



Title	THE KINETICS OF POLYMERIZATION
Author(s)	KAGIYA, Tsutomu; IZU, Masatsugu
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 16(1), 155-168
Issue Date	1968
Doc URL	http://hdl.handle.net/2115/24854
Type	bulletin (article)
File Information	16(1)_P155-168.pdf



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THE KINETICS OF POLYMERIZATION

By

Tsutomu KAGIYA and Masatsugu IZU

Department of Hydrocarbon Chemistry, Faculty of
Engineering, Kyoto University

(Received December 16, 1967)

Abstract

A comprehensive review is presented on the kinetics of polymerizations, as a summary of the studies on the polymerization kinetics performed in the authors' laboratory. Polymerizations were in the first place classified into several classes according to the relative magnitude of the rates of the elementary steps. The specific features of the kinetics were discussed by classifying into four main types, *i.e.*, stationary polymerization with slow initiation, non-stationary polymerization with slow initiation, stationary polymerization with rapid initiation, and non-stationary polymerization with rapid initiation. The kinetic studies dealing with polymerizations of these classes were summarized and some problems in the kinetic studies were pointed out.

1. Introduction

A polymerization consists of several elementary steps, and a catalyst frequently influences the rates of more than one elementary steps. Detailed kinetic studies to obtain quantitative informations of elementary steps are, therefore, particularly essential to the studies on catalyses in polymerizations.

The kinetics of free radical polymerizations has been studied in detail since the pioneer works made by STAUDINGER,¹⁾ SCHULZ,²⁾ MELVILLE,³⁾ and others,^{4~7)} and it has been established that the kinetics can be treated by a simplified analytical method based on the steady state approximation which equates the initiation and termination rates.

However, as a result of remarkable developments in polymer chemistry in recent years especially in the field of polymerizations initiated by ionic catalysts, different kinetic treatments have come to be necessitated. The kinetic studies of polymerizations in which the conventional steady state approximation was not applied have been carried out by SZWARC,⁸⁾ PEPPER,⁹⁾ MAGAT,¹⁰⁾ and the present authors;^{11~15)} SZWARC has carried out detailed kinetic studies on the anionic polymerization of styrene in which the initiation was completed very rapidly and both the termination and the transfer does not occur (a stationary

successive polymerization with rapid initiation according to the classification proposed by the present authors¹⁵⁾); PEPPER has developed a kinetic treatment on polymerizations in which the initiation is completed very rapidly and the termination occurs at a considerable rate (a non-stationary polymerization with rapid initiation); MAGAT discussed the kinetics of the free radical heterogeneous polymerization in which the termination is almost entirely due to small radicals (a non-stationary polymerization with slow initiation); the present authors have discussed specific features in the kinetics of polymerizations in which the steady state approximation is not applicable and proposed a graphical method for the interpretation of the kinetic behavior and for the evaluation of the elementary rate constants in these systems.¹⁴⁾

The aim of this article is to present a comprehensive review on the kinetics of polymerizations of various types. In the first place, the polymerizations of various types, *i. e.*, the polymerizations initiated by free radical initiators, ionic-type catalysts, and gamma-rays or light irradiation under various conditions, were classified from a kinetic point of view.¹⁵⁾ Subsequently, were discussed the specific features of the kinetics of each class.¹⁶⁾ Contents of this review is based mostly upon the discussions made by the present authors in a series of papers on the polymerization kinetics.^{11~16)}

2. Classification of Polymerizations from a Kinetic Point of View

Polymerizations have commonly been classified according to the types of initiators, kinds of monomer, modes of the addition of monomer to the propagating species, or electronic structures of the propagating species. We can conveniently express the qualitative nature of elementary reactions of a polymerization in the frame of these classifications. However, the terms which distinctly express the quantitative nature of elementary reactions, *i. e.*, the kinetic feature of a polymerization, have been used only in special cases, such as "living polymerization" and "steady state polymerization". Moreover, in consequence of the invention of manifold types of polymerization, it seems to have become difficult to express the kinetic features with the terms appearing in the usual classifications. For these reasons, the authors have proposed a classification of polymerizations from a kinetic point of view into several distinct types, each of which definitely denotes the quantitative nature of the elementary reactions. The proposed classification of polymerizations into several well-marked types is given in Table 1; each type is there characterized in detail.

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TABLE 1. Classification of Polymerization from a Kinetic Point of View

I	Slow initiation				Rapid initiation			
Value of l in $\int R_i dt = f(t^l)$	>0				$=0$			
II	Stationary		Non-stationary		Stationary		Non-stationary	
Value of m in $[P^*] = g(t^m)$	$=0$		$=0$		$=0$		$\neq 0, (<0)$	
III	Chain Successive		Chain Successive		Chain Successive		Chain Successive	
Value of n in $\bar{P} = u(t^n)$	$=0$	$\neq 0, (<0)$	$=0$	$\neq 0, (>0)$	$=0$	$\neq 0, (>0)$	$=0$	$\neq 0, (>0)$
Symbol of each type	SSC	SSS	SNC	SNS	RSC	RSS	RNC	RNS

R_i : initiation rate, *i.e.* the number of moles of propagating species produced in unit time by initiation; t : reaction time; P^* : propagating species; $[P^*]$: the number of moles of P^* ; \bar{P} : number-average degree of polymerization of the polymer obtained at reaction time t ; $f(t^l)$, $g(t^m)$ and $u(t^n)$ increase with increasing t^l , t^m and t^n .

1) Classification according to the relative magnitude of the initiation rate

The polymerizations are divided into those with rapid initiation and those with slow initiation, according to the relative magnitude of the initiation rate with reference to the rate of propagation, as is defined in Table 1. When the rate of initiation is much larger than that of propagation, the sum of polymer chains produced by initiation, ($\int R_i dt$), is independent of the reaction time; that is, all the initiation reactions are completed immediately after the polymerization reaction starts. This type of polymerization is classified as one with rapid initiation. Polymerizations with rapid initiation have been observed in those initiated by ionic catalysts and in post-effect polymerizations initiated by gamma-ray or light irradiation.

In the polymerization with a rate of initiation much smaller than that of propagation, the value of $\int R_i dt$ increases with an increase in the reaction time; that is, initiation reactions occur continuously in the course of polymerization. This type of polymerization is classified as one with slow initiation. Polymerizations with slow initiation have been observed in those initiated with free radical initiators, gamma-ray or light irradiation and some ionic catalysts.

2) Classification according to the change in the number of moles of the propagating species with an increase in the reaction time

Both of the two classes mentioned above were further divided into sta-

tionary and non-stationary polymerizations. As is defined in Table 1, in the former, the number of moles of the propagating species is approximately constant, while in the latter, it changes with an increase in the reaction time. The number of moles of the propagating species decreases with an increase in the reaction time in a non-stationary polymerization with rapid initiation. On the other hand, there are two types of non-stationary polymerizations with slow initiation; in one case, the number of moles of the propagating species increase with an increase in the reaction time, and, in the other case, that decreases.

3) Classification according to the relative magnitude of the transfer rate

As is listed in Table 1, the next sub-classification was made by estimating the change in the number-average degree of polymerization of the produced polymer with an increase in the reaction time. The authors have proposed to term the polymerizations in which the number-average degree of polymerization is independent of the reaction time, "chain polymerization", and those in which the degree of polymerization changes with an increase in the reaction time, "successive polymerization".

4) Typical kinetic feature of each class in the proposed classification

The first two classifications (1) and (2) characterize the kinetic feature with respect to the polymer yield, while the last one (3) characterizes the kinetic feature with respect to the number-average degree of polymerization of the polymer formed. The characteristic dependencies of the polymer yield and the number-average degree of the polymerization of the polymer formed upon the reaction time of each type are readily deducible according to the proposed classification.

a) *Typical kinetic feature with respect to the polymer yield*

Fig. 1 shows the change in the concentration of the propagating species with an increase in the reaction time in each classified type. As has been pointed out previously, there are two types of non-stationary polymerizations with slow initiation. Fig. 2 shows the change in the polymer yield with an increase in the reaction time, which is easily deducible from Fig. 1. It should be noted that the figures express typical cases and that intermediate cases between them have occasionally been observed. For example, when initiation is accomplished in the middle stage of the polymerization without any appreciable termination, the initial stage belongs to the polymerization with slow initiation, while the latter stage belongs to that with rapid initiation, according to the proposed classification. In addition, it should be noted that Fig. 2 represents the typical cases when the concentration of monomer does not change in the

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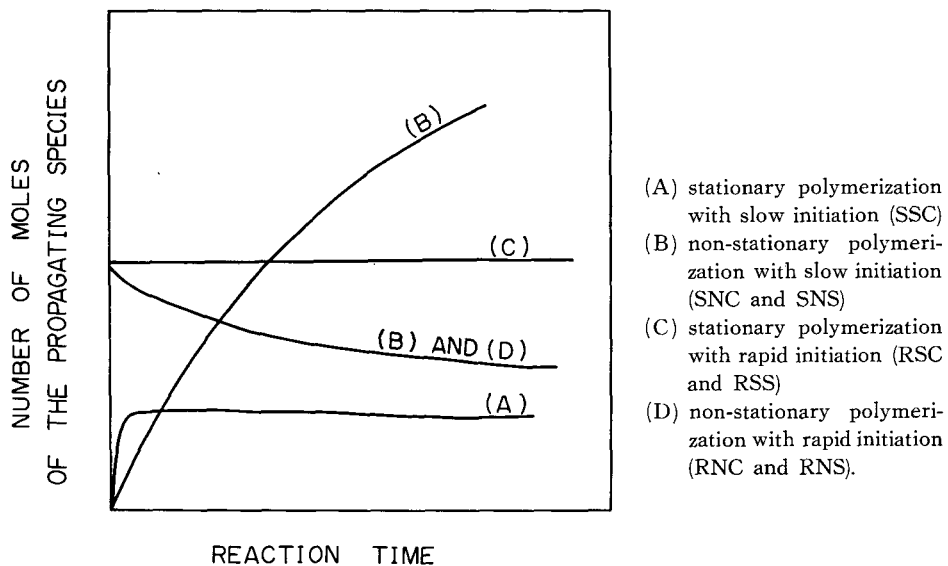


Fig. 1. Change in the number of moles of propagating species with a change in the reaction time.

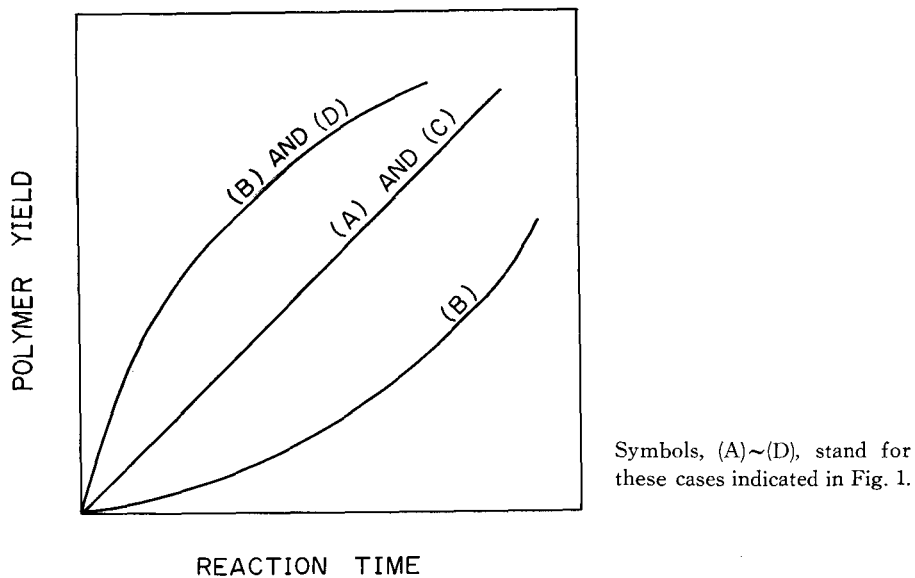


Fig. 2. Dependence of the polymer yield upon the reaction time.

course of polymerization and the propagation rate (R_p) is expressed by the equation; $R_p = k_p[P^*][M]$ (M: the monomer). If the case is otherwise, the figure should be modified.

b) *Relationship between the polymer yield and the number-average degree of polymerization of the polymer formed*

As has been defined previously, the number-average degree of polymerization of the polymer formed in a chain polymerization is independent of the polymer yield while that of the polymer formed in a successive polymerization changes with an increase in the polymer yield. The number of moles of the polymer chains defined as the ratio of the polymer yield to the number-average molecular weight of the polymer, in both stationary and non-stationary successive polymerizations with rapid initiation (RSS and RNS), are constant when the rate of transfer is negligible. Therefore, as Fig. 3 shows, a linear relationship between the polymer yield and the number-average degree of polymerization is obtained in both cases. The slope of the straight lines is equal to the number of moles of polymer chains. In the stationary polymerization with slow initiation, the number-average degree of polymerization changes when the concentration of the transfer agent increases with an increase in the reaction time, or polymer degradation occurs. This case is also shown

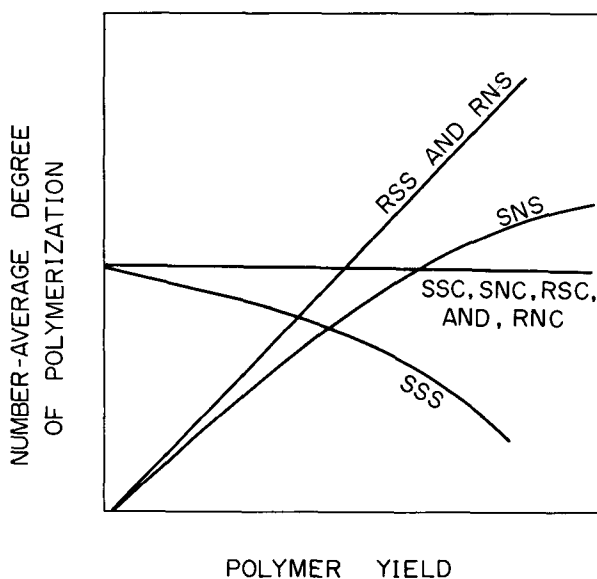


Fig. 3. Relationship between the number-average degree of polymerization of the polymer formed and the polymer yield.

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in Fig. 3, as the stationary successive polymerization with slow initiation.

3. Specific Features of the Kinetics of Each Class

1) Stationary polymerization with slow initiation

Polymerization systems, in which the initiation takes place continuously; nevertheless, the number of moles of the propagating species is constant with the reaction time, are classified as stationary polymerizations with slow initiation. These polymerizations are further divided into stationary chain polymerizations with slow initiation (SSC) and stationary successive polymerizations with slow initiation (SSS).

The change in the concentration of the propagating species of polymerization with the reaction time is expressed by the following equation:

$$\frac{d[P^*]}{dt} = R_i - R_t \quad (1)$$

R_i (the rate of initiation) is, in general, a function of the catalyst and monomer concentrations, and R_t (the rate of termination) is a function of the concentrations of P^* (the propagating species) and the terminating agent. Obviously, even if the steady state approximation, $R_i \simeq R_t$, is valid, $[P^*]$ appreciably changes with the reaction time when either of R_i or R_t changes with the reaction time. Therefore, a strict stationary state is realized under the conditions: $R_i \simeq R_t$ and at the same time, $\frac{dR_i}{dt} \simeq 0$ and $\frac{dR_t}{dt} \simeq 0$.⁴⁾ Stationary successive polymerizations are realized when the polymer degradation occurs, or when the concentration of the transfer agent changes with the reaction time. Except these cases, these polymerization systems always belong to chain polymerizations, independently of the relative magnitude of the transfer rate.⁴⁾

The kinetic data of this class are analyzed by using the conventional steady-state treatment; and the relative magnitude of the rate constants of the elementary steps can be estimated.^{4~7)}

Typical examples are the free radical polymerizations with initiators whose half-value period is much larger than the duration of polymerization in which the change in the termination rate constant with the reaction time (the Trommsdorff effect) is negligible; for instance, the polymerization of styrene by benzoyl peroxide belongs to this class.¹⁷⁾ Many photo- or radiation-induced polymerizations are also included in this category; for instance, the radiation-induced solid state polymerizations of 3, 3-bis-chloromethyloxetane¹⁸⁾ and maleimide¹⁹⁾ belong to this class. Ionic polymerizations in which the rate and the molecular weight of the polymer formed are constant with the reaction

time have often been treated as stationary chain polymerizations with slow initiation.^{20,21)} However, it appears that the validity of these treatments should be examined rigidly because these polymerizations may alternatively be treated as stationary chain polymerizations with rapid initiation (As Figs. 1-3 show, both a stationary chain polymerization with rapid initiation (RSC) and a stationary chain polymerization with slow initiation (SSC) exhibit the same kinetic behaviors.). This is an example that a type of kinetic data may be interpreted by more than one kinetic schemes. Problems like this are frequently encountered in the kinetic studies of polymerizations especially with ionic catalysts. Therefore, a strict examination of the validity of a kinetic scheme is essential to the kinetic studies of ionic polymerizations.

2) Non-stationary polymerization with slow initiation

Polymerization systems, in which the initiation takes place continuously and the number of moles of the propagating species changes with the reaction time, are classified as non-stationary polymerizations with slow initiation.

It is obvious from the discussion mentioned above that all the polymerization systems except those under the conditions: $R_i \simeq R_t$, $\frac{dR_i}{dt} \simeq 0$, and $\frac{dR_t}{dt} \simeq 0$, are included in this category. Although various types of polymerizations which are included in this class are principally considered, typical examples are realized in the following two cases: 1) when $R_i > R_t$ and the steady state approximation, $R_i \simeq R_t$, can not be applied; 2) when the steady state approximation, $R_i \simeq R_t$, is valid, but the approximation, $\frac{d[P^*]}{dt} = 0$, can not be applied because of the variation in R_i or R_t with the reaction time.

In the first case, the value of $\frac{d[P^*]}{dt}$ is positive; therefore, the number of moles of the propagating species increases with an increase in the reaction time. It depends on the relative magnitude of the transfer rate whether a polymerization of this type belongs to the successive or chain polymerization; *i. e.*, when the rate of transfer is negligible, the number-average degree of polymerizations of the polymer formed increases with an increase in the reaction time, as has been pointed out by the present authors in a previous paper,¹³⁾ whereas, the number-average degree of polymerization is constant when $R_i \ll R_t$, and, at the same time, the concentration of the transfer agent does not change. The authors have reported a general method for analyzing the kinetic data of these systems^{13,14)} and have shown that the rate constants of the elementary steps are evaluated by applying this method. MAGAT proposed a kinetic treatment of a polymerization system which is included in this class.¹⁰⁾ He has

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proposed a kinetic scheme in which termination is almost entirely due to primary radicals in order to interpret the kinetic behavior of a precipitation polymerization which proceeds by a free radical mechanism, and carried out a detailed kinetic treatment of these systems. Polymerizations with free radical initiators in the gaseous state, and in the solution where the polymer precipitates often belong to this class. The rate acceleration with an increase in the reaction time which is characteristic of this class as Fig. 2 shows, has been observed; for instance, in polymerizations with free radical initiators of ethylene,^{22,23)} vinyl chloride,²⁴⁾ and acrylonitrile.²⁵⁾ The authors have established that the polymerization of ethylene with azobisisobutyronitrile below *ca.* 60°C. is a non-stationary successive polymerization with slow initiation (SNS).²²⁾ Gamma-ray-induced polymerizations of ethylene at an ordinary temperature,^{26~28)} of vinyl chloride,²⁹⁾ of acrylamide in the solid state, and of 3,3-bis-chloromethyloxetane in the solid state in the presence of potassium hydroxide³¹⁾ belong to this class. Some polymerizations initiated by cationic catalysts^{32,33)} and complex catalysts^{34,35)} are also included in this category. But, it appears that, in few studies, maximum informations were obtained from the kinetic data by carrying out detailed analyses.

In the second case ($R_i \simeq R_t$), the number of moles of the propagating species increases when R_i increases or R_t decreases with the reaction time; whereas it decreases when R_i decreases or R_t increases. The non-stationary chain polymerization with slow initiation of this type is realized when $R_{tr} \gg R_i$ and, at the same time, the concentration of the transfer agent does not change. In the other cases, the successive polymerization is realized. The kinetic data of this type are analyzed by using the steady state approximation, $R_i \simeq R_t$, and the relative magnitude of the rate constants of the elementary steps can be estimated.^{36~39)} The "dead-end polymerization" is an example of this type;^{36,37)} in this case, R_i decreases with an increase in the reaction time owing to the consumption of the free radical initiators, and therefore, $[P^*]$ decreases with an increase in the reaction time. The polymerization which exhibits the "Trommsdorff effect" is another example of this type;^{38,39)} in this case, R_i decreased with an increase in the reaction time owing to the "gel effect", and $[P^*]$ increases with an increase in the reaction time. To the best knowledge of the present authors, polymerizations with ionic catalysts have never been treated as this type.

3) Stationary polymerization with rapid initiation

Polymerization systems, in which the initiation reactions are completed immediately after the polymerization starts and no termination takes place,

belong to stationary chain polymerizations with rapid initiation (RSC), or stationary successive polymerizations with rapid initiation (RSS). When the rate of transfer is negligible, the number-average degree of polymerization of the polymer steadily increases; this is a typical example of the stationary chain polymerization with rapid initiation and is commonly termed "living polymerization". When $R_{tr} \gg R_s$ and at the same time, the concentration of the transfer agent does not change, the number-average degree of polymerization is constant; polymerizations of this type are stationary chain polymerizations with rapid initiation. As has been pointed out above, the characteristics of the kinetic data with respect to the time-conversion and time-molecular weight relationships of this class are equal to those of the stationary chain polymerization with slow initiation (SSC).

The kinetic treatment of polymerizations of this class is simple because the initiation and the termination are not involved. SZWARC has carried out detailed kinetic studies on the anionic polymerization of styrene initiated by living polymers which is a typical example of the stationary successive polymerization with slow initiation.^{40~42)} The present authors have summarized a variety of polymerizations of this class and proposed a general method for treatment of the kinetic data.¹¹⁾ By carrying out this treatment, the efficiency factor of a catalyst, which is defined as the ratio of the number of moles of the active sites to the number of moles of the catalyst used, and the propagation rate constant can be evaluated. The authors have shown that the efficiency factor of a catalyst is independent of the kind of the monomer polymerized.

Many polymerizations with anionic catalysts have been found to belong to this class. For instance, the stationary successive polymerization with rapid initiation (RSS) is exemplified by the polymerizations of methacrylonitrile with lithium⁴³⁾ and of nitroethylene with alkylpyridine.⁴⁴⁾ Recently, it was reported that a variety of polymerizations with complex catalysts are included in this category; for instance, polymerizations of methylmethacrylate with Grignard reagents,⁴⁵⁾ of ethylene oxide with diethylmagnesium-dioxane,⁴⁶⁾ and of tetrahydrofuran with triethyloxoniumtetrafluoroborate⁴⁷⁾ and with triethylaluminum-water,⁴⁸⁾ belong to this class. One of the present authors has established that cationic polymerization of formaldehyde in carbon dioxide belonged to this class.⁴⁹⁾ Examples of the stationary chain polymerizations are often found in cationic polymerizations; for instance, polymerizations of styrene with perchloric acid in the ethylene dichloride solution^{50,51)} and of isobutene with stannic chloride⁵²⁾ are included in this class.

4) **Non-stationary polymerization with rapid initiation**

Polymerization systems in which the initiation reactions are completed immediately after the polymerization starts, and, subsequently, the concentration of the propagating species changes with an increase in the reaction time, belong to non-stationary chain polymerizations with rapid initiation (RNC) or non-stationary successive polymerizations with rapid initiation (RNS). These polymerization systems are realized when the rate of the termination of polymerizations with rapid initiation is appreciable; therefore, the rate of polymerization decreases with an increase in the reaction time in the non-stationary polymerizations with rapid initiation. When the concentration of the catalyst in these systems is small, a saturation in the polymer yield is observed. But, some polymerization systems in which the conversion reaches about 100% are also included in this category. In this case, the dependency of the initial rate of polymerization upon the concentration of the monomer is not equal to the dependency upon the concentration of the monomer estimated from the time-conversion curve at a definite monomer concentration.

A kinetic treatment of these systems has been first reported by PEPPER in the study of the polymerization of styrene with sulphuric acid in the ethylene dichloride solution.⁹⁾ The kinetic treatment has allowed the rate constants of the elementary steps to be evaluated. OKAMURA has studied the kinetics of polymerizations of this type and analyzed the kinetic data by using the equation derived by PEPPER.²⁰⁾ The authors have found that the polymerization of N-phenylethylenimine with various acids are included in this category,⁵³⁾ and analyzed the kinetic data by the graphical method proposed by the present authors to evaluate the rate constants of the elementary steps.⁵³⁾

Many cationic polymerizations have been treated as polymerizations of this type: for instance, polymerizations of styrene with sulphuric acid and with aluminium chloride,⁵⁴⁾ of isobutene with aluminium chloride⁵⁵⁾ and with titanium tetrachloride,⁵⁶⁾ of cyclopentadiene with titanium tetrachloride and with stannic chloride,²⁰⁾ and of N-phenylethylenimine with strong acid such as monochloroacetic acid and trichloroacetic acid.⁵³⁾ Polymerizations occurring from the post effect of gamma-ray or light irradiation belong to this class; for instance, the post-polymerization of trioxane by gamma-ray irradiation^{57,58)} and of acrylonitrile by light-irradiation⁵⁹⁾ are included in this class. The example of this class is very few in free radical polymerizations. One of the authors, however, succeeded in the realization of this class in the high-pressure polymerization of ethylene initiated by azobisisobutyronitrile at an ordinary temperature by using an autoclave specially designed to carry out the polymerization in the two stages;^{60,61)} in the first stage, the polymer radicals were produced by the

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initiation by azobisisobutyronitrile and, in the second stage, only the initiation was stopped by shutting the chamber in which the initiator was placed. The polymerization which occurred in the second stage is considered to be a polymerization with rapid initiation.

Acknowledgment

The authors are grateful to Professor Kenichi FUKUI for his guidance and valuable suggestions while carrying out the studies reviewed here.

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