# Redox Polymerization: Kinetics of Polymerization of Acrylonitrile Initiated by the System 2,2'-Thiodiethanol/Trichloroaquobipyridylmanganese(III) in Dilute Sulfuric Acid*

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## Synopsis

The kinetics of polymerization of acrylonitrile and methyl methacrylate initiated by the redox system 2,2'-thiodiethanol/trichloroaquobipyridylmanganese(III) have been investigated in the temperature range 20–35°C in dilute sulfuric acid. The oxidation of the substrate in the absence of monomer has also been studied. A third-order reaction involving the complex, the substrate, and H+ leads to the production of primary radicals which initiate polymerization of the monomers. The primary radicals are more reactive towards methyl methacrylate than towards acrylonitrile. The termination of polymerization with both monomers is by mutual interaction between the growing radicals. A suitable kinetic scheme has been proposed, and the rate constants evaluated.

## INTRODUCTION

The kinetics of polymerization of vinyl monomers initiated by redox systems based on Mn(III) compounds such as sulfate, perchlorate, acetate, and acetylacetonate in aqueous and nonaqueous media have been reported by us.[1–4] Bamford and co-workers have investigated metal chelates such as acetylacetonates and trifluoroacetylacetonates as initiators for polymerization of monomers like styrene, methyl methacrylate, etc.[5,6] Electron donor additives such as pyridine, 2,2'-bipyridine, 1,10-phenanthroline, etc., enhance the rate of polymerization by facilitating the elimination of the $\beta$-diketonyl radical through coordination to the metal ion.[7,8] So far, investigations on polymerizations using metal chelates have been confined to organic solvents. It was therefore felt worthwhile investigating redox polymerizations using the complex trichloroaquobipyridylmanganese(III) in combination with 2,2'-thiodiethanol as the reducing agent in aqueous acid media. The reducing action of thiodiethanol [$S(CH_2CH_2OH)_2$] has already been demonstrated.[9] In this paper some of our data on the kinetics of polymerization of acrylonitrile and methylmethacrylate initiated by the title system in dilute sulfuric acid is reported.

## EXPERIMENTAL

Trichloroaquobipyridylmanganese(III), which will be referred to hereafter as the "complex," was prepared by the method described by Goodwin and Sylva.[10] Stock solutions of the complex were prepared by weighing out the required amounts of the pure solid and dissolving in double distilled water.

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Goodwin and Sylva[10] reported that, in aqueous solution, the chloro groups of the complex undergo dissociation. When an aqueous solution of the complex, which has a deep-green color, was run through a column of Dowex 50 cation-exchange resin in the $H^+$ form and washed down with double distilled water, the eluted solution was colorless and, on titration with standard alkali, gave three equivalents of acid. It is thus probable that the complex exists as tetraaquobipyridylmanganese(III) in water.

The aqueous solutions of the complex were found to undergo the process of "aging" over a period of 6 h, the aged solutions being less active toward the reducing agent than the fresh ones. However, the electronic spectra recorded after different times of aging were identical. The diffuse refluctance spectra of the complex in $BaSO_4$ shows an absorption maximum at 550 m$\mu$.[10] However, in aqueous solution this peak is absent. The complex absorbs continuously in the visible region showing a weak shoulder at 400–420 m$\mu$ (Fig. 1). For oxidation and polymerization experiments, complex solutions aged for at least 6 h were used. Such solutions exhibited uniform reactivity.

2,2′-Thiodiethanol (TDE) was a Fluka product and was purified by distillation under reduced pressure (bp 168°C at $\approx$14 mm). Stock solutions of TDE were prepared by weighing out the required amounts of the viscous liquid and dissolving in double distilled water. The monomers acrylonitrile (AN) and methyl methacrylate (MMA) were freed from inhibitors and distilled under reduced pressure of nitrogen.

Oxidations in the absence of monomers were investigated using either a Carl-Zeiss DMR 21 or a Beckman DB-GT recording spectrophotometer. The initial slopes were obtained from the plots of optical density vs. time and converted to rates by using the appropriate extinction coefficient. The rates thus obtained were initial rates.

The batch type method was adopted for polymerizations. Reaction mixtures containing requisite amounts of all reagents except the complex were taken in reaction tubes, thermostated, and deoxygenated by nitrogen. After 20–30 min, previously deaerated complex solution was added to the reaction tubes and
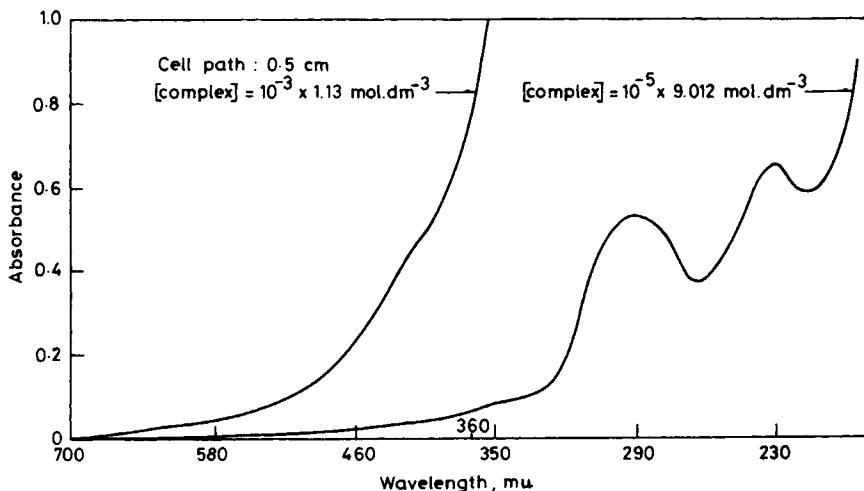


Fig. 1. Absorption spectrum of trichloroaqueobipyridyl Mn(III) in water.

stirring by nitrogen continued. Reactions were allowed to proceed to 15–20% conversions and quenched by addition of a known excess of standard ferrous ammonium sulfate solution. The polymer formed in each tube was filtered quantitatively through a tared sintered-glass crucible of IG-3 porosity. Titration of the filtrate against standard Ce(IV) solution provided data on ($-d$[complex]/$dt$) during polymerization. The polymer was then thoroughly washed with water, followed by methanol, and dried *in vacuo* to constant weight. Rates of polymerization ($-d$[M]/$dt$) were calculated from the weights of the polymer samples. Thus these rates are not initial rates but those obtained in batch type reactions where systematic variation in the concentration of each reactant was carried out at constant concentration of all other reagents.

Degrees of polymerization ($\bar{P}_n$) were obtained viscometrically using the reprecipitated polymer samples. The following equations were employed to obtain $\bar{P}_n$ from viscosity data[11]:
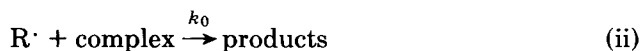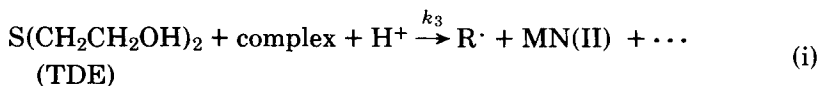
   (i)   $\log \bar{P}_n = 1.333 \log[\eta] + 3.181$ for poly(acrylonitrile) in DMF at 30°C,

   (ii)   $\log \bar{P}_n = 1.316 \log[\eta] + 3.636$ for poly(methyl methacrylate) in benzene at 30°C, where [$\eta$] refers to intrinsic viscosities.

## RESULTS AND DISCUSSION

### Oxidation of TDE in the Absence of Monomers

There was very little oxidation when no acid was added. But in the presence of 0.05–0.1M sulfuric acid the reaction proceeded smoothly at 20–30°C. All reactions were carried out in the presence of a large excess of manganous sulfate to prevent any possible disproportionation of Mn(III). The rate of disappearance of the complex ($-d$[complex]/$dt$) was proportional to the concentrations of the complex, TDE and H$^+$ (Fig. 2). There was no evidence of Michealis–Menten kinetics nor did the rates level off with increasing [H$^+$] at constant ionic strength maintained by KNO$_3$. Acid concentrations in excess of 0.1 mol·dm$^{-3}$ led to very rapid oxidation. Thus the reaction appears to be a direct third-order process without any intermediate complex. This observation is in sharp contrast to our earlier results with the TDE/Ce(IV) system in sulfuric acid medium, where a complex between the oxidant and the protonated form of TDE was indeed postulated to explain the observed kinetics.[9] Since the oxidation of pinacol as well as cyanoacetic acid by the complex[12] proceeds even in the absence of H$^+$, it is quite probable that it is the TDE which is getting protonated and not the complex. This assumption is strengthened by the fact that, in the oxidation of cyclohexanone by ferrin, protonation of the complex has not been observed.[13] Hence from the foregoing discussion it seems that protonation of TDE is a prerequisite condition for its oxidation. The oxidation can be represented by the following equations:

$$S(CH_2CH_2OH)_2 + \text{complex} + H^+ \xrightarrow{k_3} R\cdot + MN(II) + \cdots$$
$$\text{(TDE)}$$

(i)

$$R\cdot + \text{complex} \xrightarrow{k_0} \text{products}$$

(ii)

It is not readily apparent what type of radical intermediate is formed. However,
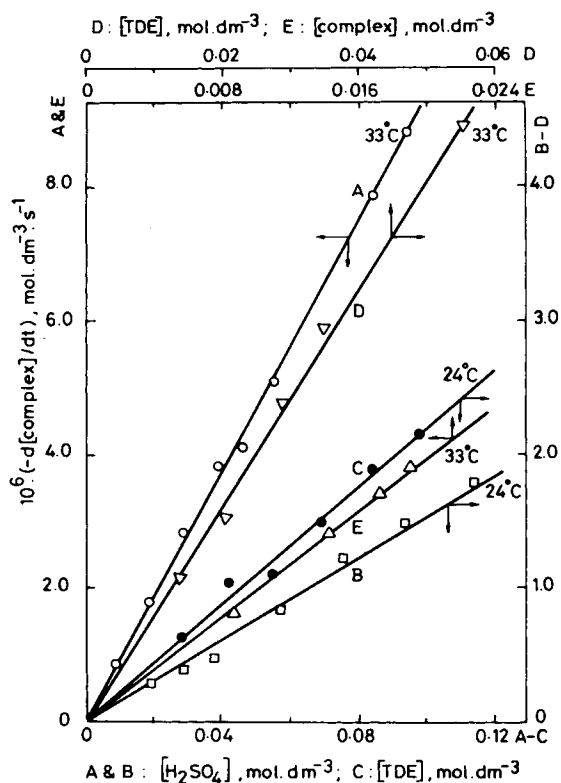
Fig. 2. Plots of $-d[\text{complex}]/dt$ vs. [complex], [H$^+$], and [TDE] in the absence of any monomer. (A, B) At [complex] = 0.00114, [Mn(II)] = 0.02, [TDE] = 0.014, and $\mu$ = 0.2 mol·dm$^{-3}$; (C, D) at [complex] = 0.00114, [Mn(II)] = 0.02, and [H$_2$SO$_4$] = 0.02 mol·dm$^{-3}$; (E) at [TDE] = 0.028, [Mn(II)] = 0.02, and [H$_2$SO$_4$] = 0.02 mol·dm$^{-3}$.

in the presence of acid and an alcohol, TDE is converted to the diether, episulfonium ion being postulated as the intermediate.[14] The rate of disappearance of the complex will be given by

$$-d[\text{complex}]/dt = 2k_3[\text{complex}][\text{TDE}][\text{H}^+] \tag{1}$$

The values of the third-order constant $k_3$ are listed in Table I.

It must, however, be mentioned that, although the absence of any levelling off of the rates with increasing [H$^+$] seems to indicate a direct third-order reac-

TABLE I
Kinetic and Thermodynamic Parameters for the System Trichloroaquobipyridyl Mn(III)—
Thiodiethanol as Initiator for Polymerization of AN and MMA

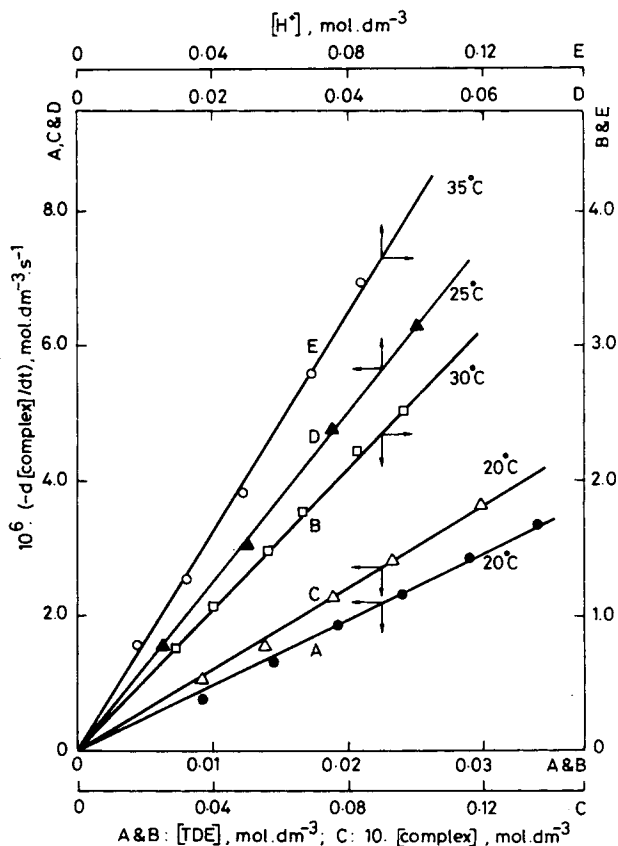| Monomer | Temp (K) | $k_3$ (dm$^6$·mol$^{-2}$·s$^{-1}$) | $E$ (kJ·mol$^{-1}$) | $k_0/k_i$ | $k_p/k_t^{0.5}$ (dm$^3$·mol$^{-1}$·s$^{-1}$)$^{1/2}$ |
|---|---|---|---|---|---|
| None | 297 | 0.520 | 109.50 | — | — |
| | 306 | 1.899 | | | |
| AN | 293 | 0.133 | 102.47 | | |
| | 298 | 0.268 | | 110 | — |
| MMA | 303 | 0.268 | 147.55 | 2.33 | 0.374 |
| | 308 | 0.689 | | 2.10 | 0.449 |

Fig. 3. Plots of $-d[\text{complex}]/dt$ vs. [complex], [H$^+$], and [TDE] in the presence of monomer. (A, C) At [Mn(II)] = 0.14, [H$_2$SO$_4$] = 0.05, and [AN] = 0.60 mol·dm$^{-3}$—[complex] = 0.0075 (A), [TDE] = 0.024 mol·dm$^{-3}$ (C). (D) at [Mn(II)] = 0.14, [TDE] = 0.026, [complex] = 0.0096, [AN] = 0.60, and $\mu$ = 1.0 mol·dm$^{-3}$; (B, E) at [Mn(II)] = 0.09, [complex] = 0.0066, and [MMA] = 0.094 mol·dm$^{-3}$—[H$_2$SO$_4$] = 0.05 mol·dm$^{-3}$ (B), [TDE] = 0.0068 and $\mu$ = 0.55 mol·dm$^{-3}$ (E).

tion, it is quite likely that there exists a protonation preequilibrium followed by the oxidation of the protonated form of TDE. Since it was not possible to increase the concentration of the acid beyond 0.12 mol·dm$^{-3}$, because the reactions became extremely rapid, evidence for levelling off of the rates at high [H$^+$] could not be obtained. Hence a third-order reaction has been postulated.
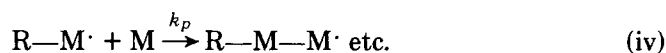
## Polymerization of Acrylonitrile (AN)

The complex did not initiate polymerization of AN (or MMA) in the absence of TDE or UV light. The rate of disappearance of the complex was considerably lowered in the presence of AN. As observed in the absence of AN, rates of oxidation were found to be proportional to [complex], [TDE], and [H$^+$] (Fig. 3) and independent of [AN] (Table II). Polymerizations started immediately without induction periods in thoroughly deaerated systems. Rates of polymerization were proportional to [M]$^{1.5}$, [TDE]$^{0.5}$, and [H$^+$]$^{0.5}$ (Fig. 4), but were insensitive to changes in the concentration of the complex (Table III). The following steps could therefore be written in addition to steps (i) and (ii) above to account for to experimental facts:

TABLE II
Variation of $-d[\text{complex}]/dt$ and $\overline{P}_n$ with [AN] at 20°C[a]

| [AN] mol·dm$^{-3}$ | $10^6$ ($-d[\text{complex}]/dt$) mol·dm$^{-3}$·s$^{-1}$ | $\overline{P}_n$ |
|---|---|---|
| 0.526 | 2.141 | 820 |
| 0.601 | 2.267 | 960 |
| 0.676 | 2.267 | 1110 |
| 0.751 | 2.267 | 1180 |

[a] [complex] = 0.00751, [Mn(II)] = 0.137, [H$_2$SO$_4$] = 0.05 and [TDE] = 0.024 mol·dm$^{-3}$.

$$R\cdot + M \xrightarrow{k_i} R\text{---}M\cdot \tag{iii}$$

$$R\text{---}M\cdot + M \xrightarrow{k_p} R\text{---}M\text{---}M\cdot \text{ etc.} \tag{iv}$$

$$2R\text{---}M_n^\cdot \xrightarrow{k_t} \text{polymer} \tag{v}$$

Applying steady-state approximations to the species $R\cdot$ and $RM_n^\cdot$, the following rate laws can be derived:

$$\frac{-d[\text{complex}]}{dt} = k_3[\text{complex}][\text{TDE}][\text{H}^+] + \frac{k_0 k_3[\text{complex}]^2[\text{TDE}][\text{H}^+]}{k_0[\text{complex}] + k_i[\text{M}]} \tag{2}$$

and

$$\frac{-d[\text{M}]}{dt} = k_p[\text{M}]^{1.5} \left[\frac{k_i k_3[\text{complex}][\text{TDE}][\text{H}^+]}{k_t(k_0[\text{complex}] + k_i[\text{M}])}\right]^{0.5} \tag{3}$$

Under conditions such that $k_0[\text{complex}] \gg k_i[\text{M}]$, we have

$$\frac{-d[\text{complex}]}{dt} = 2k_3[\text{complex}][\text{TDE}][\text{H}^+] \tag{4}$$

and

$$\frac{-d[\text{M}]}{dt} = k_p[\text{M}]^{1.5} \left[\frac{k_i k_3[\text{TDE}][\text{H}^+]}{k_t k_0}\right]^{0.5} \tag{5}$$

Equation (4) is identical to eq. (1) in the absence of AN. The values of $k_3$ can also be estimated from the oxidation data in the presence of monomer (Table I). However, these values are very much lower than those obtained in the absence of monomer. Using $k_3$ obtained from oxidation data during polymerization and the literature value of $k_p/k_t^{0.5}$ at 25°C,[15] the ratio $k_0/k_i$ has been evaluated,

TABLE III
Variation of $-d[\text{M}]/dt$ and $\overline{P}_n$ with [complex] at 20°C[a]

| [complex] mol·dm$^{-3}$ | $10^4(-d[\text{M}]/dt)$ mol·dm$^{-3}$·s$^{-1}$ | $\overline{P}_n$ |
|---|---|---|
| 0.00751 | 2.156 | 980 |
| 0.00939 | 2.094 | 966 |
| 0.01126 | 2.147 | 972 |
| 0.01314 | 2.178 | 960 |

[a] [TDE] = 0.024, [AN] = 0.60, [H$_2$SO$_4$] = 0.05, and [Mn(II)] = 0.137 mol·dm$^{-3}$.
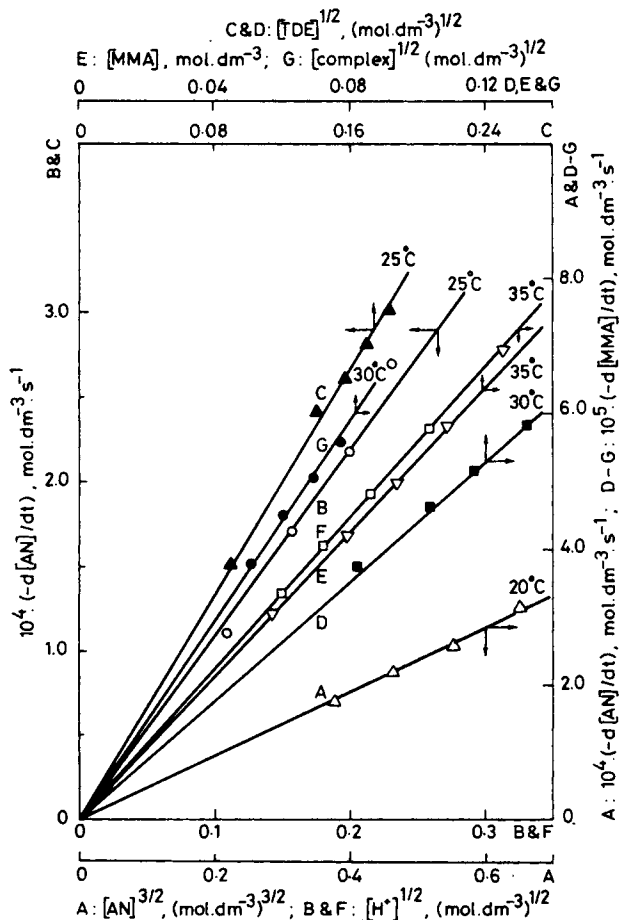
Fig. 4. Plots of $-d[M]/dt$ vs. $[H^+]^{0.5}$, $[TDE]^{0.5}$, $[AN]^{1.5}$, and $[MMA]$. (A) At $[complex] = 0.00751$, $[Mn(II)] = 0.14$, $[H_2SO_4] = 0.05$, and $[TDE] = 0.024$ $mol \cdot dm^{-3}$; (B) at $[complex] = 0.0096$, $[Mn(II)] = 0.14$, $[TDE] = 0.026$, $[AN] = 0.60$, and $\mu = 0.65$ $mol \cdot dm^{-3}$; (C) at $[complex] = 0.00725$, $[Mn(II)] = 0.14$, $[H_2SO_4] = 0.05$, and $[AN] = 0.60$ $mol \cdot dm^{-3}$; (D) at $[complex] = 0.00658$, $[Mn(II)] = 0.091$, $[H_2SO_4] = 0.05$, and $[MMA] = 0.094$ $mol \cdot dm^{-3}$; (E) at $[complex] = 0.00643$, $[Mn(II)] = 0.091$, $[H_2SO_4] = 0.05$, and $[TDE] = 0.0068$ $mol \cdot dm^{-3}$; (F) at $[complex] = 0.00645$, $[Mn(II)] = 0.091$, $[TDE] = 0.0068$, $[MMA] = 0.094$, and $\mu = 0.55$ $mol \cdot dm^{-3}$; (G) at $[Mn(II)] = 0.091$, $[H_2SO_4] = 0.05$, $[MMA] = 0.094$, and $[TDE] = 0.021$ $mol \cdot dm^{-3}$.

which is of the order of 100 (Table I). It is clear from the value of $k_0/k_i$ that $k_0[complex]$ will become comparable to $k_i[M]$ at concentrations of the complex below $5.0 \times 10^{-3}$ $mol \cdot dm^{-3}$, and hence eq. (5) ceases to be valid. The expression for the average degree of polymerization is as follows:

$$\bar{P}_n = k_p \left[ \frac{[M]}{k_i k_t k_3 [TDE][H^+]} \right]^{0.5} \tag{6}$$

The observed variation of $\bar{P}_n$ with $[M]$, $[TDE]$, and $[H^+]$ and its nondependence on $[complex]$ substantiate eq. (6) (Tables II–V).

TABLE IV
Variation of $\bar{P}_n$ with [TDE] at 20°C[a]

| [TDE] (mol·dm⁻³) | 0.00964 | 0.0145 | 0.0193 | 0.0241 | 0.0289 |
|---|---|---|---|---|---|
| $\bar{P}_n$ | 1620 | 1240 | 1050 | 935 | 840 |

[a] [complex] = 0.00751, [Mn(II)] ≈ 0.137, [H₂SO₄] = 0.05 and [AN] = 0.6 mol·dm⁻³

## Polymerization of MethylMethacrylate (MMA)

In the presence of MMA, the rates of oxidation of the substrate were proportional to [TDE] and [H⁺] (Fig. 3). But, unlike the case of AN, the order with respect to the complex was greater than unity and the rates were adversely affected by increse in the monomer concentration (Fig. 5). The rates of polymerization were proportional to [M], [TDE]$^{0.5}$, [complex]$^{0.5}$, and [H⁺]$^{0.5}$ (Fig. 4). It has been possible to explain all the above observations by the same set

TABLE V
Variation of $\bar{P}_n$ with [H⁺] at 20°C[a]

| [H₂SO₄] (mol·dm⁻³) | 0.013 | 0.025 | 0.038 | 0.050 | 0.063 |
|---|---|---|---|---|---|
| $\bar{P}_n$ | 1280 | 1220 | 1090 | 920 | 863 |

[a] [complex] = 0.0096, [TDE] = 0.026, [Mn(II)] = 0.137, [AN] 0.60, and $\mu$ = 0.65 mol·dm⁻³.



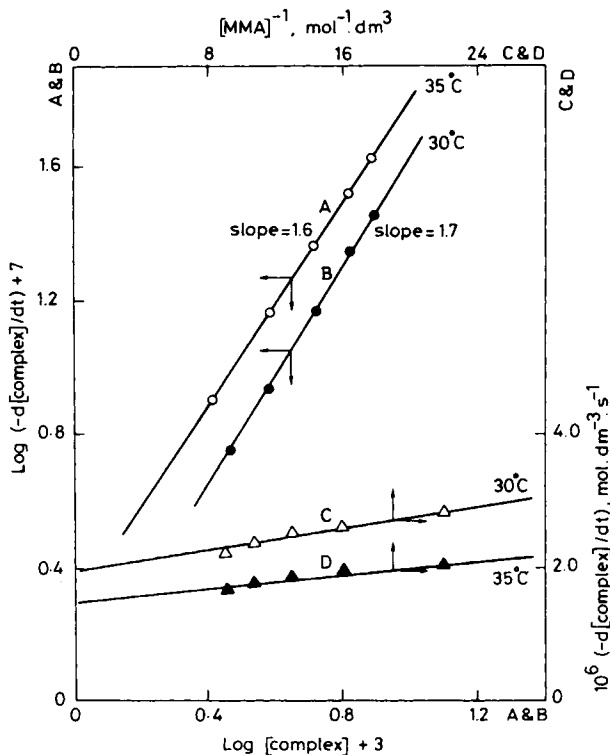Fig. 5. (A, B) Plots of log(−d[complex]/dt) vs. log[complex]. At [Mn(II)] = 0.09, [H₂SO₄] = 0.05, [MMA] = 0.094 mol·dm⁻³; [TDE] = 0.0102 mol·dm⁻³ (A) and 0.021 mol·dm⁻³ (B). (C, D) Plots of −d[complex]/dt vs. [MMA]⁻¹ at [Mn(II)] = 0.09, [H₂SO₄] = 0.05, and [complex] = 0.0065 mol·dm⁻³; [TDE] = 0.024 mol·dm⁻³ (C) and 0.00678 mol·dm⁻³ (D).

of reactions proposed for the polymerization of acrylonitrile [steps (i)–(v)] with the condition $k_i[M] > k_0[complex]$ prevailing. Hence the rate laws applicable would be

$$\frac{-d[\text{complex}]}{dt} = k_3[\text{complex}][\text{TDE}][\text{H}^+] + \frac{k_0 k_3[\text{complex}]^2[\text{TDE}][\text{H}^+]}{k_i[M]} \quad (7)$$

and

$$\frac{-d[M]}{dt} = k_p[M] \left[ \frac{k_3[\text{complex}][\text{TDE}][\text{H}^+]}{k_t} \right]^{0.5} \quad (8)$$

It can be seen that eqs. (7) and (8) are quite consistent with the experimental facts. The values of $k_3$ and those of the ratio $k_0/k_i$ could be evaluated from the plots of $-d[\text{complex}]/dt$ vs. $[M]^{-1}$ (Fig. 5). The data appear in Table I. Using $k_3$ obtained in the presence of MMA, the values of $k_p/k_t^{0.5}$ have been calculated from the polymerization data (Table I). These values compare well with those reported for the polymerization of MMA.[1] From the relative values of $k_0/k_i$ it is evident that the primary radicals are more reactive toward MMA than AN.

In conclusion it may be said that, though the present system may not be superior to the existing recipes for redox polymerization (e.g., persulfate/bisulfite system), investigating it, nevertheless, felt worthwhile from the point of view of the oxidizing properties of the complex. Using the rate data, the initiator productivity of the present system was calculated to be about 20 kg polymer per kg initiator. Calculations also indicated that even after 100% convertions there would be enough of the initiator components left to initiate polymerization if more monomer were added. However, at such high conversions the whole reaction mixture becomes a solid mass which seriously affects efficient stirring and temperature equilibration.

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