

Effect of Tris(bipyridyl)iron(III) Complex on the Polymerization of Styrene

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Received 12 March 1979; revised and accepted 3 August 1979

The polymerization of styrene initiated by 2,2'-azobisisobutyronitrile has been studied in N,N-dimethylformamide at 60° in the presence of tris(bipyridyl)iron(III) perchlorate. The complex is prepared *in situ* by mixing bipyridyl and hexakis(N,N-dimethylformamide)iron(III) perchlorate in the ratio of 3:1. The nature of the complex formed has been established by Job's method. The equilibrium constant for the reaction, $\text{Fe}^{3+} + 3\text{Bipy} \rightleftharpoons [\text{Fe}(\text{Bipy})_3]^{3+}$ is $4.0118 \times 10^4 \text{ litre}^3 \text{ mol}^{-3}$. The velocity constant for the reaction of polystyryl radical with $[\text{Fe}(\text{Bipy})_3]^{3+}$ at 60° is $5.564 \times 10^4 \text{ litre mol}^{-1} \text{ sec}^{-1}$.

THE interaction of polystyryl radical with ferric salts^{1,2} and complexes of iron(III) has been reported by many workers³⁻⁶. It has been 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 styrene⁷. This paper reports the polymerization of styrene in N,N-dimethylformamide (DMF) at 60° initiated by 2,2'-azobisisobutyronitrile (AIBN) in the presence of iron(III) bipyridyl perchlorate. The complex has been characterized by Job's method and the equilibrium constant determined by the limiting logarithmic method⁸.

Materials and Methods

The initiator, 2,2'-azobisisobutyronitrile (AIBN)⁹, N,N-dimethylformamide (DMF)⁹ and styrene¹⁰ were purified as described previously. The monomer and DMF were finally dried over Linde (4A°) molecular sieve, and the monomer was stored at low temperature under oxygen-free nitrogen atmosphere. Analar grade 2,2'-bipyridyl was used without further purification.

The method of preparation and purification of hexakis(N,N-dimethylformamide)iron(III) perchlorate $[\text{Fe}(\text{DMF})_6](\text{ClO}_4)_3$, (A), has already been described⁶.

The rates of polymerization were determined dilatometrically and gravimetrically in the usual way⁹. Before sealing off the dilatometer, the reactants were completely deoxygenated. The polymers were precipitated in excess of absolute alcohol and dried under vacuum.

The intrinsic viscosities of polymer were determined in toluene (AR) at 30° using an Ubbelohde viscometer.

The values of number average degree of polymerization \overline{DP} were calculated from the corresponding intrinsic viscosities $[\eta]$, by the use of the relationship of Bawn *et al.*¹¹.

$$[\eta] = 1.729 \times 10^{-4} (104.1 \times \overline{DP})^{0.71} 100 \text{ d.l.g}^{-1}$$

The characterization of the iron(III) complex by Job's method and determination of the equilibrium constant by the limiting logarithmic method, were carried out using a SPECORD UV-VIS spectrometer at a fixed wavelength of 500 nm.

Results and Discussion

The formation of $[\text{Fe}(\text{Bipy})_3](\text{ClO}_4)_3$ was established spectrophotometrically by Job's method of continuous variation. It was found that the maximum absorbance occurred at the $[\text{Bipy}] : [\text{A}]$ molar ratio of 3:1 at 500 nm. The appearance of an isobestic point supports the conclusion that only one complex namely, tris(bipyridyl)iron(III) is formed. The equilibrium constant was determined by the limiting

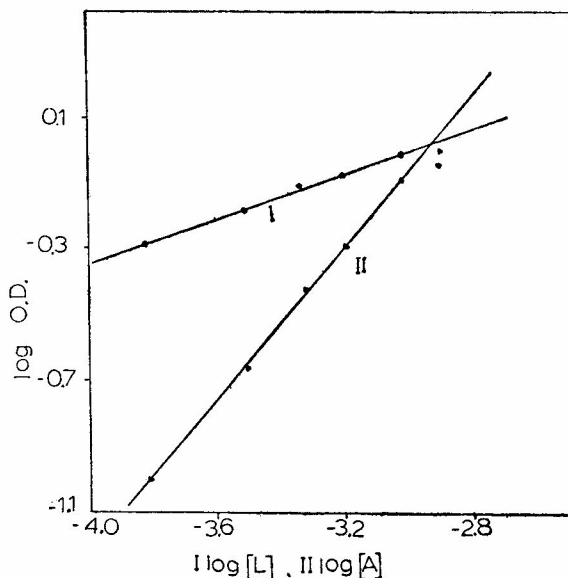
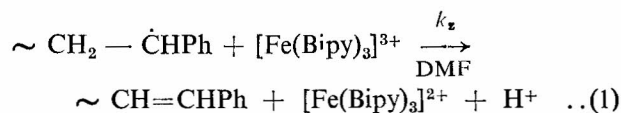


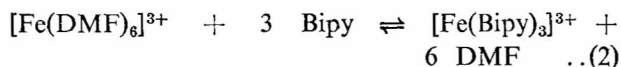
Fig. 1 — Plots of log O. D. versus log [L] or log [A] in the limiting logarithmic method [Curve I : concentration of the ligand L is kept constant at $[L] = 2.5 \times 10^{-3} \text{ M}$. Curve II : concentration of the complex A is kept constant at $[A] = 2.5 \times 10^{-3} \text{ M}$ solvent = DMF]

logarithmic method where the ratio of the slopes of the curves (II) and (I) was 3:1 (Fig. 1). At the fixed wavelength of 500 nm the value of the equilibrium constant was 4.0118×10^4 litre³ mol⁻³. The molar extinction coefficient of $[\text{Fe}(\text{Bipy})_3](\text{ClO}_4)_3$ is 2666.66 at 357 nm and 2166.66 at 500 nm.

The interaction of polystyryl radical with FeCl_3 and chloro complexes of iron(III) is well known¹⁻⁷. The same type of reaction is expected with $[\text{Fe}(\text{Bipy})_3]^{3+}$ (Eq. 1),



On addition of bipyridyl to the complex A, $[\text{Fe}(\text{Bipy})_3]^{3+}$ is expected to form and the reaction may be represented as (Eq. 2),



The high value of the equilibrium constant for the reaction. (2) indicates that all the Fe(III) ions should exist as $[\text{Fe}(\text{Bipy})_3]^{3+}$ when the molar ratio of $[\text{Bipy}]$ to $[\text{A}]$ would be 3:1. Hence,

$$\tau = \frac{[\text{Fe}(\text{Bipy})_3]^{3+}}{2k_d f [\text{I}_n]} = \frac{[\text{Fe}(\text{Bipy})_3]^{3+}}{I} \dots (3)$$

where τ , the induction period, is the time at which the rate of polymerization corresponds to $0.648 \times$ maximum rate, I is the rate of initiation and $[\text{I}_n]$ is the average concentration of the initiator, AIBN, during the reaction time. Taking k_d as 0.94×10^{-5} sec⁻¹ (ref 4), f the efficiency is found to be 0.52 which is in agreement with the literature value^{1,3}.

The experiment was repeated with $[\text{Bipy}] : [\text{A}]$ molar ratio 1:1, keeping $[\text{A}]$ fixed. It was found that the induction period τ , was reduced almost to one-third of the previous value (Fig. 2). This suggests that for a $[\text{Bipy}] : \text{A}$ ratio of 3:1 only $[\text{Fe}(\text{Bipy})_3]^{3+}$ exists in solution and it acts as an ideal retarder. The plot of $[\text{Bipy}]$ in the presence of constant $[\text{A}]$ against τ upto $[\text{Bipy}] : [\text{A}]$ molar ratio of 3:1 produced a straight line.

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

$$\begin{aligned} \tau &= \frac{k' [\text{A}]_0 - \frac{1}{3} [\text{Bipy}]_0}{I} + \frac{\frac{1}{3} [\text{Bipy}]_0}{I} \\ &= \frac{k' [\text{A}]_0}{I} + \frac{1}{3} [\text{Bipy}]_0 \left(\frac{1}{I} - \frac{k'}{I} \right) \dots (4) \end{aligned}$$

where the first term on the right hand side is the conversion factor, which allows for the conversion

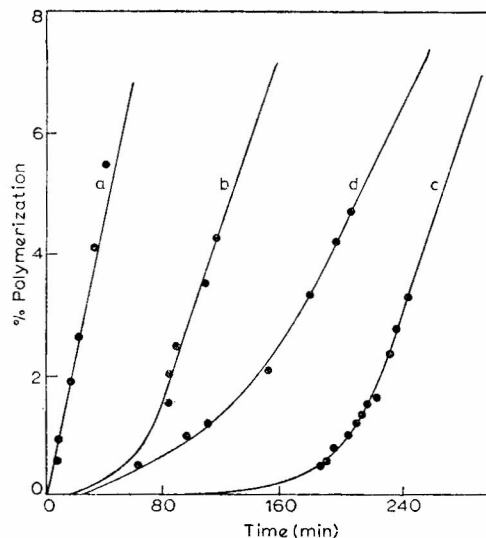


Fig. 2 — Polymerization of styrene in DMF at 60° initiated by AIBN and retarded by various Fe (III) species at $[\text{Styrene}] = 2.49M$, $[\text{AIBN}] = 7.87 \times 10^{-2} M$ and $[\text{DMF}] = 8.792M$ {Curve a : no added iron compound, Bipy, $[\text{L}] = 2.361 \times 10^{-2} M$. Curve b : $[\text{L}] : [\text{A}] = 1:1$. Curve c : $[\text{L}] : [\text{A}] = 3:1$. curve d : $[\text{L}] : [\text{A}] = 2:1$. Conc. of A = $3.935 \times 10^{-8} M$ in 6, c and d}.

of $[\text{Fe}(\text{DMF})_6]^{3+}$ to $[\text{Fe}(\text{Bipy})_3]^{3+}$ and k' is an arbitrary constant. In accordance with the prediction, the plot of τ against $[\text{Bipy}]$ is linear upto $[\text{Bipy}] : [\text{A}]$ molar ratio of 3:1. Since the line passes through the origin, the value of the conversion factor and hence k' must be zero. This indicates that all the added Bipy reacts with A to form $[\text{Fe}(\text{Bipy})_3]^{3+}$ and so the equilibrium constant for the reaction (2) must be high.

The usual reaction scheme for vinyl polymerization in solution using a constant [initiator] but varying [additive], leads to Eq. 5,

$$[\text{M}] (1/\overline{\text{DP}} - C_m) = C_i [\text{I}]' + \text{constant} \dots (5)$$

where C_m and C_i are the transfer constants to the monomer and the additive respectively, $\overline{\text{DP}}$ is the degree of polymerization and $[\text{M}]$ is the concentration of monomer. If, as observed for other systems^{9,12}, the initiator efficiency and velocity constant involved remain constant, then a plot of the left hand side of Eq. 5 against the additive, $[\text{I}]'$ should be linear, with a slope equal to C_i .

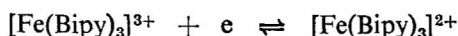
Experimentally, at a constant $[\text{Styrene}]$ and $[\text{DMF}]$, a straight line was obtained for bipyridyl. Taking the value of $C_m = 6.023 \times 10^{-5}$ (ref. 14) the transfer constant for bipyridyl, C_i , was found to be 1.2×10^{-3} . The small value of transfer constant for bipyridyl indicates that bipyridyl alone has little tendency to attack the monomer.

A more detailed analysis of a single rate curve with a 3:1 molar ratio of bipyridyl to A was done using the methods of Bamford *et al.*^{11,13} and Bengough *et al.*^{14,15}. Details of the methods of analysis are given elsewhere^{1,5,14,15}. The value of k_x at 60° calculated by Bamford and Bengough's [I and II] methods are 6.9545×10^4 , 4.9647×10^4 and

4.7728×10^4 litre mol⁻¹ sec⁻¹ respectively. Hence the average value of k_z would be 5.564×10^4 litre mol⁻¹ sec⁻¹ at 60°. This agrees with the rate constants for the interaction of polystyryl radical with complexes of iron(III)³⁻⁷.

The rate constant for the interaction of polystyryl radical with [Fe(DMF)₆]³⁺ was reported to be 847 litre mol⁻¹ sec⁻¹ at 60° but the same for the interaction between polystyryl radical and [Fe(Bipy)₃]³⁺ is found to be 5.564×10^4 litre mol⁻¹ sec⁻¹ at 60°. The mechanism of the interaction of the polymer radical with [Fe(Bipy)₃]³⁺ is uncertain but there is a possibility that electron transfer occurs by conduction through bipyridyl ligands. The rate will be high since the ligands are unsaturated and π-bonding. The type of possible metal-ligand interaction may be $p\pi-d\pi$ ¹⁶. Back donation from the metal *d*-orbital to *p*-orbital of nitrogen or π-orbitals of benzene ring may also occur. The ability of the ligands to form π-bonds, by using electron density from the appropriate *d*-orbital of Fe³⁺ will dissipate unfavourable charge distribution around metal ion. An extended π-bond may be formed between the coordinated ligands in the octahedral complex and a polystyryl radical by interaction of metal *d*-orbitals, π-orbital of the ligand and the 2*p*-orbital of the carbon atom on the polymer radical end. An extended π-bond system of this in transition state will markedly facilitate electron transfer.

The high reactivity of [Fe(Bipy)₃]³⁺ ion in the polymer radical electron transfer is in agreement with its high redox potential¹⁷ ($E_0 = 1.10$ V),



It may be noted that the rate constant¹⁷ for the reaction, $[\text{Fe}(\text{Bipy})_3]^{3+} + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} +$

$[\text{Fe}(\text{Bipy})_3]^{2+}$ was reported to be 2.7×10^4 litre mol⁻¹ sec⁻¹ at 25°.

Acknowledgement

The authors thank the UGC, New Delhi for the equipment grant to N. N. D.

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