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ALTERNATING COPOLYMERIZATION OF METHYL ACRYLATE AND ISOBUTYLENE

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Abstract

The kinetics and mechanism of copolymerization of methyl acrylate (MA) and isobutylene (IB) in the presence of AlEtCl2 and benzoyl peroxide (BPO) has been examined. It is suggested that when [IB]>[MA], the copolymerization proceeds via a homopolymerization of a three-component complexed monomer (T) to form the alternating MA-IB copolymer. When [MA]>[IB], the formation of a MA-IB copolymer rich in MA and containing MA blocks may occur through the copolymerization of a three-component complexed monomer (T) and a two-component complexed monomer (B), or simply MA.

Introduction

Two main mechanisms have been proposed in the literature (1) to account for the alternating copolymerization in the presence of Lewis acid. One is the alternating coordination of monomers, and the other is the radical polymerization of three component complex or its copolymerization with other monomer complex. Each proposed mechanism has its advantages which vary with the polymerization systems and conditions. In the previous paper (2), the synthesis and characterization of the alternating copolymer MA-IB polymerized in the presence of AlEtCl2 and benzoyl peroxide, have been described. The present paper will discuss its copolymerization mechanism based on laboratory UV information and kinetic data.

※ Polysar visiting professor

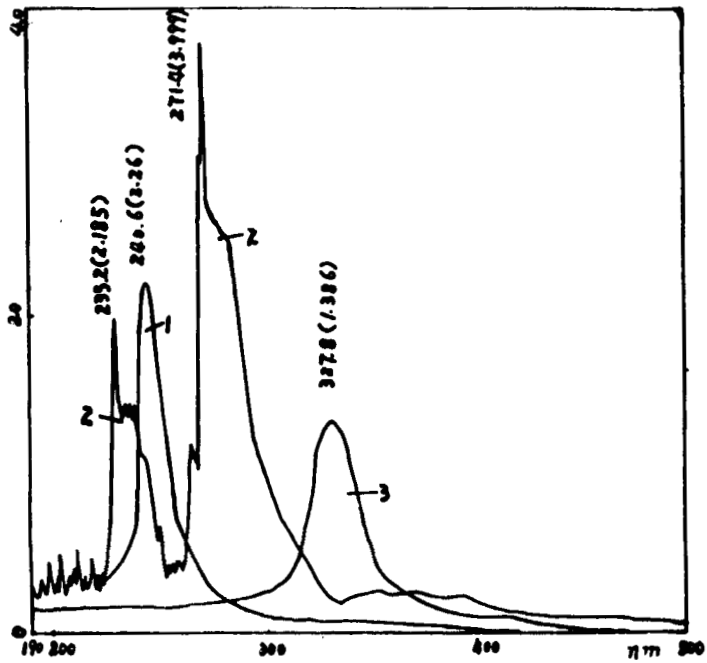


Figure 1. UV spectra 1 --- MA in CH_2Cl_2 (Reference CH_2Cl_2)
2 --- MA→$AlEtCl_2$ in CH_2Cl_2 (Reference MA in CH_2Cl_2)
3 ---(MA→$AlEtCl_2$)+IB in CH_2Cl_2 (Reference MA→$AlEtCl_2$ in CH_2

Experimental

Shimazu 260 UV photometer and dilatometer were used to obtain kinetic data. The polymerization procedure and material used here were the same as reported previously (2). The charged dilatometer was placed in a constant temperature bath. Once 50℃ was reached, the catalyst was transfered via pre-dried syringe.

Results and Discussion

1. Mechanism and Kinetics of Three-Component Complex Homopolymerization

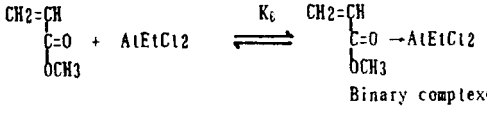
i) Formation of two-component complex (B)

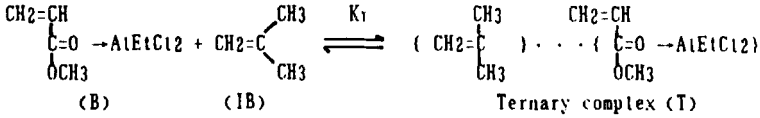
Ebdon and Gabbott (3) reported that MMA and $AlEt_{1.5}Cl_{1.5}$ formed a two-component complex and obtained its equilibrium constant $K>100(l \cdot mol^{-1})$

$$MMA + AlEt_{1.5}Cl_{1.5} \underset{}{\overset{K}{\rightleftharpoons}} (MMA\text{-}AlEt_{1.5}Cl_{1.5})$$

This complex is formed through the unshared electron pair on the carbonyl group and the unoccupied orbital on the aluminium atom. In this study, MA and (MA-AlEtCl2) complex were analysed with UV photometer. The UV spectrum of the binary complex was characterized by 271.4nm (MA in CH_2Cl_2 was taken as reference) and ternary complex by 327.8nm (binary complex in CH_2Cl_2 was taken as reference).

Cl2) This suggested that the binary and ternary complexes can be formulated as





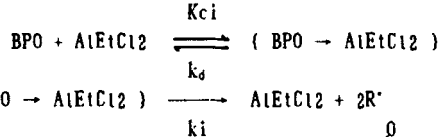
ii) Mechanism of three-component complex homopolymerization

The alternating copolymerization in this system can be deduced as the homopolymerization of new monomer (T) , the three-component complex.

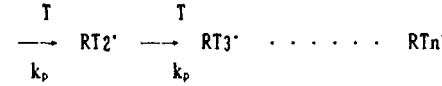
A. Formation of the new monomer (ternary complex)

[IB · · · (MA →AlEtCl2)]

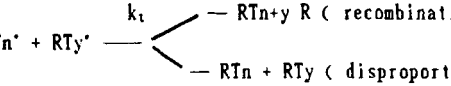
B. Chain initiation



C. Chain propagation



D. Chain termination



iii) The mechanism and kinetic equation of three-component complex homopolymerization

Based on the above mechanism, the following equation can be derived,

[BPO →AlEtCl2] = Kci [BPO] [AlEtCl2]

Concentration of two-component complex,

[B] = K_b · [MA] [AlEtCl2]

Concentration of three-component complex,

[T] = K·[B] · [IB] = $K_b \cdot K_T$ · [MA] [IB] [AlEtCl2]

Rate of initiation,

Ri = 2fkd [BPO→AlEtCl2] = 2fk_dKci [BPO] · [AlEtCl2] (I)

Rate of propagation ,

$$Rp = -d[T]/dt = kp[T^{\cdot}][T] \quad (2)$$

Rate of termination, (by recombination)

$$Rt = -d[T^{\cdot}]/dt = 2kt[T^{\cdot}]^2 \quad (3)$$

At steady state, Ri = Rt , $[T\cdot]$ can be expressed as the following,

$$[T^{\cdot}] = (Ri/2kt)^{1/2} \quad (4)$$

Substitute [T] into equation (2) with (4) and set

$$K = kp(fkdKci/kt)K_TK_B ,$$

the kinetic equation for the three-component homopolymerization can be derived as,

$$Rp = K[BPO]^{1/2}[AlEtCl2]^{3/2}[MA][IB]$$

iv) Kinetics of three-component complex homopolymerization

Experiments were carried out to demonstrate the relation betwen the polymerization rate, [BPO], [AlEtCl2], [IB] and [MA] as derived based on the three-component complex homopolymerization mechanism. The results in Figures (2) (3) and (4) respectivety show the linear relationship between the polymerization rate of [BPO] and [AlEtCl2] and [MA]. The experimental data agrees with the kinetic equation derived here in the previous section which indicated the free radicat nature of the polymerization.

2. Mechanism and Kinetics of Copolymerization of the Three-component Complex (T) and the Two-component Complex (B)

When [MA]>[IB], both three-component complex (T) and two-component complex (B), or monomer MA, exist in the system at the same time. The polymerization can be viewed as a random copolymerization of the monomers (T) and (B), or MA. Due to the equal mole of IB and MA in (T) and only MA in (B), the resulted copolymer is rich in MA. This system of copolymerization can be described with the following scheme:

$$T\cdot + T \xrightarrow{K_{TT}} TT\cdot$$

$$T\cdot + B \xrightarrow{K_{TB}} TB\cdot$$

$$B\cdot + T \xrightarrow{K_{BT}} BT\cdot$$

$$B\cdot + B \xrightarrow{K_{BB}} BB\cdot$$

The Mayo-Lewis two component copolymerization equation is therefore,

$$\frac{d[T]}{d[B]} = \frac{[T]}{[B]} \cdot \frac{[T]\cdot\gamma_T + [B]}{[B]\cdot\gamma_B + [T]}$$

Let $\gamma_T = K_{TT}/K_{TB}$ $\gamma_B = K_{BB}/K_{BT}$ $d[T]/d[B] = y$ and $[T]/[B] = x$, substitute into the above equation, and rearrange the resulted equation to

$$(y-1)\cdot x/y = x^2/y\cdot\gamma_T - \gamma_B$$

This is known as the Fineman-Ross equation.

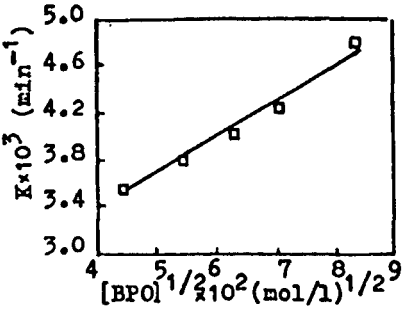


Figure 2. Correlation between polymerization rate and $[BPO]^{1/2}$

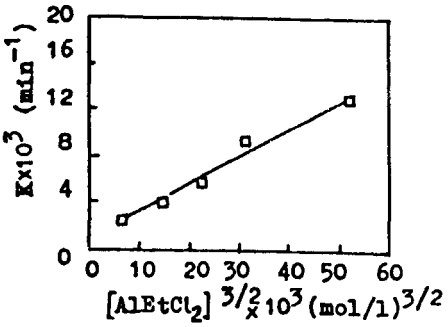


Figure 3. Correlation between polymerization rate and $[AlEtCl_2]^{3/2}$

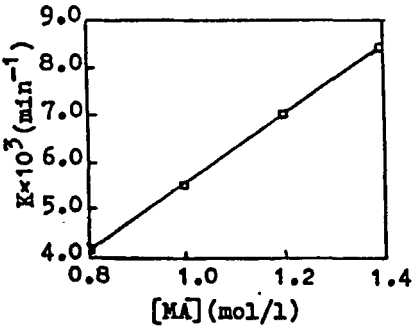


Figure 4. Correlation between polymerization rate and [MA]

Table 1 Calculation Values of x and y based on Experimental Data

	In Monomers		In Polymer		Calculated Values	
	MA%	x	MA%	y	$x(y-1)/y$	x^2/y
1	60	2.00	0.54	5.75	1.65	0.70
2	60	1.06	0.57	3.07	0.71	0.37
3	70	0.75	0.62	1.58	0.28	0.36
4	75	0.50	0.66	1.06	0.03	0.24
5	80	0.33	0.75	0.50	-0.33	0.22

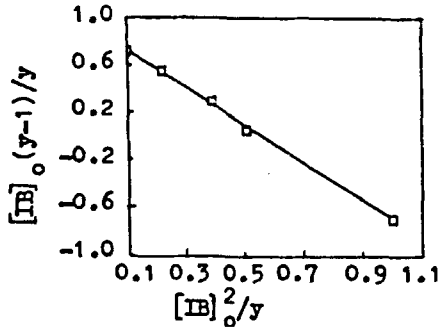


Figure 5. Correlation between
$[IB]_o \cdot y-1/y$ and $[IB]^2_o \cdot 1/y$

In the case of [MA]>[IB], the value [B] numerically equals to [MA]o -[T] and [T] equals to [IB]o in the monomer, and d[B] equals to [MA] in the copolymer. Thus the values x and y were calculated as listed in Table 1 .The plot of $x(y-1)/y$ against x^2/y is a straight line, as shown in Figure 5, with a correlation coefficient 0.97. The slop of the straight line, γ_1 is 3.5 and the point of intersection with abscissa γ_8 is 0.8. The plot agrees with the proposed mechanism that when [MA]>[IB] the mechanism is very likely follow the random copolymerization of the three component complex (T) and the two component complex (B). There was no evidence that isobutylene homopolymer or isobutylene rich copolymer existed in the system even the [IB]/[MA] mole ratio was high in the monomer mixture. This may due to the inability of forming an active isobutylene complex with the existing Lewis acid.

Conclusion

When [IB]>[MA], the copolymerization proceeds with three-component complex homopolymerization mechanism to produce an alternating copolymer. The kinetic equation derived for such copolymerization is,

$$Rp = K\ [BPO]^{1/2}\ [AlEtCl2]^{3/2}[MA]\ [IB]$$

When [MA]>[IB], the mechanism of random copolymerization of the three-component complex and the two-component complex (or MA monomer) is followed. The copolymer will be rich in MA and may contain MA blocks.

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