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## Interaction of Polystyryl Radical with Tris Azido-Iron(III) Complex

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### ABSTRACT

The polymerization of styrene initiated by 2,2'-azobisisobutyronitrile (AIBN) had been studied in *N,N*-dimethylformamide (DMF) at 60°C in presence of tris azido-iron(III) complex. The complex was prepared in situ by mixing solid sodium azide with hexakis(*N,N*-dimethylformamide)iron(III) perchlorate,  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$ , in the ratio 3:1. The nature of the complex formed was established by Job's method. The equilibrium constant for  $\text{Fe}^{3+} + 3\text{N}_3^- \rightleftharpoons \text{Fe}(\text{N}_3)_3$  determined by the limiting logarithmic method is  $6.14 \times 10^6$  liter<sup>3</sup>/mole<sup>3</sup>. The velocity constant for the polystyryl radical towards the complex is  $3.13 \times 10^4$  liter/mole-sec.

### INTRODUCTION

The interaction of polystyryl radical with ferric salts [1, 2] and complexes of iron(III) [3-6] are well known. It was established that hexakis(*N,N*-dimethylformamide)iron(III) perchlorate,  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$ , (A) retards the rate of polymerization of styrene [7]. This paper reports the polymerization of styrene in DMF at 60°C initiated by AIBN in the presence of ferric azide. The complex was characterized by Job's method [8] and the equilibrium constant was determined by the limiting logarithmic method [8].

## EXPERIMENTAL

Materials

The initiator, 2,2'-azobisisobutyronitrile (AIBN) [9], N,N-dimethylformamide (DMF) [9], and styrene [10] were purified as described previously. The monomer and DMF were finally dried over Linde 4 Å Molecular Sieves, and the monomer was stored at low temperature under oxygen-free nitrogen. Sodium azide was used without further purification. The method of preparation and purification of hexakis-(N,N-dimethylformamide)iron(III) perchlorate [ $\text{Fe}(\text{DMF})_6$ ] ( $\text{ClO}_4$ )<sub>3</sub>, has already been reported [6].

Procedure

Rates of polymerization were measured dilatometrically and gravimetrically in the usual way [9], care being taken to degas the reactants thoroughly before sealing off the dilatometer. Polymers were dried under vacuum after precipitation in excess methanol.

The intrinsic viscosity of polymers in A. R. toluene were determined at 30°C by using a Ubbelohde viscometer [10]. The number-average degrees of polymerization  $\overline{DP}$ , were calculated from corresponding intrinsic viscosities  $[\eta]$ , by use of the relationship of Bawn et al. [11]:

$$[\eta] = 1.729 \times 10^{-4} (104.1 \times \overline{DP})^{0.71} \text{ dl/g}$$

The characterization of the iron(III) complex in DMF by Job's method and the equilibrium constant by limiting logarithmic method were determined with a Specord UV-VIS spectrometer at room temperature at a fixed wavelength of 475 nm.

## RESULTS AND DISCUSSION

Spectrophotometrically the formation of  $\text{Fe}(\text{N}_3)_3$  with the mole ratio of 3:1 of  $[\text{N}_3^-]:[\text{A}]$  was established by Job's method of continuous variation (Fig. 1). By varying the mole ratios of  $\text{N}_3^-$  to A it was found that the maximum absorbancy occurred at the mole ratio of  $[\text{N}_3^-]:[\text{A}]$  of 3:1. The appearance of an isosbestic point at 400 nm suggests the formation of only one complex, tris azido-iron(III). The equilibrium constant was determined by the limiting logarithmic method where the ratio of the slopes of the curves II and I was 3:1 (Fig. 2). Whether the complex formed is inner or outer sphere or simple salt remains obscure. For simplicity it was assumed to be a simple salt  $\text{Fe}(\text{N}_3)_3$ .

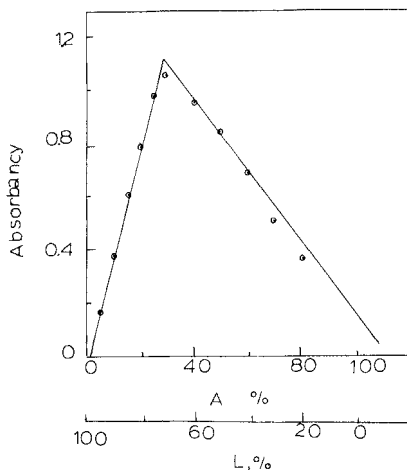


FIG. 1. Job's method of continuous variation. 100% of the complex,  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$ ,  $[\text{A}] = 7.87 \times 10^{-4}$  mole/liter; 100% of the ligand, azide,  $[\text{N}_3^-] = 7.87 \times 10^{-4}$  mole/liter. Solvent = DMF; experimental wavelength = 475 nm.

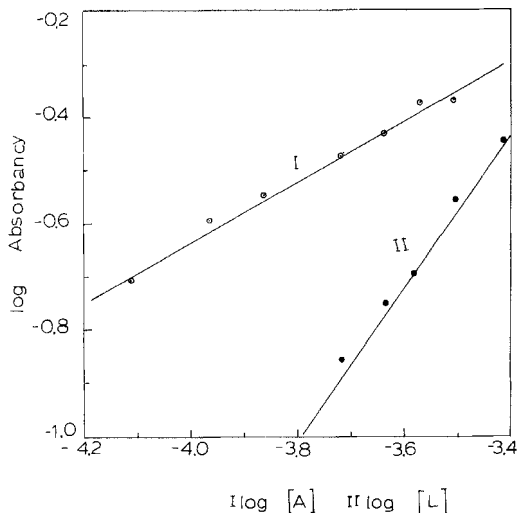


FIG. 2. Limiting logarithmic method: (I) concentration of the ligand,  $\text{N}_3^-$ , is kept constant.  $[\text{N}_3^-] = 3.935 \times 10^{-4}$  mole/liter; (II) concentration of the complex  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$ , A, is kept constant,  $[\text{A}] = 3.935 \times 10^{-4}$  mole/liter. Solvent = DMF; experimental wavelength = 475 nm.

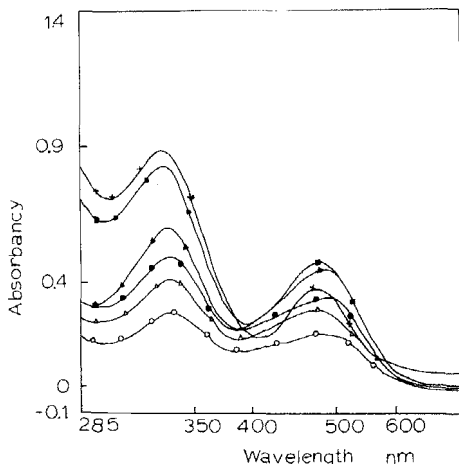
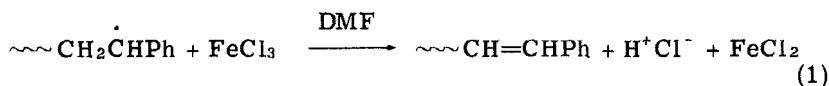


FIG. 3. Ultraviolet and visible spectra of the complex,  $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$ , A, with added  $\text{NaN}_3$  in DMF at  $30^\circ\text{C}$ : ( $\circ$ )  $[\text{A}]:[\text{N}_3^-] = 10:90$ ; ( $\triangle$ )  $[\text{A}]:[\text{N}_3^-] = 15:85$ ; ( $\bullet$ )  $[\text{A}]:[\text{N}_3^-] = 20:80$ ; ( $\times$ )  $[\text{A}]:[\text{N}_3^-] = 50:50$ ; ( $\blacktriangle$ )  $[\text{A}]:[\text{N}_3^-] = 60:40$ ; ( $\blacksquare$ )  $[\text{A}]:[\text{N}_3^-] = 25:75$ . 100% of A  $[\text{A}] = 7.87 \times 10^{-4}$  mole/liter; 100% of the ligand, azide,  $[\text{N}_3^-] = 7.87 \times 10^{-4}$  mole/liter.

Some typical experimental spectra in the ultraviolet and visible regions are shown in Fig. 3. The spectra were recorded from 280 nm since DMF, which absorbs too strongly below 270 nm [12], was used as the solvent. The peaks at 335 nm and 475 nm may be associated with  $\text{Fe}(\text{N}_3)_3$  and form due to charge-transfer [13] and d-d transitions, respectively. Assuming this to be true, the molar extinction coefficient of  $\text{Fe}(\text{N}_3)_3$  at 335 nm was found to be  $8.74 \times 10^3$  liter/mole-cm and at 475 nm to be  $4.89 \times 10^3$  liter/mole-cm. The value of the equilibrium constant at 475 nm was found to be  $6.14 \times 10^6$  liter<sup>3</sup>/mole<sup>3</sup>.  $\text{NaN}_3$  in absence of complex A, had no effect on the polymerization of styrene initiated by AIBN. However,  $\text{N}_3^-$  in the presence of complex A retarded the rate of polymerization (Fig. 4).

The interaction of polystyryl radical with  $\text{FeCl}_3$  and complexes of  $\text{Fe}(\text{III})$  is well known [1-7].



Similarly the interaction of polystyryl radical with  $\text{Fe}(\text{N}_3)_3$  may be represented by Eq. (2):

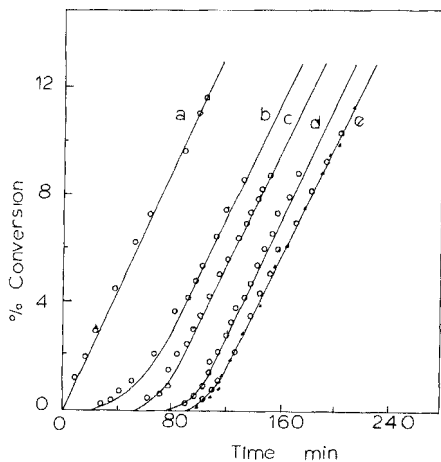
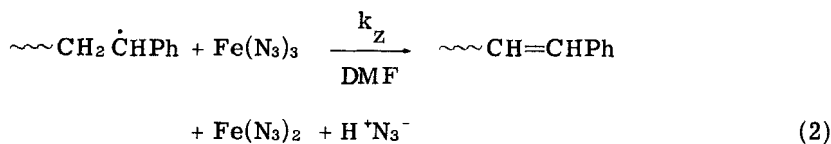
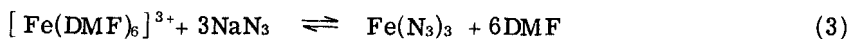


FIG. 4. Polymerization of styrene in DMF at 60°C, initiated by AIBN and inhibited by various iron(III) species: (a) No added iron compound, azide,  $[N_3^-] = 7.87 \times 10^{-3}$  mole/liter; (b) only the complex, A,  $[A] = 7.87 \times 10^{-3}$  mole/liter; (c) mole ratio  $[A]:[N_3^-] = 1:1$ ; (d) mole ratio  $[A]:[N_3^-] = 1:2$ ; (e) mole ratio,  $[A]:[N_3^-] = 1:3$  ( $\circ$ ) and  $[A]:[N_3^-] = 1:5$  ( $\blacktriangle$ ).  $[Styrene] = 1.673$  mole/liter;  $[AIBN] = 7.62 \times 10^{-2}$  mole/liter;  $[DMF] = 10.40$  mole/liter.



On addition of  $\text{NaN}_3$  to the complex A,  $\text{Fe}(\text{N}_3)_3$  was expected to form; this reaction may be represented by Eq. (3).



A high value of the equilibrium constant for Eq. (3) indicates that all the  $\text{Fe}(\text{III})$  ions should exist as  $\text{Fe}(\text{N}_3)_3$  when the mole ratio of  $[N_3^-]$  to  $[A]$  would be 3:1. The efficiency of the initiator was calculated from the induction period,  $\tau$ .

$$\begin{aligned}
 \tau &= [\text{Fe}(\text{N}_3)_3] / 2k_d f [\bar{\text{In}}] \\
 &= [\text{Fe}(\text{N}_3)_3] / I
 \end{aligned} \quad (4)$$

where  $\tau$  is defined as the time at which the rate of polymerization corresponds to the reaction time at which the rate is 0.648 times the maximum rate [1].  $I$  is the rate of initiation and  $[\bar{In}]$  is the average concentration of the initiator, AIBN, during the reaction time. Using  $k_d$  as  $0.95 \times 10^{-5} \text{ sec}^{-1}$  [4],  $f$  was found to be 0.76, which is in agreement with literature values [1, 3].

The experiment was repeated with a  $[N_3^-]:[A]$  mole ratio of 1:1. On keeping the A fixed, it was found that the induction period was reduced almost to one third if the ratio be changed from 3:1 to 1:1. This suggested that for a mole ratio of 3:1 only  $Fe(N_3)_3$  existed in solution and acted as an ideal retarder [14, 15]. The plot of  $[N_3^-]$  in the presence of A against  $\tau$  up to a mole ratio of  $[N_3^-]:[A] = 3:1$  produced a straight line. Beyond that ratio, however, the induction period did not change.

If  $[A]_0$  and  $[N_3^-]_0$  are the initial concentrations of A and  $N_3^-$ , respectively, and if the equilibrium constant is high, then the concentrations of  $[Fe(DMF)_6]^{3+}$  and  $[Fe(N_3)_3]$  ions are  $[A]_0 - \frac{1}{3}[N_3^-]_0$  and  $\frac{1}{3}[N_3^-]_0$ , respectively, when equilibrium is established. The polymerization of styrene initiated by AIBN is known [7] to be retarded by A. By analogy with Eq. (4) we have,

$$\begin{aligned} \tau &= \frac{k' \{ [A]_0 - \frac{1}{3} [N_3^-]_0 \}}{I} + \frac{\frac{1}{3} [N_3^-]_0}{I} \\ &= \frac{k' [A]_0}{I} + \frac{1}{3} [N_3^-]_0 \left( \frac{1}{I} - \frac{k'}{I} \right) \end{aligned} \quad (5)$$

where the first term on the right-hand side of Eq. (5) is the conversion factor of  $[Fe(DMF)_6]^{3+}$  to  $Fe(N_3)_3$  and  $k'$  is an arbitrary constant. In accordance with the prediction, the plot of  $\tau$  against  $[N_3^-]$  was linear up to a mole ratio of  $[N_3^-]:[A] = 3:1$ . As the line passes through the origin, the conversion factor is zero. This indicates that all the added  $N_3^-$  reacted with A instantaneously for the formation of  $Fe(N_3)_3$  and so the equilibrium constant for the reaction (3) must be high.

The usual reaction scheme for vinyl polymerization in solution, using a constant initiator concentration but varied additive concentration, leads to Eq. (6):

$$[M] \left[ \frac{1}{\overline{DP}} - C_m \right] = C_1 [I'] + \text{constant} \quad (6)$$

where  $C_m$  and  $C_1$  are transfer constants to monomer and additive respectively,  $\overline{DP}$  is the degree of polymerization, and  $[M]$  is the concentration of monomers. If, as observed for other systems [9, 15],

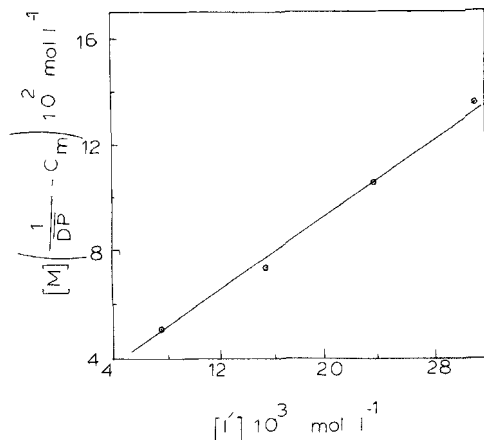


FIG. 5. Plot of  $[M] \left[ \left( \frac{1}{\overline{DP}} \right) - C_m \right] \times 10^2$  as a function of additive concentration,  $[I']$ . Temperature of polymerization =  $60^\circ\text{C}$ .

the initiator efficiency and velocity constant involved remain constant, then a plot of the left-hand side of Eq. (6) against values of the concentration of additive  $[I']$ , should be a straight line with a slope equal to  $C_i$ . Experimentally, with a constant composition of styrene and DMF, a straight line was obtained for  $\text{N}_3^-$  (Fig. 5). On assuming  $[16] C_m = 6.023 \times 10^{-5}$ ,  $C_i$  for  $\text{NaN}_3$  was  $3.40 \times 10^{-2}$ . The small value of transfer constant for  $\text{NaN}_3$  indicates a low value of  $[I']$  to attack the monomer.

A more detailed analysis of a single rate curve with a 3:1 mole ratio of  $\text{N}_3^-$  to A was done by the methods of Bamford et al. [1, 14] (Fig. 6) and Bengough et al. [17, 18] (Figs. 7 and 8). Details of the methods of analysis were given elsewhere [1, 5, 14, 17-19]. Experimental values of maximum rate of polymerization  $R_{pS}$  and concentration of monomer  $[M]$  were  $4.13 \times 10^{-5}$  mole/liter-sec and 1.673 mole/liter, respectively. Reasonable agreement was found between the experimental and theoretical plots when  $k_z [R\cdot]_s$  and  $A^*$  were  $4.3 \times 10^{-3}$  liter/mole-sec and -30.6, respectively, for Bamford's method. On assuming  $k_p$  to be 176 liter/mole-sec [20],  $k_z$  was calculated from the relation (7):

$$k_z/k_p = k_z [R\cdot]_s [M] / R_{pS} \quad (7)$$



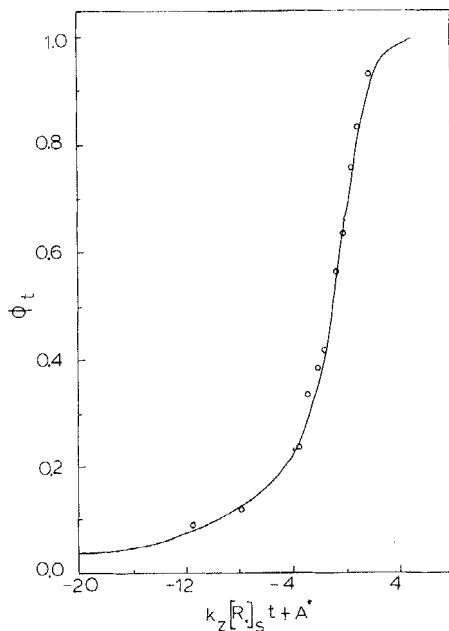


FIG. 6. Reduced rate  $\phi_t$  as a function of time: (o) experimental points; (—) calculated curve. Mole ratio of  $[A]:[N_3^-] = 1:3$ , temperature =  $60^\circ\text{C}$ ;  $[\text{Styrene}] = 1.673$  mole/liter;  $[\text{DMF}] = 10.40$  mole/liter;  $[\text{AIBN}] = 7.62 \times 10^{-2}$  mole/liter;  $[A] = 7.87 \times 10^{-3}$  mole/liter.

The value of  $k_z$  at  $60^\circ\text{C}$  calculated by Bamford and Bengough's methods I and II were  $3.06 \times 10^4$ ,  $3.06 \times 10^4$ , and  $3.26 \times 10^4$  liter/mole-sec, respectively. Hence the average value of  $k_z$  would be  $3.13 \times 10^4$  liter/mole-sec at  $60^\circ\text{C}$ . This agrees well with the rate constants for the interaction of polystyryl radical with complexes of iron(III) [3-7].

The rate constants for the interaction of polystyryl radical with  $[\text{Fe}(\text{DMF})_6]^{3+}$  was reported to be 847 liter/mole-sec at  $60^\circ\text{C}$ , but the same for the interaction between polystyryl radical and  $\text{Fe}(\text{N}_3)_3$  was found to be  $3.13 \times 10^4$  liter/mole-sec at  $60^\circ\text{C}$ . Above  $25^\circ\text{C}$  the value for interaction between  $\text{Fe}^{2+}$  and  $\text{Fe}(\text{N}_3)_3$  was reported to be  $1.9 \times 10^3$  [21]. The mechanism of interaction of the polystyryl radical with  $\text{Fe}(\text{N}_3)_3$  ion remain uncertain, but there is the possibility that electron transfer between iron(II) and iron(III) ions may be facilitated by a bridge activated complex mechanism. It may be assumed that azide ion may act as a conductor during the electron transfer process. The rates of polymerization will be high since the ligand is unsaturated and  $\pi$  bonding. The type of possible metal

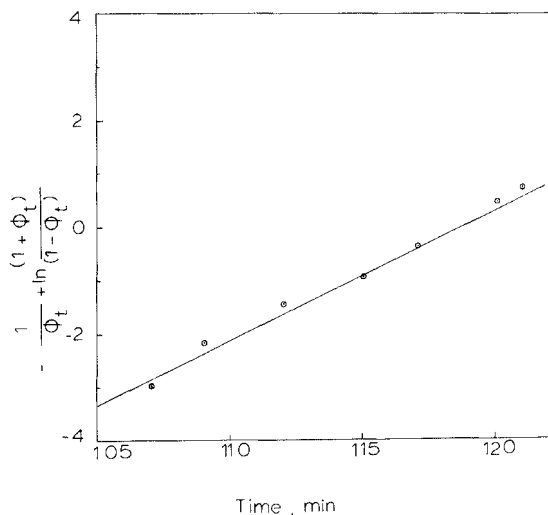


FIG. 7. Plot of  $-\frac{1}{\phi_t} + \ln\left[\frac{1 + \phi_t}{1 - \phi_t}\right]$  as a function of time for the polymerization of styrene initiated by AIBN at  $60^\circ\text{C}$ , inhibited by  $\text{Fe}(\text{N}_3)_3$ , prepared in situ. Mole ratio of  $[\text{A}]:[\text{N}_3^-] = 1:3$ ;  $[\text{Styrene}] = 1.673$  mole/liter;  $[\text{DMF}] = 10.40$  mole/liter;  $[\text{AIBN}] = 7.62 \times 10^{-2}$  mole/liter;  $[\text{A}] = 7.87 \times 10^{-3}$  mole/liter.

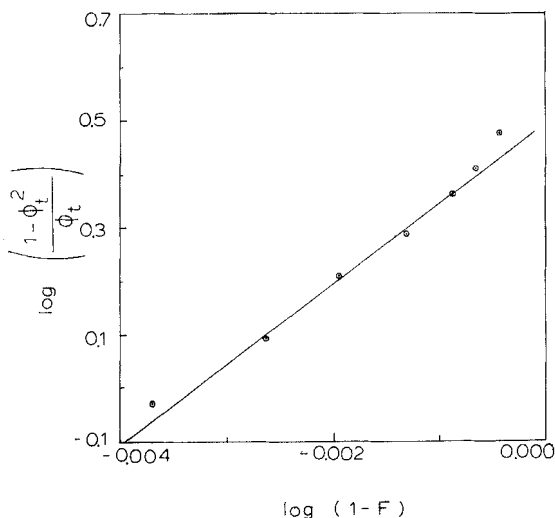


FIG. 8. Plot of  $\log\left[\frac{1 - \phi_t^2}{\phi_t}\right]$  as a function of  $\log(1 - F)$  for the polymerization of styrene initiated by AIBN at  $60^\circ\text{C}$ , inhibited by  $\text{Fe}(\text{N}_3)_3$ , prepared in situ. Mole ratio of  $[\text{A}]:[\text{N}_3^-] = 1:3$ ;  $[\text{Styrene}] = 1.673$  mole/liter;  $[\text{DMF}] = 10.40$  mole/liter;  $[\text{AIBN}] = 7.62 \times 10^{-2}$  mole/liter and  $[\text{A}] = 7.87 \times 10^{-3}$  mole/liter.

ligand interaction may be  $p\pi - d\pi$  [22]. Back donation from the metal d-orbital to p-orbital of nitrogen may also occur. The ability of the ligand to form  $\pi$  bonds by using electron density from the appropriate d-orbital of  $Fe^{3+}$  will dissipate unfavorable charge distribution around metal ion. An extended  $\pi$  bond may be formed between the coordinated ligands in the octahedral complex and a polystyryl radical by interaction of metal d-orbitals,  $\pi$  orbitals of the ligand and the 2p orbitals of the polymer radical end carbon atom. An extended  $\pi$  bond of this type in transition state will markedly facilitate electron transfer.

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