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An Energetic Consideration of the Monomer Reactivity in Catalytic Polymerization

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The elementary processes constituting the polymerization reaction are energetically considered, and the relation between the activation energy of each process and the structures of reagents or the kind of solvents is theoretically discussed. The solvation energy of ion has been evaluated with the ionization potential of anion or the electron affinity of cation, and the ionization potential or the electron affinity of the growing radical with that of the corresponding 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 calculated, and the π bond dissociation energy has been evaluated with the summation ($\lambda_{ho}+\eta_{lv}$). On the basis of these considerations, the monomer reactivity in catalytic polymerization can be compared with the relative magnitude of the electronic natures of monomer and components of catalyst, *i. e.*, ionization potential or electron affinity.

In recent years, a number of experimental informations has been accumulated on the polymerization of vinyl compounds. On the basis of the data, Alfrey and Price[1,2] have systematically made a study of the correlations between the monomer reactivities in radical polymerization and the structural factors of vinyl monomers in terms of the empirical values of Q and e. Yonezawa, Fukui and their coworkers,[3-5] from the standpoint of the simple molecular orbital theory, have calculated the stabilization energy arising from π conjugation in the transition state in radical or ionic polymerization of vinyl monomer and the

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[1] T. Alfrey, Jr. and C. C. Price, *J. Polymer Sci.*, **2**, 101 (1947).

[2] G. E. Ham, *ibid.*, **14**, 483 (1954).

[3] T. Yonezawa, K. Hayashi, C. Nagata, S. Okamura and K. Fukui, *ibid.*, **14**, 312 (1954).

[4] K. Hayashi, T. Yonezawa, C. Nagata, S. Okamura and K. Fukui, *ibid.*, **20**, 537 (1956).

[5] T. Yonezawa, T. Higashimura, K. Katagiri, K. Hayashi, S. Okamura and K. Fukui, *ibid.*, **26**, 311 (1957).

localization energy indicating the facility of the initiation reaction in ionic polymerization, and have considered the relation between these characteristic values and the reactivities of monomers.

The latest experimental results, however, have indicated that the monomer reactivity is remarkably affected by the structure of catalyst[6,7] and the nature of solvent.[8,9] Hence it appears that these theories based on the free ion model are insufficient to explain the accumulated experimental data.

The purpose of the work is to study quantitatively the monomer reactivity in catalytic polymerization. The elementary processes constituting the polymerization reaction are energetically considered in connection with the electronic structures of the monomer and the catalyst. On the basis of the conclusion, the monomer reactivity in catalytic polymerization should be correlated with the electronic structures of a monomer and components of catalyst.

Theoretical

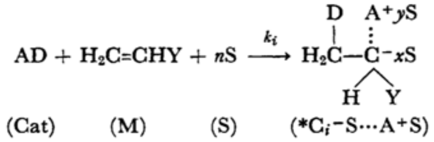
(I) The Overall Rate of Polymerization. It is generally assumed that the catalytic polymerization consists of the elementary processes of (i) the formation of the active ion-pair (the initiation), (ii) the monomer addition to the active ion-pair (the propagation), (iii) the formation of the polymer and the active ion-pair (the chain transfer) and (iv) the deactivation of the active ion-pair (the termination). In order to discuss theoretically the monomer reactivity in catalytic polymerization, an energetic consideration was forcused on the first two steps, that is, the initiation and the propagation. Then, the followings are postulated.

(i) The initiation process is that forms the solvated active ion-pair by the reaction of monomer and catalyst.

(ii) The propagation process consists of the formation reaction of the intermediate and its rearrangement reaction to make the chain growth. The former is that to form the complex in which the monomer co-ordinates to the solvated ion-pair nucleophilically and electrophilically. The latter is the unimolecular rearrangement reaction of the complex.

According to the above postulations, the elementary processes controlling the overall polymerization are illustrated by the following models for the anionic polymerization of the vinyl monomer as an example.

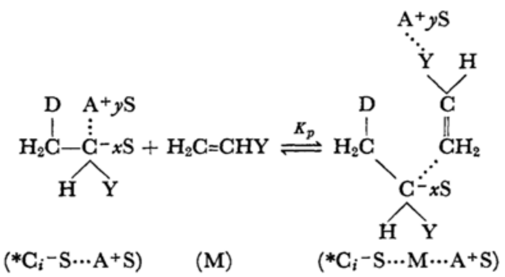
Initiation:



(1)

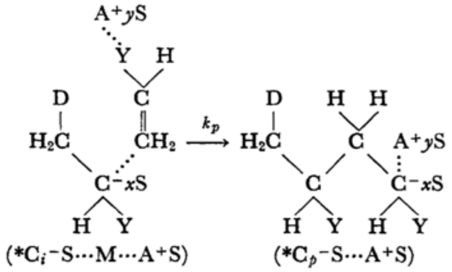
Propagation:

The formation of the intermediate complex:



(2)

The rearrangement of the intermediate complex:



(3)

In the above models, AD represents a catalyst, and the conjugated component A is an electron acceptable group and D an electron donative group. The expression in ( ) indicates the abbreviation of the model compound. Where Cat: catalyst, M: monomer, S: solvent, $^*C_i{}^-S\cdots A^+S$: initiating active ion-pair solvated, $^*C_p{}^-S\cdots A^+S$: propagating active ion-pair solvated, $^*C_i{}^-S\cdots M\cdots A^+S$: intermediate complex, Y: electron donative group such as a carbonyl group in the monomer molecule, x and y: the number of solvent molecules solvating to the anion and the cation, and $x+y=n$. k_i and k_p are the rate constants of the initiation and the rearrangement reaction, and K_p the equilibrium constant of the intermediate formation.

Based on the assumption of the first order rate with respect to all components, the rate of consumption of the catalyst is

$$-\frac{d[\mathrm{Cat}]}{dt} = k_i[\mathrm{S}][\mathrm{M}][\mathrm{Cat}] \tag{4}$$

Since the concentration of the solvent and the monomer can be regarded as constant in the first stage of the polymerization, the remaining concentration of the catalyst is expressed by Eq. (5),

$$[\mathrm{Cat}] = [\mathrm{Cat}]_0 e^{-k_i[\mathrm{S}][\mathrm{M}]t} \tag{5}$$

where $[\mathrm{Cat}]_0$ is the initial concentration of the catalyst. While, from the equilibrium reaction (2),

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[6] Y. Imanishi, T. Higashimura and S. Okamura, *Kobunshi Kagaku* (*Chemistry of High Polymers*), **18**, 333 (1961).

[7] T. Kagiya, T. Kondo and K. Fukui, This Bulletin, **41**, 2473 (1968).

[8] T. Kagiya, T. Shimidzu and K. Fukui, *Shokubai (Catalyst)*, **5**, 304 (1963).

[9] H. L. Hsieh, *J. Polymer Sci.*, **A3**, 153 (1965).

$$[{}^*C_i\text{-}S\cdots M\cdots A^+S] = K_p[M] \times ([Cat]_0 - [Cat] - [{}^*C_i\text{-}S\cdots M\cdots A^+S] - [{}^*C_p\text{-}S\cdots A^+S]) \qquad (6)$$

In the beginning of the polymerization, the polymer concentration $[{}^*C_p\text{-}S\cdots A^+S] \approx 0$, hence

$$[{}^*C_i\text{-}S\cdots M\cdots A^+S] = \frac{K_p[M][Cat]_0}{1+K_p[M]}(1-e^{-k_i[S][M]t}) \qquad (7)$$

In the case of the first order propagation reaction with respect to the intermediate, the overall rate of polymerization is generally given as follows,

$$R = \frac{d[{}^*C_p\text{-}S\cdots A^+S]}{dt} = k_p[{}^*C_i\text{-}S\cdots M\cdots A^+S][M] = \frac{k_pK_p[M][Cat]_0}{1+K_p[M]}(1-e^{-k_i[S][M]t}) \qquad (8)$$

It is apparent from Eq. (8) that the overall rate is simplified as follows by the relative magnitude of the K_p value, in both polymerization with the slow initiation ($k_i \ll 1$) and the rapid initiation ($k_i \gg 1$) defined by us previously,[10]

The polymerization with the slow initiation ($k_i \ll 1$):

$$K_p[M] \ll 1 \quad R = k_ik_pK_p[M]^2[S][Cat]_0t \qquad (9)$$

$$K_p[M] \gg 1 \quad R = k_ik_p[M][S][Cat]_0t \qquad (10)$$

The polymerization with the rapid initiation ($k_i \gg 1$):

$$K_p[M] \ll 1 \quad R = k_pK_p[M][Cat]_0 \qquad (11)$$

$$K_p[M] \gg 1 \quad R = k_p[Cat]_0 \qquad (12)$$

Equations (9) and (10) in the slow initiation system show that the polymerization rate in the early stage increases with the polymerization time.

Since the equilibrium constant K_p is considered to be small, the overall rate of polymerization can be generally discussed by Eq. (9). The observed specific rate k in the slow initiation system (9) involves that the equilibrium constant of the formation of the intermediate and both rate constants of the formation of the active ion-pair and the rearrangement reaction of the complex.

$$k = k_ik_pK_p \qquad (13)$$

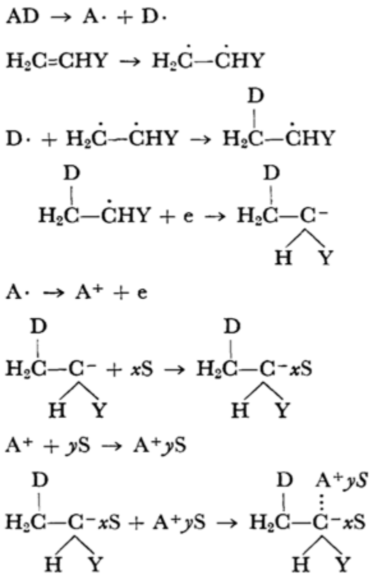
(II) An Energetic Study of the Catalytic Polymerization. Based on Eq. (13), the overall activation energy ΔE is given as follows by using each activation energy (ΔE_i, ΔE_p) and the Gibbs' free energy change (ΔG_p) of the reactions,

$$\Delta E = \Delta E_i + \Delta E_p + \Delta G_p \qquad (14)$$

In order to evaluate quantitatively the activation energy and the Gibbs' free energy change of each reaction, an energetic study was made as follows.

(a) The Overall Activation Energy of the Initiation Reaction. As shown in Eq. (1), it has been considered in ionic polymerization whether the polymerization takes place by an anionic mechanism (the formation of the D-C covalent bond) or a cationic mechanism (the formation of the A-C covalent bond) is dependent on the relative electronic properties of the catalyst and the monomer.

In order to study energetically the rate of initiation, we assume the following elementary reactions of the initiation for an anionic polymerization as an example,



$$AD \rightarrow A\cdot + D\cdot \qquad (i)$$

$$H_2C{=}CHY \rightarrow H_2\dot{C}\text{—}\dot{C}HY \qquad (ii)$$

$$D\cdot + H_2\dot{C}\text{—}\dot{C}HY \rightarrow H_2\overset{D}{\overset{|}{C}}\text{—}\dot{C}HY \qquad (iii)$$

$$H_2\overset{D}{\overset{|}{C}}\text{—}\dot{C}HY + e \rightarrow H_2\overset{D}{\overset{|}{C}}\text{—}\underset{H\ \ Y}{C^-} \qquad (iv)$$

$$A\cdot \rightarrow A^+ + e \qquad (v)$$

$$H_2\overset{D}{\overset{|}{C}}\text{—}\underset{H\ \ Y}{C^-} + xS \rightarrow H_2\overset{D}{\overset{|}{C}}\text{—}\underset{H\ \ Y}{C^-}xS \qquad (vi)$$

$$A^+ + yS \rightarrow A^+yS \qquad (vii)$$

$$H_2\overset{D}{\overset{|}{C}}\text{—}\underset{H\ \ Y}{C^-}xS + A^+yS \rightarrow H_2\overset{D}{\overset{|}{C}}\text{—}\underset{H\ \ Y}{\overset{A^+yS}{\overset{\vdots}{C^-}}}xS \qquad (viii)$$

The reactions (i) and (ii) are the bond dissociation of the catalyst AD and the π bond dissociation of the vinyl monomer, and the component radical D· of catalyst combines with the monomer radical to give the polymer end (iii). The growing radical produced by the reaction (iii) and the other component radical A· of catalyst ionize ((iv), (v)) and form the corresponding solvated ions ((vi), (vii)). The two solvated ions having an opposite charge form a solvated ion-pair by an electrostatic force (viii).

According to Polanyi - Horiuchi - Semenov's empirical rule, the overall rate of the growing radical ($H_2DC\text{-}\dot{C}HY$) formation is considered to be large as both of the bond dissociation energy B(A–D) of the A–D bond and the π bond dissociation energy B(C=C) of the monomer are small or as B(D–C) of the D–$CH_2\dot{C}HY$ large. It is supposed that the reactions (iv) and (v) take place easily when the electron affinity $E_a({}^*C_i\cdot)$ of the radical $CH_2D\dot{C}HY$ indicated by ${}^*C_i\cdot$ is large and the ionization potential $I_p(A\cdot)$ of a component A· is small, and that the reactions (vi) and (vii) occur facilely

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10) T. Kagiya, M. Izu and K. Fukui, This Bulletin, **40**, 1045 (1967).

as the solvation energies, *i. e.*, $-\Delta G_s(^*C_i^-\cdots S)$ and $-\Delta G_s(A^+\cdots S)$, of the growing anion H_2-DCHYC$^-$ indicated by $^*C_i^-$ and the counter cation A^+ are large. The two solvated ions having an opposite charge exist usually in the solution as a solvated ion-pair. It is, however, considered that the facility of the polymerization increases with a decrease in the electrostatic energy $-\Delta G_e(^*C_i^-S\cdots A^+S)$ arised between two solvated ions, because the rate of polymerization by a free ion mechanism is larger than that by an ion-pair mechanism.[11]

On the basis of the above considerations, it has been assumed that the activation energy (ΔE_i) of the initiation is expressed as follows, by the use of the free energy changes of these elementary reactions and the electronic natures of the catalyst components,

Anionic Polymerization;

$$\begin{aligned}\Delta E_{i(A)} = {} & c_1B(A\text{–}D) + c_2B(C{=}C) - c_3B(D\text{–}C)\\ & + c_4[I_p(A\cdot) - E_a(^*C_i\cdot)]\\ & + c_5[\Delta G_s(^*C_i^-\cdots S) + \Delta G_s(A^+\cdots S)]\\ & - c_6\Delta G_e(^*C_i^-S\cdots A^+S)\end{aligned} \tag{15}$$

Cationic Polymerization;

$$\begin{aligned}\Delta E_{i(C)} = {} & c_1'B(A\text{–}D) + c_2'B(C{=}C) - c_3'B(A\text{–}C)\\ & + c_4'[I_p(^*C_i\cdot) - E_a(D\cdot)]\\ & + c_5'[\Delta G_s(^*C_i^+\cdots S) + \Delta G_s(D^-\cdots S)]\\ & - c_6'\Delta G_e(^*C_i^+S\cdots D^-S)\end{aligned} \tag{16}$$

where $c_1,\cdots, c_6, c_1',\cdots, c_6'$ are the positive constants disregarding the kinds of monomer, catalyst and solvent.

(b) The Overall Activation Energy of the Propagation Reaction. As Eq. (2) shows, the formation reaction of the intermediate complex is that the monomer co-ordinates to the solvated ion-pair nucleophilically and electrophilically. Then, it is considered that the Gibbs' free energy of the co-ordination of the monomer to the growing chain and the counter ions can be estimated with the nucleophilic and electrophilic co-ordination energies and the electrostatic energy of the solvated ion-pair. Therefore, the Gibbs' free energy of the reaction is written as follows,

Anionic Polymerization;

$$\begin{aligned}-\Delta G_{p(A)} = {} & -\Delta G_c(A^+S\cdots M)\\ & - \Delta G_c(^*C_i^-S\cdots M) + \Delta G_e(^*C_i^-S\cdots A^+S)\end{aligned} \tag{17}$$

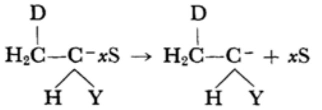
Cationic Polymerization;

$$\begin{aligned}-\Delta G_{p(C)} = {} & -\Delta G_c(D^-S\cdots M)\\ & - \Delta G_c(^*C_i^+S\cdots M) + \Delta G_e(^*C_i^+S\cdots D^-S)\end{aligned} \tag{18}$$

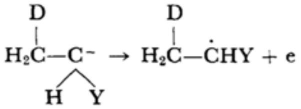
where $-\Delta G_p$ represents the Gibbs' free energy of the formation reaction of the intermediate and $-\Delta G_c$ the co-ordination energy, and the abbreviation $^*C_i^-S\cdots M$ or $^*C_i^+S\cdots M$ indicates the monomer co-ordinating to the solvated growing anion or cation and $A^+S\cdots M$ or $D^-S\cdots M$ indicates the monomer co-ordinating to the counter cation or anion.

On the other hand, in a similar manner as the initiation reaction, the following elementary reactions of the chain growth reaction of the intermediate for an anionic polymerization as an example were assumed,

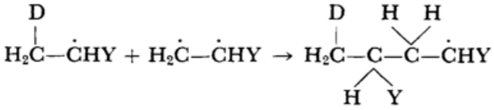
$$H_2C{=}CHY \rightarrow H_2\dot{C}-\dot{C}HY \tag{ix}$$



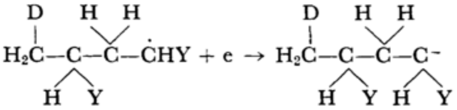
$$\overset{D}{H_2C}-\underset{H\quad Y}{C^-}xS \rightarrow \overset{D}{H_2C}-\underset{H\quad Y}{C^-} + xS \tag{x}$$



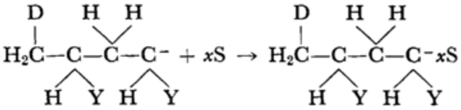
$$\overset{D}{H_2C}-\underset{H\quad Y}{C^-} \rightarrow \overset{D}{H_2C}-\dot{C}HY + e \tag{xi}$$



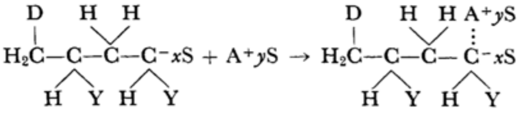
$$\overset{D}{H_2C}-\dot{C}HY + H_2\dot{C}-\dot{C}HY \rightarrow \overset{D}{H_2C}-\underset{H\quad Y}{C}-\overset{H\quad H}{\dot{C}}-\dot{C}HY \tag{xii}$$



$$\overset{D}{H_2C}-\underset{H\quad Y}{C}-\overset{H\quad H}{\dot{C}}-\dot{C}HY + e \rightarrow \overset{D}{H_2C}-\underset{H\quad Y}{C}-\overset{H\quad H}{C}-\underset{H\quad Y}{C^-} \tag{xiii}$$



$$\overset{D}{H_2C}-\underset{H\quad Y}{C}-\overset{H\quad H}{C}-\underset{H\quad Y}{C^-} + xS \rightarrow \overset{D}{H_2C}-\underset{H\quad Y}{C}-\overset{H\quad H}{C}-\underset{H\quad Y}{C^-}xS \tag{xiv}$$



$$\overset{D}{H_2C}-\underset{H\quad Y}{C}-\overset{H\quad H}{C}-\underset{H\quad Y}{C^-}xS + A^+yS \rightarrow \overset{D}{H_2C}-\underset{H\quad Y}{C}-\overset{H\quad H}{C}-\underset{H\quad Y}{\overset{A^+yS}{\overset{\vdots}{C^-}}}xS \tag{xv}$$

In the above elementary reactions, the reaction (ix) is the π bond dissociation to form the monomer radical, (x) and (xi) are the desolvation of the solvated growing ion and the formation of the growing radical, (xii) is the recombination of the growing radical with the monomer radical to make growth of the chain. The growing radical produced by the reaction (xii) ionizes (xiii) and forms the corresponding solvated ion (xiv), and the two solvated ions having an opposite charge form a solvated ion-pair by an electrostatic force (xv).

In the same way of the initiation reaction, the activation energy (ΔE_p) of the chain growth reaction may be considered to be small as the π bond dissociation energy $B(C{=}C)$ of monomer is small and the bond dissociation energy $B(^*C\text{–}C)$ of the

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

growing radical with the monomer radical large. It is supposed that the reactions (x) and (xi) are easily arised as the desolvation energy $-\Delta G_{ds}(^*C_i^-\cdots S)$ of the solvated ion $H_2DCHYC^-\cdots xS$ indicated by $^*C_i^-\cdots S$ and the ionization potential $I_p(^*C_i^-)$ of the ion H_2DCHYC^- are small, and that the reactions (xiii) and (xiv) take place easily when the electron affinity $E_a(^*C_p\cdot)$ of the radical $H_2DCHYCH_2CHYC\cdot$ indicated by $^*C_p\cdot$ and the solvation energy $-\Delta G_s(^*C_p^-\cdots S)$ of the propagating growing ion $H_2DCHYCH_2CHYC^-$ indicated by $^*C_p^-$ are large. On the basis of the reason described in the initiation reaction, it is also considered that the rate of polymerization increases with a decrease in the electrostatic energy $-\Delta G_e(^*C_p^-S\cdots A^+S)$ of (xv) arised between two solvated ions.

On the basis of the above considerations, it has been assumed that the activation energy of the chain growth reaction is expressed as follows,

Anionic Polymerization;

$$\begin{aligned}\Delta E_{p(A)} = {} & c_7B(C{=}C) - c_8B(^*C{-}C)\\ & - c_9[\Delta G_{ds}(^*C_i^-\cdots S) - \Delta G_s(^*C_p^-\cdots S)]\\ & + c_{10}[I_p(^*C_i^-) - E_a(^*C_p\cdot)]\\ & - c_{11}\Delta G_e(^*C_p^-S\cdots A^+S)\end{aligned}\tag{19}$$

Cationic Polymerization;

$$\begin{aligned}\Delta E_{p(C)} = {} & c_7'B(C{=}C) - c_8'B(^*C{-}C)\\ & - c_9'[\Delta G_{ds}(^*C_i^+\cdots S) - \Delta G_s(^*C_p^+\cdots S)]\\ & + c_{10}'[I_p(^*C_p\cdot) - E_a(^*C_i^+)]\\ & - c_{11}'\Delta G_e(^*C_p^+S\cdots D^-S)\end{aligned}\tag{20}$$

where $c_7,\cdots, c_{11}, c_7',\cdots, c_{11}'$ are the positive constants disregarding the kinds of monomer, catalyst and solvent. In Eqs. (19) and (20), the ionization potential $I_p(^*C_i^-)$ or the electron affinity $E_a(^*C_i^+)$ of the initiating anion or cation is approximately equal to the electron affinity $E_a(^*C_p\cdot)$ or the ionization potential $I_p(^*C_p\cdot)$ of the propagating radical, respectively. The desolvation energy $-\Delta G_{ds}(^*C_i^-\cdots S)$ or $-\Delta G_{ds}(^*C_i^+\cdots S)$ is also equal to the solvation energy $-\Delta G_s(^*C_p^-\cdots S)$ or $-\Delta G_s(^*C_p^+\cdots S)$. Equations (19) and (20) may, therefore, be written,

Anionic Polymerization;

$$\begin{aligned}\Delta E_{p(A)} = {} & c_7B(C{=}C) - c_8B(^*C{-}C)\\ & - c_{11}\Delta G_e(^*C_p^-S\cdots A^+S)\end{aligned}\tag{21}$$

Cationic Polymerization;

$$\begin{aligned}\Delta E_{p(C)} = {} & c_7'B(C{=}C) - c_8'B(^*C{-}C)\\ & - c_{11}'\Delta G_e(^*C_p^+S\cdots D^-S)\end{aligned}\tag{22}$$

(c) The Overall Activation Energy of the Polymerization. From a series of these energetic considerations, it seems reasonable to conclude that the overall activation energy, in any cases of the slow initiation and the rapid initiation,[10] is expressed as follows by using Eqs. (15)—(22),

The Slow Initiation System (9)

Anionic Polymerization;

$$\begin{aligned}\Delta E_{(A)} = {} & c_1B(A{-}D) + (c_2+c_7)B(C{=}C)\\ & - c_3B(D{-}C) - c_8B(^*C{-}C)\\ & + c_4[I_p(A\cdot) - E_a(^*C_i\cdot)]\\ & + c_5[\Delta G_s(^*C_i^-\cdots S) + \Delta G_s(A^+\cdots S)]\\ & + [\Delta G_c(A^+S\cdots M) + \Delta G_c(^*C_i^-S\cdots M)]\\ & - (c_6+1+c_{11})\Delta G_e(^*C_i^-S\cdots A^+S)\end{aligned}\tag{23}$$

Cationic Polymerization;

$$\begin{aligned}\Delta E_{(C)} = {} & c_1'B(A{-}D) + (c_2'+c_7')B(C{=}C)\\ & - c_3'B(A{-}C) - c_8'B(^*C{-}C)\\ & + c_4'[I_p(^*C_i\cdot) - E_a(D\cdot)]\\ & + c_5'[\Delta G_s(^*C_i^+\cdots S) + \Delta G_s(D^-\cdots S)]\\ & + [\Delta G_c(D^-S\cdots M) + \Delta G_c(^*C_i^+S\cdots M)]\\ & - (c_6'+1+c_{11}')\Delta G_e(^*C_i^+S\cdots D^-S)\end{aligned}\tag{24}$$

The Rapid Initiation System (11)

Anionic Polymerization;

$$\begin{aligned}\Delta E_{(A)} = {} & c_7B(C{=}C) - c_8B(^*C{-}C)\\ & + [\Delta G_c(A^+S\cdots M) + \Delta G_c(^*C_i^-S\cdots M)]\\ & - (1+c_{11})\Delta G_e(^*C_i^-S\cdots A^+S)\end{aligned}\tag{25}$$

Cationic Polymerization;

$$\begin{aligned}\Delta E_{(C)} = {} & c_7'B(C{=}C) - c_8'B(^*C{-}C)\\ & + [\Delta G_c(D^-S\cdots M) + \Delta G_c(^*C_i^+S\cdots M)]\\ & - (1+c_{11}')\Delta G_e(^*C_i^+S\cdots D^-S)\end{aligned}\tag{26}$$

In the above Eqs. (23)—(26), we may regard the value of $B(^*C{-}C)$ as a constant, because the dissociation energy of the $^*C{-}C$ bond is about 81 ± 3 kcal/mol. And $B(D{-}C)$ is constant (83 ± 4 kcal/mol) in the case of CH_3, OCH_3, NH_2 and OH as a component D, and $B(A{-}C)$ is constant because the hydrogen atom acts as a component A in the cationic polymerization. $B(A{-}D)$ is remarkably affected by the kind of catalyst (Table 1).[12,13] It is obvious in Table 1 that $B(A{-}D)$ varies more remarkably with the change in the electron affinity of component D than the ionization potential of component A. Then, it may be allowed that $B(A{-}D)$ is tentatively expressed as follows,

$$B(A{-}D) = c_{12} + c_{13}E_a(D) + c_{14}I_p(A) \qquad (c_{13} \gg c_{14} > 0)\tag{27}$$

where c_{12}, c_{13} and c_{14} are assumed to be the constants disregarding the kind of catalyst.

Subsequently, we tried to evaluate the solvation energy of ion with its electronic properties. Little information has, however, been reported on the

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[12] C. J. Schexnayder, Jr., "National Aeronautics and Space Administration, Technical Note," D-1791, Washington (1963).

[13] C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon, Oxford (1962).

TABLE 1. BOND DISSOCIATION ENERGY OF A-D COMPOUND*1

A	I_p(A), eV	D				
		H	OH	Br	Cl	F
		E_a(D), eV				
		0.7	2.6	3.5	3.8	4.3
H	13.6	103.1	116	86.5	102.0	133.8
Li	5.4	57.6	101.9	100.4	110.3	136.0
Na	5.1	47.2	80.9	88.5	97.7	107.2
K	4.3	42.9	86.0	90.8	101.0	116.9
Rb	4.2	39.2	—	90.5	101.9	119.9
Cs	3.8	41.5	91.0	90.9	101.0	122.8

*1 In units of kcal/mol. Data in Ref. 12 and 13.

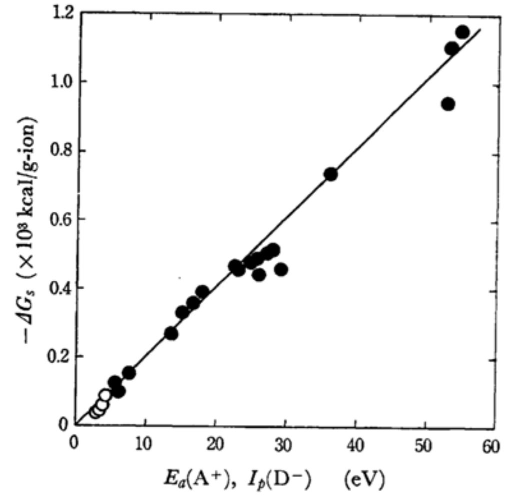

Fig. 1. Relation between the hydration energy ($-\Delta G_s$) of ion and the electron affinity ($E_a(A^+)$) of cation or the ionization potential ($I_p(D^-)$) of anion.

● metal cation, ○ halogen anion

solvation energies of ions determined in the various organic solvents all but water. Then, the plots of the hydration energies of ions[14] against the electron affinities of cations and the ionization potentials of anions were drawn in Fig. 1. In Fig. 1, as an electron affinity of divalent cation, the sum of the first and the second electron affinities was used, which is required to make the radical from the divalent cation. The hydration energy of the metal cation or the halogen anion has a linear relation through an origin with the electron affinity of cation or the ionization potential of anion. If there is a linear free energy relationship between the solvation energy in organic solvent and the hydration energy, the solvation energy of ion is generally expressed as follows,

$$-\Delta G_s(A^+\cdots S) = c_{15}E_a(A^+) + c_{16} \qquad (c_{15} > 0) \qquad (28)$$

$$-\Delta G_s(D^-\cdots S) = c_{15}'I_p(D^-) + c_{16}' \qquad (c_{15}' > 0) \qquad (29)$$

where c_{15}, c_{16}, c_{15}' and c_{16}' are the constants depending on the kind of solvents.

Moreover, it may be considered that the solvation energy of the polymer chain anion or cation is a constant in the same solvent system in consideration of the sufficient length of the polymer chain.

$$-\Delta G_s(^*C_i^-\cdots S) = c_{17} \qquad (30)$$

$$-\Delta G_s(^*C_i^+\cdots S) = c_{17}' \qquad (31)$$

On the other hand, it seems reasonable, from a point of quantum chemical view, that the nucleophilicity or the electrophilicity of monomer is approximately estimated by its ionization potential or electron affinity, respectively. That is, the nucleophilicity of monomer increases with a decrease in its ionization potential and the electrophilicity of monomer increases with an increase in its electron affinity. Hence, it is assumed that the co-ordination energy of monomer to ion and the electrostatic energy arised between two solvated ions are tentatively expressed as follows,

$$-\Delta G_c(A^+S\cdots M) = c_{18}E_a(A^+) - c_{19}I_p(M) + c_{20} \qquad (c_{18},\ c_{19} > 0) \qquad (32)$$

$$-\Delta G_c(D^-S\cdots M) = c_{18}'I_p(D^-) + c_{19}'E_a(M) + c_{20}' \qquad (c_{18}',\ c_{19}' > 0) \qquad (33)$$

$$-\Delta G_c(^*C_i^-S\cdots M) = c_{21}E_a(M) + c_{22} \qquad (c_{21} > 0) \qquad (34)$$

$$-\Delta G_c(^*C_i^+S\cdots M) = -c'_{21}I_p(M) + c_{22}' \qquad (c_{21}' > 0) \qquad (35)$$

$$-\Delta G_e(^*C_i^-S\cdots A^+S) = c_{23}E_a(A^+) - c_{24}I_p(^*C_i^-) + c_{25} \qquad (c_{23}, c_{24} > 0) \qquad (36)$$

$$-\Delta G_e(^*C_i^+S\cdots D^-S) = -c_{23}'I_p(D^-) + c_{24}'E_a(^*C_i^+) + c_{25}' \qquad (c_{23}', c_{24}' > 0) \qquad (37)$$

where $c_{18}, \cdots, c_{25}, c_{18}', \cdots, c_{25}'$ are constants. And Eqs. (34) and (35) are simplified by using the relations (30) and (31).

The ionization potential and the electron affinity

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[14] J. D. Bernal and R. H. Fowler, *J. Chem. Phys.*, **1**, 515 (1933).

of the initiating growing radical can be considered in connection with the electronic porperties of the corresponding monomer. Although these values of all monomers are scarcely available up to the present, it is possible to evaluate those with the method of the molecular orbital theory or using some values relating to those. For instance, the ionization potential and the electron affinity are approximately expressed by the energies of the highest occupied ε_{ho} and the lowest vacant ε_{lv} π orbitals, respectively.

$$\varepsilon_{ho} = \alpha + \lambda_{ho}\beta = -I_p \tag{38}$$

$$\varepsilon_{lv} = \alpha - \eta_{lv}\beta = -E_a \tag{39}$$

$(\alpha, \beta$: negative constants)

It is apparent from the above equations that the ionization potential is large as the λ_{ho} value is large, and that the electron affinity is large as the η_{lv} value is small.

The observed ionization potential[15] or the observed electron affinity[16] of the radical is plotted against the λ_{ho} or η_{lv} value of the corresponding monomer (in Figs. 2 and 3). Figure 4 shows the linear relation between the ionization potential of the radical and that of the monomer. From these figures, it is found that the ionization potential or the electron affinity of the initiating radical and ion is expressed by that of the corresponding monomer, as follows,

$$E_a(^*C_i\cdot) = I_p(^*C_i^-) = c_{26}E_a(M) + c_{27} \quad (c_{26} > 0) \tag{40}$$

$$I_p(^*C_i\cdot) = E_a(^*C_i^+) = c_{26}'I_p(M) + c_{27}' \quad (c_{26}' > 0) \tag{41}$$

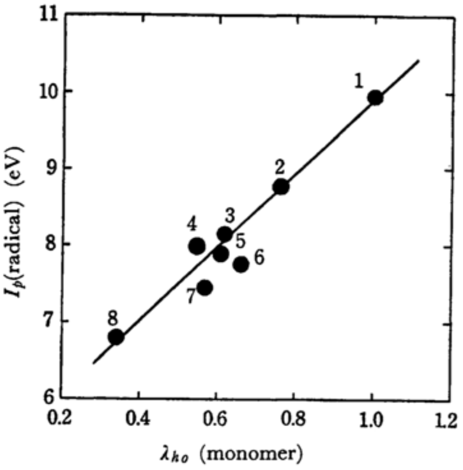


Fig. 2. Relation between the ionization potential of radical and the λ_{ho} value of monomer.
Monomer (radical); (1) $CH_2=CH_2$ ($\cdot CH_3$), (2) $CH_2=CHCH_3$ ($\cdot CH_2CH_3$), (3) $CH_2=CHCH=CH_2$, ($\cdot CH_2CH=CH_2$), (4) $CH_2=C(CH_3)CH=CH_2$ ($\cdot CH_2C(CH_3)=CH_2$), (5) $CH_2=C(CH_3)_2$ ($\cdot CH(CH_3)_2$), (6) $CH_2=CH\text{-}\phi$ ($\cdot CH_2\text{-}\phi$), (7) $CH_2=CH\text{-}\phi\text{-}p\text{-}CH_3$ ($\cdot CH_2\text{-}\phi\text{-}p\text{-}CH_3$), (8) $CH_2=CH\text{-}\phi\text{-}p\text{-}OCH_3$ ($\cdot CH_2\text{-}\phi\text{-}p\text{-}OCH_3$)

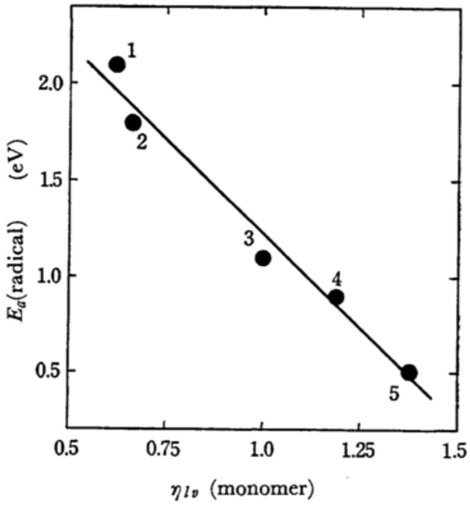


Fig. 3. Relation between the electron affinity of radical and the η_{lv} value of monomer.
Monomer (radical); (1) $CH_2=CHCH=CH_2$ ($\cdot CH_2\text{-}CH=CH_2$), (2) $CH_2=CH\text{-}\phi$ ($\cdot CH_2\text{-}\phi$), (3) $CH_2=CH_2$ ($\cdot CH_3$), (4) $CH_2=CHCH_3$ ($\cdot CH_2CH_3$), (5) $CH_2=C(CH_3)_2$ ($\cdot CH(CH_3)_2$)

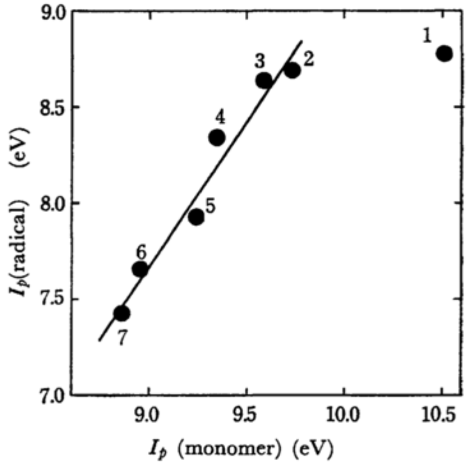
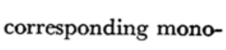


Fig. 4. Comparison of the ionization potential of radical with that of monomer.
Monomer (radical); (1) $CH_2=CH_2$ ($\cdot CH_2CH_3$), (2) $CH_2=CHCH_3$ ($\cdot CH_2CH_2CH_3$), (3) $CH_2=CHCH_2CH_3$ ($\cdot CH_2CH_2CH_2CH_3$), (4) $CH_2=C(CH_3)_2$ ($\cdot CH_2CH(CH_3)_2$), (5) $CH_3CH=CHCH_3$ ($\cdot CH(CH_3)CH_2CH_3$), (6) , (7) $CH_3CH=C(CH_3)_2$ ($\cdot CH(CH_3)CH(CH_3)_2$)

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[15] A. Streitwieser, Jr., "Progress in Physical Organic Chemistry," Vol. 1, ed. by S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Interscience Publishers, New York. N. Y. (1963).

[16] H. O. Pritchard, *Chem. Revs.*, **52**, 529 (1953).

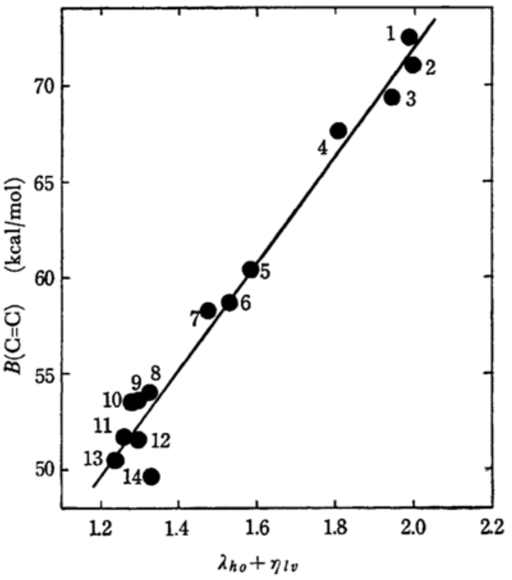

Fig. 5. Relation between the π bond dissociation energy B(C=C) and the ($\lambda_{ho}+\eta_{lv}$) value of monomer.
(1) Isobutylene, (2) Ethylene, (3) Propylene, (4) Vinyl acetate, (5) Methyl vinyl ketone, (6) Methyl acrylate, (7) Acrolein, (8) Styrene, (9) *p*-Methylstyrene, (10) *p*-Chlorostyrene, (11) Acrylonitrile, (12) α-Methylstyrene, (13) Butadiene, (14) Methyl methacrylate

Lastly, we tried to evaluate the π bond dissociation energy B(C=C) of monomer $H_2C{=}CHY$ with its characteristic values of the electronic structures. The observed values of B(C=C) have, however, been reported. Then, we estimated B(C=C) in term of the localization energy.[17]

$$H_2C{=}CHY \rightarrow H_2\dot{C}{-}\dot{C}HY \qquad \text{(ii)}$$

On the assumption that the two odd electrons of the product in the above reaction are the p-electrons, it is considered that B(C=C) may be expressed by the difference between the total energies of the radical and the monomer, as follows,

$$B(\mathrm{C{=}C}) = \sum_i^{occ} \nu_i \varepsilon_{i(\mathrm{CH_2Y})} + \varepsilon_{(\mathrm{CH_3})} - \sum_j^{occ} \nu_j \varepsilon_{j(\mathrm{CH_2=CHY})} \qquad (42)$$

$$= \sum_i^{occ} \nu_i \lambda_i \beta_{(\mathrm{CH_2Y})} - \sum_j^{occ} \nu_j \lambda_j \beta_{(\mathrm{CH_2=CHY})} \qquad (43)$$

In Eq. (42), the first, the second and the third terms indicate the total energies of π electrons of the radicals CH_2Y and CH_3 and the monomer $CH_2{=}CHY$, respectively. Where $\sum^{occ}$ means a summation with respect to the occupied orbitals, ε_i is the π energy of the ith orbital, λ_i the coefficient of β_i in Eq. (38) and ν_i the number of π electron in the ith orbital.

It is found from the results that B(C=C) of monomer $CH_2{=}CHY$ varies remarkably with the kind of substituent Y. In order to evaluate B(C=C) with its characteristic values, the plots of B(C=C) against the summation ($\lambda_{ho}+\eta_{lv}$) of the coefficinets of β in the highest occupied and the lowest vacant π orbitals of monomer were drawn in Fig. 5. From the linear relationship between B(C=C) and ($\lambda_{ho}+\eta_{lv}$), the π bond dissociation energy may be expressed as follows,

$$B(\mathrm{C{=}C}) = c_{28}(\lambda_{ho} + \eta_{lv}) + c_{29} \quad (c_{28} > 0) \qquad (44)$$

$$= c_{30}(I_p(\mathrm{M}) - E_a(\mathrm{M})) + c_{31} \quad (c_{30} > 0) \qquad (45)$$

From a series of the above considerations (27)—(45), it is concluded that the overall activation energy of ionic polymerization may be expressed as follows,

The Slow Initiation System (9)
Anionic Polymerization;

$$\Delta E_{(\mathrm{A})} = k_1 + k_2 E_a(\mathrm{D}) \pm k_3 I_p(\mathrm{A}) - k_4 E_a(\mathrm{M}) + k_5 I_p(\mathrm{M}) \qquad (46)$$

Cationic Polymerization;

$$\Delta E_{(\mathrm{C})} = k_1' + k_2' I_p(\mathrm{A}) - k_3' E_a(\mathrm{D}) + k_4' I_p(\mathrm{M}) - k_5' E_a(\mathrm{M}) \qquad (47)$$

where $k_1, \cdots, k_5, k_1' \cdots, k_5'$ are the positive constants. The coefficient of $I_p(\mathrm{A})$ in Eq. (46) represents the term, $(c_4+c_{23}+c_1c_{14}+c_6c_{23}+c_{11}c_{23})-(c_{18}+c_5c_{15})$, and might change in sign since the constants c_{15}, c_{18} and c_{23} are those to depend on the kind of solvent.

The Rapid Initiation System (11)
Anionic Polymerization;

$$\Delta E_{(\mathrm{A})} = k_6 \pm k_7 I_p(\mathrm{A}) - k_8 E_a(\mathrm{M}) + k_9 I_p(\mathrm{M}) \qquad (48)$$

Cationic Polymerization;

$$\Delta E_{(\mathrm{C})} = k_6' - k_7' E_a(\mathrm{D}) + k_8' I_p(\mathrm{M}) - k_9' E_a(\mathrm{M}) \qquad (49)$$

where $k_6, \cdots, k_9, k_6', \cdots, k_9'$ are the positive constants and the coefficient of $I_p(\mathrm{A})$ in Eq. (48) might change in sign by the kind of solvent.

In the polymerization that the contribution to the activation energy of the monomer co-ordination to the growing ion is larger than that to the counter ion, these equations lead to the reasonable conclusion that the monomer reactivity in anionic polymerization increases as the electron affinity of the monomer increases, and that in cationic polymerization increases as the ionization potential of

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[17] G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

the monomer decreases.[*1] On the attention to the catalyst in the polymerization of the same monomer, the catalytic activity in anionic polymerization increases as the electron affinity of component D decreases, whereas that in cationic polymerization increases as the electron affinity of D increases and as the ionization potential of A decreases.

On the basis of these energetic considerations, the monomer reactivity and the catalytic activity will be quantitatively discussed in the subsequent paper.

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

[*1] As Eq. (41) shows, $I_p(\mathrm{M})$ is positively proportional to $I_p({}^*\mathrm{C}_i\cdot)$. It is found in a homologous series that there exists the positive linear relation between $I_p({}^*\mathrm{C}_i\cdot)$ and $I_p({}^*\mathrm{C}_i{}^-)$, *cf.*, $I_p({}^*\mathrm{C}_i\cdot)$ and $I_p({}^*\mathrm{C}_i{}^-)$ for the alkyl radicals are in units of eV 9.95 and 1.1 for methyl, 8.78 and 0.9 for ethyl, 8.69 and 0.8 for *n*-propyl, 8.64 and 0.65 for *n*-butyl, and 7.90 and 0.5 for isopropyl radical. According to this relation, the activation energy of the anionic polymerization is given as follows, $\Delta E_{(\mathrm{A})}=k_{10}-k_{11}E_a(\mathrm{M})+k_{12}I_p({}^*\mathrm{C}_i{}^-)$. This equation indicates that the activation energy of the anionic polymerization decreases as the electron affinity of monomer is large and the ionization potential of the corresponding growing anion is small, in other words, that it is dominated with the energetic difference between the lowest vacant level of monomer and the highest occupied level of the growing anion. Similarly, the activation energy of the cationic polymerization is given as follows, $\Delta E_{(\mathrm{C})}=k_{10}'+k_{11}'I_p(\mathrm{M})-k_{12}'E_a({}^*\mathrm{C}_i{}^+)$, and it is dominated with the energetic difference between the highest occupied level of monomer and the lowest vacant level of the growing cation. In words of the quantum chemical view, the concept that one may discuss the reactivity of monomer in ionic polymerization with the relative difference of the electronic states between the monomer and the growing ion, can be considered to correspond to the treatment of the zero-order perturbation.