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Mechanism of Donor-Acceptor Alternating Copolymerization

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ABSTRACT

The alternating copolymerization of butadiene and an acrylic compound in the presence of ethyl aluminum dichloride and vanadium oxychloride as complexing agents was studied kinetically for the comparison of two mechanisms, i.e., one involving an intermediate of a ternary complex of butadiene–acrylic monomer–$EtAlCl_2$ and the other without the complex formation. The rate of propagation was found to attain a maximum at a definite monomer composition, and this composition is not varied by changing the amount of $EtAlCl_2$ but decreased with increasing the concentration of total monomer. This fact is explained only by the mechanism of the ternary complex intermediate. In relation to the mechanism, NMR study of the ternary complex, ESR study of the growing radical NMR study of the regularity of the copolymer, and the elementary reaction of the propagation are reviewed with discussion.

INTRODUCTION

Several kinds of alternating copolymerizations controlled by such factors as the steric hindrance of the substituent of monomers, the coordination ability of monomers, and the polar nature of the reaction sites of monomers have been found. Among these, the alternating copolymerization of electron-donating monomer and electron-accepting monomer is of special interest because it gives a copolymer with an extremely high degree of alternation. However, the mechanism is not fully established; a mechanism involving the formation of a donor-acceptor complex as an intermediate is believed to be correct, but there is a possible alternative mechanism involving a Lewis-Mayo-type copolymerization without the formation of the intermediate complex.

The author studied in detail the copolymerization of butadiene and such acrylic monomers as acrylonitrile and methyl methacrylate in the presence of ethylaluminum dichloride ($EtAlCl_2$) and vanadyl chloride ($VOCl_3$), which are a complexing agent and a promotor, respectively.

This paper includes a summary of previously published work together with the recent study.

RESULTS AND DISCUSSION

Kinetic Study [1, 2]

In the polymerization with varied concentrations of ethylaluminum dichloride [Al], vanadyl chloride [V], butadiene [BD], and acrylic monomer [A], the overall rate of polymerization R_p was found to be expressed by

$$R_p = k_p[Al]^{1.5}[V]^{0.5}[BD]^m[A]^n \tag{1}$$

where k_p is a rate constant of polymerization. The order m and n for butadiene and acrylic monomer, respectively, were both zero for the copolymerization of butadiene and methyl methacrylate (MMA) while they were 1 and 2 for the copolymerization of butadiene and acrylonitrile (AN).

The molecular weight of the resulting polymer increases linearly with an increasing extent of polymerization or polymer yield, but the increase in molecular weight is slowed down at a large degree of polymerization. This fact is compatible with the assumption that the polymerization involves rapid initiation, step-growth propagation, and some chain transfer reaction. Equation (2) describes the relationship of the weight of polymer W and its molecular weight M:

$$W/M = a + bW \tag{2}$$

where a is the number of active species and b the ratio of the transfer reaction to the propagation reaction if these reaction rates are proportional to each other. The constants a and b were measured at various concentrations of the catalyst components, and the following relationship was obtained:

$$a \propto [\mathrm{Al}]^{0.5}\,[\mathrm{V}]^{0.5} \tag{3}$$

Since the step-growth polymerization is proportional to the concentrations of the active species C* and the monomer:

$$R_p = k_p[\mathrm{C}^*][\text{monomer}] \tag{4}$$

Comparing Eqs. (1), (2), (3), and (4), it follows that

$$[\mathrm{C}^*] \propto [\mathrm{Al}]^{0.5}\,[\mathrm{V}]^{0.5} \tag{5}$$

and

$$[\text{monomer}] \propto [\mathrm{Al}] \tag{6}$$

It is concluded that the actual monomer responsible for propagation contains 1 mole of aluminum compound as a complexing agent. A ternary complex of butadiene, acrylic monomer, and ethylaluminum dichloride was assumed to be formed and to be responsible for the alternating copolymerization. The order of monomer concentration can be explained by taking into account the formation of the ternary complex. There are several kinds of complexes among ternary components:

$$A + EtAlCl_2 \underset{}{\overset{K_1}{\rightleftharpoons}} A\cdot EtAlCl_2$$

$$2A + EtAlCl_2 \overset{K_1'}{\rightleftharpoons} A_2\cdot EtAlCl_2$$

$$A + BD + EtAlCl_2 \overset{K_2}{\rightleftharpoons} A\cdot BD\cdot EtAlCl_2 \text{ or } A\cdot BD\cdot al$$

The concentration of the ternary complex is expressed by a Langumuir-type equation:

$$[A\cdot BD\cdot al] = \frac{K_2\,[al]\,[A]\,[BD]}{1 + k_1\,[A]^n + K_2\,[A][BD]} \qquad (7)$$

Equation (7) can be simplified according to the magnitude of K_1 and K_2. The following equation hold for the case of $K_2 \gg K_1$, and 1:

$$[A\cdot BD\cdot al] = [al] \qquad (8)$$

and for the case of $K_1 \gg K_2$, and 1:

$$[A\cdot BD\cdot al] = K_2\,[al]\,[A]^{1-n}[BD] \qquad (9)$$

Equations (8) and (9) seem to correspond to the copolymerization of butadiene and methyl methacrylate and that of butadiene and acrylonitrile, respectively.

Formation of Binary Complex or Ternary Complex among Acrylic Monomer, Butadiene, and Aluminum Compounds [3]

The formation of binary complex between an acrylic monomer and $EtAlCl_2$ was confirmed by the cryoscopic method. The following equilibria were observed:

$$2MMA + [EtAlCl_2]_2 \rightleftharpoons [MMA\cdot EtAlCl_2]_2$$

$$2MAN + [EtAlCl_2]_2 \rightleftharpoons [MAN\cdot EtAlCl_2]_2$$

$$AN + [EtAlCl_2]_2 \rightleftharpoons AN\cdot[EtAlCl_2]_2$$

$$AN\cdot[EtAlCl_2]_2 + AN \rightleftharpoons 2AN\cdot EtAlCl_2$$

The formation of the ternary complex was not detected by the cryoscopic method but observed by NMR and UV spectra. In the NMR spectrum of a system of MMA and $EtAlCl_2$, an up-field shift of the ethyl group of $EtAlCl_2$ and a down-field shift of various protons of MMA were observed. Further addition of benzene as a donor agent to the binary system caused a change in the above shifts, with the MMA-proton shifts being recovered to some extent whereas the $EtAlCl_2$-protons remained unaffected. This fact was taken as evidence of the direct complexation of benzene to MMA without changing the electronegativity of $EtAlCl_2$.

In a system of butadiene, MMA, and $EtAlCl_2$, polymerization takes place at room temperature. The NMR measurement was made at -78°C without polymerization. The addition of butadiene to the binary system MMA-$EtAlCl_2$ induces a shift of the MMA protons, which attains a maximum value at a 1:1 ratio of butadiene to MMA-$EtAlCl_2$. This fact suggests the formation of a ternary complex of 1:1:1 with respect to three components.

In the UV spectrum of ternary systems of BD, AN, and $EtAlCl_2$ or of BD, MMA, and $EtAlCl_2$ the absorption was observed at 360 or 340 nm, respectively. These absorptions are not observed in binary systems. The ternary complex may be associated with polymerization because its rate of polymerization is greatly enhanced by irradiation with UV light, especially at the above-mentioned wavelengths. In the experiment with light of various wavelengths, a maximum rate of initiation and propagation is shown at the above wavelengths.

Comparison of Two Mechanisms of the Lewis-Mayo Type and a Ternary Complex One by Kinetic Study [4]

In the alternating copolymerization of butadiene and MMA there exists a maximum rate of polymerization at a definite molar ratio of MMA to butadiene almost equal to 1:1. This fact can be explained by the Lewis-Mayo mechanism as well as ternary complex one, but in a different way. In the Lewis-Mayo mechanism the rate of the step-growth type of copolymerization of A and B monomers is expressed by

$$R_p = \frac{2k_{AB}k_{BA}[A][B]}{k_{AB}[B] + k_{BA}[A]}[P^*] \qquad (10)$$

Equation (10) can be rewritten in terms of the fraction x of monomer A and M (total monomer):

$$\frac{[M][P^*]}{R_p} = \frac{1}{k_{BA}(1 - x)} + \frac{1}{k_{AB}x} \tag{11}$$

Equation (11) gives a maximum at

$$\frac{x}{1 - x} = \frac{[A]}{[B]} = \left(\frac{k_{AB}}{k_{BA}}\right)^{1/2} \tag{12}$$

In the presence of $EtAlCl_2$ the monomer A is complexed with $EtAlCl_2$. If the complexed monomer $A \cdot EtAlCl_2$ is an actual monomer copolymerized with B monomer (butadiene), their ratio is changed by changing not only [A] : [B] ratio but also the [Al] : [A] ratio. The concentration of the A•Al-complex is almost equal to the concentration of [Al] when [Al] is less than [A], and the equilibrium constant of complex formation is high enough to give

$$[A \cdot al] = \frac{K[Al][A]}{1 + K[A]} \tag{13}$$

Then, instead of Eq. (12), the following equation is used:

$$\frac{x}{1 - x} = \left(\frac{k_{AB}}{k_{BA}[Al]K}\right)^{1/2} \tag{14}$$

If K is very large, and [A–Al] is almost equal to [Al], there is no maximum.

Experiments were carried out with varied amount of $EtAlCl_2$. It was found that the maximum rate exists at a MMA fraction of 0.3, and this is not affected by the amount of aluminum compound added. In the experiment in which the total monomer concentration was varied from 1.6 to 8.0 mole/liter, the MMA fraction for the maximum rate decreases with an increase in the MMA fraction. That is, Eq. (14) is not in agreement with the experimental results.

The above fact is compatible with the ternary complex mechanism. In this mechanism the rate of polymerization is proportional to the concentration of the ternary complex [al·A·B] if the concentration of the growing species [P*] is kept constant.

This assumption is based on the fact that the amount of polymer is mainly produced by the transfer reaction, or, in other words, bW ≫ a in Eq. (2):

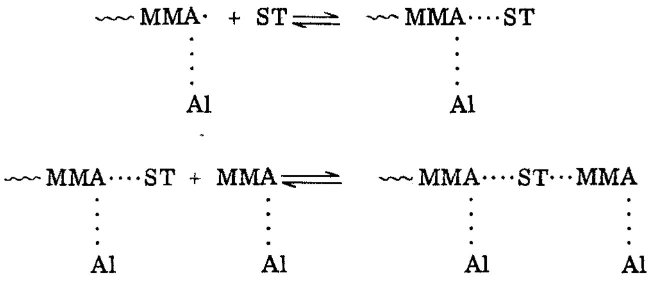
$$R_p \propto [\mathrm{Al}\cdot\mathrm{A}\cdot\mathrm{B}][\mathrm{P}^*] = \frac{K_2[\mathrm{M}]^2 x(1-x)[\mathrm{Al}]}{1 + K_1[\mathrm{M}]^n x^n + K_2[\mathrm{M}]^2 x(1-x)}[\mathrm{P}^*] \qquad (15)$$

Equation (15) gives a maximum for the cases of n = 1 or 2 at

$$x = \frac{[\mathrm{A}]}{[\mathrm{A}] + [\mathrm{B}]} = \frac{(K_1[\mathrm{M}]^n + 1)^{1/2} - 1}{K_1[\mathrm{M}]^n} \leqq \frac{1}{2} \qquad (16)$$

where [M] is a total monomer concentration. In this equation, x, the mole fraction of A in the monomer giving the maximum rate, is not affected by [Al] but by [M]. An increase of the total monomer concentration [M] causes a decrease of x from a value of 0.5, and this is in complete agreement with the experimental results.

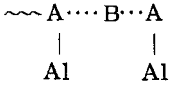
Hirooka [5] proposed a modified mechanism in which a ternary complex is formed in the vicinity of the growing polymer radical. This mechanism is useful in the case where no complex is detected or the concentration of the complex is very small, for example, where the formation of the ternary complex occurs only at the growing polymer end. In some cases a 1:1 monomer-monomer complex is formed, but there is no maximum rate at a definite monomer composition. This is also explicable for the case where the actual complex forming at the growing polymer terminal is different from the complex formed in the absence of a growing polymer terminal. However, Hirooka's mechanism leaves a problem concerning the structure of the complex at the polymer terminal. He preferred the following scheme for the copolymerization of styrene or propylene with MMA in the presence of $EtAlCl_2$:



$$\sim\!\!\sim\underset{\underset{\mathrm{Al}}{\vdots}}{\mathrm{MMA}}\cdot + \mathrm{ST} \rightleftharpoons \sim\!\!\sim\underset{\underset{\mathrm{Al}}{\vdots}}{\mathrm{MMA}}\cdots\mathrm{ST}$$

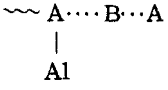
$$\sim\!\!\sim\underset{\underset{\mathrm{Al}}{\vdots}}{\mathrm{MMA}}\cdots\mathrm{ST} + \underset{\underset{\mathrm{Al}}{\vdots}}{\mathrm{MMA}} \rightleftharpoons \sim\!\!\sim\underset{\underset{\mathrm{Al}}{\vdots}}{\mathrm{MMA}}\cdots\mathrm{ST}\cdots\underset{\underset{\mathrm{Al}}{\vdots}}{\mathrm{MMA}}$$

The growing polymer terminal composed of a MMA radical is somewhat stabilized by complexation with styrene and is not able to propagate. The propagation takes place when the ternary complex is formed by the further attack of the MMA•Al monomer. Applying this mechanism to the system of butadiene (B) and an acrylic compound (A), the following ternary complexes were considered:



$$\sim\!\!\sim\underset{\underset{\mathrm{Al}}{|}}{\mathrm{A}}\cdots\mathrm{B}\cdots\underset{\underset{\mathrm{Al}}{|}}{\mathrm{A}}$$

a



$$\sim\!\!\sim\underset{\underset{\mathrm{Al}}{|}}{\mathrm{A}}\cdots\mathrm{B}\cdots\mathrm{A}$$

b

The concentration for complex a is

$$[\mathrm{complex}] = \frac{K_1'K_2'[B][Al]}{1 + K_1'[B] + K_1'K_2'[Al][B]}$$

or

$$\frac{1}{[\mathrm{complex}]} = \frac{1}{K_1'K_2'[M][Al](1 - x)} + \frac{1}{K_2'[Al]} + 1 \qquad (17)$$

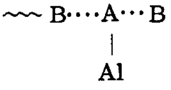
and for complex b:

$$\frac{1}{[\mathrm{complex}]} = \frac{1}{K_1'K_2'[M]^2 x(1 - x)} + \frac{1}{K_2'[M]x} + 1 \qquad (18)$$

There is no maximum for the complex formation in Eq. (17), whereas a maximum occurs in Eq. (18) at

$$\frac{x}{1 - x} = (1 \quad K_1'[M])^{1/2} \geqq 1 \tag{19}$$

However, Eq. (19) does not fit the experimental data. For other types of complexes occurring at the growing terminal, such as



$$\sim\!\sim\!\sim B\cdots A\cdots B \text{ (with Al below A)}$$

c

$\sim\!\sim\!\sim B\cdots A\cdots B$

d

the corresponding equations are used for complex c:

$$\frac{1}{[\text{complex}]} = \frac{1}{K_1'K_2'[M][Al](1 - x)} + \frac{1}{K_2'[M](1 - x)} + 1 \tag{20}$$

and for complex d:

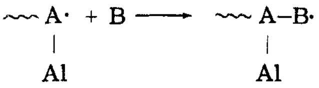
$$\frac{1}{[\text{complex}]} = \frac{1}{K_1'K_2'[M]^2 x(1 - x)} + \frac{1}{K_2'[M](1 - x)} + 1 \tag{21}$$

Equation (20) does not indicate a maximum. Only Eq. (21) gives a maximum similar to Eq. (15), but unlike Eq. (15), it does not involve the function of aluminum compounds.

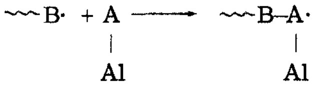
Consequently, the mechanism through the complex occurring at the polymer terminal is ruled out in this case.

Model Reaction of Alternating Addition

The main difference between a Lewis-Mayo-type mechanism and a ternary complex mechanism is in the propagation step. The former is composed of two kinds of addition reactions:

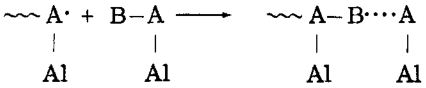


$$\sim\!\!\sim\underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}}\cdot + \mathrm{B} \longrightarrow \sim\!\!\sim\underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}}\text{–}\mathrm{B}\cdot \tag{a}$$



$$\sim\!\!\sim\mathrm{B}\cdot + \underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}} \longrightarrow \sim\!\!\sim\mathrm{B}\text{–}\underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}}\cdot \tag{b}$$

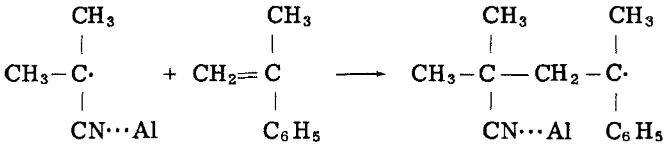
and the latter



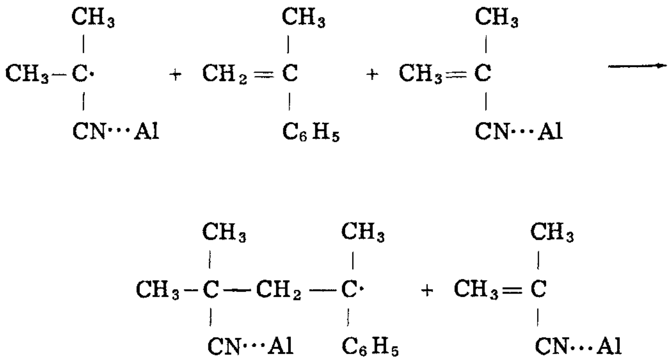
$$\sim\!\!\sim\underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}}\cdot + \mathrm{B}\text{–}\underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}} \longrightarrow \sim\!\!\sim\underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}}\text{–}\mathrm{B}\cdots\underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}} \tag{c}$$

$$\sim\!\!\sim\underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}}\text{–}\mathrm{B}\cdots\underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}} \longrightarrow \sim\!\!\sim\underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}}\text{–}\mathrm{B}\text{–}\underset{\overset{|}{\mathrm{Al}}}{\mathrm{A}}\cdot \tag{d}$$

Consequently, the difference exists in (a) and (c) and/or in (b) and (d). For a comparison of (a) with (c), a reaction of isobutyronitrile radical with α-methylstyrene was investigated in the absence and in the presence of methacrylonitrile (MAN).

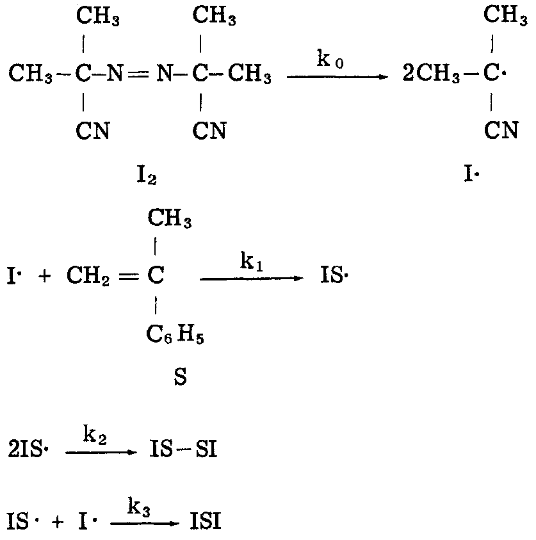


$$\mathrm{CH_3}\text{–}\underset{\underset{\mathrm{CN\cdots Al}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}\cdot + \mathrm{CH_2}{=}\underset{\underset{\mathrm{C_6H_5}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}} \longrightarrow \mathrm{CH_3}\text{–}\underset{\underset{\mathrm{CN\cdots Al}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}\text{—}\mathrm{CH_2}\text{–}\underset{\underset{\mathrm{C_6H_5}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}\cdot \tag{e}$$



$$\begin{gathered}\mathrm{CH_3}\text{–}\underset{\underset{\mathrm{CN\cdots Al}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}\cdot + \mathrm{CH_2}{=}\underset{\underset{\mathrm{C_6H_5}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}} + \mathrm{CH_3}{=}\underset{\underset{\mathrm{CN\cdots Al}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}} \longrightarrow \\ \mathrm{CH_3}\text{–}\underset{\underset{\mathrm{CN\cdots Al}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}\text{—}\mathrm{CH_2}\text{—}\underset{\underset{\mathrm{C_6H_5}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}\cdot + \mathrm{CH_3}{=}\underset{\underset{\mathrm{CN\cdots Al}}{|}}{\overset{\overset{\mathrm{CH_3}}{|}}{\mathrm{C}}}\end{gathered} \tag{f}$$

In reaction (e) without MAN, it was found that the product ISI or ISSI is formed without any polymer. Consequently, the reactions involved are



$$\underset{I_2}{CH_3-C(CH_3)(CN)-N=N-C(CH_3)(CN)-CH_3} \xrightarrow{k_0} \underset{I\cdot}{2CH_3-C\cdot(CH_3)(CN)}$$

$$I\cdot + \underset{S}{CH_2=C(CH_3)(C_6H_5)} \xrightarrow{k_1} IS\cdot$$

$$2IS\cdot \xrightarrow{k_2} IS-SI$$

$$IS\cdot + I\cdot \xrightarrow{k_3} ISI$$

At the stationary state, Eq. (22) is obtained:

$$\frac{ISI}{ISSI} = \frac{k_3^2\,[I\cdot]^2}{k_2\{k_0\,[I_2] - k_1[I\cdot][S]\}} \tag{22}$$

which indicates that the ratio of ISI/ISSI is decreased as k_1 or k_3, viz., the reactivity of the I· radical, is increased. The ratio is calculated from mass analysis of the reaction products.

It was found that the amount of the IS fragment or its ratio to the amount of AIBN decomposed is not significantly affected by the addition of $EtAlCl_2$. In other words, the reactivity of the radical of methacrylonitrile is almost the same irrespective of the presence of the complexing agent. The same result is obtained by the calculation of the IS fragment from the molecular weight of the product. The ratio of the yield to the molecular weight or the number of molecule produced is not changed.

The experiment in the presence of methacrylonitrile is complicated, because a considerable amount of the polymeric product is formed. The mass analysis of product seems to give an increased amount of IS fragment as compared with that obtained in the absence of methacrylonitrile, but the true amount of IS fragment is not obtained. The number of molecule of the reaction product is almost constant irrespective of the presence of methacrylonitrile, but the calculation of IS fragment has not been made. The comparison of the reactivity in reactions (b) and (d) has not been completed. However, the fact that the reactivity of methacrylonitrile radical is not significantly affected by the aluminum compound suggests that the high alternating tendency arises from reaction (d) enhanced by the complexation with $EtAlCl_2$. The enhancement of reaction (d) is explained not merely by the activation of methacrylonitrile monomer but by the formation of such clusters as $\sim\!\!\sim B\cdot \cdots A{-}Al$. These results seem to favor the mechanism involving the ternary complex intermediate which is formed prior to or during the propagation.

Binary and Ternary Complex among Acrylic Monomer, $EtAlCl_2$, and Toluene

As previously reported, the protons of methyl, methoxyl, and olefinic protons (cis and trans with respect to the ester group) of methyl methacrylate are shifted downfield by the complexation with $EtAlCl_2$, and the ethyl protons of $EtAlCl_2$ are shifted upfield. The addition of benzene to the binary system affects the above shift of MMA but not that of $EtAlCl_2$. The product of MMA fraction, f, and the additional shift, $\Delta\tau_c$, caused by further complexation of toluene shows a maximum value at a 1:1 composition in MMA-$EtAlCl_2$ and toluene.

These facts suggest the formation of the 1:1:1 complex of $EtAlCl_2$-acrylic monomer-toluene.

In the measurement of NMR at various temperatures, a significant temperature dependence is observed in protons of acrylic monomer but not in those of $EtAlCl_2$. The magnitude of the temperature dependence of each protons is in the order

$$\text{MAN:}\ H_c > H_t > \alpha\text{-}CH_3$$

and

$$\text{MMA:}\ OCH_3 > H_t \cong \alpha\text{-}CH_3 > H_c$$

These are almost the same as the changes in the magnitude of the shift caused by the complexation of an equimolar amount of toluene, i.e.,

MAN: $H_c > H_t > \alpha\text{-}CH_3$

MMA: $OCH_3 \cong H_t > \alpha\text{-}CH_3 > H_c$

These changes were also compared with the shift caused by the addition of toluene in various amounts. The order of the shift difference between toluene and methylene dichloride solutions, $\delta_{(\text{toluene})} - \delta_{(\text{methylene dichloride})}$, is

MAN: $H_c > H_t > \alpha\text{-}CH_3$

MMA: $OCH_3 > H_t > \alpha\text{-}CH_3 > H_c$

An almost similar tendency in shift change in these experiments suggests that these change run parallel to the effect of toluene in complexation, from which the location of toluene in the complex is assumed to be in the vicinity of olefinic protons in MAN and in that of olefinic H_t protons and methoxyl protons in MMA. However, the slope of the temperature dependence curves suggests that the energy for complexation is rather small. In addition to this, the fact that the NMR is composed of an intermediate shift between the ternary complex and the component indicates the formation of a loose complex whose rate of formation or dissociation is rapid as compared with the NMR time scale.

Other Methods for Comparison

Thus the mechanism through an intermediate complex seems to be more likely than a simple Lewis-Mayo mechanism. In an ESR study made by Zubov [6] to determine the intermediate radical during the polymerization of dimethylbutadiene and t-butyl acrylate in the presence of diethylaluminum monochloride, it was claimed there was a simple Lewis-Mayo mechanism because the two radical species were observed in an almost equimolar ratio at -100°C. However, his experiment was carried out at temperature too low to examine the radical species responsible for the polymerization. In recent work by Ohtsu et al. [7] using 2-methyl-2-nitrosopropane as a spin-trapping agent, only one radical species was observed in the copolymerization of styrene and acrylic monomers in the presence of zinc chloride, and it arose from the styrene unit.

Recent improvements in NMR enables the sequence regularity to be determined more precisely at times. If a detailed regularity of more than triad is obtained, the following relation may be examined among diads (F_{ij}), triads (F_{ijk}), etc. in a Lewis-Mayo mechanism of the first Markov chain statistics:

$$\frac{F_{11}}{F_{12}} = \frac{F_{111}}{F_{112}} = \frac{F_{211}}{F_{212}} = \frac{F_{ij11}}{F_{ij12}} = r_1 u \qquad (23)$$

and

$$\frac{F_{22}}{F_{21}} = \frac{F_{122}}{F_{121}} = \frac{F_{222}}{F_{221}} = \frac{F_{ij22}}{F_{ij21}} = r_2/u \qquad (24)$$

where $u = [M_1]/[M_2]$ and r_1 and r_2 are monomer reactivity ratios.

In the intermediate complex mechanism, Eqs. (23) and (24) similar to the Lewis-Mayo type are also available, if the following alternating processes are considered:

$$M_2{*} + M_1 \cdots M_2 \xrightarrow{k_{21}} M_2{-}M_1{*} \cdots M_2$$

$$M_2{-}M_1{*} \cdots M_2 \xrightarrow{k_{12}} M_2{-}M_1{-}M_2{*}$$

Only special condition for this case is $r_1 = 0$ in contrast to the condition for the Lewis-Mayo mechanism that $r_1 \cong 0$. However, these two conditions are not necessarily discriminated.

There has been some reports on the tacticity of the copolymer in relation to its alternating regularity. However, the role of the complex formation may not always be the same in stereo and sequence regulations if the intermediate complex is of a rather loose structure; it may not be as effective for stereo control as for sequence control.

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