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Redox Polymerization of Acrylamide Initiated by the System Trisacetylacetonato Vanadium(III)-Benzoyl Peroxide in Dimethylformamide

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ABSTRACT

The kinetics of polymerization of acrylamide (AA) initiated by the redox system $V(III)(acac)_3$-benzoyl peroxide (BPO) in DMF were investigated in the temperature range 40-45°C. A direct second-order reaction between $V(III)(acac)_3$ and BPO was evident from the oxidation kinetics. Rates of polymerization varied as $[AA]^{3/2}$ and $[BPO]^{1/2}$ but were independent of $[V(III)(acac)_3]$. Extensive reduction of primary radicals by $V(III)(acac)_3$ with mutual termination of growing radicals accounts for the kinetics. Degrees of polymerization increased with increasing [AA] and decreased with increasing [BPO] but remained unchanged with variation in $[V(III)(acac)_3]$ as required by the mechanism proposed.

INTRODUCTION

Organic peroxides such as t-butyl hydroperoxide (t-BHP), cumene hydroperoxide (CHP), benzoyl peroxide (BPO) and lauroyl peroxide can be activated by metal ions such as Co(III), V(III), Mn(III) [1],

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Fe(II) [2, 3], Rh(I) [4], and Cr(II) [5, 6]. These metal ion-peroxide redox systems are efficient polymerization initiators, and polymerization can be initiated at lower temperatures than normally required for peroxides alone. Roda and Harabok [4] have used the system Rh(I)-BPO for the polymerization of methyl methacrylate and shown that the rates varied as $[\text{MMA}]^{1.0}$, $[\text{BPO}]^{1/2}$, and $[\text{Rh(I)}]^{1/2}$. Lee and Minoura [5, 6] have reported that the redox system chromous acetate-BPO initiates polymerization even at -28° C. With this system at higher concentrations of initiator and lower concentrations of monomer, termination by the initiating radicals generated in the redox reaction Cr(II) + BPO, has been observed [5]. These authors have also reported that with an aged solution of Cr(II)-BPO the polymerization proceeds through a terminationless mechanism [6]. The radicals remain within the ligand field of the metal ion and are protected from attack by primary radicals, thus leading to living radical polymerization. However, the system Cr(II)-CHP did not show this kind of living radical polymerization. We have been investigating redox systems based on V(III) as polymerization initiators and have earlier reported [7] the polymerization of acrylamide using the system V(III)(acac)_3-NH_2OH in dimethylformamide (DMF). This paper reports the use of the V(III)(acac)_3-BPO system in DMF medium.

EXPERIMENTAL

The preparation and purification of V(III)(acac)_3 has been reported [7]. Benzoyl peroxide and dimethylformamide were purified by standard methods. Details of oxidation [7] and polymerization [8] procedures have also been reported. Oxidation reactions were followed by using a Carl Zeiss DMR 21 model recording spectrophotometer. Polymerizations were arrested by the addition of a methanolic solution of hydroquinone, and the rates were followed gravimetrically.

RESULTS AND DISCUSSION

The kinetics of oxidation were investigated in the temperature range 40-45° C. With BPO as oxidant the product of oxidation is VO(acac)_2, and this was confirmed by visible spectral studies (Fig. 1). The rate of formation of the product VO(acac)_2 was followed at 800 nm. From plots of absorbance versus time the concentration of V(III)(acac)_3 at any time, $[\text{V(III)}]_t$ was calculated by the method reported earlier [7], using a value 43.2 $\text{dm}^3\ \text{mol}^{-1}\ \text{cm}^{-1}$ for the molar extinction coefficient of VO(acac)_2 in DMF containing excess BPO. The stoichiometry of the reaction was found to be 2 mol of V(III)(acac)_3 per mole of BPO. This was determined by reacting a limited amount of oxidant with excess V(III)(acac)_3 and estimating the amount of V(III)(acac)_3 consumed for complete oxidation. Plots of log $[\text{V(III)}]_t$ versus time are linear (Fig. 2), indicating a first-order dependence of the rates on

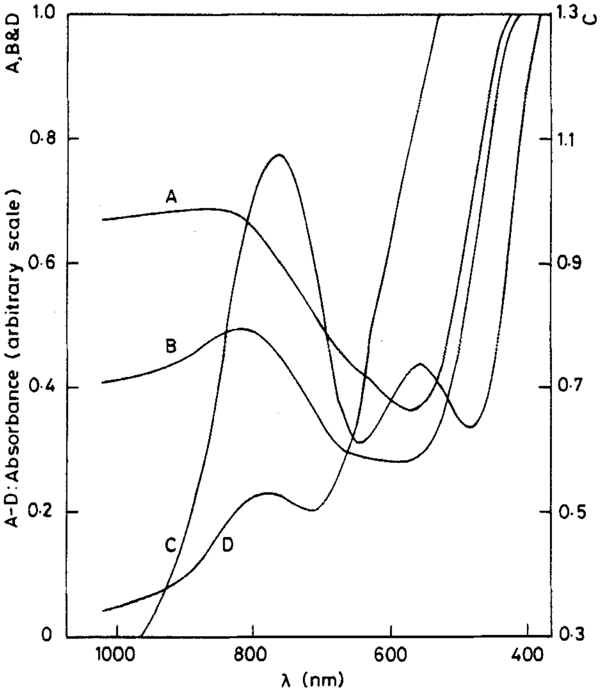

FIG. 1. Absorption spectra of chelates. Curve A: 0.03141 mol/dm^3 $VO(acac)_2$ + excess BPO. Curve B: 0.02309 mol/dm^3 $V(III)(acac)_3$ + excess BPO. Curve C: 0.0449 mol/dm^3 $VO(acac)_2$. Curve D: 0.0483 mol/dm^3 $V(III)(acac)_3$. Cell path length: 0.5 cm.

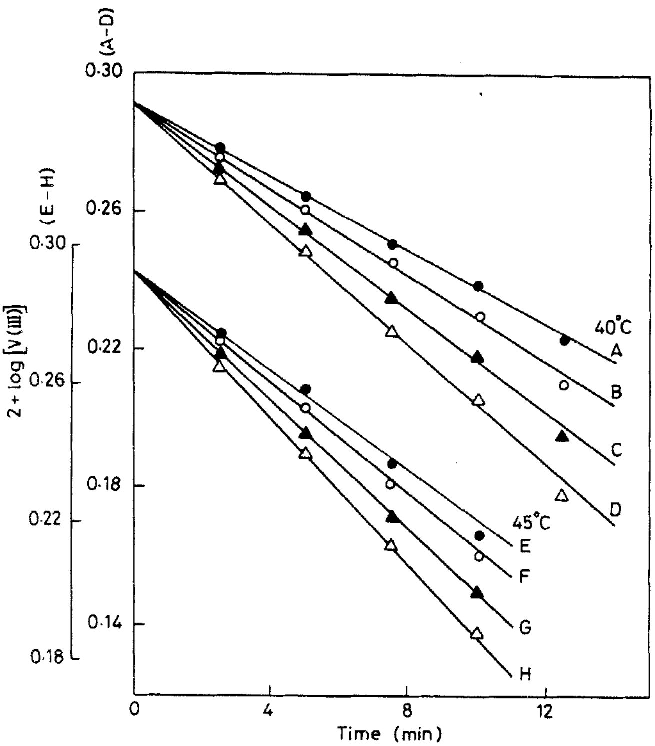

FIG. 2. Plots of log [V(III)]$_t$ versus time. [V(III)(acac)$_3$] = 1.92×10^{-2} mol/dm^3. [BPO] = 0.469 M (A, E); 0.527 M (B, F); 0.615 M (C); 0.644 M (G); 0.732 M (D, H).

TABLE 1. Variation of k_{ob} with [BPO]^a

[BPO] (mol/dm^3)	40°C 10^4 k_{ob} (s^{-1})	40°C 10^4 k_r (dm^3 mol^{-1} s^{-1})	45°C 10^4 k_{ob} (s^{-1})	45°C 10^4 k_r (dm^3 mol^{-1} s^{-1})
0.469	2.12	2.26	2.76	2.95
0.527	2.39	2.28	3.07	2.92
0.615	2.84	2.31	-	-
0.644	-	-	3.56	2.77
0.732	3.30	2.25	4.05	2.76

^{a}Where $k_r = k_{ob}/2[\mathrm{BPO}]$; $[\mathrm{V(III)(acac)_3}] = 1.95 \times 10^{-2}$ mol/dm^3.

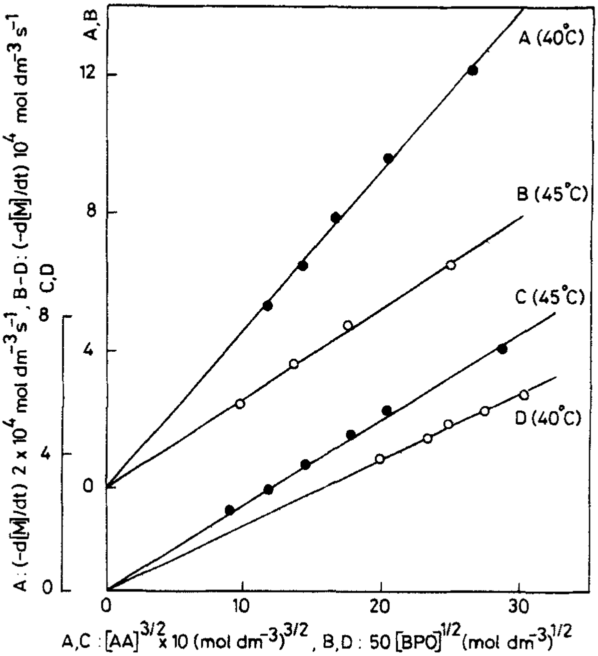

FIG. 3. Plots of $-d[M]/dt$ versus $[AA]^{3/2}$ and $[BPO]^{1/2}$. [AA] = 1.124 M (B); 1.129 M (D). 10^2 [BPO] = 9.52 M (A); 6.1 M (C). 10^2 [V(III)(acac)$_3$] = 4.55 M (A); 2.36 M (B, C, D).

TABLE 2. Variation of -d[M]/dt with [V(III)(acac)$_3$]

10^2 [V(III)] (mol/dm^3)	40°C, rate × 10^4 (mol dm^{-3} s^{-1})^a	45°C, rate × 10^4 (mol dm^{-3} s^{-1})^b
2.64	4.01	2.93
5.28	4.13	3.10
13.2	3.97	3.02
29.0	3.89	2.98
36.9	3.99	2.99

^{a}[AA] = 1.132 mol/dm^3 and [BPO] = 0.1630 mol/dm^3.
^{b}[AA] = 1.113 mol/dm^3 and [BPO] = 0.0602 mol/dm^3.

[V(III)(acac)$_3$]. The constancy of the ratio $k_{ob}/2$[BPO] (Table 1) indicates that the order with respect to [BPO] is also unity. The following rate law is applicable to the above data:

$$-d[\mathrm{V(III)}]/dt = 2\,k_r[\mathrm{V(III)(acac)_3}][\mathrm{BPO}] \tag{1}$$

The kinetics of polymerization were also investigated in the temperature range 40-45°C, and the reactions were allowed to proceed for 10-15 min. Within this time no polymer was obtained due to peroxide alone in the absence of the chelate. However, when V(III)-(acac)$_3$ was present, polymerization proceeded almost instantaneously as was evident from precipitation of the polymer. The rates of polymerization varied as [AA]$^{3/2}$ and [BPO]$^{1/2}$ (Fig. 3) but were independent of [V(III)(acac)$_3$] (Table 2). The following mechanism can be written for polymerization with V(III) and V(IV) representing the respective chelates:

$$\mathrm{V(III) + BPO} \xrightarrow{k_r} \mathrm{PhCOO^{\bullet} + PhCOO^{-} + V(IV)}$$

$$\mathrm{PhCOO^{\bullet} + V(III)} \xrightarrow[\text{fast}]{k_0} \mathrm{PhCOO^{-} + V(IV)}$$

$$\mathrm{PhCOO^{\bullet} + M} \xrightarrow{k_i} \mathrm{M_1^{\bullet}}$$

TABLE 3. Variation of $\overline{P}_n$ with [AA], [BPO], and [V(III)(acac)$_3$] at 45°C

[AA] (mol/dm^3)^a	$\overline{P}_n$^{a}	10^2[V(III)] (mol/dm^3)^b	$\overline{P}_n$^{b}	10^2[BPO] (mol/dm^3)^c	$\overline{P}_n$^{c}
0.577	139	2.64	259	3.79	285
0.922	183	5.28	266	7.69	252
1.268	229	13.2	261	12.7	213
1.614	261	29.0	263	18.9	188
1.893	293	-	-	25.3	159

[a] [V(III)(acac)$_3$] = 0.0243 mol/dm^3; [BPO] = 0.0789 mol/dm^3.

[b] [BPO] = 0.0602 mol/dm^3; [AA] = 1.113 mol/dm^3.

[c] [V(III)(acac)$_3$] = 0.0236 mol/dm^3; [AA] = 1.124 mol/dm^3.

$$M_1^{\bullet} + M \xrightarrow{k_p} M_2^{\bullet}$$

$$M_n^{\bullet} + M_n^{\bullet} \xrightarrow{k_t} \text{polymer}$$

Under conditions such that $k_0[\mathrm{V(III)}] \gg k_i[\mathrm{M}]$, the following expression can be derived:

$$-d[\mathrm{M}]/dt = \frac{k_p k_i^{1/2} k_r^{1/2} [\mathrm{AA}]^{3/2} [\mathrm{BPO}]^{1/2}}{(2k_t k_0)^{1/2}} \qquad (2)$$

which explains the kinetic data obtained. The expression for the degrees of polymerization can be derived as

$$\overline{P}_n = \frac{k_p k_0^{1/2} [\mathrm{AA}]^{1/2}}{(2k_t k_i k_r [\mathrm{BPO}])^{1/2}} \qquad (3)$$

Thus $\overline{P}_n$ decreased with increasing [BPO] and increased with increasing [AA] but remained unchanged with [V(III)(acac)$_3$] (Table 3). Despite the evidence for the reaction of V(III)(acac)$_3$ with primary radicals, there is no evidence for linear termination in this system. From the data on polymerization and oxidation we can estimate the values of the composite constant $k_p k_i^{1/2}/(k_t k_0)^{1/2}$ to be 7.5×10^{-4} and 10.5×10^{-4} $(dm^3\ mol^{-1}\ s^{-1})^{1/2}$ at 40 and 45°C, respectively.

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