BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 40 1045—1049 (1967)

A Classification of Polymerizations from a Kinetic Point of View

Tsutomu KAGIYA, Masatsugu IZU and Kenichi FUKUI
Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

(Received September 27, 1966)

Polymerizations were classified from a kinetic point of view. The polymerizations were divided into those with a rapid initiation and those with a slow initiation, according to the magnitude of the initiation rate in relation to the propagation rate. Both of these groups were then divided into stationary and non-stationary polymerizations according to the change in the number of moles of the propagating species with the reaction time. The next sub-classification, into chain and successive polymerizations, was made by estimating the change, with the reaction time, in the number-average degree of the polymerization of the polymer formed. Each proposed class was shown to possess a characteristic kinetic feature. Several examples of each class were collected.

Polymerizations have commonly been classified according to the types of initiators, monomers, modes of the addition of the monomers to the propagating species, or electronic structures of the propagating species. We can conveniently express the qualitative nature of the elementary reactions of a polymerization in the frame of these classifications. However, the terms which distinctly express the quantitative nature of elementary reactions, that is, the kinetic features of a polymerization, have been used only in special cases, such as "living polymerization" or "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.

We will propose in this paper a mode of the classification of polymerization reactions from a kinetic point of view into several distinct types, each of which definitely denotes the quantitative nature of the elementary reactions.

Classification of Polymerizations

The classification proposed in this paper has been intended to satisfy two requirements: 1) Each class should possess a quantitative nature of elementary reactions clearly distinguished from the others. 2) The type of a polymerization should be able to be determined readily by means of its kinetic features, that is, the dependencies of the polymer yield and the molecular weight of the polymer formed upon the reaction time. In order to attain these requirements, we have classified polymerization reactions according to the relative magnitude of elementary reaction rates. A proposed classification of polymerizations into several well-marked types is given in Table 1; each type is there characterized in detail.

1) Classification According to the Relative Magnitude of the Initiation Rate. As we pointed out previously,[1] the polymerizations are divided into those with a rapid initiation and those with a 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, $\left(\int R_i \mathrm{d}t\right)$, 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 a rapid initiation. Polymerizations with a rapid initiation have been observed in those initiated by ionic catalysts, and in the post-effect polymerizations initiated by γ-ray or by light irradiation.

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

2) Classification According to the Change in the Number of Moles of the Propagating Species with the Reaction Time. Both of the two classes mentioned above were further divided into stationary and non-stationary polymerizations. As is defined in Table 1, in the former, the mole of the propagating species is approximately constant, while, in the latter the mole of the propagating species changes

---

[1] T. Kagiya, S. Machi, M. Gotoda and K. Fukui, *Kōbunshi Kagaku*, **22**, 752 (1965).

TABLE 1. CLASSIFICATION OF POLYMERIZATIONS FROM A KINETIC POINT OF VIEW

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

R_i: initiation rate, *i. e.* the number of moles of the propagating species produced in unit time by initiation; t: reaction time; P*: propagating species; [P*]: the number of moles of P*; $\overline{P}$: 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.

with the reaction time. The stationary state in the polymerization with a slow initiation is realized when the rate of initiation is practically equal to that of termination; this state has commonly been called the "steady state." The stationary state in a polymerization with a rapid initiation is realized when the rate of termination is negligible. The mole of the propagating species decreases with the reaction time in a non-stationary polymerization with a rapid initiation, whereas the mole of the propagating species increases with the reaction time in a non-stationary polymerization with a slow initiation. The former is the case in rapidly-initiated polymerizations with an appreciable termination, while the latter is the case in slowly-initiated polymerizations with a very slow termination or without termination.

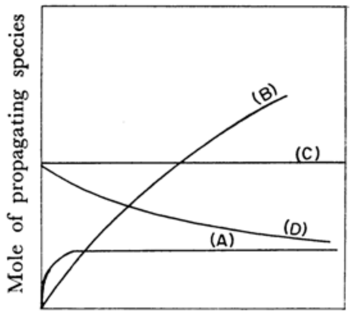
3) *Classification According to the Relative Magnitude of the Transfer Rate.* As listed in Table 1, the next sub-calssification was made by estimating the change of the number-average degree of polymerization of the produced polymer with the reaction time. We propose to term the polymerizations in which the number-average degree of polymerization is independent of the reaction time, as "chain polymerization," and those in which the polymerization degree changes with the reaction time, as "successive polymerization."

Various factors may influence the number-average degree of polymerization. But, the change in the number-average degree of polymerization with the reaction time can be estimated as follows, in typical cases where the concentration of the transfer agent is constant and polymer degradation does not occur. Stationary polymerizations with a slow initiation always belong to the chain polymerization, because the number-average degree of the polymerization of the polymer formed in the system is apparently independent of the reaction time, regardless of the relative magnitude of the transfer rate. In other cases, it depends on the relative magnitude of the transfer rate whether a polymerization belongs to a chain polymerization or to a successive polymerization. The former is the case when the mole of polymer chains produced by transfer during a certain period is much larger than that produced by initiation, that is, $\int R_{tr}\mathrm{d}t \gg \int R_i \mathrm{d}t$. The latter is the case in the opposite situation, that is, $\int R_{tr}\mathrm{d}t \ll \int R_i \mathrm{d}t$.

It should be noted that, in this proposed classification, we excluded the polymerizations in which the overall rate constant varies with the reaction time, for instance, the polymerization which has a Trommsdorff effect in the latter stage of polymerization. We also excluded the polymerizations in which the reverse reactions of the elementary steps are appreciable.

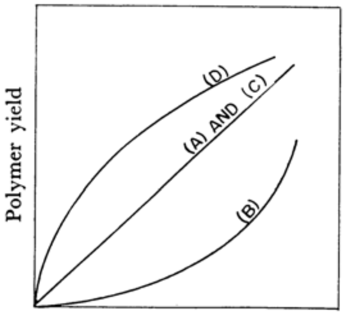
Typical Kinetic Feature of Each Type

As has been described above, we have classified polymerizations into proposed types, intending each type to possess its characteristic kinetic feature. 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.



Reaction time

Fig. 1. Change in the mole of propagating species with the reaction time.
(A) = Stationary polymerization with a slow initiation (SSC)
(B) = Non-stationary polymerization with a slow initiation (SNC and SNS)
(C) = Stationary polymerization with a rapid initiation (RSC and RSS)
(D) = Non-stationary polymerization with a rapid initiation (RNC and RNS)



Reaction time

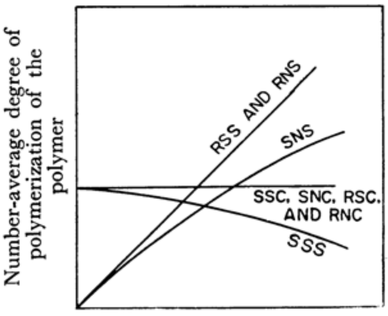
Fig. 2. Dependence of the polymer yield upon the reaction time. Symbols, (A)—(D), stand for those cases indicated in Fig. 1.

1) Typical Kinetic Feature with Respect to the Polymer Yield. Figure 1 shows the change in the concentration of the propagating species with the reaction time in each classified type of polymerization. Figure 2 shows the change in the polymer yield with 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 a slow initiation, while the later stage belongs to that with a rapid initiation, according to the proposed classification. In addition, it should be noted that Fig. 2 represents the typical cases when the concentration of the monomer does not change in the course of polymerization and when the propagation rate (R_p) is expressed by the equation $R_p=k_p[P^*][\mathrm{M}]$. If the case is otherwise, the figure should be modified.

As Figs. 1 and 2 show, since the mole of the propagating species shows a constant value which is independent of the reaction time in stationary polymerizations, it can be said that the polymerization proceeds at a constant rate. The overall rate of the non-stationary polymerization with a slow initiation increases with the reaction time, because of the increase in the mole of propagating species. The overall rate of the non-stationary polymerization with a rapid initiation decreases with the reaction time because the mole of the propagating species decreases with the reaction time.

2) Relationship between the Polymer Yield and the Number-average Degree of Polymerization of Each Type. As has been defined previously, the number-average degree of the polymerization of the polymer formed in a chain polymerization is constant and independent of the polymer yield, while that of the polymer formed in a successive polymerization changes with an increase in the polymer yield. The moles of the polymer chains in both stationary and non-stationary successive polymerizations with a rapid initiation (RSS and RNS), which are defined as the ratio of the polymer yield to the number-average molecular weight of the polymer, are constant if 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 mole of polymer chains. In the stationary polymerization with a slow initiation, the number-average degree of polymerization changes when the concentration of the transfer agent increases with the reaction time, or polymer degradation occurs. This case is also shown in Fig. 3 as the stationary successive polymerization with a slow initiation.

From these figures, it can be seen that each type in the proposed classification exhibits a



Polymer yield

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

characteristic kinetic feature. Accordingly, the class to which a polymerization belongs can be distinctly determined by means of its kinetic data. It should be noted, however, that both the stationary chain polymerization with a rapid initiation (RSC) and the stationary chain polymerization with a slow initiation (SSC) exhibit the same kinetic behavior, as is shown in Figs. 2 and 3. Accordingly, such an assignment of the class should be made by only after a careful consideration of the nature of the initiation.

Practical Examples of Each Type

Slow Initiation. Polymerizations initiated by radical initiators, those induced by γ-ray irradiation or by light irradiation, and thermal polymerizations mostly belong to this type. Some polymerizations with ionic catalysts are also included in this category.

1) Polymerizations with a Radical Initiator. Polymerizations with a radical initiator in the homogeneous liquid phase, where the termination rate between propagating radicals is relatively large, are mostly stationary polymerizations with a slow initiation (SSC). On the other hand, polymerizations with a radical initiator in the gaseous state and in the solution where the polymer precipitates are often non-stationary polymerizations with a slow initiation (SNC and SNS). The rate acceleration, which is characteristic of this type, as Fig. 2 shows, has been observed; for instance, in the polymerizations with a radical initiator of ethylene,[2,3] vinyl chloride,[4] and acrylonitrile in solution.[5] We have established that the polymerization of ethylene with AIBN below *ca.* 60°C is a non-stationary successive polymerization with a slow initiation (SNS).[3]

2) Polymerizations with γ-Ray or Light Irradiation. Homogeneous liquid state polymerizations with γ-ray or light irradiation are mostly stationary polymerizations with a slow initiation (SSC). Solid state polymerizations have occasionally been found to belong to this type also. For instance, the steady state approximation with respect to the propagating species has been observed to be applicable in the γ-ray-induced solid state polymerizations of 3, 3-bischloromethyloxetane[6] and maleimide.[7]

On the other hand, non-stationary systems with a slow initiation (SNC and SNS) have been observed in polymerizations in the solid state, in the gaseous state, and in the solution in which the precipitation of polymers takes place. For instance, the rate acceleration which is characteristic of this type has been observed in γ-ray-induced polymerization of ethylene at an ordinary temperature,[8,9] in vinyl chloride,[10] in acrylamide in the solid state,[11] and in 3, 3-bischloromethyloxetane in the solid state in the presence of KOH.[12] The polymerizations of ethylene and 3, 3-bischloromethyloxetane in the presence of KOH have been found to belong to the group of non-stationary successive polymerizations with a slow initiation (SNS), because the number-average degree of polymerization of the polymer formed increases with the irradiation time.

3) Polymerizations with Ionic Catalysts. Some polymerizations with ionic catalysts have been treated as a stationary polymerization with a slow initiation (SSC), in which a steady-state assumption with respect to the propagating species is applicable. However, the mode of the steady state is quite different from that in free radical polymerization, for the subsequent initiation which balances termination is considered to be caused by a catalyst recovered from the propagating species in the case of polymerizations with an ionic catalyst. For example, the polymerization of styrene catalyzed by potassium amide in liquid ammonia might be classified into this type.[13] As has been pointed out above, the kinetic feature of a stationary polymerization with a slow initiation (SSC) is equal to that of a stationary chain polymerization with a rapid initiation (RSC). Accordingly, there seems to be no objection to treating this system as RSC by regarding the termination as the transfer. A more detailed discussion of this type will be undertaken at the next opportunity.

The rate acceleration phenomena, which are characteristic of non-stationary polymerizations with a slow initiation (SNC and SNS), have been observed in polymerizations with both anionic[14,15] and cationic catalysts. As to the latter, Allen and Plesch have summarized the data on this type of polymerization.[16]

---

[2] R. Buchdahl, *Discussions Faraday Soc.*, **22**, 150 (1956).

[3] S. Machi, T. Sakai, M. Gotoda and T. Kagiya, *J. Polymer Sci.*, **B3**, 709 (1965).

[4] E. Jenckel, H. Eckmans and B. Rumbach, *Makromol. Chem.*, **4**, 15 (1949).

[5] C. H. Bamford and A. D. Jenkins, *Proc. Royal Soc.*, **A261**, 515 (1953).

[6] T. Kagiya, M. Izu and K. Fukui, unpublished results.

[7] T. Kagiya, M. Izu, S. Kawai and K. Fukui, *J. Polymer Sci.*, in press.

[8] S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, *ibid.*, **B2**, 765 (1964).

[9] S. Machi, M. Hagiwara, M. Gotoda and T. Kagiya, *ibid.*, **A3**, 2931 (1965).

[10] A. Chapiro, *J. Chem. Phys.*, **55**, 512 (1956).

[11] B. Baysal, G. Adler, D. S. Ballantine and P. Colombo, *J. Polymer Sci.*, **44**, 117 (1960).

[12] T. Kagiya, M. Izu and K. Fukui, *Makromol. Chem.*, **102**, 39 (1967).

[13] W. C. E. Higginson and N. S. Wooding, *J. Chem. Soc.*, **1952**, 760.

[14] F. J. Whelch, *J. Am. Chem. Soc.*, **81**, 1345 (1959).

[15] A. A. Kototkov, N. N Chesnokova and L. B. Trukhmanova, *Vysokomol. Soedin.*, **1**, 46 (1959).

[16] P. E. M. Allen and P. H. Plesch, "The Chemistry of Cationic Polymerization," ed. by P. H. Plesch, Pergamon Press. Ltd., Oxford (1963), p. 119.

Rapid Initiation. Some polymerizations with ionic catalysts, and polymerizations occurring from the post-effect of γ-ray or light irradiation belong to this type.

1) Post-effect in Polymerizations with γ-Ray and Light Irradiations. Polymerizations in which the life-time of their propagating species is long show a post-effect after irradiation is stopped. Most solid-state polymerizations possess a post-effect, and the kinetic features of these polymerizations mostly belong to polymerizations with a rapid initiation.[11,17,18] The radiation-induced polymerization of vinyl chloride[10] and the photopolymerizations of acrylonitrile[19] have also been found to possess a post-effect.

2) Polymerizations with Ionic Catalysts. Many polymerizations have been found to belong to this type. The stationary successive polymerization with a rapid initiation (RSS) is exemplified by the polymerizations of methacrylonitrile with Li,[20] of methylmethacrylate with RMgX,[21] of ethylene oxide with a coordinated catalyst of diethylmagnesium-dioxane,[22] and of nitroethylene with alkylpiridine.[23]

The polymerization of styrene by sulfuric acid has been established by Pepper to be a non-stationary polymerization[24] with a rapid initiation.

We were able to classify polymerizations from their kinetic data into classes which characterized the quantitative nature of elementary reactions. A kinetic interpretation and evaluation of the elementary rate constants of several classes using a graphical method is presented in a subsequent paper.

---

[17] H. Morawetz and I. D. Rubin, *J. Polymer Sci.*, **57**, 669 (1962).

[18] S. Okamura, K. Hayashi and Y. Nakamura, *Isotopes and Radiation (Japan)*, **3**, 416 (1960).

[19] C. H. Bamford and A. D. Jenkins, *J. Polymer Sci.*, **20**, 405 (1956).

[20] C. G. Overberger, E. M. Pearce and N. Mayens, *ibid.*, **34**, 109 (1959).

[21] A. Nishioka, H. Watanabe, K. Abe and Y. Sono, *ibid.*, **48**, 241 (1960).

[22] T. Kagiya, K. Toba and K. Fukui, presented at the 13th annual conference on polymer (Japan).

[23] D. J. Grodzensky, A. Katchalsky and D. Vofsi, *Makromol. Chem.*, **44**, 591 (1961).

[24] M. J. Hayes and D. C. Pepper, *Proc. Chem. Soc.*, **1958**, 228.