SEC curves were converted to MWD, as shown in Figure 2, by using a calibration curve obtained with polystyrene (PS) and poly(methyl methacrylate) (PMMA) in the following manner. A calibration curve for PS in the THF solvent was prepared by measuring the SEC of PS in the THF. The calibration curve for PS in THF was converted to PMMA in the THF by using a correlation, $\text{MW}_{\text{PMMA}} = 1.967\ \text{MW}_{\text{PS}}^{0.918}$ (Mori, 1989). The SEC for a PMMA standard with MW distribution was measured and the integrated MWD for PMMA in the THF was obtained by using the calibration curve for PMMA in the THF. The SEC for the PMMA standard was measured in the HFIP solvent, and the integrated MWD for PMMA in the HFIP was obtained. A calibration curve for PMMA in the HFIP was prepared from these integrated MWDs for PMMA in the THF and HFIP. The SEC curves for PET and the decomposition products were then converted to the MWD by using the calibration curve for PMMA in the HFIP.

For comparison with the MWD for the decomposition products, the MWD of the original PET is also shown in Figure 2. As the reaction time was longer, the molecular weight of the polymer was decreased. PET with a weight-average molecular weight of about 47,000 (polymerization degree: $n = 240$ to 250) was decomposed to an oligomer with that of

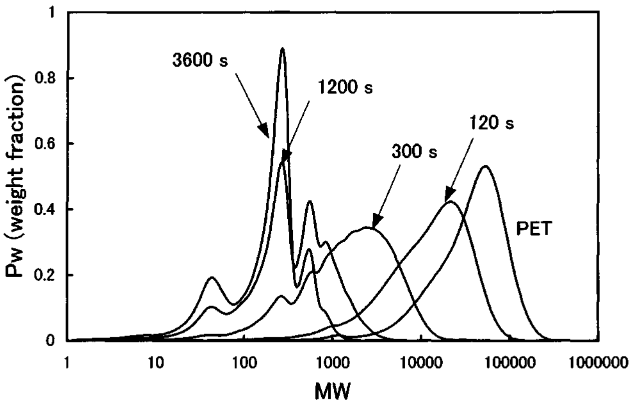


Figure 2. Molecular-weight distribution for the decomposition products

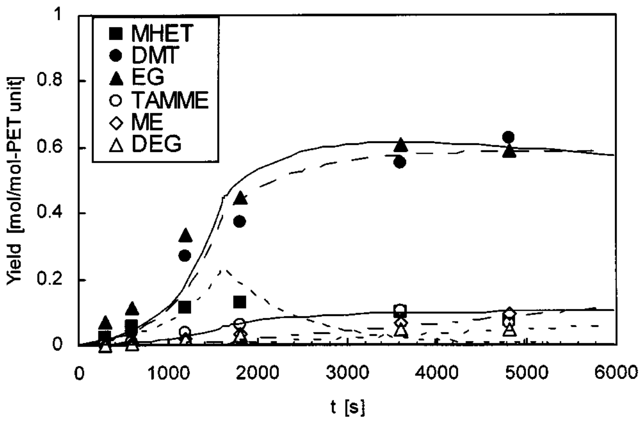


Figure 3. Yield of monomer products.

3,000 (polymerization degree: $n = 15$) in 300 s and with that of 1,000 (polymerization degree : $n = 5$) in 600 s in supercritical methanol. The main three peaks observed after the 1,200 s reaction were MHET, DMT, and TAMME, whose MWs are 224, 194, and 180, respectively. The MW of these peaks in Figure 2 is smaller than their real MW, because SEC was calibrated for a polymer with an MW much larger than the monomer components, and thus an MW for smaller molecules is inaccurate. MHET is a 1:1 monomer of DMT and EG, and TAMME is a byproduct produced in the side reaction. After the 1200 s reaction time, PET decomposed to the components of monomer size, and the DMT peak gradually became larger.

The reaction scheme of PET decomposition in supercritical methanol is shown in Figure 1. PET is degraded by random scission to a polymer with a smaller MW. Then it is continuously depolymerized to yield MHET, DMT, and EG by end scission. Produced MHET reacts further with methanol to produce DMT and EG. The following reactions can occur as side reactions. Dimerization of EG produces DEG. ME is produced by the reaction of EG and methanol. TAMME is also produced from a polymer, oligomer, or MHET in the presence of water, which is produced in the reactions yielding DEG and ME.

Figure 3 shows the yields of each component as a function of reaction time. The yields of each component were evaluated by the following equation

$$\text{Yield[mol \%]} = \frac{\text{Moles of specific products}}{\text{Moles of PET units}} \times 100. \quad (73)$$

The yields of DMT and EG increased with time, and the MHET yield increased at up to a 1800 s reaction, after which it decreased gradually. This tendency agrees with the mechanism in which MHET decomposes to DMT and EG. The largest yield of DMT was 80 mol % at 7,200 s, and that of EG was 60 mol % at 3,600 s. TAMME and ME were produced about 10 mol % in 7,200 s. A small amount of DEG dimerized from EG was also observed up to 2.5 mol %. Although another byproduct related to EG was observed in an amount comparable to DEG, it was not identified. Therefore, when PET was decomposed in supercritical methanol, both monomers, DMT and EG, were obtained efficiently without catalyst, and with fewer of byproducts, TAMME and ME. The yield of EG was much higher than that for the reaction in supercritical water (Yamamoto et al., 1996; Adschiri et al., 1997).

The rate constants for specific degradation-producing monomers were determined by the zero moments for specific products at different reaction times. At a short reaction time, the rate equations are approximated by using $\exp(k_r t) \approx 1 + k_r t$

$$p^{(0)}(t)/p_0^{(0)} \approx 1 + k_r t \quad (74)$$

$$q_1^{(0)}(t)/p_0^{(0)} \approx k_1 t \quad (75)$$

$$q_2^{(0)}(t)/\left(p_0^{(0)} t\right) \approx k_2 - (k_1 k_5/2)t \quad (76)$$

$$q_3^{(0)}(t)/\left(p_0^{(0)} t\right) \approx k_3 - (k_1 k_6/2)t \quad (77)$$

$$q_4^{(0)}(t)/p_0^{(0)} \approx k_4 t. \quad (78)$$

These equations indicate that the parameters could be roughly estimated from the plots by the following procedure. A plot of $p^{(0)}/p_0^{(0)}$ vs. t gives a straight line with a slope of k_r. A plot of $q_1^{(0)}/p_0^{(0)}$ vs. t gives a straight line with a slope of k_1. Plots of $q_2^{(0)}(t)/(p_0^{(0)}\ t)$ vs. t and $q_3^{(0)}(t)/(p_0^{(0)}\ t)$ vs. t give k_2, k_3, k_5, and k_6. A plot of $q_4^{(0)}/p_0^{(0)}$ vs. t gives a straight line with a slope of k_4. The parameters obtained in this manner with linear optimization were used as initial-guess values to optimize the parameters nonlinearly by fitting with experimental data.

The MWD of PET was represented by gamma distribution with parameters $\alpha = 2.24$, $\beta = 2.49 \times 10^4$, $x^{\text{avg}} = 4.84 \times 10^4$, $x^{\text{var}} = 1.39 \times 10^9$. As shown in Figure 2, an SEC of the reaction products gave the MWD for a mixture of polymer, oligomer, and monomers. Since even for monomers there is a distribution in SEC due to the dispersion and mass-transfer process in chromatography, we have expressed the monomer elution curves in SEC by gaussian distributions. The parameters in the gaussian distribution were obtained from the MWD for the reaction at 3,600 s, where large monomer peaks were observed. The concentration of monomers was determined by GC analysis. The MWD for a product mixture was then

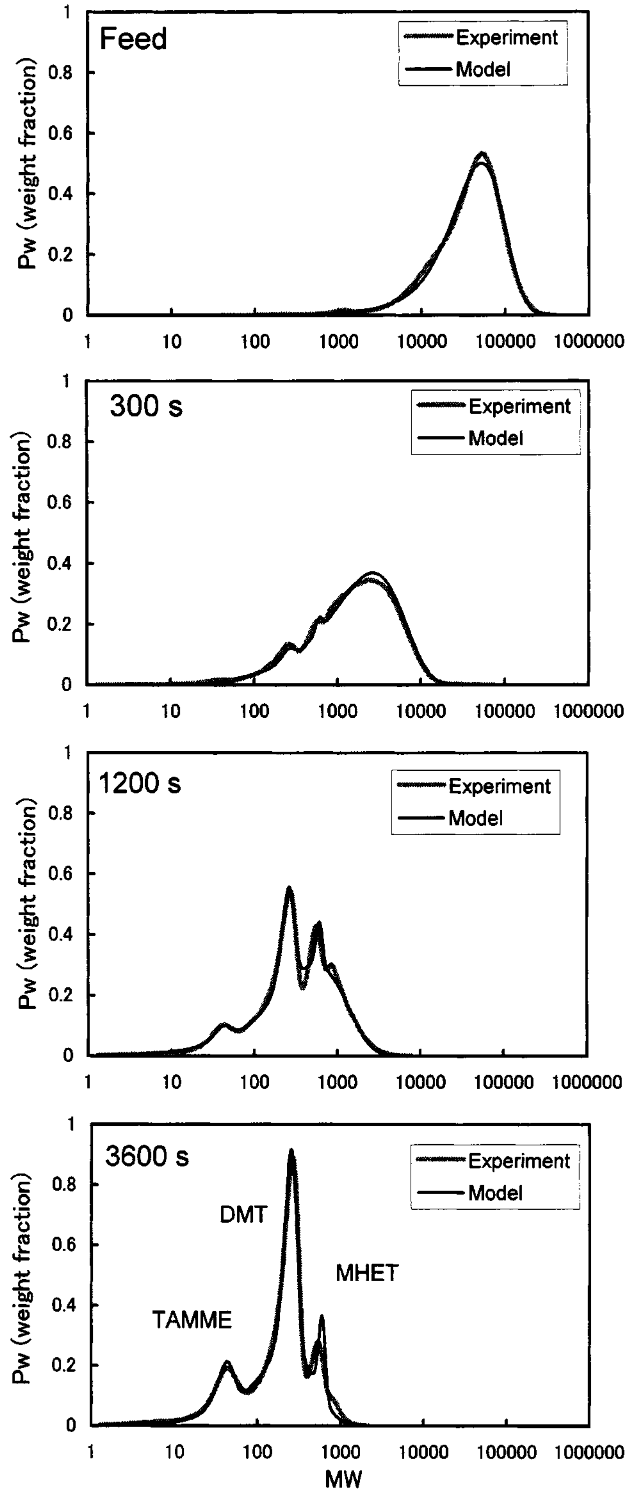


Figure 4. Comparison between measured MWD and simulated MWD.

expressed by combining the gamma distribution for polymer and the monomer peaks expressed as gauss distributions. Figure 4 shows a comparison of estimated MWD and experimental MWD obtained by SEC. The experimental MWDs were simulated by superimposing gamma distributions for polymer and gaussian distributions for monomers. The monomer yield changes were also calculated and compared in Figure 3 as a function of reaction time. The parameters used in the calculation are $1/k_r = 518$ s, $1/k_1 = 415$ s, $1/k_2 = 529$ s, $1/k_3 = 595$ s, $1/k_4 = 485$ s, $1/k_5 = 980$ s, $1/k_6 = 407$ s, $1/k_7 = 25{,}000$ s, and $k_8 = 1.0 \times 10^{-6}$ $\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$.

As Figure 4 indicates, the fit of the reaction kinetics model with data was excellent (correlation coefficient = 0.990–0.998).

Conclusion

Decomposition of PET in supercritical methanol was carried out in a batch reactor. The decomposition behavior of PET in supercritical methanol was observed in terms of the evolution of the MWD, and yields for monomer products. The reaction scheme of the decomposition of PET was estimated from the monomer products. Continuous kinetics, including random and specific scissions and secondary reactions for monomer components, was developed and applied to the analysis of the decomposition behavior. Changes in the MWD and monomers as a function of time were simulated by the continuous kinetics.

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Notation

$A(x)$ = polymer molecule having molecular weight x
D = polydispersity
k_i = rate coefficients for specific degradation
k_r = rate coefficient for random degradation
$k(x)$ = rate coefficient for polymer degradation
M_n = molar average molecular weight
M_w = mass average molecular weight
$P(x)$ = polymer
$p(x,t)$ = MWDs of the reaction mixtures based on molar fraction
$p_0(x)$ = MWD for the feed polymer
$p^{(n)}$ = nth-order MW moments of the reaction mixture
$Q_i(x_i)$ = specific products
$q_i(x_i,t)$ = molar concentration of the specific products
$q_{si}(x_i,t)$ = molar concentration of the secondary reaction products
$q_i^{(n)}$ = nth-order MW moments of the specific products
x = molecular weight
x_i = molecular weights for the specific products
x_p = molecular weight at the peak maximum for a gamma distribution
x_s = lowest molecular weight for a gamma distribution
x^{avg} = number-average molecular weight for the reaction mixtures
x_0^{avg} = number-average molecular weight for the feed polymer
x^{var} = variance
y = dimensionless molecular weight

Greek Letters

α = parameter in a gamma distribution
β = parameter in a gamma distribution
Γ = gamma function
Ω = stoichiometric kernel

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