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ALTERNATING COPOLYMERIZATION OF ETHYL ACRYLATE AND α-METHYL STYRENE. 2. KINETIC AND MECHANISM

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ABSTRACT

The formation of the ternary molecular complex composed of α-methylstyrene (α-MS), ethyl acrylate(EA) and diethylaluminum chloride (AlEt$_2$Cl) in of CH$_2$Cl$_2$ were examined by UV spectroscopy. The polymerization rate was first order in monomer concentration. The rate depends linearly on the square root of benzoyl peroxide(BPO) concentration and on the cube root of the AlEt$_2$Cl concentration. These results can be explained by a mechanism involving the homopolymerization of a ternary molecular complex.

INTRODUCTION

Since Hirooka et al. [1-3] reported the alternating copolymerization of styrene and acrylate in presence of alkylalumium halides, three main mechanisms have been proposed: (a) the cross-propagation mechanism [4, 5], (b) the radical complex mechanism [6], (c) the ternary molecular complex homopolymerization mechanism [7]. The kinetics and mechanisms of the α-MS-EA- AlEt$_2$Cl system has not been reported. In the previous paper [8], the synthesis and characterization of the alternating copolymer α-MS-EA copolymerized in the presence of AlEt$_2$Cl and BPO was described.

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In this paper, the the formation of the complex between EA and $AlEt_2Cl$ and for the formation of the ternary molecular complex composed of EA, α-MS and $AlEt_2Cl$ are identifed using UV spectroscopy. By using these equilibrium values, the alternating copolymerization of α-MS and EA in the presence of $AlEt_2Cl$ is kinetically analyzed, and the reaction mechanism is discussed.

METHODS

The polymerization procedure and materials used here were the same as in the previously reported paper [8]. Shimazu 260 UV photometer and dilatometer were used to obtain kinetic data. The whole process was kept under nitrogen. Kinetic data were processed by the following equation:

$$\text{Conversion \%} = \frac{\text{dry rubber weight(g)} \times V_t}{\text{theoretical rubber weight(g)} \times V_\infty} \times 100\%$$

where V_t was the volume or height at time (t) and V_∞ was the total volume or height at the end of the reaction .

RESULTS AND DISCUSSION

1. Polymerization mechanism

From the results obtained from the α-MS-EA-$AlEt_2Cl$-BPO system [9], the following conclusions have been drawn: 1) Polymerization time had little effect on the molecular weight of the copolymer and had a significant effect on monomer conversion. 2) Without BPO, the α-MS-EA-$AlEt_2Cl$ system was essentially inactive. The conversion was found to increase with BPO, while the molecular weight decreased. This decrease in Mw indicate that BPO acts as free radical initiator. 3) The reaction rate varies linearly with BPO.

$AlEt_2Cl$ as a complex agent, has two functions:

(I) It complexes with BPO, rendering it more active. UV spectra (Figure 1) shows the dependence of $AlEt_2Cl$ and BPO: The λ_{max} of BPO is 242 nm ($\lg\varepsilon = 2.408$) and 274 nm ($\lg\varepsilon = 1.108$) in CH_2Cl_2. Adding an equivalent of $AlEt_2Cl$, the interaction

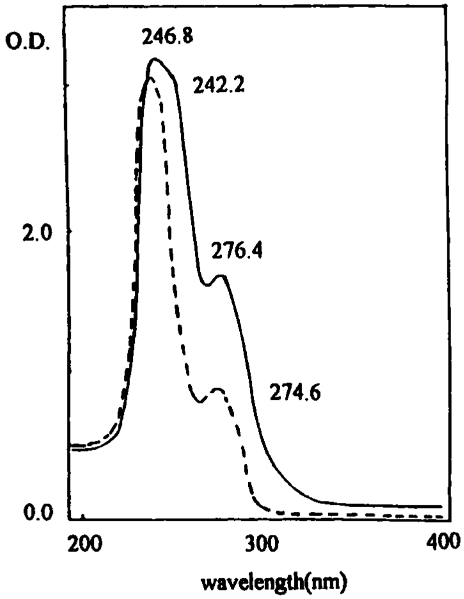
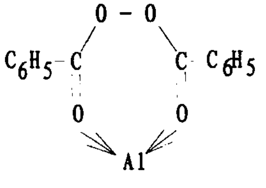


Fig.1 UV spectra of BPO- $AlEt_2Cl$
(---)BPO
(—)BPO- $AlEt_2Cl$
in CH_2Cl_2

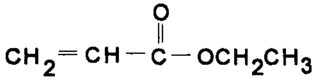
between $AlEt_2Cl$ and BPO increased the conjugated system of the complex, and lowered the transition energy of the excited state of π-π*. π-π* bands underwent a red shift toward longer wavelength. The complex caused the λ_{max} to shift to 246nm (lgε = 2.602) and 276nm (lgε = 1.6203), accompanied by an increase in absorption intensity.

Above all, the conversion increased when $AlEt_2Cl$ was added to the polymerization system. It has been suggested [10] that the complex of BPO and $AlEt_2Cl$ consists of a ring as show below:



The complexation reduces the electron density on -O-O- bond and makes it easier to break. This reduce the decomposition energy of BPO, and significantly shortens its half-life[11, 12]. This made it possible to initiate copolymerization at 0 °C.

(II) It complexes with α-MS, EA and $AlEt_2Cl$ to form ternary molecular complex The UV spectrum of the $AlEt_2CI$ and EA coplex (B) is shown in Figure 2.

EA( $CH_2{=}CH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OCH_2CH_3$) was considered as conjugated system. The λ_{max} of EA was 240 nm (lgε=2.018) in CH_2Cl_2. When an equivalent amount of $AlEt_2Cl$ was added, the absorb peak shift to longer wavelenth, and intensity enhanced. The red shift and increased intensity illustrates that the conjugated π-electron system were increased, and that the complex of EA and $AlEt_2Cl$ resulted in a redistrabution of electrons (including metal atoms). The electron density of the double bonds decreased resulting in an increase in lewis acidity, and the possibility of complexation with α-MS is increased.

After α-MS was added to the EA-$AlEt_2Cl$ system, the absorption peak move to long wavelenth and the intensity increased. The absorbance of the α-MS-$AlEt_2Cl$ was observed at 288nm, with lgε=0.302, indicating that the conjugation of EA-$AlEt_2Cl$ was enhanced by the adding of α-MS. This also indicates that α-MS-EA-$AlEt_2Cl$ ternary molecular complex (T), a charge-transfer complex, exists. It also suggests that binary complexes of α-MS-$AlEt_2Cl$ and EA-$AlEt_2Cl$ preobably exist.

From the experimental results, the scheme for this alternating copolymerization may be proposed as follows:

A) Formation of the new monomer(ternary molecular complex)

$$\alpha\text{-MS} + (EA \rightarrow AlEt_2Cl) \overset{K_T}{=} \underset{(T)}{[(\alpha\text{-MS})(EA \rightarrow AlEt_2Cl)]}$$

where ($EA \rightarrow AlEt_2Cl$), [(α-MS)($EA \rightarrow AlEt_2Cl$)] represented binary molecular complex and ternary molecular complex respectively. K_T was the equilibrium constant of the formation of the ternary molecular complex, while T is the charge-transfer complex.

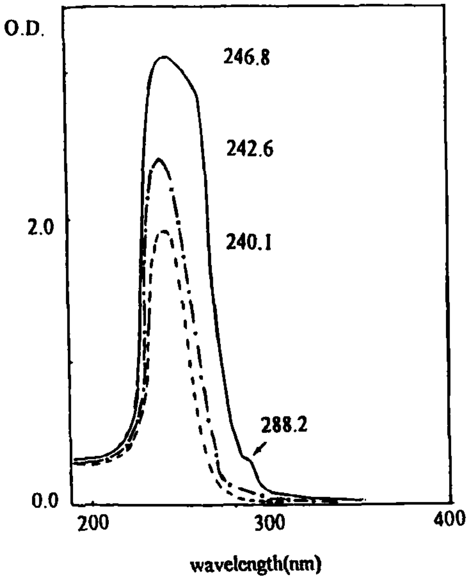


Fig.2 UV spectra of α-MS-EA- $AlEt_2Cl$
(---)EA (-.-)EA- $AlEt_2Cl$
(—)α-MS-EA-$AlEt_2Cl$
in CH_2Cl_2

B) Chain initiation

$$BPO + AlEt_2Cl \overset{Kci}{=} (BPO \rightarrow AlEt_2Cl)$$

$$(BPO \rightarrow AlEt_2Cl) \xrightarrow{K_d} AlEt_2Cl + 2R\bullet \qquad (R\bullet = C_6H_5COO\bullet)$$

$$R\bullet + T \xrightarrow{K_i} RT\bullet$$

where ($BPO \rightarrow AlEt_2Cl$), R• , and RT • represent the BPO complex, the initiating radical, and the propagating radical, respectively; Kc_i was the complex formation constant between BPO and $AlEt_2Cl$; K_d and k_i are the decomposition and initiation rate constants.

C) Chain propagation

$$RT_1\bullet \xrightarrow[Kp_1]{T} RT_2\bullet \xrightarrow[Kp_2]{T} RT_3\bullet \xrightarrow[Kp_3]{T} \ldots RT_n\bullet$$

$$(Kp_1 = Kp_2 = Kp_3 = \ldots Kp_n = Kp$$

where kp_i is the propagation rate constants.

D) Chain termination

$$Rt_n\bullet + Rt_m\bullet \xrightarrow{Kt} \begin{cases} \text{---}RT_nRT_m & \text{(recombination)} \\ \text{---}\ RT_n + RT_m & \text{(disproportionation)} \end{cases}$$

where K_t is the termination rate constant .

Base on the above mechansm, the following equation could be derived:

$$[BPO \rightarrow AlEt_2Cl] = Kc_i[BPO][AlEt_2Cl] \qquad (1)$$

Concentration of ternary molecular complex:

$$[T] = [(\alpha\text{-MS})(EA \rightarrow AlEt_2Cl)] = K_T[\alpha\text{-MS-EA}][AlEt_2Cl] \qquad (2)$$

Initiation rate:

$$R_i = 2fK_d[BPO \rightarrow AlEt_2Cl] = 2fK_dKc_i[BPO][AlEt_2Cl] \qquad (3)$$

Propagation rate:

$$R_p = -(\frac{d[T]}{dt})_p = K_p[T]\sum[RT_i\cdot] = K_p[T\cdot][T] \qquad (4)$$

where $[T\bullet] = [RT\bullet]$

Termination rate (predominantly by recombination):

$$R_t = -\frac{d[T\cdot]}{dt} = 2K_t[T\cdot]^2 \qquad (5)$$

Where the subdcript p and t represent chain propagation and termination.
At steady state, $R_i = R_t$,[T•] could be expressed as follows:

$$[T\cdot] = (\frac{R_i}{2K_t})^{\frac{1}{2}} \qquad (6)$$

Substitute equations (2) with (6) into equation (4) results in

$$R = K_p(\frac{fK_dKc_t}{K_t})^{\frac{1}{2}} K_T[BPO]^{\frac{1}{2}}[AlEt_2Cl]^{\frac{3}{2}}[\alpha - MS - EA]$$

$$\text{set } K = K_p(\frac{fK_dKc_t}{K_t})^{\frac{1}{2}} K_T$$

the kinetic equation for the ternary molecular complex homopolymerization could be derived as:

$$R_p = K[BPO]^{\frac{1}{2}}[AlEt_2Cl]^{\frac{3}{2}}[\alpha - MS - EA]$$

2. Kinetic experiments

Experiments were carried out to demonstrate the relationship between the polymerization rate and [BPO], [AlEt$_2$Cl], [α-MS], [EA] as derived based on the ternary molecular complex homopolymerization mechanism.

(1) Overall activation energy

Figure 3 depicts the dependence of polymerization time on conversion.
At the beginging of reaction(t→0), the yield of the copolymerization increaseed linearly with time, while the rate of reaction increases proportionally with the temperature.

Rate of reaction: $R_p = -\frac{d[M]}{dt} = K_p[M_t]^{\alpha}$

where [M$_t$] was the mole concentration of reactants at time t.

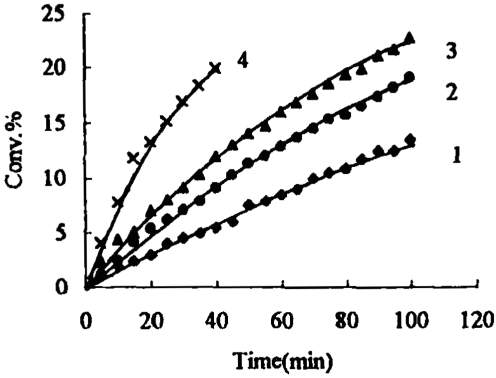


Fig.3 Correspond between conv% and time
1. 20 °C 2. 30 °C 3. 40 °C 4. 50 °C
in toluene

Set conversion to be (x):

$$-\frac{d[M_o(1-x)]}{dt} = K_p[M_o(1-x)]^{\alpha}$$

where M_0 is the initial concentration of reactant.

$$M_o\frac{dx}{dt} = K_pM_o^{\alpha}(1-x)^{\alpha}$$

Set $K_pM_o^{\alpha-1} = K$ then

$$\ln\frac{dx}{dt} = \ln K_p + \alpha\ln(1-x)$$

where $\frac{dx}{dt}$ was the rate of reaction Rp.

The slope of curve at t→0 reprents the reaction rate (R_p) at this time, and Arrehenius plot is

$$K = Ae^{-\frac{E}{RT}}$$

$$\ln K_p = \ln A - \frac{E}{RT}$$ (let [Mo] = 1.0 mol/l then Rp = K)

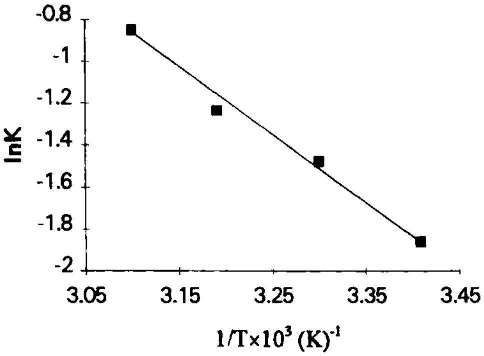


Fig.4 Correpond of lnK and 1/T

The overall activation energy of the alternating copolymerization was determined to be 27.4 KJ/mol, which is lower than that of normal radical polomerization. This indicates that $AlEt_2Cl$ enhances the trends of alternating copolymerization, and deduces the decomposition energy of BPO (Fig.4).

(2) Kinetic equation

A dilatometer was used to obtain the kinetic data.

(A) Figure 5 depicts the dependence of conversion on polymerization time for the different concentration of BPO. The slope of the curved at $t \to 0$ was suggested to be the corresponding reaction rate R_p at that [BPO] concentration, see figure 6. Figure 6 depicts the dependence of the rate of alternating copolymerization on the concentration of benzoyl peroxide. The rate of the alternating copolymerization increased linearly with the square root of the concentration of benzoyl peroxide, which indicates that the reaction was terminated by the recombination.

(B) Figure 7 depicts the dependence of conversion on polymerization time at difference concentration of $AlEt_2Cl$.

The slope at $t \to 0$ was suggested to be the corresponding reaction rate R_p at [$AlEt_2Cl$] see figure 8.

Fig.8 depicts the dependence of the rate of alternating copolymerization on the concentration of $AlEt_2Cl$. The rate of the alternating copolmerization increases linearly with $AlEt_2Cl$ concentration to the power 3/2.

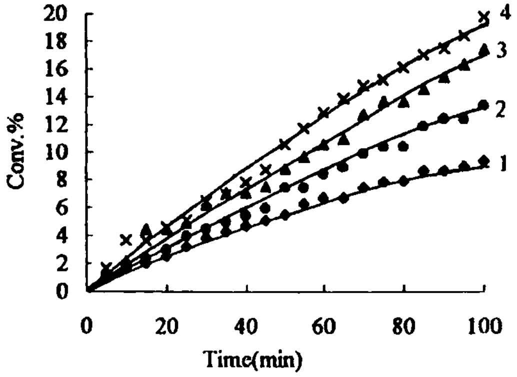


Fig.5 Dependence of conversion on polymerization time

1.0.005 2.0.015 3.0.020 4.0.030(mol/l)

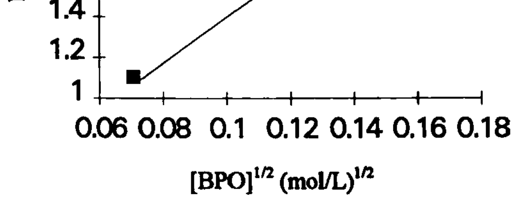


Fig.6 Correlation between polymerization rate and $[BPO]^{1/2}$

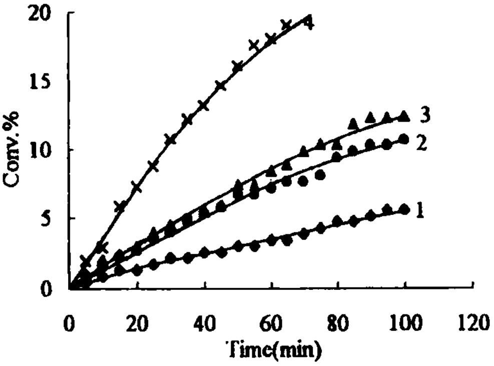


Fig.7 Conversion vs polymerization time
1.0.10 2.0.15 3.0.20 4.0.30 (mol/l)

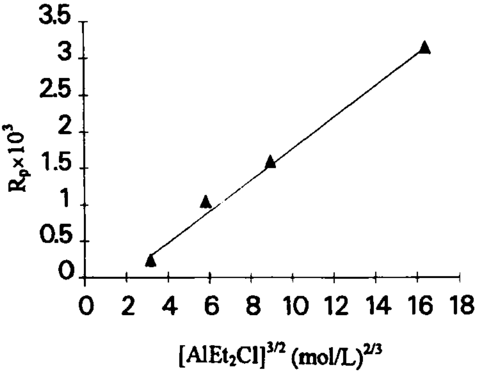


Fig.8 Correlation of polymerization rate and $[AlEt_2Cl]^{3/2}$

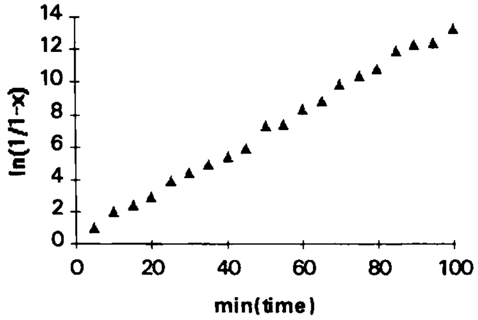


Fig.9 Correlation of ln 1/(1-x) and polymerization time
[α-MS]=[EA]=1.0 mol/l, [$AlEt_2Cl$]=0.2 mol/l, [BPO]=0.015mol/l

(C) Dependence of conversion on total monomers concentration

Figure 9 depicts the dependence of $\ln\frac{1}{1-x}$ vs time .
From figure 9, $\ln\frac{1}{1-x}$ increases linearly with time,which indicates that the rate of the alternating copolymerization was proportional to the first order of the total monomer concentration.

From these results,the kinetic equation of the alternating copolymerization could be derived:

$$R_p = K[BPO]^{\frac{1}{2}}[AlEt_2Cl]^{\frac{3}{2}}[\alpha - MS - EA]$$

This kinetic equation,which was obtained from the exprimental data,agrees with that derived here in the previous section,based on free radical nature of the polymerization. The ternary molecular complex mechanism could reasonably explain this alternating copolymerization.

CONCLUSION

(1) The complex of $AlEt_2Cl$ and BPO was examined by UV spectra. Complexation reduced the decomposition energy of BPO, such that the reaction could be carried out at 0 °C. Complexation of $AlEt_2Cl$ and EA increased the accepting property of EA, and then a ternary molecular complex of α-MS-EA-$AlEt_2Cl$ was easily formed.

(2) The kinetic equation derived based on the free radical polymerization of the ternary molecular complex agreed with the results obtained in the kinetic experiments:

$$R_p = K[BPO]^{0.5}\,[AlEt_2Cl]^{1.5}\,[\alpha\text{-MS - EA}]$$

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