Studies on Thermal Degradation of Synthetic Polymers. XV. Estimation of the Product Yield on the Basis of Intensity Function for Thermal Gasification of Isotactic and Atactic Polypropylenes

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Synopsis

The kinetic equation for the pyrolysis gasification reaction of isotactic and atactic polypropylenes has been established. The difference in tacticity of the samples does not much affect the kinetic parameters. The exponent a of the intensity function $I_F = T\theta^a$ (K·sec^a), concerning the severity of decomposition conditions, has been approximated as 0.039 (isotactic) and 0.040 (atactic), respectively from the kinetic parameters in this experiment. The calculated values of the product yield from Arrhenius equations, $k = 2.0 \times 10^{10} \exp(-40.9 \times 10^3/RI_F)$ (isotactic) and $k = 1.2 \times 10^{10} \exp(-41.4 \times 10^3/RI_F)$ (atactic), for the I_F standard agree with the experimental values.

INTRODUCTION

From the point of view of energy diversification and chemical resources, attention has been directed not only to coal and heavy oils of the petroleum group, but also to plastic waste matter and recovery of resources by pyrolysis. The most suitable control method of recovery by pyrolysis requires development of a way for estimating product yield corresponding to the decomposition conditions. The prediction of product yield should be made on the basis of kinetics, i.e., by the analysis of the equations of material balance maintained through various elementary reactions which occur by free radical mechanisms. However, the analysis of the elementary reactions, even in the thermal decomposition of petroleum hydrocarbons,[1] becomes very difficult with an increase in the number of carbon atoms in a sample, and it is impossible to analyze the elementary reactions in the case of polymers. The authors therefore have directed their attention to the parameter that expresses the degree of severity of the decomposition conditions, i.e., the intensity function ($I_F = T\theta^a$), and has good correlation with the product yield. From experience, 0.06[2] is used as the value for the exponent a, and this value is also applied for the pyrolysis of crude petroleum.[3] The authors[4-7] introduced the concept of I_F for polymers; and in cases where property values differ completely from naphtha, crude petroleum, etc., an experimental induction method for the value of a was established. It was demonstrated that I_F has a good correlation with the product yield. Moreover, the value of a for polymers differs from that for petroleum hydrocarbons, and it was suggested that the value of a is dependent on the molecular structure of the sample and that it is correlated with the kinetic parameter (activation energy).[4]

I_F is useful as a means for estimating product yield, and it is clear that the value of a depends considerably on the pyrolysis reaction according to the type of material.

In order to use the concept of I_F for the pyrolysis reaction with a wide range of hydrocarbons, it is necessary to elucidate the value of a theoretically. Davis and Farrell[2] have recently indicated a definition of I_F (I_F corresponds to the temperature required to obtain an optical conversion ratio x in a residence time of 1 sec) and established an I_F standard kinetic equation using $a = 0.062$. It is noteworthy as a first attempt that elucidation of the relation between I_F and kinetics was made from the definition of I_F. Recently, the authors[8] have established a kinetic equation for the pyrolysis gasification reaction of polyethylene-low polymers, theoretically clarified I_F, which is conventionally considered an important parameter, from a kinetic point of view, and clarified the dependence of the kinetic parameters on the value of the exponent a of I_F. Moreover, the authors have developed a useful means for estimating the product yield from I_F on the basis of the kinetic parameter, which quantitatively reflects the pyrolysis reactions.

In this study, I_F is shown to be applicable to the thermal gasification of isotactic and atactic polypropylenes.

Calculation of Product Yield on the Basis of the Theoretical Relation between I_F and Kinetics

The relation between the value for the exponent a on I_F and the kinetic parameters have been described in a previous report.[8]

The intensity function equation, first-order reaction velocity equation, and Arrhenius equation are as follows:

$$I_F = T\theta^a \tag{1}$$

$$\frac{dx}{d\theta} = k(1 - x) \tag{2}$$

or

$$k = \ln (1 - x)^{-1}/\theta$$
$$k = A \exp(-E/RT) \tag{3}$$

where I_F is the intensity function (K·sec^a); T, the reaction temperature (K), θ = the residence time (sec); a, the constant; x, the conversion ratio (gasification ratio); k, the reaction velocity constant (sec^{-1}); A, the frequency factor (sec^{-1}); E, the activation energy (cal/mole); and R, the gas constant (cal/mole K). Equations (4) and (5) are obtained when the above definition of I_F is introduced into eqs. (2) and (3):

$$k_{I_F} = \ln (1 - x)^{-1} \tag{4}$$

$$k_{I_F} = A_{I_F} \exp(-E_{I_F}/RI_F) \tag{5}$$

with k_{I_F} = I_F standard reaction velocity constant (sec^{-1}), A_{I_F} = I_F standard frequency factor (sec^{-1}), and E_{I_F} = I_F standard activation energy (cal/mole). Accordingly, the value of a can be expressed by the following equation:

$$a = \frac{-\ln (1 - \ln \theta \cdot RT/E)}{\ln \theta} \tag{6}$$

If $A = A_{I_F}$ and $E = E_{I_F}$ hold in the variable range of $\theta \neq 1$, eq. (6) becomes a general formula.

Comparison of eqs. (7) and (8) permits evaluation of the value of a obtained from eq. (6) by kinetic consideration:

$$\theta_2 = \theta_1 \left(\frac{T_1}{T_2}\right)^{1/a} \tag{7}$$

$$\theta_2 = \theta_1 \exp\left[\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\frac{E}{R}\right] \tag{8}$$

Therefore, computation of the product yield on the basis of I_F is carried out by the following equation:

$$x = 1 - \frac{1}{\exp[A \exp(-E/RI_F)]} \tag{9}$$

EXPERIMENTAL

Sample. In this experiment, the commercial isotactic and atactic forms of polypropylene were used without further purification. The molecular weights and the tacticity are given in Table I.

Apparatus and Procedure. The apparatus used and the procedure for this experiment have been described in a previous report[8] in detail. The samples were melted according to the reaction conditions at 200°C (isotactic) and 85°C (atactic) by constant electric heating.

Analysis. The gaseous product was analyzed by a Shimadzu 4B-PT gas chromatograph. The conditions for the analysis of each object have already been reported.[5] The average molecular weight was determined by gel permeation chromatography using a Toyo Soda HLC-811 high-speed liquid chromatograph. The calibration line was produced by standard polystyrene, and 26.4 (ref. 9) was used as the Q factor. The tacticity was obtained by ^{13}C NMR spectrometry using a Jeol JNM-FX 100 spectrometer.

Definition of Terms. Definition of the residence time, the effective reactor volume, and the gasification ratio, etc. have been described in a previous report.[8]

TABLE I
Characteristization of Samples Used

| Sample | $\overline{M}_n \times 10^{-3}$ | $\overline{M}_w \times 10^{-4}$ | Microtacticity | | |
			mm	mr	rr
Isotactic	54.8	36.4	0.92	0.06	0.02
Atactic	3.20	1.68	0.46	0.28	0.26

RESULTS AND DISCUSSION

Effect of Reaction Conditions on Gasification

The IR spectra for liquid products obtained under conditions of differing gasification ratios are shown in Figure 1.   Up to a gasification ratio of approximately 0.5, the main constituent in liquid products was formed by such aliphatic olefins as the terminal vinylidene (1780, 888 cm^{-1}) type.   With a gasification ratio of 0.5 or more, aromatics (1600, 1500 cm^{-1}, etc.) could be observed, and their absorption appeared stronger with an increase in the gasification ratio.   Figure 2 shows the composition of gaseous products for the gasification ratio.   With
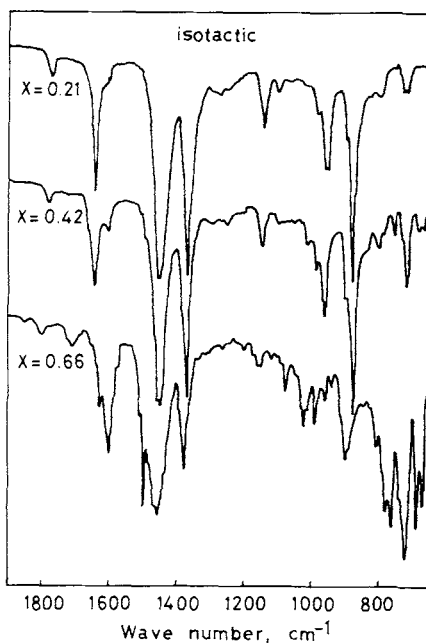
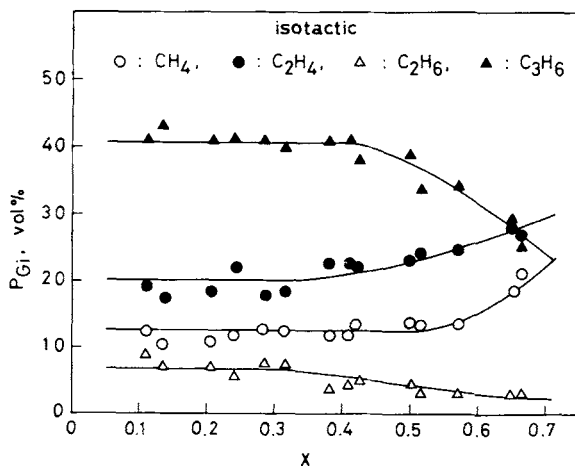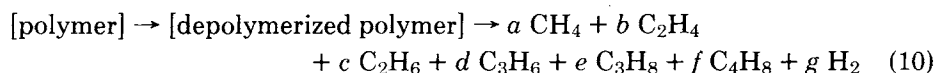Fig. 1. IR spectra of pyrolysis products from isotactic polypropylene.

Fig. 2. Composition of gaseous products corresponding to the gasification ratio.

a gasification ratio near 0.5, the product gas composition showed a constant ratio. With a gasification ratio of 0.5 or more, the composition showed a remarkable change. It is believed that secondary reactions such as the redecomposition of olefins take place, and these olefins are the initial products of the gasification reaction and the formation of aromatics by condensation, etc. The IR spectra characterization and the composition for atactic forms are similar to those for isotactic forms mentioned above.

For the gasification reaction of polypropylenes, and polyethylene-low polymers[8], two reaction ranges can be observed: the first-stage reaction occurs within a gasification ratio range of up to 0.5, where the gas composition is formed at fixed ratio; and the second-stage reaction occurs within a gasification ratio range of 0.5 or higher, where the secondary reactions of the product gas are brought about. For the first-stage reaction range, the following quantitative chemical equation is obtained:

$$[\text{polymer}] \rightarrow [\text{depolymerized polymer}] \rightarrow a\ CH_4 + b\ C_2H_4$$
$$+ c\ C_2H_6 + d\ C_3H_6 + e\ C_3H_8 + f\ C_4H_8 + g\ H_2 \quad (10)$$

The coefficients of each component are expressed by mole fraction in the gaseous products. The coefficients are given in Table II.

Kinetics of Gasification and I_F

As shown in eqs. (2) and (10), these experiments on polypropylenes, as well as polyethylene-low polymers,[8] are governed by overall first-order reaction kinetics in regard to the depolymerized polymer weight fraction for the complicated gasification reaction, and the gasification velocity is analyzed.

A linear relation is established for the plot of $-\ln(1-x)$ vs. θ in the range of short residence times. For the long residence times, the above-mentioned secondary reaction of olefins occurs and linearity is lost. The various reaction velocity constants of the first-stage reaction range are obtained from the slope of the straight line and are shown in the Arrhenius equation (Fig. 3) as
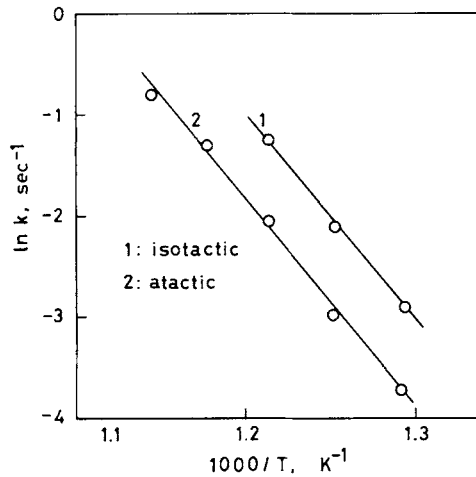
$$k = 2.0 \times 10^{10} \exp\left(\frac{-40.9 \times 10^3}{RT}\right) \text{ (isotactic)} \quad (11)$$

$$k = 1.2 \times 10^{10} \exp\left(\frac{-41.4 \times 10^3}{RT}\right) \text{ (atactic)} \quad (12)$$

TABLE II
Coefficients of Each Component in Eq. (10)

| Component	Coefficient[a]	Sample	
		Isotactic	Atactic
CH_4	a	0.13	0.13
C_2H_4	b	0.19	0.17
C_2H_6	c	0.07	0.07
C_3H_6	d	0.42	0.40
C_3H_8	e	0.02	0.02
C_4H_8	f	0.15	0.14
H_2	g	0.02	0.07

[a] Mole fraction in the gaseous products.

Fig. 3.   Arrhenius plot for k.

As shown in Table II and in eqs. (11) and (12), the difference in the tacticity of both samples dose not have much effect on the gasification reactions.

Comparison of eqs. (3) and (5) clearly shows good coincidence of $A = A_{I_F}$ as well as $E = E_{I_F}$ (ref. 8).   Accordingly, it becomes clear that the value of a can be calculated by the kinetic parameters shown in eq. (6).   Figure 4 shows the change range corresponding to the experimental conditions for the value of a in eq. (6). Since the change range for the value of a is determined by the residence time, reaction temperature, activation energy, frequency factor, and the conversion ratio (gasification ratio), an approximated value can be obtained within the experimental conditions wherein the kinetic parameters are definite.   Since the value of a obtained from the kinetic parameters in this experiment changes in the shaded part of the figure, a is approximated as 0.039 (isotactic) and 0.040 (atactic).

Evaluation of the value of a obtained from the kinetic parameters is determined by a comparison of eq. (7) with eq. (8).   Figure 5 shows the change of T_2
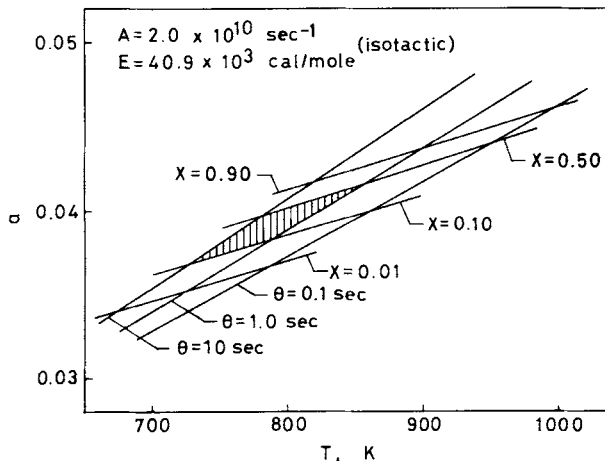
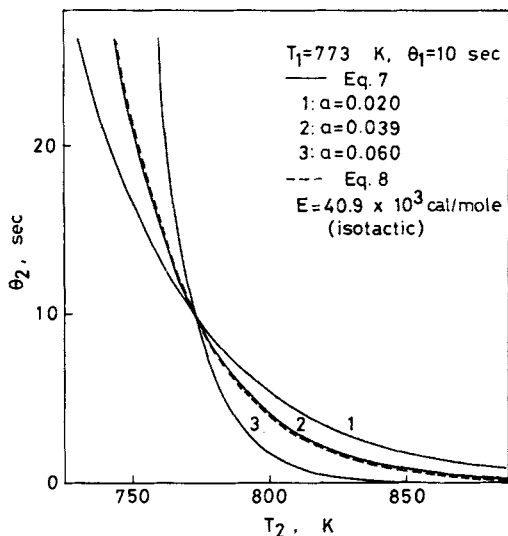Fig. 4.   Change range for the value of a in eq. (6).

Fig. 5.   Comparison of eqs. (7) and (8).

and θ_2 for given values of T_1 and θ_1.   Equation (7), using $a = 0.039$ (isotactic) as obtained from the kinetic parameters for this experiment, and eq. (8), using $E = 40.9 \times 10^3$ cal/mole (isotactic), show good coincidence.   This figure also shows considerable dependence of the value of a on the activation energy.
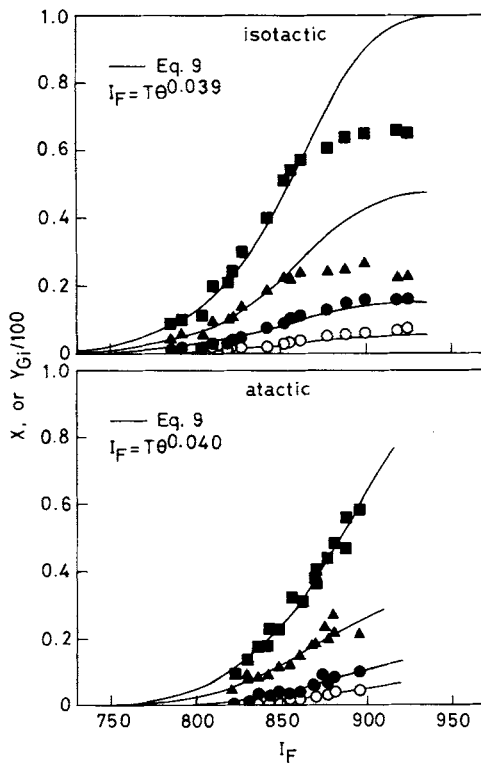

Fig. 6.   Comparison of the experimental values with the calculated values for the various product yields on I_F: (■) X; (○) CH_4; (●) C_2H_4; (▲) C_3H_6.

Figure 6 shows a comparison of the experimental values with the calculated values for various product yields based on I_F, as shown in eq. (9). The calculated and experimental values show good coincidence up to a gasification ratio near 0.5 (first-stage reaction range)

As mentioned above, it has been demonstrated that the theory of I_F for estimating product yield is also applicable to the thermal gasification of polypropylene.

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