BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2247—2253 (1968)

A Structural Study on the Catalytic Activity in Ionic Polymerization

Tsutomu KAGIYA, Yūzō SUMIDA and Tetsuya NAKATA
Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

(Received December 29, 1967)

According to the theoretical conclusion reported previously on the activation energy of the catalytic polymerization, the experimental results relating to the monomer reactivity and the catalytic activity in anionic or cationic polymerization were interpreted. The catalytic activity in ionic polymerization can be quantitatively compared with the relative magnitude of the ionization potential or the electron affinity of monomer and components (A, D) of catalyst (AD). As a measure of the ionization potential or the electron affinity of monomer, the energy of the highest occupied ($\varepsilon_{ho}=\alpha+\lambda_{ho}\beta$) or the lowest vacant ($\varepsilon_{lv}=\alpha-\eta_{lv}\beta$) π level of the monomer has been used, and as a measure of the electron affinity of component D, the pK_a of the acid HD or the σ_I value. In anionic polymerization, it was found that the polymerization by the catalyst with the same component A took place only in the combination of the monomer and the catalyst in which the $\eta_{lv}/\mathrm{p}K_a$ value was less than about 2.5×10^{-2}, and that the catalytic activity, with the same component D, depends on the kind of solvent. The results in cationic polymerization were also discussed in connection with the electron affinity of component D or co-catalyst. And the monomer reactivity in ionic polymerization with the same catalyst was quantitatively discussed with the η_{lv} or λ_{ho} value of monomer. From the accordance between the theoretical consideration and the experimental data, the present treatment was found to be useful for the purpose of the quantitative study of the catalytic activity and the monomer reactivity in ionic polymerization.

In the past ten years, many works on ionic polymerization have been accumulated. Little attention has, however, been paid to the relation between the catalytic activity and the structure of the catalyst.

In the previous paper,[1] the authors made a study on the energetic consideration of ionic polymerization and reported that the monomer reactivity could be compared with the relative magnitude of the electronic natures of monomer and catalyst components.

---

[1] T. Kagiya, Y. Sumida and T. Nakata, This Bulletin, **41**, 2239 (1968).

The purpose of this paper is to determine the relation between the catalytic activity and the structure of the catalyst on the basis of the energetic study reported previously. It was found that the relative magnitude of the catalytic activity is closely related to the electronic structures of catalyst and monomer. The theoretical treatment was found to be useful for the purpose of a systematical interpretation of many kinds of experimental results.

Theoretical

As have been described in the previous paper,(1) the overall activation energy of ionic polymerization with the slow or the rapid initiation(2) is expressed as follows,

The Slow Inititation System

Anionic Polymerization;

$$\varDelta E_{(A)} = k_1 + k_2 E_a(\mathrm{D}) \pm k_3 I_p(\mathrm{A}) - k_4 E_a(\mathrm{M}) + k_5 I_p(\mathrm{M}) \qquad (1)$$

Cationic Polymerization;

$$\varDelta E_{(C)} = k_1' - k_2' E_a(\mathrm{D}) + k_3' I_p(\mathrm{A}) + k_4' I_p(\mathrm{M}) - k_5' E_a(\mathrm{M}) \qquad (2)$$

The Rapid Initiation System

Anionic Polymerization;

$$\varDelta E_{(A)} = k_6 \pm k_7 I_p(\mathrm{A}) - k_8 E_a(\mathrm{M}) + k_5 I_p(\mathrm{M}) \qquad (3)$$

Cationic Polymerization;

$$\varDelta E_{(C)} = k_6' - k_7' E_a(\mathrm{D}) + k_8' I_p(\mathrm{M}) - k_5' E_a(\mathrm{M}) \qquad (4)$$

where $k_1, \cdots, k_8, k_1', \cdots, k_8'$ are the positive constants. k_3 and k_7 depend on the kind of solvents. M: monomer, AD: catalyst, D: conjugated component acting as the electron donor, A: conjugated component acting as the electron acceptor. E_a and I_p are an electron affinity and an ionization potential, respectively. In the polymeriaztion that the contribution to the activation energy of the monomer co-ordination to the growing ion is larger than that to the counter ion, the last terms in these equations (1)—(4) contribute less to the change in the overall activation energy of the polymerization.

According to the energetic consideration of the catalytic polymerization, the catalyst give mainly an effect on the initiation and propagation reactions.(1,3) And, since the activation energy of the initiation reaction is larger than that of the propagation in the polymerization with the slow initiation, the overall catalytic activity can be discussed quantitatively with Eqs. (1) and (2). It is evident from Eqs. (1) and (2) that the overall activation energy of the anionic polymerization decreases as the electron affinity of D decreases, whereas that of the cationic polymerization decreases as that of D increases. The electron accepting component A of the catalyst is usually a metal or hydrogen atom, and the data of the ionization potentials of their compounds have been reported, while those of the electron affinities of D have not.

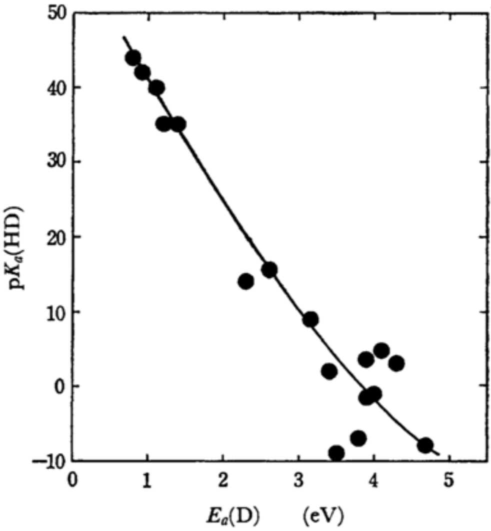


Fig. 1. Relation between the electron affinity of component D and the $\mathrm{p}K_a$ value of the conjugated acid HD.

In order to evaluate the electron affinity of D with the parameter corresponding to it, the relation between the $E_a(\mathrm{D})$ value and the $\mathrm{p}K_a$ value of the conjugated acid HD(4,5) was investigated as shown in Fig. 1. $E_a(\mathrm{D})$ can be approximately evaluated with $\mathrm{p}K_a(\mathrm{HD})$ as follows,

$$E_a(\mathrm{D}) = -k_9 \mathrm{p}K_a(\mathrm{HD}) + k_{10} \quad (k_9 > 0) \qquad (5)$$

Therefore, the overall activation energy of the polymerization with the slow initiation by the catalyst with the same component A is given as follows, neglecting the last terms,

$$\varDelta E_{(A)} = k_{11} - k_{12} \mathrm{p}K_a(\mathrm{HD}) - k_4 E_a(\mathrm{M}) \qquad (6)$$

$$\varDelta E_{(C)} = k_{11}' + k_{12}' \mathrm{p}K_a(\mathrm{HD}) + k_4' I_p(\mathrm{M}) \qquad (7)$$

where k_{11}, k_{12}, k_{11}' and k_{12}' are constants.

Since the electron affinity of D is one of the measures of the electron withdrawing character of D, it is considered to be related to the inductive substituent constant σ_I. Figure 2 shows the relation between them. In a similar manner as described above, the overall activation energy can

---

(2) T. Kagiya, M. Izu and K. Fukui, *ibid.*, **40**, 1045 (1967).

(3) T. Kagiya, T. Kondo and K. Fukui, This Bulletin in press.

(4) D. J. Cram, "Fundamentals of Carbanion Chemstry," Academic Press, New York and London (1965), pp. 4—19.

(5) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," First Edition, Methuen & Co., Ltd. (1962).

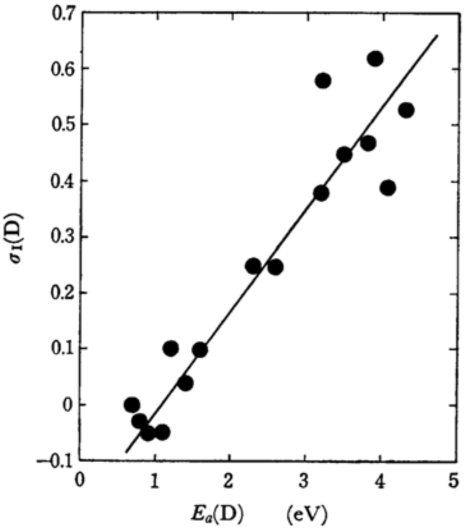


Fig. 2. Relation between the electron affinity of component D and the inductive substituent constant σ_I.

be expressed by the following equations, neglecting the last terms, instead of Eqs. (1) and (2),

$$\Delta E_{(A)} = k_{13} + k_{14}\sigma_I(D) - k_4 E_a(M) \quad (k_{14}>0) \tag{8}$$

$$\Delta E_{(C)} = k_{13}' - k_{14}'\sigma_I(D) + k_4' I_p(M) \quad (k_{14}'>0) \tag{9}$$

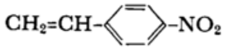
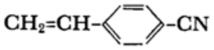
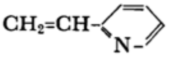
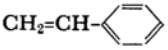
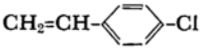
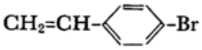
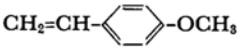
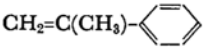
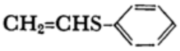
where k_{13}, k_{14}, k_{13}' and k_{14}' are constants.

The Eqs. (1)—(9) were used to discuss whether a certain compound in connection with the structures of catalyst and monomer has a catalytic activity or not.

Interpretation of Experimental Data

Monomer Reactivity and Catalytic Activity in Anionic Polymerization. As have been described in the preceding chapter, the monomer reactivity and the catalytic activity in anionic polymerization can be compared with the electron affinity of monomer and catalyst component D. Little information has, however, been reported on the electron affinities of various monomers except those of some components D. Then, as described in the previous paper,[1] the η_{lv} values of vinyl monomers were calculated as the parameter relating to the electron affinity and the results were summarized in Table 1 in the order of the smaller value. The observed half wave reduction potential[6] relating to the electron affinity is also tabulated in Table 1.

TABLE 1. MONOMER REACTIVITY IN ANIONIC POLYMERIZATION AND ENERGY OF THE LOWEST VACANT π LEVEL OF MONOMER

Monomer	*1	η_{lv}*2	$-E_{1/2}$*3
	+	0.2658	
$CH_2=CHNO_2$	+	0.2714	
$CH_2=C(CN)_2$	+	0.3106	
$CH_2=CHCHO$	+	0.3147	(2.50)*4
$CH_2=C(COOCH_3)_2$	+	0.3346	
	+	0.3845	
$CH_2=CHCN$	+	0.4065	2.90
$CH_2=C(CH_3)CN$	+	0.4311	3.13
$CH_2=CHCOCH_3$	+	0.4476	(2.65)*4
$CH_2=CHCOOCH_3$	+	0.4527	2.95
$CH_2=C(CH_3)COOCH_3$	+	0.4872	3.07
$CH_3CH=CHCHO$	+	0.4917	
	+	0.5709	
$CH_2=CHCH=CH_2$	+	0.6180	3.27
	+	0.6622	3.19
	−	0.6742	
	−	0.6769	
	−	0.7065	
	+	0.7163	
$CH_2=CHCl$	−	0.8556	no wave
$CH_2=CHOCOCH_3$	−	0.9581	no wave
	−	0.9600	
$CH_2=CH_2$	+	1.0000	
$CH_2=CHOCH_3$	−	1.1175	
$CH_2=CHCH_3$	?	1.1838	
$CH_2=C(CH_3)_2$	—	1.3808	

*1 + and − indicate the occurrence and the nonoccurrence of the anionic polymerization.

*2 η_{lv} is the coefficient of the energy of the lowest vacant π level, $\varepsilon_{lv}=\alpha-\eta_{lv}\beta$.

*3 $-E_{1/2}$ is the half wave reduction potential in units of eV. Data in Ref. 6.

*4 An approximate value.

There is a general tendency that the monomer polymerizes more easily as its η_{lv} value is small, and that the order of the monomer reactivity is nearly in accordance with the empirical informations. In order to discuss quantitatively this fact, Fig. 3 was drawn. The half wave reduction potential was adopted as a measure of the electron affinity, and the reactivity[7] of monomer with the CH_3O^- or n-$C_{12}H_{25}S^-$ anion as its reactivity in anionic polymerization.

---

6) N. Yamazaki, I. Tanaka and S. Nakahama, paper presented at the 16th Symposium on Polymer Chemistry, Kyushu, October 1967, preprint, p. 91.

7) Y. Yasuda and T. Tsuruta, paper presented at the 16th Symposium on Polymer Chemistry, Kyushu, October 1967, preprint, p. 105.

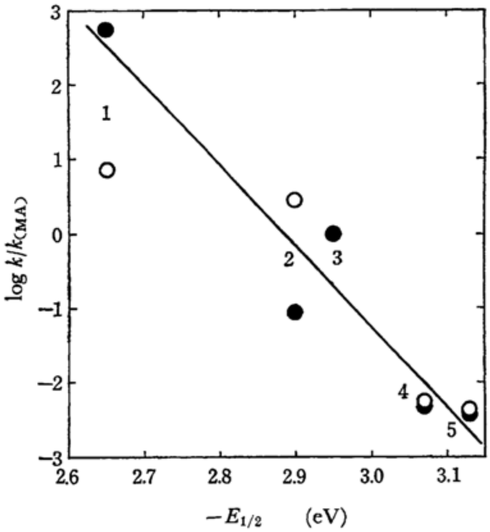


Fig. 3. Relation between the reactivity of monomer with CH_3^- or n-$C_{12}H_{25}S^-$ anion and the half wave reduction potential of monomer.
○ CH_3O^-, ● n-$C_{12}H_{25}S^-$
(1) Methyl vinyl ketone, (2) Acrylonitrile, (3) Methyl acrylate, (4) Methyl methacrylate, (5) Methacrylonitrile

On the other hand, Higginson *et al.*[8] studied the reactivity of some vinyl monomers catalysed by the sodium salts of various weak acids and pointed out that the occurrence of the polymerization had some relations to the pK_a of the original acids and the color resulting from the addition of the catalyst into the monomer.

In Eq. (6), the overall activation energy of anionic polymerization with the same component A is given by the following equation,

$$\varDelta E_{(A)} = k_{15} - k_{12}\mathrm{p}K_a(\mathrm{HD}) + k_{16}\eta_{lv}(\mathrm{M}) \qquad (k_{12},\ k_{16}>0) \quad (10)$$

In order to discuss the catalytic activity in connection with the property of monomer, it is necessary to claculate the value of $(-k_{12}\mathrm{p}K_a(\mathrm{HD})+k_{16}\eta_{lv}(\mathrm{M}))$. This value, however, cannot be calculated in practice. Then the $\eta_{lv}/\mathrm{p}K_a$ value was examined here and summarized in Table 2. Table 2 shows that the polymerization occurs in the combination of the monomer and the catalyst in which the $\eta_{lv}/\mathrm{p}K_a$ value is less than about 2.5×10^{-2}.

Tsuruta *et al.*[9] discussed the possibility of the anionic polymerization in connection with the structures of monomer and catalyst as shown in Table 3. In Table 3, (a) group of catalyst gives the polymer of the monomer in group (A), (B) and (C), (b) group (B) and (C) groups but not (A), and (c) group (C) group but not (A) and (B) groups. In order to study the result by using the above conclusion, the $\eta_{lv}/\mathrm{p}K_a$ values have been calculated. The results obtained also indicate that the polymerization takes place only in the combination of the catalyst and the monomer in which the $\eta_{lv}/\mathrm{p}K_a$ value is less than about 2.5×10^{-2}. It is concluded from the above facts that $\eta_{lv}/\mathrm{p}K_a$ value is an important parameter for evaluation of the catalytic activity in anionic polymerizations.

It is also considered that the analogous condition described above is preserved in the propagation reaction in anionic polymerization. In order to examine this inference, the $\eta_{lv}/\mathrm{p}K_a$ value was calculated as to the several vinyl monomers, where CH_3Y may be considered to be employed as the conjugated acid CH_2DCHY-CH_2CH_2Y of the propagating anion CH_2DCHY-CH_2C^-HY of the monomer $CH_2{=}CHY$. It is apparent in Table 4 that the $\eta_{lv}/\mathrm{p}K_a$ parameter is a good index to predict the occurrence of the anionic polymerizations.

Szwarc *et al.*[10] studied the anionic polymerization of styrene in tetrahydrofuran and in dioxane, and observed that the rate of propagation is dependent on the kind of counter ions and the nature of solvents. This result may be also discussed by Eq. (3). In the case of the same monomer and the

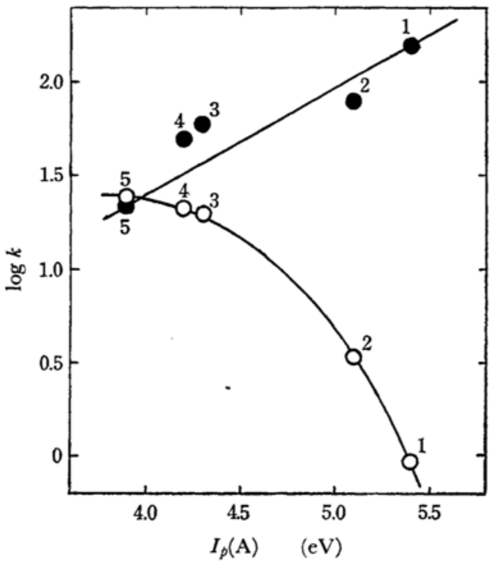


Fig. 4. Effect of the ionization potential of counter metal on the rate constant of propagation in anionic polymerization of styrene.
●, tetrahydrofuran; ○, dioxane.
(1) Li, (2) Na, (3) K, (4) Rb, (5) Cs

---

[8] N. S. Wooding and W. C. Higginson, *J. Chem. Soc.*, **1952**, 774.

[9] T. Tsuruta, "Atarashii Kobunshi Gosei Kagaku (Kagaku Zokan 13)," ed. by E. Imoto, M. Imoto, R. Oda, S. Kambara, J. Furukawa and S. Murahashi, Kagaku Dojin (1964), p. 109.

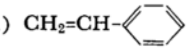
[10] D. N. Bhattacharyya, J. Smid and M. Szwarc, *J. Phys. Chem.*, **69**, 612, 624 (1965).

Table 2. The ratio of the η_{lv} value of the energy of the lowest vacant π level of monomer to the pK_a value of the original acid of the catalyst

Original acid	pK_a	Cloro of anion	$\eta_{lv}/\mathrm{p}K_a \times 10^2$ *		
			Acrylonitrile $\eta_{lv}=0.4065$	Methyl methacrylate $\eta_{lv}=0.4872$	Styrene $\eta_{lv}=0.6622$
Methanol	16	Colorless	+ 2.54	− 3.05	− 4.14
Ethanol	18	Colorless	+ 2.26	− 2.71	− 3.68
Acetophenone	19	Yellow	+ 2.14	− 2.57	− 3.48
Triphenylcarbinol	19	Green	+ 2.14	− 2.57	− 3.48
Indene	21	Yellow	+ 1.94	+ 2.32	− 3.16
Phenylacetylene	21	Colorless	+ 1.94	+ 2.32	− 3.16
Diphenylamine	23	Colorless	+ 1.77	+ 2.12	− 2.88
Fluorene	25	Red	+ 1.63	+ 1.95	− 2.65
Acetylene	26	Colorless	+ 1.56	+ 1.87	− 2.55
Aniline	27	Colorless	+ 1.50	+ 1.81	+ 2.45
p-Methoxyaniline	27	Colorless	+ 1.50	+ 1.81	+ 2.45
Xanthen	29	Red	+ 1.40	+ 1.68	+ 2.28
Triphenylmethane	33	Red	+ 1.23	+ 1.48	+ 2.01
Ammonia	35	Colorless	+ 1.16	+ 1.39	+ 1.89

* + indicates the formation of polymer, − indicates the absence of polymer.

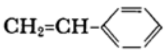
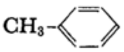
Table 3. The ratio of the η_{lv} value of the energy of the lowest vacant π level of monomer to the pK_a value of the conjugated acid of the catalyst

Catalyst	Conjugated acid	pK_a*[1]	$\eta_{lv}/\mathrm{p}K_a \times 10^2$	Monomer	η_{lv}*[2]
(a) NaR	RH	35		(A) 	0.6622
(b) NaOR	ROH	17		(B) CH_2=CHCN	0.4065
(c) (H_2O)	H_2O	15		(C) CH_2=$CHNO_2$	0.2714

*[1] Data of Refs. 4 and 5.

*[2] η_{lv} is the coefficient of the energy of the lowest vacant π level, $\varepsilon_{lv}=\alpha-\eta_{lv}\beta$.

Table 4. The η_{lv} value of the energy of the lowest vacant π level of monomer and the pK_a value of the conjugated acid

Monomer	η_{lv}*[1]	Conjugated acid	pK_a*[2]	*[3]	$\eta_{lv}/\mathrm{p}K_a \times 10^2$
CH_2=$CHNO_2$	0.2714	CH_3NO_2	11	+	2.47
CH_2=$C(CN)_2$	0.3106	$CH_2(CN)_2$	12	+	2.59
CH_2=CHCHO	0.3147	CH_3CHO	14.5	+	2.17
CH_2=$C(COOCH_3)_2$	0.3346	$CH_2(COOCH_3)_2$	13.3	+	2.52
CH_2=CHCN	0.4065	CH_3CN	25	+	1.63
CH_2=$CHCOCH_3$	0.4476	CH_3COCH_3	20	+	2.24
CH_2=$CHCOOCH_3$	0.4527	CH_3COOCH_3	24.5	+	1.85
	0.6622		35	+	1.89
CH_2=CHCl	0.8556	CH_3Cl	22	−	3.89
CH_2=$CHOCOCH_3$	0.9581	CH_3OCOCH_3	24.5	−	3.91
CH_2=CH_2	1.0000	CH_4	40	+	2.50
CH_2=$CHCH_3$	1.1838	CH_3CH_3	42	?	2.81
CH_2=$C(CH_3)_2$	1.3808	$CH_3CH_2CH_3$	44	−	3.14

*[1] η_{lv} is the coefficient of the energy of the lowest vacant π level, $\varepsilon_{lv}=\alpha-\eta_{lv}\beta$.

*[2] Data of Refs. 4 and 5.

*[3] + and − indicate the occurrence and the nonoccurrence of the anionic polymerization.

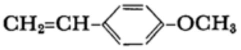
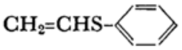
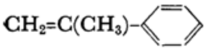
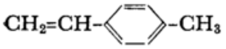
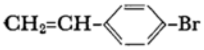
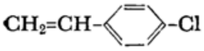
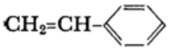
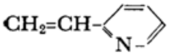
same conjugated component D of catalyst, Eq. (3) may be written as follows,

$$\log k = k_{17} \pm k_{18} I_p(\mathrm{A}) \quad (k_{18}>0) \qquad (11)$$

where k is a rate constant of the propagation reaction, k_{17} and k_{18} are constants, and k_{18} depends on the kind of solvent. Figure 4 indicates that Eq. (11) can approximately express the change of the propagation rate with the counter metals.

Monomer Reactivity and Catalytic Activity in Cationic Polymerization. As the same manner, the λ_{ho} values of various vinyl monomers were calculated in the order of the smaller value as shown in Table 5. There is a general tendency that the monomer polymerizes more easily as its λ_{ho} value is smaller, and that the monomer whose ionization potential[11-14] is larger than about 10.2 eV occurs no longer a cationic polymerization. The order of the monomer reactivity is nearly in accordance with the empirical informations. Figure 5 shows the relation between the rate constant of propagation in the cationic polymerization of the styrene derivatives[15] and their ionization potentials.[11] These results also lead to the conclusion that the quantitative treatment in the previous paper[1] represents satisfactorily many experimental data on the monomer reactivity in the cationic polymerization.

TABLE 5. MONOMER REACTIVITY IN CATIONIC POLYMERIZATION AND ENERGY OF THE HIGHEST OCCUPIED π LEVEL OF MONOMER

Monomer	*1	λ_{ho}*2	$-I_p$*3
	+	0.3424	7.92
$CH_2=CHOCH_3$	+	0.3542	9.97
$CH_2=C(CH_3)CH=CH_2$	+	0.5460	8.86
	+	0.5654	
	+	0.5793	(8.2)*4
	+	0.5793	8.20
	+	0.5875	
	+	0.6051	8.47
$CH_2=C(CH_3)_2$	+	0.6082	9.35
$CH_2=CHCH=CH_2$	+	0.6180	9.07
	+	0.6622	8.47
	−	0.7176	
$CH_2=C(CH_3)CN$	−	0.7202	(10.5)*4
$CH_2=CHCH_3$	+	0.7632	9.70
$CH_2=CHOCOCH_3$	−	0.8500	(10.5)*4
$CH_2=CHCN$	−	0.8547	10.75
$CH_2=CHCl$	−	0.9420	10.39
$CH_3CH=CHCHO$	+	0.9905	9.73
$CH_2=CHCOOCH_3$	−	1.0774	(10.7)*4
$CH_2=CHCOCH_3$	+	1.1368	(10.2)*4
$CH_2=CHCHO$	+	1.1607	10.10

*1 + and − indicate the occurrence and the non-occurrence of the cationic polymerization.

*2 λ_{ho} is the coefficient of the energy of the highest occupied π level, $\varepsilon_{ho}=\alpha+\lambda_{ho}\beta$.

*3 I_p is the ionization potential in units of eV. Data in Refs. 11, 12, 13 and 14.

*4 An approximate value.

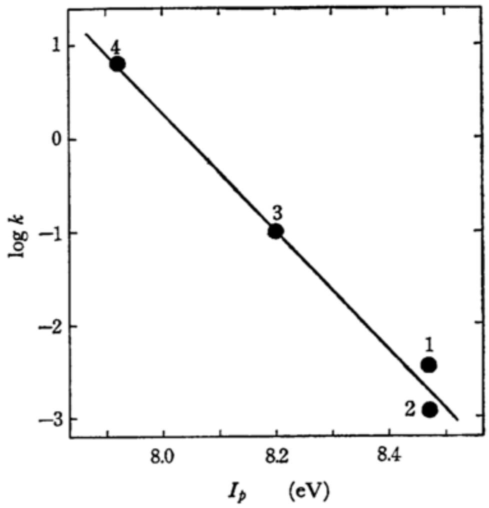


Fig. 5. Relation between the rate constant of propagation in cationic polymerization of styrene derivative and its ionization potential.
(1) Styrene, (2) *p*-Chlorostyrene,
(3) *p*-Methylstyrene, (4) *p*-Methoxystyrene

On the other hand, Yokota *et al.*[16] studied the kinetics of the polymerization of formaldehyde by the various proton acids in liquid carbon dioxide, and reported that this polymerization belonged to a type of the stationary successive with the rapid initiation[2] and the catalytic activity was remarkably changed by the kind of counter anions. Substituting Eq. (5) into Eq. (4), it is expected that the following relation exists between the rate of polymerization and the pK_a value of the acid of the catalyst,

$$\log R = k_{19} - k_{20}\mathrm{p}K_a(\mathrm{HD}) \qquad (k_{20}>0) \qquad (12)$$

where R is a rate of polymerization, k_{19} and k_{20}

---

11) N. Tamura, M. Hatano and S. Kambara, paper presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, March 1967, preprint IV, p. 277.

12) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

13) K. Watanabe, T. Nakayama and J. Mottl, "Final Report on Ionization Potentials of Molecules by a Photoionization Method," December, 1959, Dept. Army No. 5B-99-01-004, ORD TB2-0001-OOR-1624.

14) A. Streitwieser, *J. Am. Chem. Soc.*, **82**, 4123 (1960).

15) N. Kanoh, T. Higashimura and S. Okamura, *Makromol. Chem.*, **56**, 65 (1962).

16) H. Yokota and M. Kondo, *J. Polymer Sci.*, *Part A*, in press.

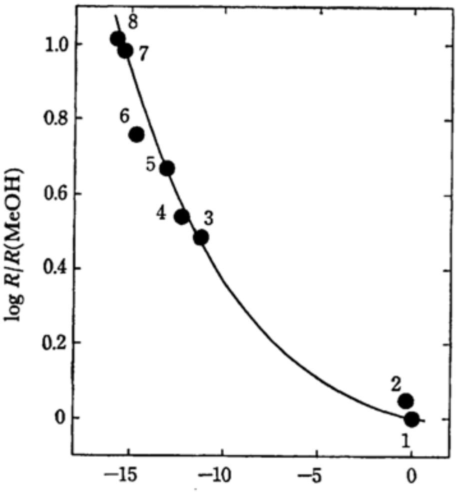


Fig. 6. Effect of the pK_a value of catalyst on the rate of cationic polymerization of formaldehyde. (1) Methanol, (2) Water, (3) Acetic acid, (4) Formic acid, (5) Monochloroacetic acid, (6) Dichloroacetic acid, (7) Trichloroacetic acid, (8) Trifluoroacetic acid.

are constants. As shown in Fig. 6, the relation (12), that is, Eq. (4) holds good in the cationic polymerization.

In both of the cationic polymerization of styrene catalysed by Lewis acids[17] and the racemization of 1-phenylethyl chloride,[18] the cationic activity of Lewis acids is in the order as follows,

$$\underset{(252)}{SbCl_5} \gg \underset{(175)}{TiCl_4} > \underset{(163)}{AlBr_3} > \underset{(133)}{SnCl_4} \gtrsim \underset{(141)}{FeCl_3} >$$

$$\underset{(57)}{ZnCl_2} > \underset{(52)}{HgCl_2}$$

These Lewis acids react with the co-catalyst to form the counter anions of the growing chain end. Therefore, it is expected that an increase in the cationic activity of Lewis acid is arised from an increase in its acidity. Okamura *et al.*[17] employed the heat of solution of Lewis acid and ethyl acetate as a measure of the acidity of Lewis acid. Present authors used the shift of the characteristic band of the carbonyl group in the infrared spectrum of the Lewis acid-xanthone complex,[19] and reported[20] that an increase in the shift showed an increase in the acidity of Lewis acid. The values in parentheses in the above relation represent the magnitude of the carbonyl shift. There is a good correlation between the catalytic acitivity and the carbonyl shift in the Lewis acid-xanthone complex.

Similarly, the activity of co-catalysts in the polymerization system of the same monomer and the same Lewis acid catalyst, for example, in the cationic polymerization of isobutene catalysed by tin chloride,[21] decreases in the order,

$$\underset{(pK_a=0.64)}{CCl_3COOH} > \underset{(2.87)}{CH_2ClCOOH} > \underset{(4.76)}{CH_3COOH}$$

$$> \underset{(9)}{CH_3CH_2NO_2} > \underset{(11)}{CH_3NO_2} > \underset{(10)}{C_6H_5OH} > \underset{(15)}{H_2O}$$

As the pK_a value of co-catalyst decreases, its activity increases, and Eq. (7) is satisfied.

As described above, in any cases of anionic and cationic polymerization the energetic treatment in the previous paper was found to be useful to explain quantitatively many kinds of experimental data.

The authors are grateful to Professor Kenichi Fukui and Professor Teijiro Yonezawa for their valuable suggestions while carrying out this study.

---

[17] S. Okamura, T. Higashimura and H. Sakurada, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **61**, 1640 (1958).

[18] K. Bodendorf and H. Boehme, *Ann.*, **516**, 1 (1935).

[19] D. Cook, *Can. J. Chem.*, **41**, 522 (1963).

[20] T. Kagiya, Y. Sumida and T. Inoue, This Bulletin, **41**, 767 (1968).

[21] K. E. Russell, *Trans. Faraday Soc.*, **48**, 114 (1952).