

Using isothermal kinetic results to estimate kinetic triplet of pyrolysis reaction of polypropylene

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Abstract

This paper describes how to estimate the Arrhenius parameters as well as the reaction model of the pyrolysis of polypropylene (PP) from isothermal kinetic results. We introduced a custom-made thermobalance that is able to record weight decrease with time under pure static condition. A best fit of experimental reduced-time-plot (RTP) to theoretical ones led to a conclusion that the pyrolysis reaction model and Arrhenius parameters of PP vary with reaction temperature. The pyrolysis reaction model of PP is accounted for by “Contracting Cylinder” model at lower-temperature reactions (683–693 K), whereas that of PP by “Avrami-Erofeev” model at higher-temperature reactions (728–738 K). Medium-temperature reactions (693–728 K) manifest the shift pattern of reaction model from “Contracting Cylinder” model to “Avrami-Erofeev” model. There is a critical temperature (705–720 K) that triggers the explosive generation of volatiles, leading to bubble nucleation and growth, simulating the “Avrami-Erofeev” model. The n th order model adopted by most previous studies appears to be inappropriate to represent the pyrolysis reaction model of PP. Consequently, the Arrhenius parameters derived from the assumption of n th order model would be improper as well.

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1. Introduction

A pyrolysis reaction is uniquely represented by one set of “kinetic triplet”: activation energy, pre-exponential factor, and reaction model. Based on the assumption that the reaction model would be represented by n th order model, various kinetic analysis methods have been developed to estimate the Arrhenius parameters of pyrolysis reactions of polymers. However, little effort has been made on verifying the assumption of the n th order model.

Most previous studies [1–7] also assumed the n th order model to be the pyrolysis reaction model of polypropylene (PP). It is, hence, essential to check the validity of the n th order

model for the pyrolysis reaction model of PP. Incorrect reaction model can also lead to a deviation of the Arrhenius parameters.

Isothermal reduced-time-plot (RTP) was taken as an effective tool to identify the reaction model of the thermal decomposition of solids [8–13]. We confirmed the applicability of the isothermal RTP to identify the pyrolysis reaction models of high-density polyethylene (HDPE) [11,12] and linear low-density polyethylene (LLDPE) [13].

This paper determined the pyrolysis reaction model of the PP using the isothermal RTP, consequently checking the validity of the n th order kinetics. Accordingly, the Arrhenius parameters were estimated. The validity of the kinetic triplet derived here was verified indirectly in consequence of comparing with the activation energy value estimated from model-free method.

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Nomenclature

A	pre-exponential factor
E	activation energy
$f(\alpha)$	reaction model
$g(\alpha)$	integrated form of the reaction model, $g(\alpha) = \int_0^\alpha [f(\alpha)]^{-1} d\alpha$
N	number of experimental measurements
k	reaction constant (min^{-1})
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
S^2	residual sum of squares
t	time (min)
T	absolute temperature (K)
<i>Greek letters</i>	
α	extent of conversion
<i>Subscripts</i>	
i	certain reaction temperature
j	certain extent of conversion

2. Theoretical

Single step kinetics for solid state decomposition takes the following kinetic equation:

$$\frac{d\alpha}{dt} = k(T) f(\alpha) \quad (1)$$

Arrhenius equation generally expresses the explicit temperature dependency of the rate constant:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (2)$$

The A , E , and $f(\alpha)$ are called as kinetic triplet that can characterize a unique pyrolysis reaction. The reaction model can be expressed in various forms, some of which are shown in Table 1.

From isothermal experiments, the RTPs were constructed by plotting α as a function of a reduced time, t/t_α , where t_α is the

time that it takes to attain a specific conversion ($\alpha = 0.9$). In case of a single reaction, the RTPs constructed at different isothermal temperatures are superimposable within an experimental error. Reaction model can be chosen among the various reaction models by means of comparing experimental RTPs with theoretical ones described in Table 1. The goodness of fit of theoretical RTP to experimental one can be judged by the residual sum of squares [9]:

$$S^2 = \frac{1}{N-1} \sum_{j=1}^N \left(\frac{t_j}{t_{0.9}} - \frac{g(\alpha_j)}{g(0.9)} \right)^2 \quad (3)$$

After identifying the reaction model, we can determine rate constant at a temperature from the slope of a plot of $g(\alpha)$ versus t (Eq. (4)), which can be deduced from integrating Eq. (1):

$$g(\alpha) = k(T)t \quad (4)$$

The rate constants can be assayed from the slopes of Eq. (4) at various temperatures and then, the Arrhenius parameters can be estimated from the Arrhenius plot of the rate constants as follows:

$$\ln k(T_i) = \ln A - \left(\frac{E}{R}\right) \frac{1}{T_i} \quad (5)$$

3. Experimental

Powdered PP with an average molecular weight of 182,000 was used in this study and supplied by Samsung Chemical Co. (HJ500 Powder). The samples were dried in a desiccator before analyses.

For dynamic experiments, a thermogravimetric analyzer (Model: Cahn TG-2121 manufactured by ATI Instruments, Inc.) was used and the amount of sample was 7.0 ± 0.1 mg. The temperature was raised up to 923 K at the three linear heating rates of 10, 15, and 20 K min^{-1} . Nitrogen was used as a carrier gas at a flow rate of 50 mL min^{-1} .

A custom-made thermobalance was used for isothermal kinetic experiments. The thermobalance was designed and manufactured for isothermal kinetic experiments (Fig. 1). It consisted of a laboratory scale pyrolysis reactor and a weight

Table 1
Reaction models employed to describe the solid state reaction

	Reaction model	Symbol	$f(\alpha)$	$g(\alpha)$
1	Power law	P4	$4\alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	P3	$3\alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	P2	$2\alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	P2/3	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion	D1	$1/2\alpha^{-1}$	α^2
6	Mample (first-order)	F1	$1 - \alpha$	$-\ln(1 - \alpha)$
7	Avrami-Erofeev	A4	$4(1 - \alpha)[-\ln(1 - \alpha)]^{3/4}$	$[-\ln(1 - \alpha)]^{1/4}$
8	Avrami-Erofeev	A3	$3(1 - \alpha)[-\ln(1 - \alpha)]^{2/3}$	$[-\ln(1 - \alpha)]^{1/3}$
9	Avrami-Erofeev	A2	$2(1 - \alpha)[-\ln(1 - \alpha)]^{1/2}$	$[-\ln(1 - \alpha)]^{1/2}$
10	Three-dimensional diffusion	D3	$2(1 - \alpha)^{2/3}(1 - (1 - \alpha)^{1/3})^{-1}$	$[(1 - (1 - \alpha)^{1/3})]^{2/3}$
11	Contracting Sphere	R3	$3(1 - \alpha)^{2/3}$	$1 - (1 - \alpha)^{1/3}$
12	Contracting Cylinder	R2	$2(1 - \alpha)^{1/2}$	$1 - (1 - \alpha)^{1/2}$
13	Second-order	F2	$(1 - \alpha)^2$	$(1 - \alpha)^{-1} - 1$

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