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Rate Constant of Initiation Reaction in Cationic Polymerization of Vinyl Monomers. I. Polymerization of Styrene Derivatives Catalyzed by Triphenylmethyl Stannic Pentachloride

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Summary

To investigate the method of measurement of the initiation rate constant in cationic polymerization, styrene and α -methylstyrene are polymerized by triphenylmethyl stannic pentachloride ($\text{Ph}_3\text{CSnCl}_5$). Adding these monomers to a solution of $\text{Ph}_3\text{CSnCl}_5$, the strong absorption of triphenylmethyl cation at 400 to 450 $m\mu$ disappears. The rate of disappearance of the absorption at 430 $m\mu$ is proportional to the concentration of $\text{Ph}_3\text{CSnCl}_5$ and monomer. It is confirmed that this disappearance of the absorption is due to the conversion of triphenyl cation to styryl or α -methylstyryl cation. Therefore, the rate of consumption of triphenylmethyl cation corresponds to that of the addition of triphenylmethyl cation to the olefinic double bond in a monomer, that is, the rate of the initiation reaction. Considering the dissociation constant of $\text{Ph}_3\text{CSnCl}_5$, the initiation rate constants of styrene and α -methylstyrene in ethylene chloride solution at 30°C are 11.6×10^{-2} and 2.85 liters/mole-min, respectively. These values seem to be much smaller than the propagation rate constant of each monomer. However, the effect of polymerization conditions, for example, the kind of a monomer and the polarity of a solvent, on the initiation rate constant is the same as in the propagation reaction. This fact suggests the similarity of a reaction mechanism in both elementary reactions.

INTRODUCTION

To clarify the reaction mechanism of the cationic polymerization based on the kinetic study, we have to know the rate constants of

elementary reactions and discuss the mechanism founded on these values. For such a purpose, the propagation reaction was studied by Hayes and Pepper (1) and the present authors (2), and the rate constants of termination and transfer reaction were measured for the same reaction systems (3,4). On the other hand, although the elaborate studies of the initiation reaction were carried out to elucidate the problem of cocatalyst, there was little research on the rate of the initiation reaction [one example is the study of the dimerization of 1,1-diphenylethylene derivatives by Evans et al. (5)]. Both the rate and stereochemistry of the addition of proton or halogen to an olefinic double bond were discussed in detail. However, the reaction condition in these reports was different from the usual polymerization reaction.

We want to elucidate the mechanism of the initiation reaction as well as that of the propagation reaction. The method of measurement of the rate constant for the initiation reaction has not yet been established. Therefore, in this paper, styrene and α -methylstyrene were polymerized by a stable carbonium ion salt, triphenylmethyl stannic pentachloride ($\text{Ph}_3\text{CSnCl}_5$), because its concentration is easily determined by UV spectra. During this experiment, a paper concerned with $\text{Ph}_3\text{CCl-HgCl}_2$ initiator (6) was published. This result will be discussed together with ours.

EXPERIMENTAL

Materials

Triphenylchloromethane (m.p. 111 to 112°C) was dissolved in purified benzene and excess stannic chloride was added to the solution at room temperature (7). Then $\text{Ph}_3\text{CSnCl}_5$ was precipitated from benzene solution. Excess benzene and stannic chloride were evaporated in vacuo. Sn content obtained by gravimetric analysis was 23.8% (calcd. value 22.0%).

Styrene and α -methylstyrene were purified by the usual method. They were washed by dilute aqueous alkali solution and distilled in vacuo over CaH_2 . The solvents were purified by the usual method and distilled over CaH_2 before use.

Procedures

Monomer solution was introduced into a flask sealed with a rubber cap. A catalyst solution was added to the monomer solution

with a syringe and the polymerization proceeded under dried air. In this procedure the water concentration in the reaction system was 1 to 2 mmoles/liter. The polymerization rate was measured by a dilatometric method and a molecular weight of polystyrene was calculated from the intrinsic viscosity number $[\eta]$ (benzene solution, 30°C) according to (1)

$$[\eta] = 4.37 \times 10^{-4} \bar{M}_n^{0.66} \quad (1)$$

The rate of a consumption of triphenylmethyl cation was measured from the absorption at 430 m μ by a Beckman UV spectrometer equipped with a thermostat.

RESULTS

Absorption Spectra of $\text{Ph}_3\text{CSnCl}_5$

$\text{Ph}_3\text{CSnCl}_5$ shows a strong absorption at 400 to 450 m μ in ethylene chloride solution. Optical density at 430 m μ is proportional to the concentration of $\text{Ph}_3\text{CSnCl}_5$, as shown in Fig. 1. From this result the apparent molar extinction coefficient can be obtained. In nitrobenzene, the results deviate from the Lambert-Beer law and the exact molar extinction coefficient cannot be obtained.

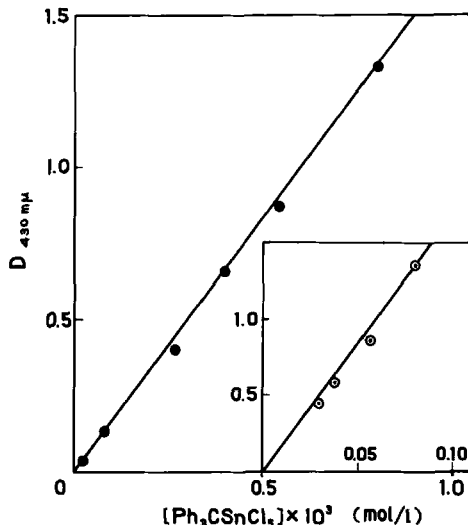


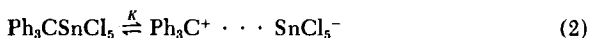
FIG. 1. Relationship between optical density at 430 m μ and the concentration of $\text{Ph}_3\text{CSnCl}_5$. Solvent, $(\text{CH}_2\text{Cl})_2$, 30°C; thickness of cell: ●, 0.10 cm; ○, 1.00 cm.

TABLE I

Equilibrium Constant between $\text{Ph}_3\text{CSnCl}_5$ and $\text{Ph}_3\text{C}^+ \cdots \text{SnCl}_5^-$ at 30°C
 ($\text{Ph}_3\text{CSnCl}_5$: 0.2×10^{-4} to 1.5×10^{-4} mole/liter)

Solvent	$\epsilon_{430 \text{ m}\mu}$ liters/mole-cm	K
$(\text{CH}_2\text{Cl})_2$	1.69×10^4	0.84
$(\text{CH}_2\text{Cl})_2$ (90 vol. %) + C_6H_6 (10 vol. %)	1.59×10^4	0.76
$(\text{CH}_2\text{Cl})_2$ (80 vol. %) + C_6H_6 (20 vol. %)	1.27×10^4	0.52

Evans et al. (8) reported that the shape and position of an absorption was not changed by the ratio of a free ion to an ion pair in tri-*p*-tolylmethyl chloride. Therefore, it is assumed in this paper that there is no difference between a free ion and an ion pair from the viewpoint of the absorption spectra. Ionic species seem to be mainly an ion pair, because the Lambert-Beer law is established over a wide range of catalyst concentration. Also, the molar extinction coefficient of triphenylmethyl cation, which completely dissociates in concentrated H_2SO_4 , is 3.7×10^4 liters/mole-cm (9). Then the dissociation constant K of $\text{Ph}_3\text{CSnCl}_5$ defined by Eq. (2) is calculated if the molar extinction coefficient is independent of the



type of solvent. The values of dissociation constants obtained by this method are summarized in Table I. The dissociation constant increases with increasing solvent polarity.

Rate of Consumption of $\text{Ph}_3\text{CSnCl}_5$ in the Reaction with Styrene

The optical density of the absorption of triphenylmethyl cation decreases with increasing reaction time in the presence of styrene, as shown in Fig. 2. The optical density at 430 $\text{m}\mu$ in time zero yields different values depending upon the concentration of styrene, even in the same concentration of $\text{Ph}_3\text{CSnCl}_5$. This may be due to the decrease of polarity of a reaction system by the increase of monomer concentration.

In the case of no addition of styrene, the optical density at 430 $\text{m}\mu$ does not change, as shown by the dashed line in Fig. 2. Therefore, the decrease of absorption at 430 $\text{m}\mu$ by an addition of styrene

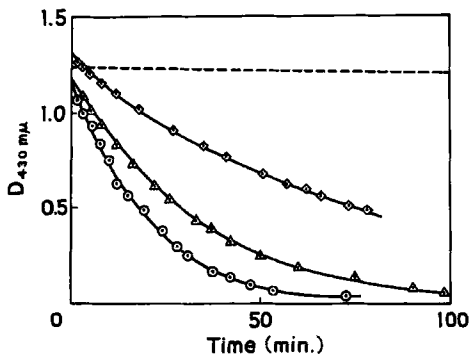
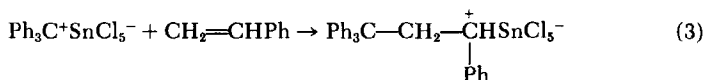
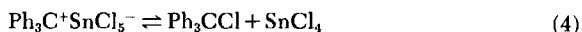


FIG. 2. Consumption of $\text{Ph}_3\text{CSnCl}_5$ in the presence of styrene. $\text{Ph}_3\text{CSnCl}_5$, 7.0×10^{-5} mole/liter; solvent, $(\text{CH}_2\text{Cl})_2$, 30°C ; styrene (moles/liter): \odot , 0.86; \triangle , 0.52; \diamond , 0.17; ----, 0.

is due to the change of triphenylmethyl cation to benzyl cation by the reaction of $\text{Ph}_3\text{CSnCl}_5$ with styrene,



Otherwise, the decomposition of $\text{Ph}_3\text{CSnCl}_5$ might cause the disappearance of the absorption of triphenylmethyl cation, as shown by



When a large amount of stannic chloride is added to the system, the absorption of $430 \text{ m}\mu$ disappears on the addition of styrene. This fact means that the dissociation reaction in equilibrium (4) does not occur and triphenylmethyl cation is not regenerated by the reaction with stannic chloride.

In this experiment, water concentration is larger than the initiator concentration, and water concentration has no effect on the rate of reaction of $\text{Ph}_3\text{CSnCl}_5$ with styrene in the range 1 to 3 mmoles/liter of water. As triphenylmethyl cation does not disappear in the presence of water, as shown in Fig. 2, $\text{Ph}_3\text{CSnCl}_5$ may not react with a small amount of water even if water can react with benzyl cation. Therefore, it is concluded that the disappearance of the absorption at $430 \text{ m}\mu$ is due to the reaction shown in Eq. (3).

Figure 3 shows a first-order plot concerned with the concentration of triphenylmethyl cation, where the initial concentration of

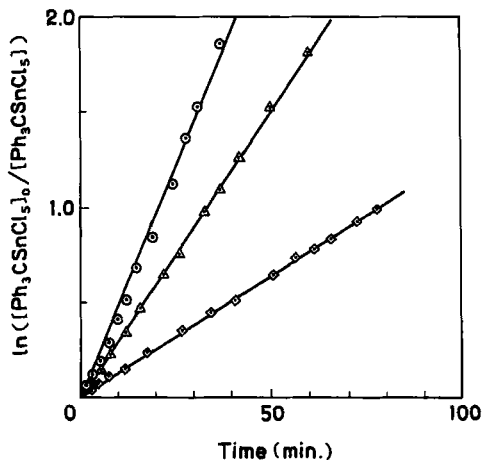


FIG. 3. First-order plot for the consumption of $\text{Ph}_3\text{CSnCl}_5$ in the presence of styrene. (From Fig. 2.)

triphenylmethyl cation is the value estimated from the optical density at $430\text{ m}\mu$ at time zero. This first-order plot is established in the whole range of conversion. From the inclination of this straight line, it is found that the rate of the consumption of triphenylmethyl cation is proportional to the initial concentration of styrene, as shown in Fig. 4.

When the reaction is carried out at various initiator concentrations and the same monomer concentration, the first-order plot of

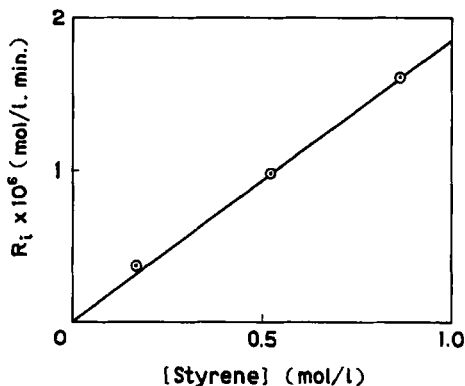


FIG. 4. Effect of monomer concentration on the rate of consumption of $\text{Ph}_3\text{CSnCl}_5$. (From Fig. 3.)

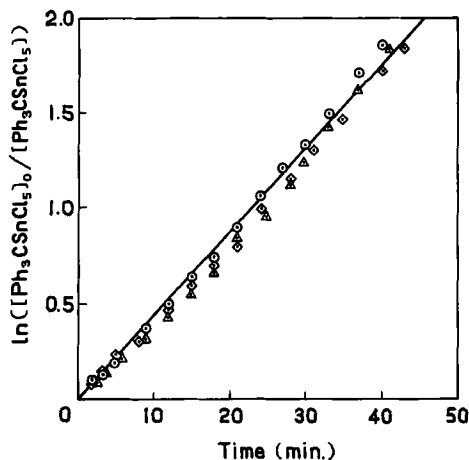
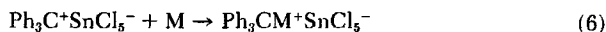


FIG. 5. First-order plot for the consumption of $\text{Ph}_3\text{CSnCl}_5$ in various concentration of $\text{Ph}_3\text{CSnCl}_5$. Styrene, 0.86 mole/liter; solvent, $(\text{CH}_2\text{Cl})_2$, 30°C ; $\text{Ph}_3\text{CSnCl}_5$ (moles/liter): \circ , 8.5×10^{-5} ; \triangle , 5.9×10^{-5} ; \diamond , 3.6×10^{-5} .

triphenylmethyl cation is given by one straight line, as shown in Fig. 5. This result supports the fact that the rate of reaction is proportional to the concentration of the initiator. Therefore, the rate of the consumption of the initiator is given by

$$-d[\text{C}]/dt = k_i'[\text{C}][\text{M}] \quad (5)$$

In this reaction, a part of $\text{Ph}_3\text{CSnCl}_5$ is ionized as shown in equilibrium (2), and ionized $\text{Ph}_3\text{C}^+\text{SnCl}_5^-$ can easily be added to a monomer. When the ionized $\text{Ph}_3\text{C}^+\text{SnCl}_5^-$ is immediately supplied from a neutral $\text{Ph}_3\text{CSnCl}_5$ after the consumption of triphenylmethyl cation by



the measurable rate constant k_i' is different from the true rate constant of the initiation reaction (k_i). If it can be assumed that equilibrium (2) is immediately established after the consumption of triphenylmethyl cation, k_i is given by k_i' and K as shown in

$$k_i[K]/(K + 1) = k_i' \quad (7)$$

This means that k_i can be calculated from observed k_i' and K , and both values of k_i and k_i' are given in this paper. There is no large

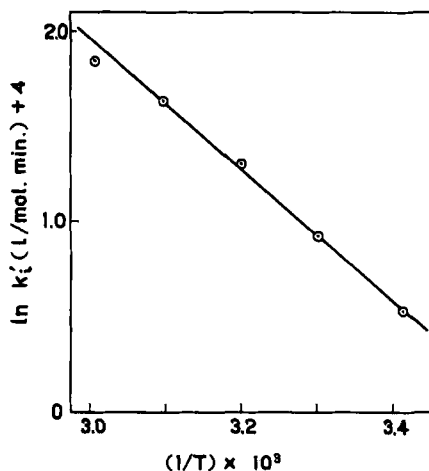


FIG. 6. Arrhenius plot for k'_i in the styrene- $\text{Ph}_3\text{CSnCl}_5$ system. Styrene, 0.86 mole/liter, $\text{Ph}_3\text{CSnCl}_5$, 6.2×10^{-5} mole/liter; solvent, $(\text{CH}_2\text{Cl})_2$.

difference between k_i and k'_i under the conditions of this experiment.

The effect of temperature on the rate of reaction was studied in ethylene chloride solution. Figure 6 shows that an Arrhenius plot of k'_i is established in the range 20 to 60°C and the activation energy is 6.7 kcal/mole. In this temperature range, as optical density at 430 μ is not changed by temperature, and the activation energy concerned with k_i has the same value as that of k'_i . The frequency factor is about 10^4 liters/mole-sec, a low value compared with the usual bimolecular reaction.

The polarity of a solvent affects the rate of reaction as expected from a general ionic reaction. When a small amount of benzene is

TABLE 2

Rate Constant of Addition Reaction of $\text{Ph}_3\text{CSnCl}_5$ to Styrene
[styrene: 0.86 mole/liter (10 vol. %), 30°C]

Solvent	k'_i , liters/ mole-min	k_i , liters/ mole-min	E , kcal/mole
$(\text{CH}_2\text{Cl})_2$	5.3×10^{-2}	11.6×10^{-2}	6.7
$(\text{CH}_2\text{Cl})_2$ (80 vol. %) + C_6H_6 (10 vol. %)	3.8×10^{-2}	8.8×10^{-2}	—
$(\text{CH}_2\text{Cl})_2$ (70 vol. %) + C_6H_6 (20 vol. %)	2.7×10^{-2}	7.9×10^{-2}	—

added to ethylene chloride to decrease the polarity of a reaction system, the rate of reaction decreases. The first-order plot established in these systems and the results obtained are summarized in Table 2. The decrease of polarity of a solvent causes not only a decrease of equilibrium constant K in Eq. (2), but also that of the rate constant k_i .

Rate of Consumption of $\text{Ph}_3\text{CSnCl}_5$ in the Reaction with α -Methylstyrene

Although α -methylstyrene cannot polymerize in our experimental condition due to the ceiling temperature of α -methylstyrene, there are no problems in measuring the rate of addition of triphenylmethyl cation to the carbon-carbon double bond of α -methylstyrene. The rate of reaction with α -methylstyrene is much larger than that of styrene and is proportional to the concentration of monomer and initiator as well, as in the case of styrene. Figures 7 and 8 are examples of the kinetic results of reaction in ethylene chloride and show the effect of a concentration of monomer and initiator, respectively. The rate constants in various solvents are summarized in Table 3.

Activation energy is also obtained in ethylene chloride, as shown

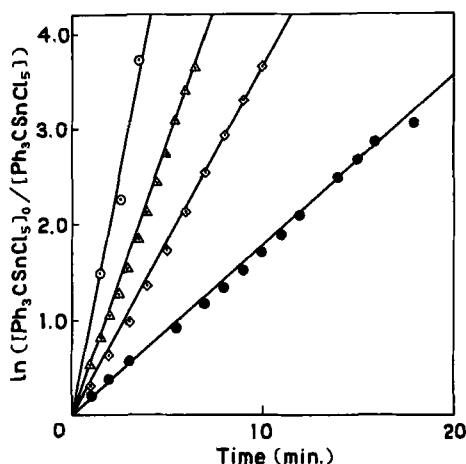


FIG. 7. First-order plot for the consumption of $\text{Ph}_3\text{CSnCl}_5$ in the presence of α -methylstyrene. $\text{Ph}_3\text{CSnCl}_5$, 6.5×10^{-5} mole/liter; solvent, $(\text{CH}_2\text{Cl})_2$, 30°C ; α -methylstyrene (moles/liter): \circ , 0.77; \triangle , 0.46; \diamond , 0.31; \bullet , 0.15.

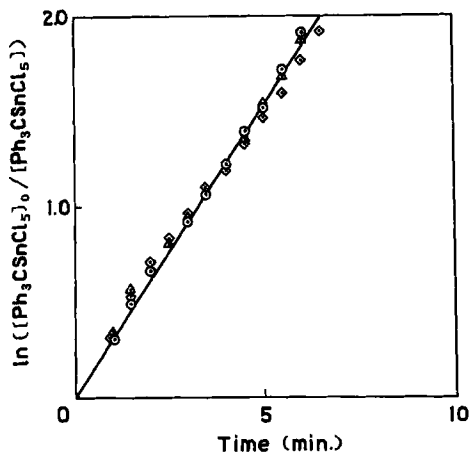


FIG. 8. First-order plot for the consumption of $\text{Ph}_3\text{CSnCl}_5$ in various concentrations of $\text{Ph}_3\text{CSnCl}_5$ in the presence of α -methylstyrene. α -methylstyrene, 0.31 mole/liter; solvent, $(\text{CH}_2\text{Cl})_2$, 30°C ; $\text{Ph}_3\text{CSnCl}_5$ (moles/liter): \circ , 5.2×10^{-5} ; \triangle , 4.2×10^{-5} ; \diamond , 3.1×10^{-5} .

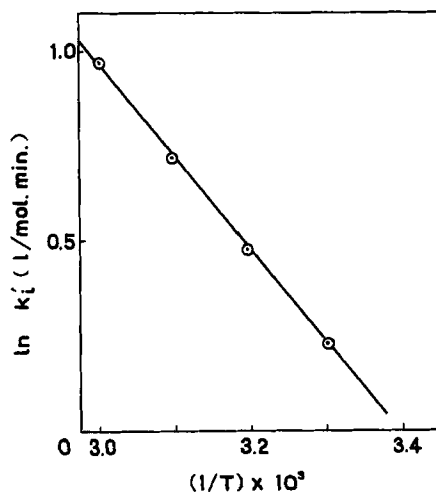


FIG. 9. Arrhenius plot for k'_i in the α -methylstyrene- $\text{Ph}_3\text{CSnCl}_5$ system. α -Methylstyrene, 0.31 mole/liter; $\text{Ph}_3\text{CSnCl}_5$, 7.4×10^{-5} mole/liter; solvent, $(\text{CH}_2\text{Cl})_2$.

TABLE 3
Rate Constant of Addition Reaction of $\text{Ph}_3\text{CSnCl}_5$ to α -Methylstyrene
[α -methylstyrene: 0.31 mole/liters (4 vol. %), 30°C]

Solvent	k'_i , liters/ mole-min	k_i , liters/ mole-min	E_i , kcal/mole
$(\text{CH}_2\text{Cl})_2$	1.30	2.85	5.0
$(\text{CH}_2\text{Cl})_2$ (86 vol. %) + C_6H_6 (10 vol. %)	0.84	1.95	—
$(\text{CH}_2\text{Cl})_2$ (76 vol. %) + C_6H_6 (20 vol. %)	0.47	1.37	—

in Fig. 9. Activation energy is about 5 kcal/mole and this value is smaller than that of styrene, but the frequency factor has the same value as with styrene.

Polymerization of Styrene by $\text{Ph}_3\text{CSnCl}_5$

In higher concentrations of $\text{Ph}_3\text{CSnCl}_5$ than that in the case of the measurement of the rate constant of the initiation reaction, styrene is polymerized at an appreciable rate, as shown in Fig. 10. In a situation such as Fig. 10 ($[\text{M}]_0$, ca. 1 mole/liter; $[\text{C}]$, 1 to 5 mmoles/liter; $[\text{H}_2\text{O}]$, 1 to 2 mmoles/liter), a time-conversion curve consists of two parts: a part with a slow rate in the initial stage and a part with a fast rate in the later stage. The polymerization behavior

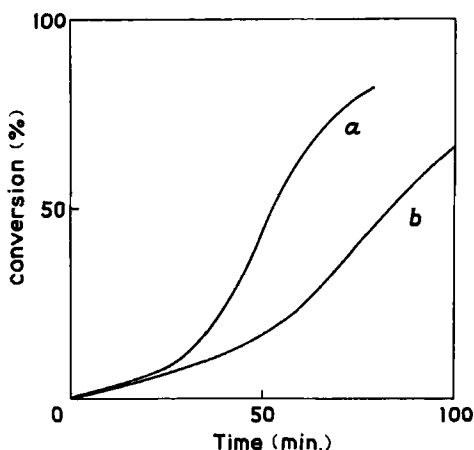


FIG. 10. Time-conversion curves of polymerization of styrene catalyzed by $\text{Ph}_3\text{CSnCl}_5$. $\text{Ph}_3\text{CSnCl}_5$, 2.4×10^{-3} mole/liter; solvent, $(\text{CH}_2\text{Cl})_2$, 30°C ; styrene (moles/liter): a, 1.38, b, 0.86.

will be discussed only briefly because the main subject of this paper is the initiation reaction.

The maximum rate of polymerization is proportional to the square of monomer concentration and independent of initiator concentration. The molecular weight of the resultant polymer is roughly proportional to monomer concentration and decreases with increasing initiator concentration. These facts show that $\text{Ph}_3\text{CSnCl}_5$ may act as a transfer or terminating agent as well as an initiator.

DISCUSSION

When $\text{Ph}_3\text{CSnCl}_5$ is used as an initiator, it is found that the rate of reaction of $\text{Ph}_3\text{CSnCl}_5$ with a monomer can be measured by the rate of disappearance of an absorption at $430\text{ m}\mu$. As optical density at $430\text{ m}\mu$ does not change in the absence of styrene or α -methylstyrene, the consumption of triphenylmethyl cation should be due to the reaction with a monomer.

Vofsi and Tobolsky (11) reported that the rate of polymerization of tetrahydrofuran by the stable ion was not proportional to catalyst concentration and in the higher concentration range deviated from linearity observed with respect to catalyst concentration. They explained this phenomenon by the idea that the activity of cation was quite different from a catalyst concentration in a solvent with a low dielectric constant. Fortunately, because in our experiment the rate of reaction is proportional to the catalyst concentration in the wide range of catalyst concentration, it is not necessary to consider the dissociation to a free ion from an ion pair. Also, it was reported that an absorption at about $420\text{ m}\mu$ was observed during polymerization of styrene (12). However, we could not observe such an absorption during polymerization in a dark place and did not attend to the absorption of the polymerizing system of styrene in this experiment. One bit of evidence supporting this assumption is that the relation of Eq. (5) is established in a wide range of concentration of $\text{Ph}_3\text{CSnCl}_5$.

As the value of the propagation rate constant in this system is not obtained, comparison between the rate constant of initiation and propagation of the $\text{Ph}_3\text{CSnCl}_5$ catalyst is not possible. However, the propagation rate constant in a styrene-stannic chloride-water system is about 25 liters/mole-min at 30°C (13) and the structure of the counterion in this case seems to be similar to the case of

$\text{Ph}_3\text{CSnCl}_5$. A small value of the initiation rate constant compared with the propagation rate constant is due to the difference between the reactivity of benzyl and triphenylmethyl cation.

From the results obtained above, the effect of various conditions on the initiation rate constant is discussed. The initiation rate constant of α -methylstyrene is about 25 times as large as that of styrene. The increase in reactivity in α -methylstyrene is due to the inductive effect of the α -methyl group and is not caused by the difference in frequency factor but by that of activation energy.

In our experiment, temperature does not affect a dissociation constant in equilibrium (2). Therefore, the observed activation energy corresponds to that in an addition of triphenylmethyl cation to monomer. Although cleavage of a covalent bond requires a large amount of energy, the ionic initiator is polarized and the initiation reaction in cationic polymerization will not need a high energy. As the activation energy in the initiation reaction of radical polymerization is usually 20 to 30 kcal/mole, it is concluded that the activation energy is very low in cationic polymerization. The frequency factor of styrene and α -methylstyrene is about 10^4 moles/liter-sec, and this value is similar to the frequency factor of the propagation rate constant of styrene derivatives catalyzed by iodine (14). The similarity of the frequency factor in both reactions suggests that the addition reaction of $\text{Ph}_3\text{CSnCl}_5$ to styrene derivatives is also an ion-pair mechanism.

It is easily estimated that the polarity of a solvent affects the rate of reaction. However, the polarity of a reaction system cannot be changed over a wide range, because $\text{Ph}_3\text{CSnCl}_5$ is insoluble in a hydrocarbon solvent, and optical density at $430\text{ m}\mu$ decreases slightly in nitrobenzene without addition of styrene. Even with a slight decrease in solvent polarity, the value of the initiation rate constant decreases remarkably, as shown in Tables 2 and 3. The degree of variation of the initiation rate constant by a change of polarity is comparable with that of the propagation rate constant in the styrene-perchloric acid-ethylene chloride system (15).

Sambhi and Treloar (6) reported that the initiation rate constant in the $\text{Ph}_3\text{CCl-HgCl}_2$ -styrene-ethylene chloride system was 3.7×10^{-3} liter²/mole²-min at 25°C. The difference between this value and the one in our system may be due to the difference of the ionizing power of metal halide (16).

As mentioned above, factors that affect the rate of reaction of $\text{Ph}_3\text{CSnCl}_5$ with styrene are the structure of a monomer, the polarity of a solvent, and the type of catalyst. The tendency of these factors to influence the reaction rate is exactly the same in both reactions—initiation and propagation. This fact suggests the similarity of the reaction mechanism in both elementary reactions.

It is found for the $\text{Ph}_3\text{CSnCl}_5$ initiator that the rate constant of initiation can be measured from the disappearance of absorption at $430\text{ m}\mu$ due to triphenylmethyl cation. Although the kinds of reagents used as monomer and catalyst are limited, one method of measurement for the initiation rate constant is established, and values of the initiation rate constant can be obtained under a variety of conditions.

REFERENCES

1. M. Hayes and C. C. Pepper, *Proc. Roy. Soc. (London)*, **A263**, 63 (1961), and a series of their papers.
2. S. Okamura, N. Kanoh, and T. Higashimura, *Makromol. Chem.*, **47**, 19 (1961), and a series of their papers.
3. D. H. Jenkinson and D. C. Pepper, *Proc. Roy. Soc. (London)*, **A263**, 82 (1961).
4. T. Higashimura and N. Kanoh, *Kobunshi Kagaku*, **23**, 114 (1966).
5. A. G. Evans, N. Jones, and J. H. Thomas, *J. Chem. Soc.*, **1955**, 1824, and a series of their papers.
6. M. S. Sambhi and F. E. Treloar, *Polymer Letters*, **3**, 445 (1965).
7. D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, **1957**, 674.
8. A. G. Evans, A. Price, and J. H. Thomas, *Trans. Faraday Soc.*, **52**, 332 (1956).
9. A. Bentley, A. G. Evans, and J. Halpern, *Trans. Faraday Soc.*, **47**, 711 (1951).
10. e.g., J. E. Leffer, *The Reactive Intermediates of Organic Chemistry*, Wiley (Interscience), New York, 1956.
11. D. Vofsi and A. V. Tobolsky, *J. Polymer Sci.*, **A3**, 3261 (1965).
12. e.g., D. O. Jordan and F. E. Treloar, *J. Chem. Soc.*, **1961**, 729, 734; A. Gandini and P. H. Plesch, *Proc. Chem. Soc.*, **1964**, 240; *Polymer Letters*, **3**, 127 (1965).
13. N. Kanoh, T. Higashimura, and S. Okamura, *Kobunshi Kagaku*, **19**, 181 (1962).
14. N. Kanoh, T. Higashimura, and S. Okamura, *Makromol. Chem.*, **56**, 65 (1962).
15. D. C. Pepper and P. J. Reilly, *J. Polymer Sci.*, **58**, 639 (1962).
16. J. L. Cotter and A. G. Evans, *J. Chem. Soc.*, **1959**, 2988.

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Zusammenfassung

Um die Messmethodik zur Bestimmung der Wachstumsgeschwindigkeitskonstante der kationischen Polymerisation zu untersuchen, wurden

Styrol und α -Methylstyrol mittels Triphenylmethylzinn-pentachlorid ($\text{Ph}_3\text{CSnCl}_5$) polymerisiert. Bei der Zugabe dieser Monomeren zu einer Lösung von $\text{Ph}_3\text{CSnCl}_5$ verschwindet die starke Absorption des Triphenylmethylkations bei 400–450 $m\mu$. Die Geschwindigkeit mit der die Absorption bei 430 $m\mu$ verschwindet ist der Konzentration von $\text{Ph}_3\text{CSnCl}_5$ und der Monomeren proportional. Es konnte bestätigt werden, dass das Verschwinden dieser Absorption auf die Umwandlung des Triphenylkations in ein Styrol- oder α -Methylstyrolkation zurückzuführen ist. Deshalb entspricht die Geschwindigkeit des Verbrauchs an Triphenylmethylkation der Addition des Triphenylmethylkations an die olefinische Doppelbindung in einem Monomeren, d.h. der Geschwindigkeit der Startreaktion. Unter Berücksichtigung der Dissoziationskonstanten von $\text{Ph}_3\text{CSnCl}_5$ sind die Startgeschwindigkeitskonstanten für Styrol in Äthylchlorid als Lösungsmittel bei 30°C 11.6×10^{-2} und für α -Methylstyrol 2.85 l/mol. min. Diese Werte scheinen viel kleiner zu sein als die Wachstumsgeschwindigkeitskonstanten für jedes der Monomeren. Der Einfluss der Polymerisationsbedingungen, z.B. die Art des Monomeren und die Polarität des Lösungsmittels, auf die Startreaktionsgeschwindigkeitskonstante ist jedoch derselbe wie bei der Wachstumsreaktion. Diese Tatsache weist auf die Ähnlichkeit im Reaktionsmechanismus in beiden Elementarreaktionen hin.

Résumé

Dans le but d'étudier la méthode de mesures des constantes de vitesse de la réaction d'amorçage d'une polymérisation cationique, on a polymérisé le styrène et l' α -méthylstyrène à l'aide du pentachlorure d'étain-triphénylméthyl ($\text{Pn}_3\text{CSnCl}_5$). Par addition de ces monomères à une solution de $\text{Ph}_3\text{CSnCl}_5$, la forte absorption du cation triphénylméthyl à 400–500 $m\mu$ disparaît. La vitesse de la disparition d'absorption à 430 $m\mu$ est proportionnelle à la concentration du $\text{Ph}_3\text{CSnCl}_5$ et du monomère. On a confirmé que cette disparition d'absorption est due à la transformation du cation triphényl en cation styryl ou α -méthylstyryl. La vitesse de la consommation du cation triphénylméthyl correspond donc à la vitesse d'addition de ce cation à la double liaison olefinique du monomère c.a.d. à la vitesse de la réaction d'amorçage. Tenant compte de la constante de dissociation du $\text{Ph}_3\text{CSnCl}_5$ les vitesses d'amorçage sont 11.6×10^{-2} et 2.85 l/mol. min. respectivement pour le styrène et l' α -méthylstyrène à 30°C dans une solution de chlorure d'éthylène. Ces valeurs semblent plus faibles que les constantes de vitesse de propagation de chaque monomère. Cependant, l'effet des conditions de polymérisation, par ex., de la nature du monomère et de la polarité du solvant sur la constante de vitesse d'amorçage et le même que dans la réaction de propagation. Ce fait suggère que le mécanisme réactionnel de ces deux réactions est analogue.