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# POLYMERIZATION OF METHYL METHACRYLATE AND *p*-FLUOROSTYRENE WITH THE FERRIC ACETYLACETONATE–TRIETHYLALUMINUM CATALYST SYSTEM

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## ABSTRACT

The kinetics of the polymerization of methyl methacrylate and *p*-fluorostyrene with the catalyst system Fe(III) acetylacetonate-triethylaluminum at 60°C in benzene was studied. Maximum conversion of the polymer was obtained when the aging time of the catalyst was 15 min. Maximum activity of the catalyst was found at an Al/Fe ratio of 4. The rate of polymerization was first order with respect to monomer. The orders with respect to the catalyst and cocatalyst were found to be 0.5 and 1.5, respectively. The overall activation energies for the polymerization of methyl methacrylate and *p*-fluorostyrene were found to be 43.9 and 51.1 kJ/mol, respectively. A free-radical mechanism is postulated.

## INTRODUCTION

Although most catalysts in Ziegler-type polymerizations are heterogeneous, several soluble catalysts have been reported [1-5]. Overberger et al. [6] and Allen and Obaid [7] reported that a soluble catalyst system consisting of di-

cyclopentadienyltitanium chloride and aluminum alkyl can polymerize styrene. Chromium acetylacetonate and triethylaluminum, a soluble catalyst system, was used for a kinetic study of the polymerization of butadiene [8]. It has been established that a soluble catalyst system containing chromium acetylacetonate with triethylaluminum [9] or triisobutylaluminum [10] is active for the polymerization of methyl methacrylate at high ratios of Al/Cr. The mechanism of polymerization is anionic in the case of triethylaluminum and chromium acetylacetonate and free radical in the case of triisobutylaluminum with chromium acetylacetonate. The catalyst system of chromium acetylacetonate with triethylaluminum [11] has high activity for the polymerization of styrene at an Al/Cr ratio of 3, and the mechanism of polymerization is coordinate anionic. Kalyanam et al. [12] reported that the microstructures of the polymers prepared by the free-radical initiators and by the cobalt acetylacetonate-triethylaluminum catalyst system are very similar. The polymerization of methyl methacrylate and styrene by the cobalt acetylacetonate-diethylaluminum bromide catalyst system was reported to proceed by an anionic mechanism [13]. Kambara et al. [14] reported that propylene oxide could be polymerized by the use of triethylaluminum and acetylacetonates of transition metals. The catalyst system based on iron acetylacetonate-triethylaluminum was used for the polymerization of alkylene oxides [15]. However, the literature reveals no detailed kinetic investigation on Ziegler catalysts containing iron acetylacetonate and triethylaluminum.

In the present investigation the kinetics of polymerization of methyl methacrylate (MMA) and *p*-fluorostyrene (FS) with a homogeneous catalyst system,  $\text{Fe}(\text{acac})_3\text{-AlEt}_3$  in benzene, are reported, and the mechanism of the reaction is discussed.

## EXPERIMENTAL

Benzene was treated with concentrated sulfuric acid, washed many times with water, and stored over sodium after distillation. It was refluxed overnight on sodium under nitrogen and redistilled immediately prior to use. Ethanol was refluxed over calcium oxide and distilled to collect the middle fraction.

Methyl methacrylate was freed of the inhibitor by washing with a 5% solution of alkali in water. Later, it was washed well with water to remove the alkali and dried over anhydrous calcium chloride. The monomer was distilled in the presence of nitrogen under reduced pressure, and the middle fraction was collected in a colored bottle which was kept in the cold.

*p*-Fluorostyrene was synthesized from *p*-fluoroacetophenone. To a stirred solution of *p*-fluoroacetophenone, sodium borohydride was added in small amounts at room temperature. After 2 h the excess of borohydride was destroyed by adding glacial acetic acid. The reaction product was extracted with ether, and the *p*-fluorophenyl methyl carbinol was vacuum distilled. The dehydration of the carbinol was done according to the method of Brooks [16]. *p*-Fluorostyrene was distilled in the presence of nitrogen under reduced pressure, and the middle fraction was collected and preserved in the cold.

Aluminum triethyl [17] and Fe(acac)<sub>3</sub> [18] were prepared in accordance with known literature methods. For use, a 0.25 *M* solution of Fe(acac)<sub>3</sub> and a 0.5 *M* solution of AlEt<sub>3</sub> in benzene were freshly prepared.

### POLYMERIZATION

All experiments were carried out inside a dry box which was maintained anhydrous under an atmosphere of dry, oxygen-free nitrogen. The catalyst complex was prepared by successively adding solutions of Fe(acac)<sub>3</sub> and AlEt<sub>3</sub> in benzene in a conical flask provided with a B-19 conical joint. After aging of the catalyst system, the monomer was introduced into the reaction mixture. The reaction flask was tightly stoppered and kept in a thermostat adjusted to 60°C. After the desired reaction time, the resultant mixture was poured into acidified ethanol. The precipitate was filtered through a sintered glass crucible, dried, and weighed.

The viscosity of polymethyl methacrylate (PMMA) was measured at 30°C in benzene, and the molecular weight was calculated by the relationship [19]

$$[\eta] = 5.2 \times 10^{-5} \times M^{0.76}.$$

The viscosity of poly(*p*-fluorostyrene) (PFS) were measured at 25°C in benzene, and the molecular weight was calculated from the relationship [20]

$$[\eta] = 4.08 \times 10^{-4} \times M^{0.58}.$$

The <sup>13</sup>C NMR spectrum of PMMA was recorded on a Jeol FX 90 Q, FT NMR instrument at room temperature by using a solution of the polymer in chloroform.

## RESULTS AND DISCUSSION

The  $\text{Fe}(\text{acac})_3\text{-AlEt}_3$  catalyst complex forms a homogeneous solution in benzene. The rose-colored solution of iron acetylacetonate turned dark red on addition of aluminum triethyl, and there was no solid formation, indicating the homogeneous nature of the catalyst system. Further addition of the monomer to the catalyst system did not change its color, indicating that there was no complex formation with the monomer. The catalyst behavior was determined by the order in which the catalyst components were mixed [21, 22]. The presence of monomer during catalyst formation may influence the stereospecificity of the catalyst [23]. In our investigation, aluminum triethyl was added to the benzene solution of iron acetylacetonate followed by the monomer.

The conversion of methyl methacrylate and *p*-fluorostyrene increased linearly with time up to 2 h and later remained almost constant up to 5 h (Fig. 1). The molecular weight of the polymers, viz., PMMA and PFS, increased with the time of polymerization (Table 1). The polymer PMMA gelled at 25% conversion. This type of behavior was reported by Schulz and Harborth [24] for free-radical polymerization of methyl methacrylate with benzoyl peroxide at 70°C. The aging time of the catalyst was varied from 5 to 25 min. The percent conversion of methyl methacrylate and *p*-fluorostyrene reached a maximum when the catalyst system was aged for 15 min. A further increase of aging time decreased the efficiency of the catalyst (Fig. 2). It is well known that too much aging of the catalyst decreases catalytic activity [25, 26]. The molecular weight of both polymers increased with the aging time (Table 2).

TABLE 1. Effect of Reaction Time on Molecular Weight

Time, h	MW $\times 10^{-4}$	
	PMMA	PFS
1	4.6	2.4
2	7.3	3.6
3	9.3	3.9
4	14.3	6.5
5	15.2	6.9

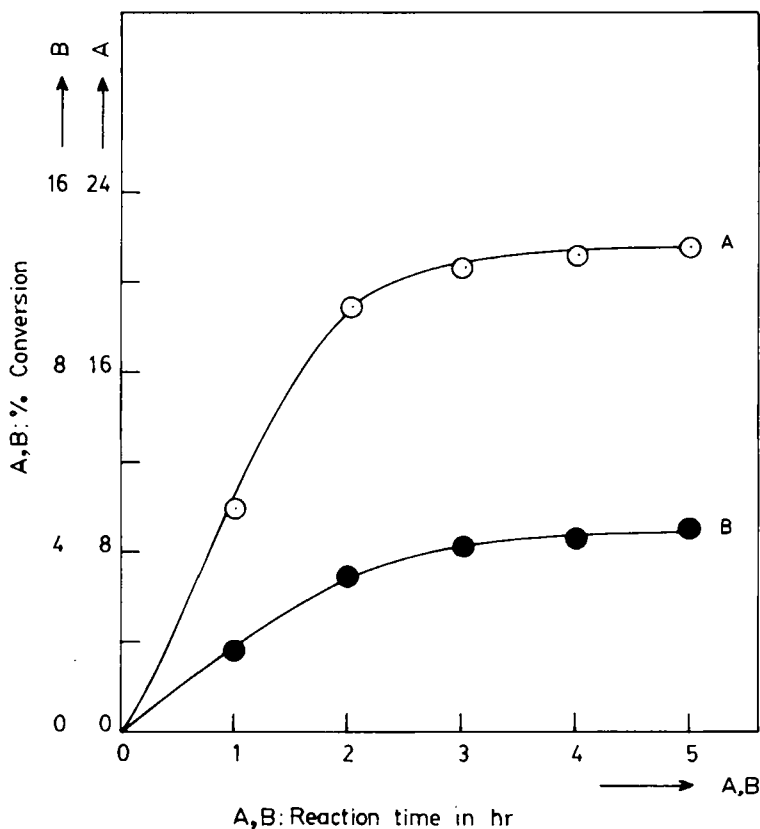


FIG. 1. Effect of reaction time on conversion of PMMA ( $\circ$ ) and PFS ( $\bullet$ ) obtained with  $\text{Fe}(\text{acac})_3$  and  $\text{AlEt}_3$  catalyst.  $[\text{Fe}(\text{acac})_3] = 0.025 \text{ mol/L}$ ;  $[\text{MMA}] = [p\text{-fluorostyrene}] = 2 \text{ mol/L}$ ;  $\text{Al/Fe} = 2$ ; aging time = 15 min;  $60^\circ\text{C}$ .

The polymerization reactions were carried out at different Al/Fe ratios by keeping the  $\text{Fe}(\text{acac})_3$  concentration constant and changing the concentration of aluminum triethyl. As shown in Fig. 3, at the Al/Fe ratio of 4, the maximum yield of polymer was obtained. The molecular weight was also found to be maximum at the Al/Fe ratio of 4 (Table 3). Deshpande et al. [27] also observed maximum polymerization of styrene at the Al/Cr ratio of 4, which was attributed to a coordinate anionic mechanism. However, the molecular weight of the polymer was the lowest as against the highest in the present study. The

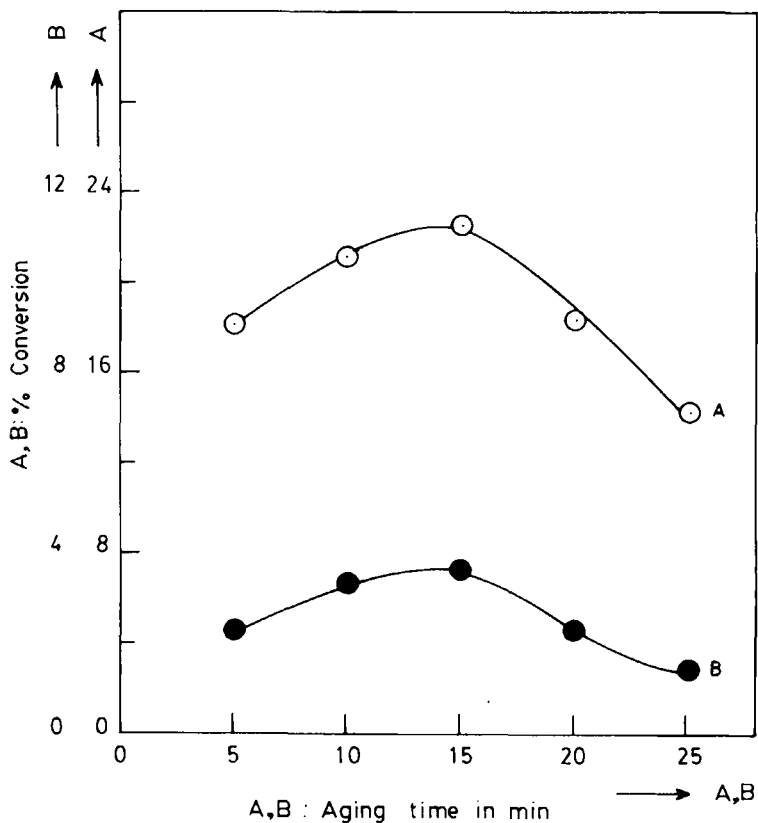


FIG. 2. Effect of aging time on conversion of PMMA (○) and PFS (●) obtained with  $\text{Fe}(\text{acac})_3$  and  $\text{AlEt}_3$  catalyst.  $[\text{Fe}(\text{acac})_3] = 0.025 \text{ mol/L}$ ;  $[\text{MMA}] = [\textit{p}\text{-fluorostyrene}] = 2 \text{ mol/L}$ ;  $\text{Al/Fe} = 2$ ; reaction time = 3 h;  $60^\circ\text{C}$ .

same authors observed a different result with the same catalyst system on changing the monomer to methyl methacrylate [9]. The rate of polymerization increased suddenly around the  $\text{Al/Cr}$  ratio of 12 and later remained almost steady. The molecular weight decreased with increasing ratio of  $\text{Al/Cr}$ , which was attributed to the transfer reaction by  $\text{AlEt}_3$ . An anionic mechanism was postulated for the polymerization of the polar monomer. The polymerization of the same monomer was constant at the  $\text{AlEt}_3/\text{VOCl}_3$  ratio of 1-2, but increased to a maximum at the ratio of 4. The molecular weight at this ratio was

TABLE 2. Effect of Aging Time on Molecular Weight

Aging time, min	MW $\times 10^{-4}$	
	PMMA	PFS
5	4.7	2.4
10	5.7	2.7
15	9.1	3.6
20	9.7	4.9
25	10.5	5.5

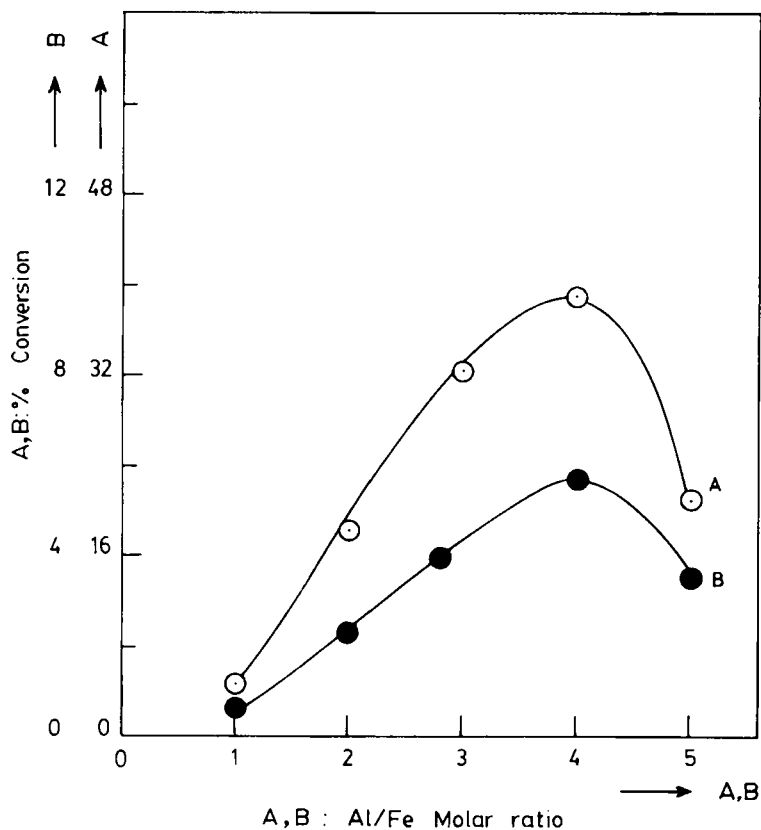


FIG. 3. Effect of Al/Fe ratio on conversion of PMMA (○) and PFS (●) obtained with  $\text{Fe}(\text{acac})_3$  and  $\text{AlEt}_3$  catalyst.  $[\text{Fe}(\text{acac})_3] = 0.025 \text{ mol/L}$ ;  $[\text{MMA}] = [p\text{-fluorostyrene}] = 2 \text{ mol/L}$ ; reaction time = 3 h; aging time = 15 min;  $60^\circ\text{C}$ .



TABLE 3. Effect of Al/Fe Ratio on Molecular Weight

[AlEt <sub>3</sub> ], mol/L	Al/Fe	MW × 10 <sup>-4</sup>	
		PMMA	PFS
0.025	1	7.6	3.4
0.050	2	9.2	3.6
0.075	3	9.4	5.6
0.100	4	9.7	5.7
0.125	5	7.0	2.9

the lowest, and a coordinate anionic mechanism has been postulated for this system [28]. The rate of polymerization of styrene decreased sharply up to the Sn(*n*-C<sub>3</sub>H<sub>7</sub>)<sub>4</sub>/VOCl<sub>3</sub> ratio of 1.5 and remained constant. The molecular weight of the polymer increased up to the ratio of 1.5 and then decreased [29]. This is the opposite of the results obtained in the present investigation and has been explained by the authors with an anionic mechanism. The rate of polymerization of methyl methacrylate was maximum at a Al/Ti ratio of 7, and the molecular weight also decreased with a further increase of the catalyst ratio [30]. The maximum conversion of methyl methacrylate and fluoro-styrene observed in the present investigation at the Al/Fe ratio of 4 may be attributed to the formation of the catalyst complex (Reaction 1). The decrease in conversion on increasing the catalyst ratio further may be attributed to the transfer reaction by the aluminum triethyl (Reaction 7).

The order with respect to the aluminum triethyl concentration was found to be 1.5 (Fig. 4). This experimental observation is in agreement with the kinetic scheme derived (Eq. 15) on the basis of initiation by the ethyl radicals and termination by mutual combination. It is interesting to compare the widely divergent experimental observations on the order with respect to the aluminum alkyl concentration reported by different workers and the mechanisms suggested. Dixit et al. [31] observed a square root dependence on the aluminum alkyl concentration for the polymerization of methyl methacrylate. It was interpreted in terms of a coordinate anionic mechanism. The same mechanism was proposed by Otta and Parravano [32] to explain the inverse dependence on the square root of the aluminum alkyl concentration for the polymerization of styrene, though the order changed to -1.5 on changing the catalyst from TiCl<sub>3</sub> to VOCl<sub>3</sub>. Even the zero-order dependence observed by Berger and Grievson [33] for the polymerization of ethylene was interpreted by

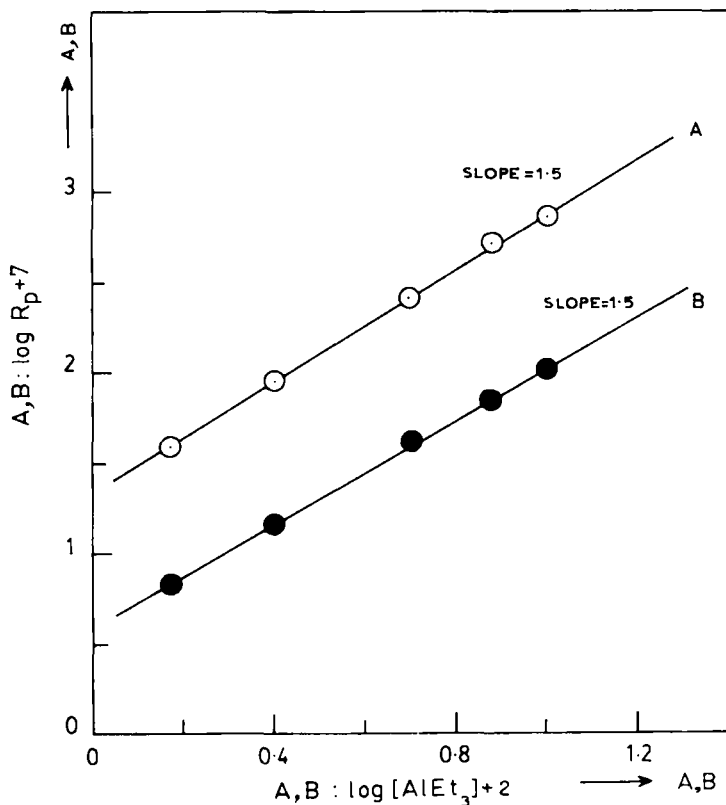


FIG. 4. Effect of Al/Fe ratio on rate of polymerization of PMMA ( $\circ$ ) and PFS ( $\bullet$ ) obtained with  $Fe(acac)_3$  and  $AlEt_3$  catalyst.  $[Fe(acac)_3] = 0.025$  mol/L;  $[MMA] = [p\text{-fluorostyrene}] = 2$  mol/L; reaction time = 3 h; aging time = 15 min;  $60^\circ C$ .

coordinate anionic mechanism. The inverse function of the aluminum triethyl concentration observed by Bawn et al. [8] for the polymerization of butadiene was not explained in terms of a reaction mechanism. Thus the role played by the cocatalyst in the Ziegler-Natta polymerization appears to be complex, sensitive to the nature of the complex and to the nature of the monomer. The kinetic orders observed appeared to be fitted to the different mechanisms in a fortuitous manner.

The rate of polymerization of methyl methacrylate was found to be proportional to the square root of the concentration of the catalyst,  $[Fe(acac)_3]$

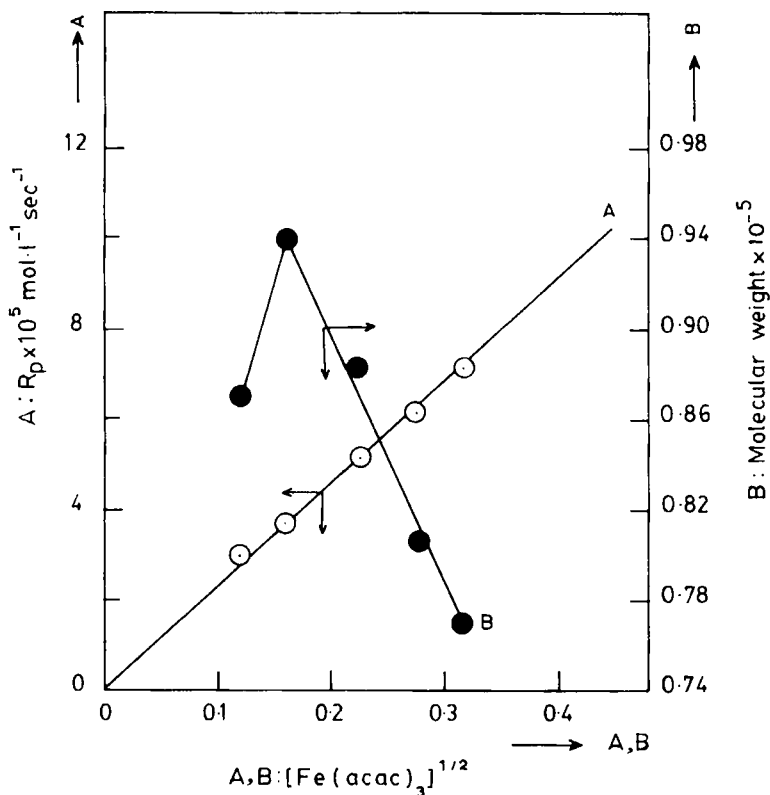


FIG. 5. Effect of catalyst concentration on rate of polymerization (○) and molecular weight (●) of PMMA obtained with  $Fe(acac)_3$  and  $AlEt_3$  catalyst.  $[MMA] = 2 \text{ mol/L}$ ;  $Al/Fe = 2$ ; aging time = 15 min; reaction time = 3 h;  $60^\circ C$ .

(Fig. 5). The molecular weight decreased at higher concentrations of the catalyst, indicating chain transfer with the complex. The rate of polymerization was found to be proportional to the monomer concentration (Fig. 6), and the molecular weight increased with the monomer concentrations (Table 4), indicating that the monomer did not take part in the chain transfer. This type of behavior was reported [10] for the free-radical polymerization of methyl methacrylate with the  $Cr(acac)_3-Al(i-Bu)_3$  catalyst system. The overall activation energies of the polymerization of methyl methacrylate and *p*-fluorostyrene were found to be 43.9 and 51.1 kJ/mol, respectively (Fig. 7). Since the values

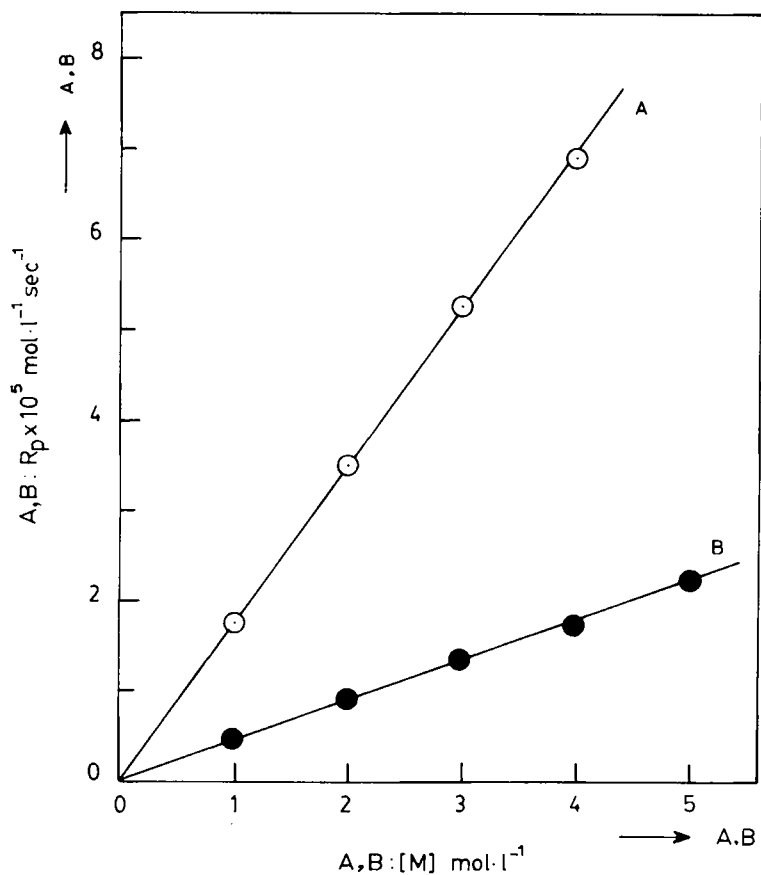


FIG. 6. Effect of monomer concentration on rate of polymerization of MMA (○) and PFS (●).  $[\text{Fe}(\text{acac})_3] = 0.025 \text{ mol/L}$ ; ratio of Al/Fe = 2; aging time = 15 min; reaction time = 3 h;  $60^\circ\text{C}$ .

TABLE 4. Effect of Monomer Concentration on Molecular Weight

[M], mol/L	MW $\times 10^{-4}$	
	PMMA	PFS
1	7.7	2.7
2	9.2	3.4
3	11.5	4.8
4	13.4	5.8
5	16.1	6.4

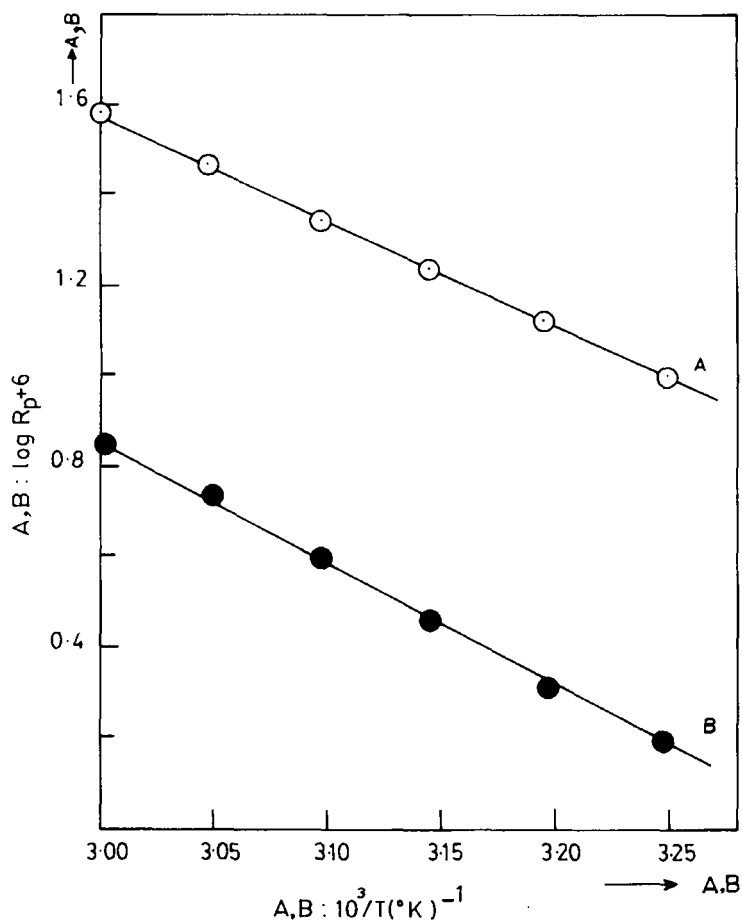


FIG. 7. Activation energy of  $\text{Fe}(\text{acac})_3$  and  $\text{AlEt}_3$  catalyst for PMMA (○) and PFS (●).  $[\text{Fe}(\text{acac})_3] = 0.025 \text{ mol/L}$ ; ratio of  $\text{Al/Fe} = 2$ ;  $[\text{MMA}] = [\text{p-fluorostyrene}] = 2 \text{ mol/L}$ ; aging time = 15 min; reaction time = 3 h.

obtained were not outside the range reported for free-radical polymerizations, a free-radical mechanism may be assumed to operate.

The rate of polymerization of methyl methacrylate dropped considerably on the addition of a polymerization inhibitor, such as hydroquinone, to the reaction system, which suggests the presence of free radicals in the reaction

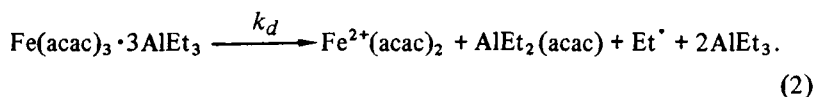
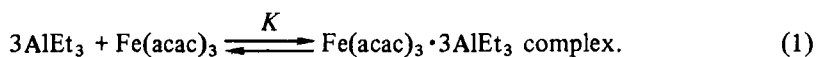
TABLE 5. Effect of Hydroquinone on  $R_p$  and Viscosity of PMMA<sup>a</sup>

Hydroquinone, mg	$R_p \times 10^5$ , mol/(L·s)	Intrinsic viscosity, dL/g
0	5.4	0.310
50	2.1	0.449

<sup>a</sup>Polymerization conditions:  $[\text{Fe}(\text{acac})_3] = 0.025$  mol/L;  $[\text{AlEt}_3] = 0.05$  mol/L; reaction time = 3 h; Al/Fe = 2;  $[\text{MMA}] = 2$  mol/L; total volume = 2 mL.

system (Table 5). The <sup>13</sup>C NMR spectrum (Fig. 8) of PMMA obtained with the catalyst system  $\text{Fe}(\text{acac})_3\text{-AlEt}_3$  compares very well with the tacticities (Table 6) of PMMA obtained by the free-radical initiators [10, 34]. This gives further support for a free-radical polymerization of methyl methacrylate.

Based on the above observations the following mechanism is proposed:



Initiation:



Propagation:



Termination:



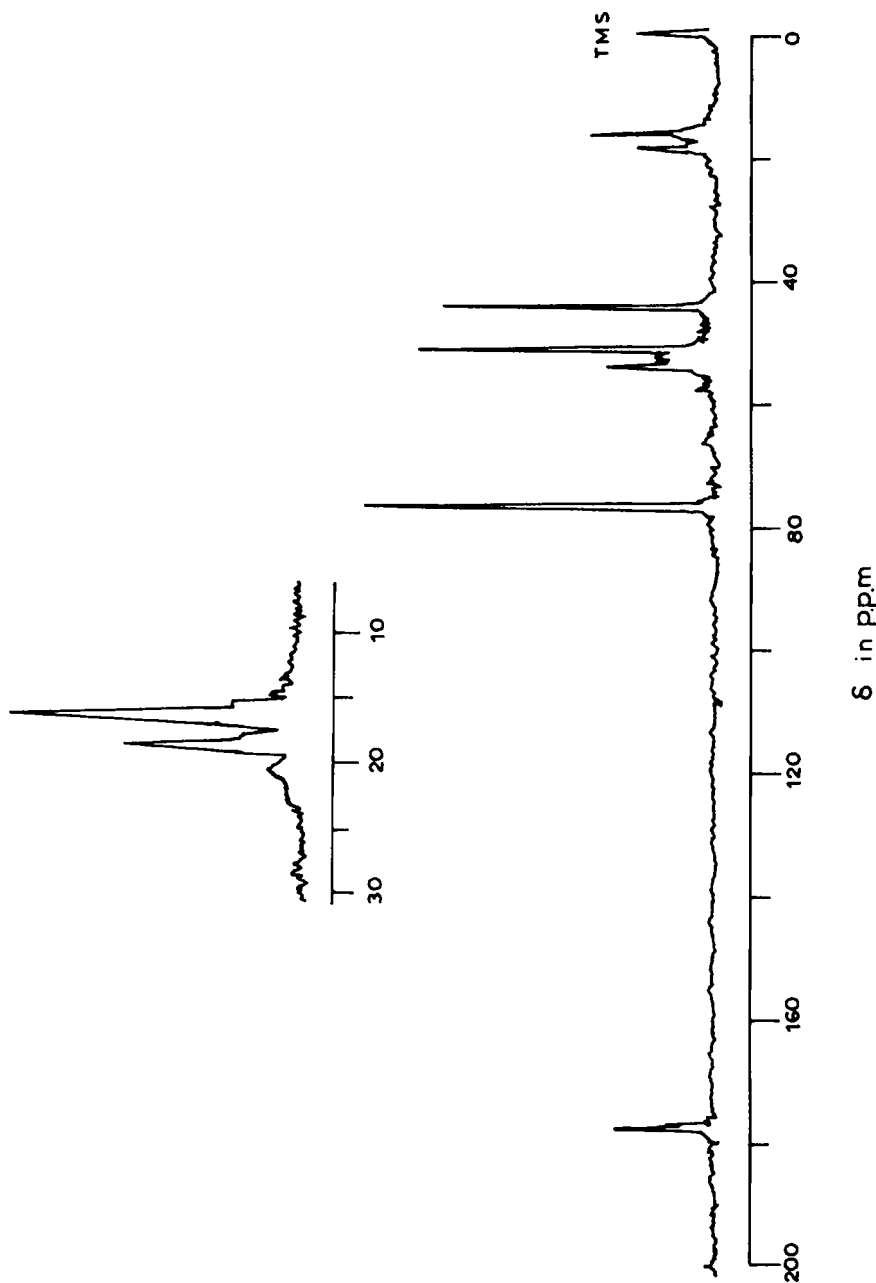


FIG. 8.  $^{13}\text{C}$  NMR spectrum of PMMA obtained at an Al/Fe ratio of 2.

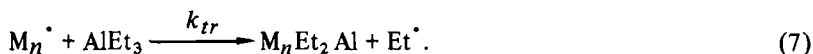
TABLE 6. Comparison of Fractional Intensities of PMMA Obtained by the  $\text{Fe}(\text{acac})_3\text{-AlEt}_3$  Catalyst System with That Obtained by the Free-Radical Initiators<sup>a</sup>

Catalyst system	Molar ratio of catalyst components	Relative area for $\alpha$ -methyl peak in the NMR spectrum <sup>a</sup>			Ref.
		I, %	H, %	S, %	
Azobisisobutyronitrile	—	6.3	37.6	56.0	34
Lauroyl peroxide	—	10.5	35.8	53.8	34
Benzoyl peroxide	—	4.9	30.8	64.2	34
$\text{Cr}(\text{acac})_3\text{-Al}(i\text{-Bu})_3$	Al/Cr = 2	6.0	31.0	63.0	10
$\text{Fe}(\text{acac})_3\text{-AlEt}_3$	Al/Fe = 2	6.0	35.0	59.0	Present study

<sup>a</sup>For evaluation of the area of the syndiotactic S, heterotactic H, and isotactic I, the  $\alpha\text{-CH}_3$  triad peaks of Bovey and Tiers [34] were used.



Transfer:



Applying the steady-state approximation for the radical  $M_n^{\cdot}$ :

$$\frac{d[M_n^{\cdot}]}{dt} = k_i[Et^{\cdot}][M] - k_t[M_n^{\cdot}]^2 - k_{tr}[M_n^{\cdot}][AlEt_3] = 0. \quad (8)$$

Applying the steady-state approximation for the radical  $Et^{\cdot}$ :

$$\frac{d[Et^{\cdot}]}{dt} = k_d[\text{complex}] - k_i[Et^{\cdot}][M] + k_{tr}[M_n^{\cdot}][AlEt_3] = 0. \quad (9)$$

$$k_i[Et^{\cdot}][M] = k_d[\text{complex}] + k_{tr}[M_n^{\cdot}][AlEt_3]. \quad (10)$$

Substituting Eq. (10) into Eq. (8):

$$k_t[M_n^{\cdot}]^2 = k_d[\text{complex}]. \quad (11)$$

$$[M_n^{\cdot}] = \left( \frac{k_d[\text{complex}]}{k_t} \right)^{1/2}, \quad (12)$$

$$= \left( \frac{k_d K [Fe(acac)_3] [AlEt_3]^3}{k_t} \right)^{1/2}. \quad (13)$$

The rate of polymerization is given by

$$R_p = k_p[M_n^{\cdot}][M]. \quad (14)$$

Substituting Eq. (13) in Eq. (14):

$$R_p = \frac{k_p k_d^{1/2} K^{1/2}}{k_t^{1/2}} [Fe(acac)_3]^{1/2} [AlEt_3]^{3/2} [M]. \quad (15)$$

It may be further concluded that the polymerization of methyl methacrylate and *p*-fluorostyrene occurs by a free-radical mechanism, the kinetic results being in agreement with the proposed mechanism.

## ACKNOWLEDGMENT

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