

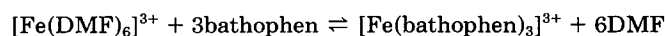
# Effect of Tris(bathophenanthroline)iron(III) on the Polymerization of Styrene

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## SYNOPSIS

The polymerization of styrene at 60°C initiated by 2,2'-azobisisobutyronitrile (AIBN) was studied in *N,N*-dimethylformamide (DMF) in the presence of tris(bathophenanthroline)iron(III) complex, [Fe(bathophen)<sub>3</sub>]<sup>3+</sup>. The complex was prepared *in situ* by mixing hexakis(*N,N*-dimethylformamide)iron(III) perchlorate with bathophenanthroline (systematic IUPAC nomenclature: 4,7-diphenyl-1,10-phenanthroline) in the molar ratio of 1 : 3. The equilibrium constant for



was  $3.12 \times 10^3 \text{ L}^3 \text{ mol}^{-3}$ . The transfer constant for bathophenanthroline was found to be  $0.38 \pm 0.01$  for the styrene/DMF system at 60°C. Mean velocity constant at 60°C for interaction of polystyryl radical with [Fe(bathophen)<sub>3</sub>]<sup>3+</sup> was  $3.73 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ . © 1996 John Wiley & Sons, Inc.

## INTRODUCTION

The interest in the field of kinetics of inhibition and ideal retardation by a transition metal salt in a non-aqueous media has received considerable attention recently.<sup>1-5</sup> A review of literature on the effect of metal ions in a polymerization system indicates that the metal ions play a significant role in the polymerization of vinyl monomers, but the part played by various ligands is not fully understood.<sup>6-8</sup> Bamford et al.<sup>1,2</sup> considered the role of complexation between FeCl<sub>3</sub> and DMF in the free radical polymerization process and concluded that the complexes are less active than the free salt. This aspect was also studied by Bengough and O'Neill,<sup>3</sup> and they have derived a kinetic treatment for systems in which two retarders, e.g., Cu(II) and Cu(I), were present. A similar result was also reported by Billingham et al.<sup>4</sup> Iron(III) chloride or copper(II) chloride, when dissolved in a non-aqueous solvent, pro-

duces a number of complexes; and the electron transfer from polymer free radical to the central metal ion was reported to be accelerated, even if one of the solvent ligand was substituted by Cl<sup>-</sup> ion. Apparently, two types of reactions are going on simultaneously<sup>1</sup>: (1) mutual termination of macroradicals and (2) termination by an ideal retarder. If reaction (2) predominates, definite induction periods are produced, and the rate constant for the interaction between polymer radicals with the ideal retarder can be calculated from the kinetic schemes with the aid of the stationary state assumption.<sup>5-7</sup> The effect of changing the type of organic ligands on the reactivity of the complex with central iron(III) and copper(II) cations towards polystyryl radical attack is very intriguing.<sup>5-7</sup> By using the group termination coefficient procedure on the kinetics of polymerization, recently, Bamford<sup>9,10</sup> reported that the mean radical sizes are reduced by the presence of a retarder and so the size-dependent termination is probably significant. This paper reports the kinetic investigations of polymerization of styrene in DMF at 60°C initiated by AIBN in the

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presence of tris(bathophenanthroline)iron(III) complex,  $[\text{Fe}(\text{bathophen})_3]^{3+}$ .

## EXPERIMENTAL

### Materials

AIBN, DMF, and styrene were purified and stored as described previously.<sup>7</sup> Bathophenanthroline (systematic IUPAC nomenclature: 4,7-diphenyl-1,10-phenanthroline) from Loba Chemie was used without further purification.  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$ , (A) was prepared as described previously.<sup>7</sup>

### Procedure

Rates of polymerization were measured dilatometrically at 60°C, with care being taken to degas the reactants thoroughly before sealing off the dilatometer.

The characterization of iron(III) complex in DMF was done on a JASCO model 7800 (CRT) spectrophotometer at room temperature.

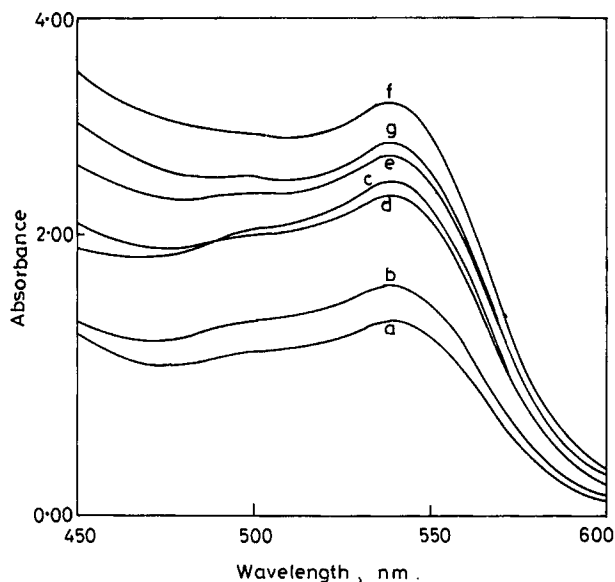
Gel permeation chromatography (GPC) was performed at 25°C with distilled THF as eluent using a Waters Associates GPC unit. Elution was conducted with a flow rate of 1 mL/min. The GPC column combination was  $10^6$ ,  $10^5$ ,  $10^4$ , and 500 Å. A universal calibration curve, based on elution volumes of 9 narrow MWD polystyrene samples from Waters Associates was used to compute the molecular weights of polymer samples.

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer PC series DSC 7 with 2–5 mg of polymer samples weighed in aluminum pans. Heating scans for the analysis of glass transition temperature ( $T_g$ ) of polymers were carried out at a heating rate of 10°C/min. All experiments were carried in a nitrogen atmosphere, and the measurement was started as soon as the heat flow in the DSC cell had stabilized.

## RESULTS AND DISCUSSION

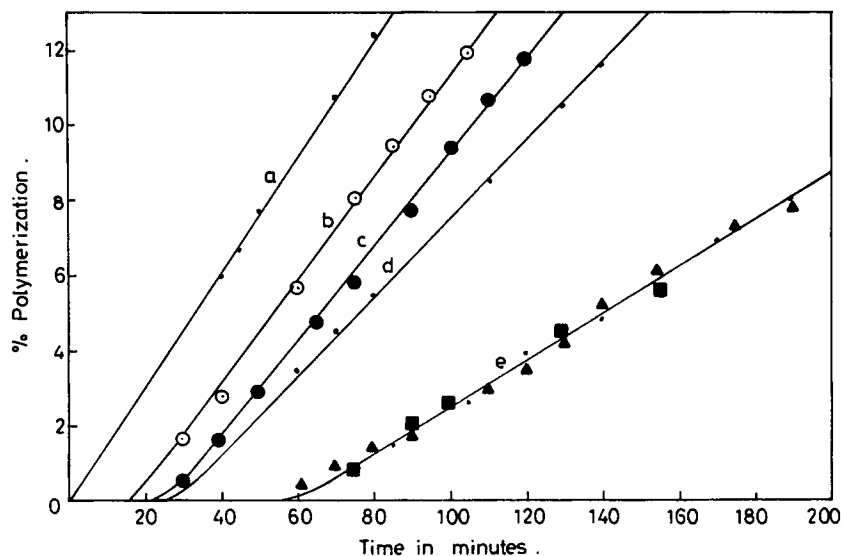
### Characterization of the Complex $[\text{Fe}(\text{bathophen})_3]^{3+}$

The formation of  $[\text{Fe}(\text{bathophen})_3]^{3+}$  with 1 : 3 molar ratio of [A] : [bathophen] was established spectrophotometrically.<sup>11</sup> A few of the experimental spectra in the visible regions are shown in Figure 1. The visible spectral curves of different solution with varied amounts of complex A and bathophen showed two

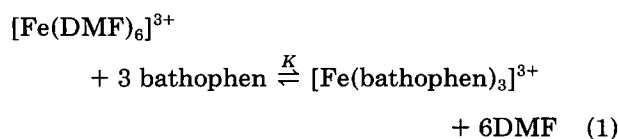


**Figure 1** Visible spectra of the complex  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$  [A] with added bathophen in DMF at 25°C. 100% of [A] =  $1.20 \times 10^{-3}$  mol L<sup>-1</sup>; 100% of the ligand [bathophen] =  $1.20 \times 10^{-3}$  mol L<sup>-1</sup>. Molar ratio [A] : [bathophen] for (a) = 9 : 1; (b) = 3 : 1; (c) = 1 : 1; (d) = 1.5 : 1; (e) = 1 : 1.5; (f) = 1 : 3; (g) = 1 : 4.

distinct peaks at  $335 \pm 3$  and 538.5 nm, whereas the complex A alone showed only one peak at 335 nm in DMF. Presumably, the peak at 335 nm exhibited by  $[\text{Fe}(\text{DMF})_6]^{3+}$  might be due to the charge-transfer (CT) transition from coordinated solvent ligand to *d*-orbital of Fe(III). CT complexes of transition metals involving ligand to metal electron transfer is expected from the availability of nonbonding or antibonding orbitals of the metal; the reverse process, however, also takes place. Up to 1 : 3 molar ratio of [A] : [bathophen], a shift in peak position at 335 nm was observed; but beyond 1 : 3 molar ratio of [A] : [bathophen], i.e., after complete conversion of  $[\text{Fe}(\text{DMF})_6]^{3+}$  into  $[\text{Fe}(\text{bathophen})_3]^{3+}$ , no such change was observed. The peak at 538.5 nm exhibited by  $[\text{Fe}(\text{bathophen})_3]^{3+}$  was due to *d-d* transition. By varying the molar ratios of [A] to [bathophen], it was found that the maximum absorbency at 538.5 nm occurred at 1 : 3 molar ratio of [A] to [bathophen], so the peak must be due to  $[\text{Fe}(\text{bathophen})_3]^{3+}$ . Whether the complex formed is inner or outer sphere or a simple salt remained obscure. However, for the sake of simplicity, it is assumed to be an inner complex  $[\text{Fe}(\text{bathophen})_3]^{3+}$ . Assuming this to be true, the molar extinction coefficient of  $[\text{Fe}(\text{bathophen})_3]^{3+}$  at 538.5 nm was found to be  $1.015 \times 10^3$  L mol<sup>-1</sup> cm<sup>-1</sup>. The equilibrium constant, *K*, for the formation of  $[\text{Fe}(\text{bathophen})_3]^{3+}$  may be represented as follows:



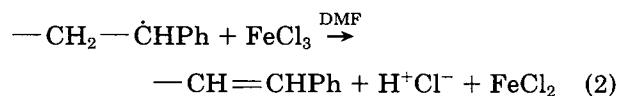
**Figure 2** Polymerization of styrene in DMF at 60°C initiated by AIBN and inhibited by various iron (III) species. [Styrene] = 1.75 mol L<sup>-1</sup>; [DMF] = 10.40 mol L<sup>-1</sup>; [AIBN] = 4.12 × 10<sup>-2</sup> mol L<sup>-1</sup>; [A] = 2.00 × 10<sup>-3</sup> mol L<sup>-1</sup>. Curve (a) = only AIBN. Molar ratios [A] : [bathophen] corresponding to curves (b) = 1 : 0.5; (c) = 1 : 1; (d) = 1 : 2. Curve (e): (●) = 1 : 3; (▲) = 1 : 4; (■) = 1 : 6.



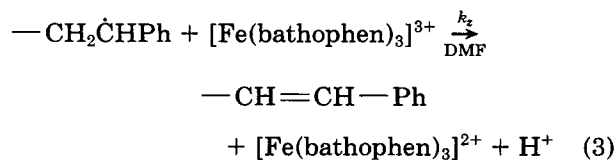
and the calculated value of  $K$  at 538.5 nm was found to be 3.12 × 10<sup>3</sup> L<sup>3</sup> mol<sup>-3</sup>.

#### Effect of Adding Bathophenanthroline to Complex A on the Rates of Polymerization

The reaction between polystyryl radical and FeCl<sub>3</sub> may be represented as follows<sup>1</sup>:



The polymerization of styrene initiated by AIBN at 60°C in DMF is retarded<sup>6</sup> by [Fe(DMF)<sub>6</sub>]<sup>3+</sup>, but the tris(bathophenanthroline) iron(III) complex, [Fe(bathophen)<sub>3</sub>]<sup>3+</sup>, produces well-defined induction periods. [Fe(bathophen)<sub>3</sub>]<sup>3+</sup> was produced *in situ* by adding quantitative amount of bathophen to complex A. Evidently, such a bidentate ligand must act as a conductor<sup>6-8</sup> for electron transfer from the polymer radical to the central metal ion. The reaction pathway between polystyryl radical and [Fe(bathophen)<sub>3</sub>]<sup>3+</sup> may be represented as follows:



where  $k_z$  is the rate constant for the interaction of polystyryl radical with [Fe(bathophen)<sub>3</sub>]<sup>3+</sup>.

It was found experimentally that bathophen in the absence of complex A had practically no effect on the AIBN-initiated polymerization of styrene at 60°C. However, when bathophen was added to a reaction mixture of constant composition of styrene, DMF, AIBN, and complex A, retarded polymerization was observed with well-defined induction periods. A few of the experimental curves of percent polymerization versus reaction time at 60°C is shown in Figure 2. Experimentally, it was found that the induction period increased gradually when the ratios of [A] : [bathophen] were increased and became steady when the ratio became 1 : 3. Beyond this ratio, the induction periods remained constant. In a polymerization system containing a powerful ideal retarder, the rate of polymerization during the induction period will be negligible until the concentration of the retarder is markedly reduced. These conditions will prevail until a sufficient amount of ideal retarder has been consumed so that the retarder can no longer effectively compete with monomer for all active radicals.<sup>12</sup> From this, it is apparent

that the ideal retarder must be almost completely consumed before the monomer can be polymerized. During the induction period, interaction between the polystyryl radical and  $[\text{Fe}(\text{bathophen})_3]^{3+}$  took place; after the induction period, i.e., after complete oxidation of polystyryl radical, the rate of polymerization increases until it finally reaches a stationary state value corresponding to the unretarded polymerization.

The efficiency of the initiator  $f$  was evaluated from the equivalent induction period  $\tau$  by analogy<sup>1</sup> with the equation

$$\tau = \frac{[[\text{Fe}(\text{bathophen})_3]^{3+}]}{2fk_d[\overline{\text{In}}]} = \frac{[[\text{Fe}(\text{bathophen})_3]^{3+}]}{I} \quad (4)$$

where  $\tau$  is defined as the time at which the rate of polymerization corresponds to a reaction time, at which the rate is 0.648 times the final maximum rate.<sup>1</sup> Thus,  $\tau$  is a more reliable quantity than the experimentally obtained induction period.  $I$  is the rate of initiation, and  $[\overline{\text{In}}]$  is the average concentration of the initiator during the reaction time. The experimental value of  $\tau$  was found to be 65 min, and using  $k_d$  as<sup>13</sup>  $0.95 \times 10^{-5} \text{ s}^{-1}$ ,  $f$  was found to be 0.66, which tallied well with the value in the literature.<sup>1,12</sup>

The experiment was repeated with [A] to [bathophen] molar ratio of 1 : 1, keeping [A] fixed, and it was found that the induction period was reduced almost to one third. The same trend of decrease of induction period was observed for the molar ratio of [A] to [bathophen] of 1 : 2. Therefore, it may be concluded that for a molar ratio of 1 : 3 of [A] : [bathophen], only  $[\text{Fe}(\text{bathophen})_3]^{3+}$  should exist in solution and it should act as an ideal retarder.<sup>1,12</sup>

The reaction scheme for free radical initiated vinyl polymerization in solution, in which termination occurred exclusively by combination and initiator concentration is constant, leads to the modified Mayo equation<sup>14</sup>

$$[\text{M}] \times \left( \frac{1}{\overline{DP}} - C_m \right) = C_s[\text{S}] + \overline{DP}_0 \quad (5)$$

where  $C_m$  and  $C_s$  are transfer constants for the monomer and additive,  $DP$  is the degree of polymerization and  $\overline{DP}_0$  is the value of  $\overline{DP}$  in the absence of transfer, and  $[\text{M}]$  and  $[\text{S}]$  are the mean concentrations of monomer and additive, respectively. A plot of the left hand side of eq. (5) against  $[\text{S}]$  is shown in Figure 3. Using a value of  $C_m$ <sup>12</sup> equal to

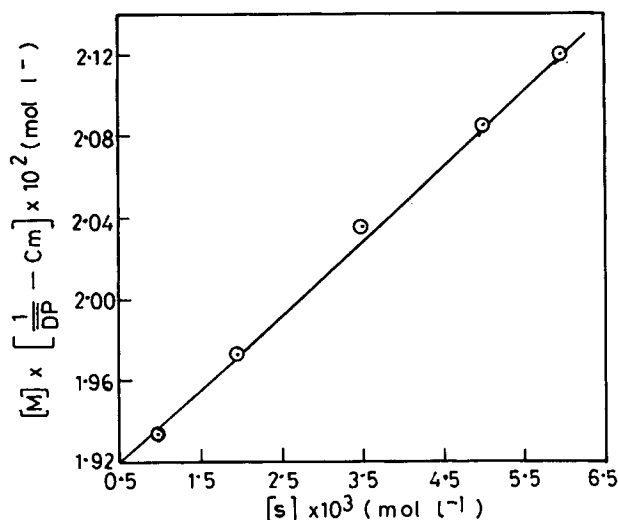


Figure 3 Plot of  $[\text{M}] \times (1/\overline{DP} - C_m) \times 10^2$  as a function of bathophenanthroline concentration  $[\text{S}]$ ; polymerization temperature =  $60^\circ\text{C}$ .

$6.00 \times 10^{-5}$ , from the slope of the plot, the value of  $C_s$  for bathophen was calculated as  $0.38 \pm 0.01$ . This value of transfer constant for bathophen indicated a low tendency of S to attack the monomer.

Assuming the steady-state approximation during the initial stages of polymerization of vinyl monomers retarded by an ideal retarder, Z, Bamford et al. showed that<sup>1,2</sup>

$$I = k_z[\text{R}'][\text{Z}] + 2k_t[\text{R}'^2] \quad (6)$$

where  $I$  is the rate of initiation.

The treatment is valid when (1) the initial rate is sufficiently small, (2) the retardation is ideal, and (3) the monomer and initiator concentrations are effectively constant.

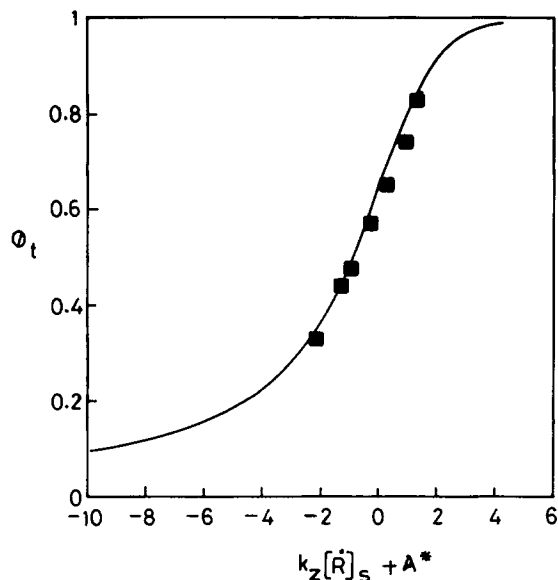
When the inhibitor is completely exhausted then  $[\text{Z}]$  is zero, and the concentration of the polymer radical attains a maximum value,  $[\text{R}'_s]$ , given by,

$$I = 2k_t[\text{R}'_s]^2 \quad (7)$$

The fraction of total termination occurring by mutual reactions of polymer radicals during the induction period is sufficiently small to be neglected, and a stationary state treatment leads to eq. (8).

$$-(1/\varnothing_t) + \ln[(1 + \varnothing_t)/(1 - \varnothing_t)] = k_z[\text{R}'_s]t + A^* \quad (8)$$

where  $\varnothing_t$  is the ratio of the rate at any time  $t$ ;  $R_p$ , in the presence of the retarder to the final maximum



**Figure 4** Reduced rate  $\phi_t$  as a function of time  $t$  expressed as  $k_z[\dot{R}]_s t + A^*$ ; experimental points (■); calculated curve (---); temperature = 60°C.  $\phi_t$  is the ratio of the rate at any time  $t$ ;  $R_p$ , in the presence of the retarder to the final maximum rate;  $R_{ps}$ , when the inhibition has disappeared, i.e.,  $\phi_t = R_p/R_{ps}$ ;  $k_z$  is the rate constant for the interaction of polystyryl radical with  $[\text{Fe}(\text{bathophen})_3]^{3+}$ , prepared *in situ*, and  $A^*$  is the integration constant. Molar ratio of  $[\text{A}] : [\text{bathophen}] = 1 : 3$ ;  $[\text{Styrene}] = 1.75 \text{ mol L}^{-1}$ ;  $[\text{AIBN}] = 4.12 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[\text{DMF}] = 10.40 \text{ mol L}^{-1}$ ;  $[\text{A}] = 2.00 \times 10^{-3} \text{ mol L}^{-1}$ .

rate;  $R_{ps}$ , when the inhibitor has disappeared, i.e.,  $\phi_t = R_p/R_{ps}$ ;  $k_z$  is the rate constant for the interaction of polystyryl radical with  $\text{Fe}^{3+}$ ; and  $A^*$  is the integration constant.

A detailed analysis of the rate curve measured with 1 : 3 molar ratio of  $[\text{A}] : [\text{bathophen}]$  was done by Bamford's method,<sup>1,2</sup> and a plot of  $\phi_t$  versus  $k_z[\dot{R}]_s t + A^*$  is shown in Figure 4, where it was assumed that only the  $[\text{Fe}(\text{bathophen})_3]^{3+}$  complex was present, and  $k_z$  refers to eq. (3). Reasonable agreement was found between experimental and theoretical plots when  $k_z[\dot{R}]_s$  was  $2.1 \times 10^{-3} \text{ s}^{-1}$  and  $A^*$  was  $-7.8$ . The theoretical curve was obtained by plotting  $\phi_t$  versus  $-(1/\phi_t) + \ln[(1 + \phi_t)/(1 - \phi_t)]$ , and the experimental one by plotting  $\phi_t$  versus  $k_z[\dot{R}]_s t + A^*$ .

The value of  $k_z$  was also calculated by Bengough's methods I and II, where  $0.8 > \phi_t > 0.15$  (Figs. 5 and 6). The details of these methods are given elsewhere.<sup>1,3</sup>

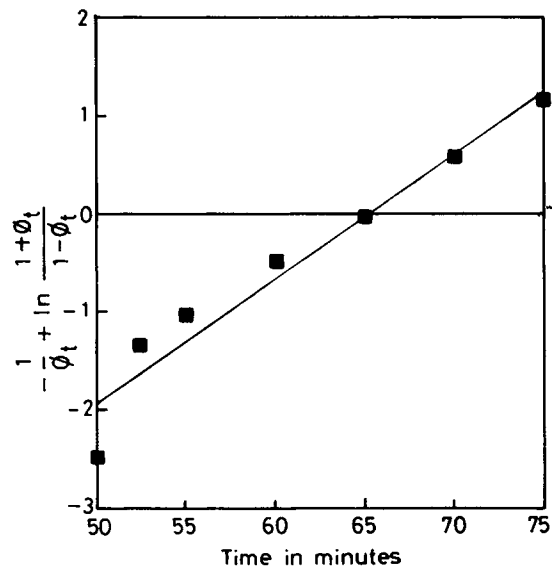
Experimental values of maximum rates of polymerization  $R_{ps}$  and concentration of monomer  $[\text{M}]$  were  $1.80 \times 10^{-5} \text{ mol L}^{-1} \text{ s}^{-1}$  and  $1.75 \text{ mol L}^{-1}$ , re-

spectively. Assuming<sup>12</sup>  $k_p$  to be  $176 \text{ L mol}^{-1} \text{ s}^{-1}$ , the value of  $k_z$  calculated by Bamford's and Bengough's methods I and II were  $3.74 \times 10^4$ ,  $3.71 \times 10^4$ , and  $3.77 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ , respectively. Hence, the average value of  $k_z$  would be  $3.73 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ . This agrees well with the rate of constants for the interaction of polystyryl radical with various complexes of iron(III).<sup>6-8</sup>

The rate constant for the interaction of polystyryl radical with  $[\text{Fe}(\text{DMF})_3]^{3+}$  was reported<sup>7</sup> to be  $847 \text{ L mol}^{-1} \text{ s}^{-1}$  at 60°C, which was much less than the corresponding value with  $[\text{Fe}(\text{bathophen})_3]^{3+}$ , which was  $3.73 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ .

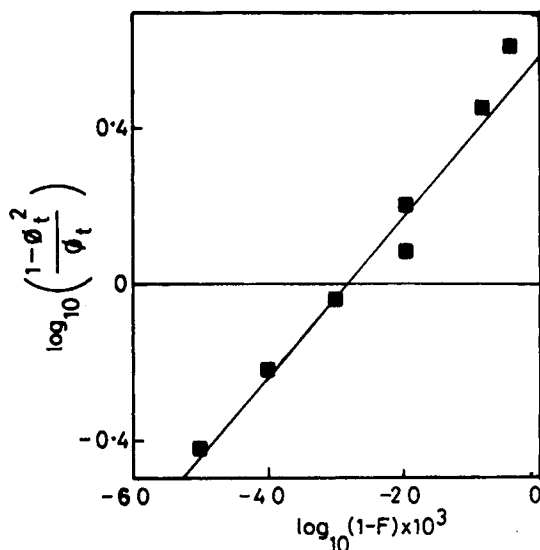
The effect of varying the  $[\text{A}] : [\text{bathophen}]$  molar ratio on the molecular weights of polystyrene are shown in Table I. As expected,<sup>8</sup> the molecular weight of polymers formed were found to decrease with increasing  $[\text{A}] : [\text{bathophen}]$  molar ratio.

Glass transition temperatures ( $T_g$ ) of polystyrene decrease with the increase of  $[\text{A}] : [\text{bathophen}]$  up to 1 : 3 molar ratio (Table I). This indicates that  $T_g$  of polystyrene is a function of its molecular weight.<sup>15,16</sup> Beyond 1 : 3 molar ratio of  $[\text{A}] : [\text{bathophen}]$ ,  $T_g$  remains unchanged with the variation of molar ratio. Therefore, it is difficult to draw a definite conclusion from these results.



**Figure 5** Analysis of the result for the polymerization of styrene initiated by AIBN at 60°C and inhibited by  $[\text{Fe}(\text{bathophen})_3]^{3+}$ , prepared *in situ*, where  $\phi_t = R_p/R_{ps}$ , and  $k_z$  is the rate constant for the interaction of polystyryl radical with  $[\text{Fe}(\text{bathophen})_3]^{3+}$ . Molar ratio of  $[\text{A}] : [\text{bathophen}] = 1 : 3$ ;  $[\text{Styrene}] = 1.75 \text{ mol L}^{-1}$ ;  $[\text{AIBN}] = 4.12 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[\text{DMF}] = 10.40 \text{ mol L}^{-1}$ ;  $[\text{A}] = 2.00 \times 10^{-3} \text{ mol L}^{-1}$ .

The mechanism of the interaction of the polymer radical with the  $[\text{Fe}(\text{bathophen})_3]^{3+}$  ion remains uncertain, but there is the possibility that the electron transfer occurs by conduction of electron through the bathophen ligands. Chelating nitrogen ligands form more stable complexes, and these strong field ligands form low spin complexes, which can be crystallized from solution with large anions such as perchlorate.<sup>17</sup> In the octahedral  $[\text{Fe}(\text{bathophen})_3]^{3+}$  ion, the low spin  $d^6$  configuration for  $\text{Fe}^{3+}$  provides the maximum number of  $t_{2g}$  electrons to take part in the bond formation and the lower oxidation,  $\text{Fe}^{2+}$  is stabilized. The  $[\text{Fe}(\text{bathophen})_3]^{3+}$  ion is therefore kinetically less reactive than the  $[\text{Fe}(\text{bathophen})_3]^{2+}$  ion. So  $[\text{Fe}(\text{bathophen})_3]^{3+}$  ion will behave as an ideal retarder when it reacts with the polystyryl radical. It may be concluded that the more extensive is the bonding is between the ligand and the central metal ion, the more rapid the electron transfer process from the free radical to the central metal ion will be.<sup>6</sup> An extended  $\pi$  bond may be formed between the coordinated ligand in the octahedral complex and a polystyryl radical by the interaction of metal  $d$ -orbital,  $\pi$ -orbital of the ligand, and  $2p$ -orbital of the polymer radical end carbon atom. An extended  $\pi$  bond of this type will markedly welcome electron transfer.<sup>6-8</sup>



**Figure 6** Analysis of the result for the polymerization of styrene initiated by AIBN at 60°C and inhibited by  $[\text{Fe}(\text{bathophen})_3]^{3+}$ , prepared *in situ*, where  $\phi_t = R_p/R_{ps}$ , and  $F$  is the fraction conversion of the monomer to polymer; i.e.,  $F = ([M]_0 - [M])/[M]_0$ , and  $k_z$  is the rate constant for the interaction of polystyryl radical with  $[\text{Fe}(\text{bathophen})_3]^{3+}$ . Molar ratio of  $[\text{A}] : [\text{bathophen}] = 1 : 3$ ,  $[\text{Styrene}] = 1.75 \text{ mol L}^{-1}$ ;  $[\text{AIBN}] = 4.12 \times 10^{-2} \text{ mol L}^{-1}$ ;  $[\text{DMF}] = 10.40 \text{ mol L}^{-1}$ ;  $[\text{A}] = 2.00 \times 10^{-3} \text{ mol L}^{-1}$ .

**Table I** Molecular Weight ( $\bar{M}_n$ ) and Glass Transition Temperature ( $T_g$ ) of Polystyrene Determined by GPC and DSC Respectively<sup>a</sup>

[A] : [bathophen]	$\bar{M}_n$	$T_g$ (°C)
Without additive	45,800	107.9
1 : 0.5	40,900	104.5
1 : 1	37,100	98.6
1 : 3	33,600	97.0
1 : 6	31,800	96.3

<sup>a</sup>  $[\text{Styrene}] = 1.75 \text{ mol L}^{-1}$ ;  $[\text{A}] = 2.00 \times 10^{-3} \text{ mol L}^{-1}$ ;  $[\text{AIBN}] = 4.12 \times 10^{-2} \text{ mol L}^{-1}$ ; temperature = 60°C.

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