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Polymerization of acrylamide photoinitiated by $Co(NH_3)_5N_3^{2+}$ with long wavelength visible light in aqueous solution

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Abstract

The 546 nm continuous irradiation of acidic aqueous solutions of $Co(NH_3)_5N_3^{2+}$ and acrylamide (AA) results in the formation of polyacrylamide. Excitation of $Co(NH_3)_5N_3^{2+}$ yields Co_{aq}^{2+} and $N_3^{\cdot}$ radicals; the latter species initiate the free-radical chain reaction via oxidative electron and/or H atom transfer with the monomer. The positive dependence of the rate of polymerization on the square root of the absorbed light intensity and [AA] suggests that the termination step of the chain reaction involves the mutual annihilation of the macroradicals. ESR spin-trapping experiments demonstrate unequivocally that $N_3^{\cdot}$ radicals are present in the system. $Co(NH_3)_5N_3^{2+}$ is a suitable photosensitizer for the initiation of free-radical polymerization with visible light.

Keywords: Polymerization; Acrylamide; Photoinitiation; Cobalt complex

1. Introduction

Photochemically induced free-radical polymerization permits on–off control of the process as well as the selection of the wavelength of excitation; the ability to use visible light is particularly important in order to minimize degradation of the reactants and products and to record holograms with Ar (488 nm) and He–Ne (633 nm) lasers. Previous studies in our laboratories have focused on visible- or near-UV-initiated polymerization sensitized by Cr(IV) complexes [1–3], $Cr(H_2O)_6^{3+}$ [4] and $Cr(bpy)_3^{3+}$ (bpy ≡ 2,2′-bipyridine) [5]. In addition, recent work has been directed towards the recording of holograms using free-radical polymerization techniques [6].

We have chosen to use $Co(NH_3)_5N_3^{2+}$ as a convenient photosensitizer to initiate the polymerization of acrylamide (CH_2=$CHCONH_2$; AA) in aqueous solution with 546 nm light; this paper has a special emphasis on the primary mechanism of initiation. Natarajan and Santappa [7] have already reported on this reaction at wavelengths up to 435 nm; we wished to move the wavelength of excitation beyond 500 nm. The photolysis of $Co(NH_3)_5N_3^{2+}$ in aqueous solution yields $N_3^{\cdot}$ radicals at wavelengths as long as 550 nm [8–10]; $N_3^{\cdot}$ radicals are strong oxidizing agents with a reduction potential of 1.34 V [11]. In addition, in as much as the yield of Co_{aq}^{2+} is exactly the same as that of the $N_3^{\cdot}$ radicals, the system possesses an internal actinometer. $N_3^{\cdot}$ radicals can also be easily generated via radiation chemical techniques and have been used to oxidize organic and biochemical molecules [12]. We have previously used $Co(NH_3)_5N_3^{2+}$ as a photosensitizer for the oxidation of *o*- [13], *m*- and *p*-phenylphenol [14] and dimethylphenol [15].

2. Experimental details

2.1. Materials

$[Co(NH_3)_5N_3](ClO_4)_2$ was prepared as described in the literature [16] and was recrystallized at least once, but generally twice. Acrylamide (Puriss) was purchased from Fluka and was used without further purification. The solutions were prepared with doubly distilled water and were deaerated when necessary by bubbling with Ar for 45 min. The pH of the solutions was adjusted with $HClO_4$ to ±0.02 units; the ionic strength was not controlled.

2.2. Procedures

Irradiations at 546 nm were performed with a high pressure mercury lamp (Osram HBO 200 W) equipped with a grating

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monochromator; a 325 nm cut-off filter was employed to remove high energy harmonics. The beam was parallel and the reactor was a square cuvette with a 1 cm path length. The incident light intensity (I_0) was determined by chemical actinometry with actinochrome N (*meso*-diphenylhelianthrene); the light intensity absorbed by the photosensitizer (I_a) was calculated from Beer's law. UV–visible spectra were recorded on a Cary 3 double-beam spectrophotometer and ESR spectra were obtained with a Brucker ER 200D spectrometer at 9.3 GHz with a modulation field of 100 kHz. An Xe–Hg Hanovia lamp with a 495 nm cut-off filter was used for irradiations in the ESR spectrometer cavity. Spin-trapping experiments were performed with DMPO (5,5-dimethyl-1-pyrroline-*N*-oxide) as a trap. DPPH (diphenylpicrylhydrazyl) was used as an internal standard.

The quantum yields of disappearance of $Co(NH_3)_5N_3^{2+}$ were determined by high performance liquid chromatography (HPLC); a Waters 540 liquid chromatography system equipped with a Waters 990 diode array UV–visible detector was used in conjunction with a reverse phase Beckman (250 mm × 4 mm) column and a mixture of 5:1 (v/v) aqueous CH_3CO_2Na (0.03 M, pH 5.0)–CH_3CN as the eluent. The concentration of Co_{aq}^{2+} formed was determined by the method of Katakis and Allen [17]; the calibration curve was obtained with Co(II)-acetylacetonate. The polymer was precipitated by pouring the irradiated solution into methanol; the polymer was separated and weighed, which offered a measure of the fractional conversion of acrylamide into polymer. The rate of polymerization, R_p, was taken from the slope of the initial linear portion of the plot of per cent of monomer conversion vs. irradiation time; the precision of the values of R_p is estimated to be ± 10%. In order to study the effect of I_a on the polymerization rate, neutral density filters were placed in front of the cell in order to alter I_0.

3. Results

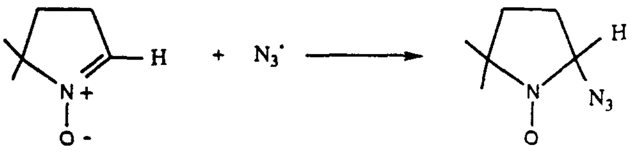
3.1. Photochemical behaviour

In as much as the presence of O_2 does not affect the rate of photochemical reaction of the photosensitizer, all experiments related to the determination of the quantum yields of formation of Co_{aq}^{2+} (Φ_{Co}) were performed in the presence of air. The experimental conditions were $[Co(NH_3)_5N_3^{2+}] = 0.25$ mM, $[AA] = 1.0$ M, pH = 2.5. The results yielded $\Phi_{Co} = 0.020 \pm 0.002$.

The progress of the reaction was also followed by UV–visible spectroscopy (monitored at 302 and 516 nm; Fig. 1) and by HPLC. Regardless of the measurement, the value of the quantum yield of the disappearance of $Co(NH_3)_5N_3^{2+}$ was 0.016 ± 0.002. It should be noted that both measurements could not distinguish between $Co(NH_3)_5N_3^{2+}$ and the known aquation product, $Co(NH_3)_4(H_2O)N_3^{2+}$, which would be expected to have similar absorption spectra and HPLC retention times; $Co(NH_3)_5H_2O^{3+}$ shows a far longer retention time.

3.2. ESR spectroscopy

Spin-trapping experiments with DMPO were performed to trap $N_3^{\bullet}$ radicals formed upon irradiation.



The incident beam, filtered to pass light of λ > 495 nm, was absorbed only by $Co(NH_3)_5N_3^{2+}$. The ESR spectrum of the adduct is shown in Fig. 2; a quartet of triplets at $g = 2.0061$ was observed. The formation of a quartet of trip-

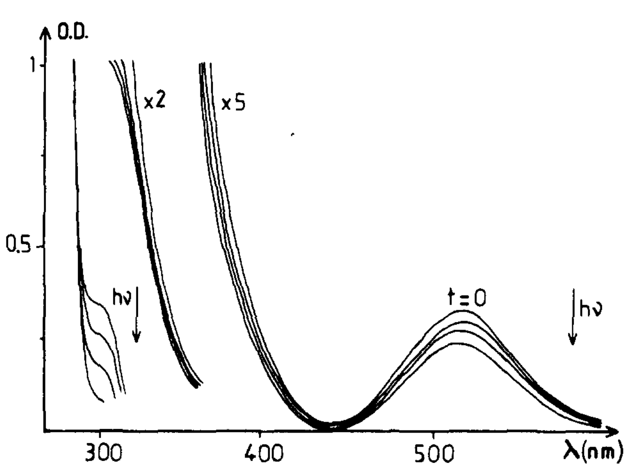


Fig. 1. Spectral evolution from photolysis of an aerated solution containing $[Co(NH_3)_5N_3^{2+}] = 0.25$ mM and [AA] = 1.0 M at pH 2.5; $\lambda_{ex} = 546$ nm.

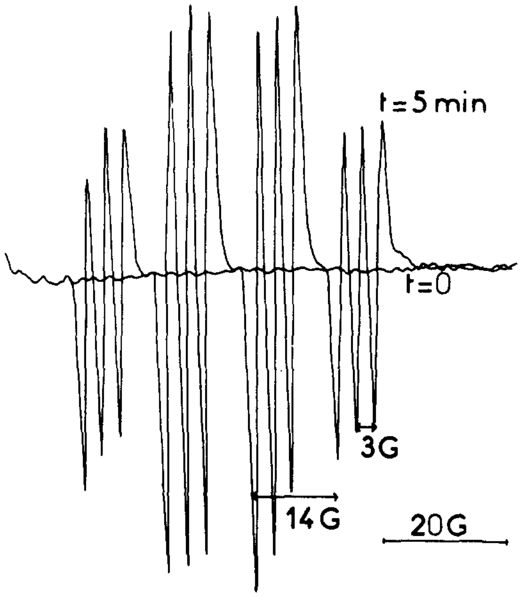


Fig. 2. ESR spectrum at ambient temperature of a solution containing $[Co(NH_3)_5N_3^{2+}] = 0.25$ mM and [AA] = 1.0 M at pH 2.5 in the presence of DMPO; $\lambda_{ex} > 495$ nm. Photolysis time 5 min.

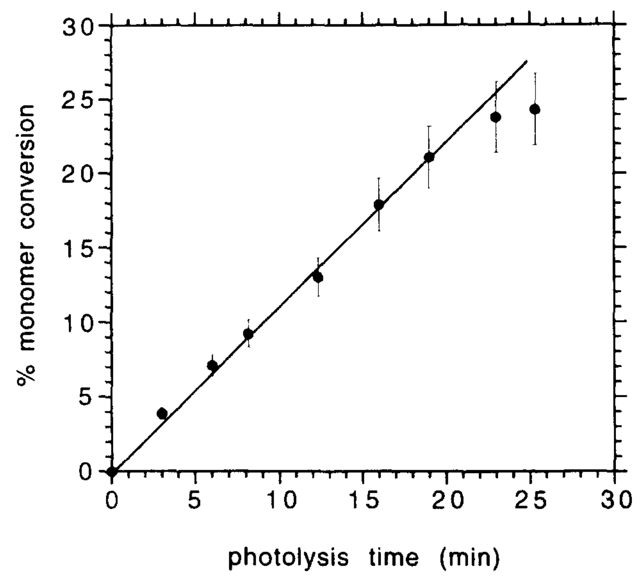


Fig. 3. Per cent conversion of monomer as a function of photolysis time for a deaerated solution containing $[Co(NH_3)_5N_3^{2+}]=0.25$ mM and $[AA]=1.0$ M at pH 2.5.

lets instead of a triplet of doublets is due to the identical value of the coupling constant between O and N on one hand and between N and H on the other ($a = 14$ G). The nitrogen atoms of the N_3 group provoke a splitting into a triplet with $a=3$ G. The intensity of the signal as a function of irradiation time increased from zero at $t=0$ to a maximum, then slowly decreased. No adduct with a radical arising from the monomer or the polymer was detected.

3.3. Polymerization

All the experiments were performed in the absence of air; in aerated solution only traces of polymer were observed. Fig. 3 shows a plot of the per cent of monomer conversion as a function of photolysis time; no induction period was discerned. When the extent of conversion was less than 20%, the polymerization rate was constant. The variation in R_p as a function of $[Co(NH_3)_5N_3^{2+}]$ is given in Table 1. Experiments on the dependence of R_p on I_a were performed at $[Co(NH_3)_5N_3^{2+}]=0.25$ and 5.0 mM (Table 2); R_p as a function of [AA] was also determined (Table 3).

4. Discussion

From the results it is possible to infer the following simplified sequence of events for the polymerization of acrylamide photosensitized by $Co(NH_3)_5N_3^{2+}$.

4.1. Excitation of the photosensitizer

Excitation of $Co(NH_3)_5N_3^{2+}$ in aqueous solution leads to the photoaquation of NH_3, but not N_3^-, at all wavelengths. Photoredox, with the formation of Co_{aq}^{2+} and $N_3^{\bullet}$ radicals, results from excitation into the ligand-to-metal charge transfer bands in the UV [8,10] but is not believed to occur directly from ligand field excitation in the visible; it apparently does so through secondary photolyses [18]. Regardless of the detailed mechanism, there is no doubt about the generation of $N_3^{\bullet}$ radicals (and an equivalent amount of Co_{aq}^{2+}) in this system.

Table 1
R_p as a function of $[Co(NH_3)_5N_3^{2+}]$ [a]

$[Co(NH_3)_5N_3^{2+}]$ (mM)	I_a (10^{-5} Einstein l^{-1} s^{-1})	R_p (10^{-4} mol l^{-1} s^{-1})
0.113	0.52	2.3
0.150	0.69	2.5
0.250	1.1	3.6
0.500	2.1	4.4
1.00	3.9	6.4
1.50	5.6	7.3
1.75	6.0	7.7
2.00	6.5	8.0
2.50	7.9	8.6
3.50	9.2	10.7
4.25	9.9	10.2
5.00	10.6	9.5

[a] $[AA]=1.0$ M; pH 2.5; $I_0=1.2\times10^{-4}$ Einstein l^{-1} s^{-1}.

Table 2
R_p as a function of I_a [a]

I_a (10^{-5} Einstein l^{-1} s^{-1})	R_p (10^{-4} mol l^{-1} s^{-1})
$[Co(NH_3)_5N_3^{2+}]=0.25$ mM	
0.179	1.22
0.214	1.59
0.355	1.74
0.711	2.70
0.735	2.84
1.57	3.98
$[Co(NH_3)_5N_3^{2+}]=5.0$ mM	
2.69	1.90
2.81	2.10
3.18	2.56
5.38	5.00
11.5	6.30
24.4	10.1

[a] $[AA]=1.0$ M; pH 2.5; I_0 varied with neutral density filters in front of the cell.

Table 3
R_p as a function of [AA] [a]

[AA] (M)	R_p (10^{-4} mol l^{-1} s^{-1})
0.50	0.96
1.0	1.8
1.5	4.9
2.0	7.5
2.5	8.5

[a] $[Co(NH_3)_5N_3^{2+}]=0.25$ mM; pH 2.5.

Our value of Φ_{Co} (0.020) at 546 nm is not inconsistent with that of an earlier determination (0.011 at $\lambda \geqslant 550$ nm) [19]. The very similar value of the quantum yield of complex loss (0.016) indicates that regardless of the involvement of secondary photolyses or the question of the spectral or HPLC separation of $Co(NH_3)_4(H_2O)N_3^{2+}$, the transformation of $Co(NH_3)_5N_3^{2+}$ into Co_{aq}^{2+} and $N_3^{\bullet}$ is a clean process and can be represented by reaction (1) with an overall quantum yield ϕ. The rate of formation of $N_3^{\bullet}$ is expressed as ϕI_a, which is independent of [AA]; ϕ can be taken as 0.020.

$$Co(NH_3)_5N_3^{2+} \xrightarrow{h\nu} Co^{2+} + N_3^{\bullet} + 5NH_3 \qquad (1)$$

4.2. Initiation

$N_3^{\bullet}$ radicals can oxidize AA via electron or H atom transfer (reaction (2)), generating monomer radicals ($M^{\bullet}$). The steady state concentration of $N_3^{\bullet}$ ($[N_3^{\bullet}]_{ss}$) is $\phi I_a/(k_i[AA]+k_d)$, where k_d represents the rate constants and concentrations in the rate laws of all the other processes by which $N_3^{\bullet}$ disappears. In as much as the rate of initiation (R_i) equals $k_i[N_3^{\bullet}]_{ss}[AA]$, $R_i = k_i\phi I_a[AA]/(k_i[AA]+k_d)$. It can be assumed that the combination reaction of $N_3^{\bullet}$ radicals ($k = 4.4 \times 10^9$ M^{-1} s^{-1} [20]) is slow compared with reaction (2) owing to the very low value of $[N_3^{\bullet}]_{ss}$ under continuous photolysis conditions.

$$N_3^{\bullet} + AA \xrightarrow{k_i} N_3^- + M^{\bullet} \qquad (2)$$

4.3. Propagation

The propagation of the reactive radicals can be written as reactions (3)–(5). The rate of propagation (R_p) is equal to $k_p[P^{\bullet}][AA]$, where $[P^{\bullet}]$ is the total concentration of the organic radicals.

$$M^{\bullet} + AA \xrightarrow{k_1} M_2^{\bullet} \qquad (3)$$

$$M_2^{\bullet} + AA \xrightarrow{k_2} M_3^{\bullet} \qquad (4)$$

...

$$M_{n-1}^{\bullet} + AA \xrightarrow{k_p} M_n^{\bullet} \qquad (5)$$

4.4. Termination

One can visualize three different processes, involving the organic radicals, that could contribute to the overall termination of the chain reaction: mutual annihilation (reaction (6)), reaction with $Co(NH_3)_5N_3^{2+}$ (reaction (7)) and reaction with $N_3^{\bullet}$ radicals (reaction (8)). R_t is the rate of termination.

$$M_n^{\bullet} + M_m^{\bullet} \xrightarrow{k_t} \text{polymer} \qquad (6)$$

$$M_n^{\bullet} + Co(III) \xrightarrow{k_t} Co_{aq}^{2+} + \text{polymer} \qquad (7)$$

$$M_n^{\bullet} + N_3^{\bullet} \xrightarrow{k_t} N_3^- + \text{polymer} \qquad (8)$$

4.4.1. Mutual annihilation

According to reaction (6), $R_t = k_t[P^{\bullet}]^2$. When the hypothesis of quasi-stationarity ($R_t = R_i$) is applied, R_p is given by Eq. (9). If the $N_3^{\bullet}$ radicals do not disappear by any route other than reaction (2), Eq. (9) simplifies to $R_t = k_p[AA](\phi I_a/k_t)^{1/2}$, predicting that R_p should be proportional to $(I_a)^{1/2}$ and [AA] but independent of [Co(III)].

$$R_p = k_p[AA]\left(\frac{k_i\phi I_a[AA]}{k_t(k_i[AA]+k_d)}\right)^{1/2} \qquad (9)$$

A test of the validity of this termination step would be a linear plot of R_p vs. $(I_a)^{1/2}$ at constant [AA] with a slope of $k_p[AA](\phi/k_t)^{1/2}$ and a y intercept of zero. The data in Table 1 reflect the variation in I_a through a change in [Co(III)] and are shown in Fig. 4; the data in Table 2 are for two concentrations of Co(III) and the variation in I_a through a change in I_0 and are shown in Fig. 5. Quantitatively, the slopes of the plots in Figs. 4, 5(A) and 5(B) are very similar: 1.0, 1.0 and 0.76 respectively. Corresponding plots of R_p vs. I_a are decidedly non-linear. Another test of this termination step would be a linear plot of R_p vs. [AA] at constant I_a; Fig. 6 shows the data from Table 3. In as much as Figs. 4–6 show acceptable linear fits, we can conclude that reaction (6) is the dominant termination step. It is to be noted, however, that the y intercepts in Figs. 5 and 6 are negative, indicating that R_p would be predicted go to zero before I_a and [AA] did; this suggests that one or both of the other termination steps may be operative, at least to a small extent.

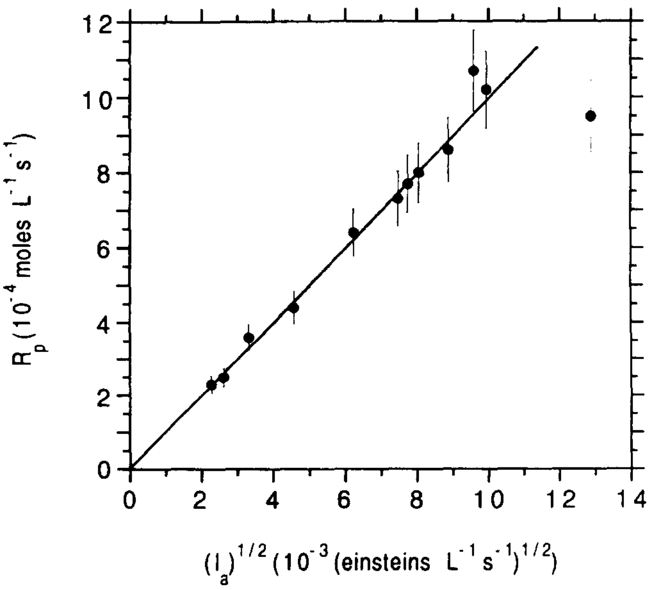


Fig. 4. R_p as a function of $(I_a)^{1/2}$ for [AA] = 1.0 M at pH 2.5 with (A) $[Co(NH_3)_5N_3^{2+}]$ = 0.113–5.0 mM. Data are taken from Table 1.

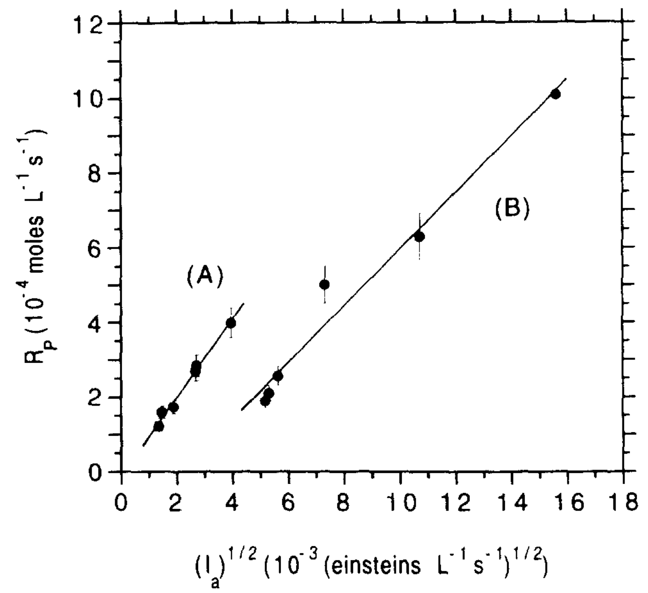


Fig. 5. R_p as a function of $(I_a)^{1/2}$ for [AA] = 1.0 M at pH 2.5 with (A) $[\mathrm{Co(NH_3)_5N_3}^{2+}]$ = 0.25 mM and (B) $[\mathrm{Co(NH_3)_5N_3}^{2+}]$ = 5.0 mM. Data are taken from Table 2.

4.4.2. Reaction with Co(III)

According to reaction (7), $R_t = k_t[\mathrm{Co(III)}][\mathrm{P}^\bullet]$. Then $R_p = k_p[\mathrm{AA}]\Phi I_a / k_t[\mathrm{Co(III)}]$ if the only pathway for $\mathrm{N_3}^\bullet$ radicals is reaction (2). This simplified equation contains interlocking variables in as much as I_a is a function of [Co(III)] and R_p is a function of I_a. Therefore the kinetically meaningful plot at constant [AA] is that of R_p/I_a vs. 1/[Co(III)], which is predicted to be linear with a y intercept of zero. Such a plot from the data in Table 1 is presented in Fig. 7, showing that reaction (7) cannot be an important step in the overall mechanism.

4.4.3. Reaction with $N_3^\bullet$

If reaction (8) were important, $R_t = k_t[\mathrm{P}^\bullet][\mathrm{N_3}^\bullet]$ and $k_d = k_t[\mathrm{P}^\bullet]$. However, if the radical–radical reaction (8) were slow relative to the radical–acrylamide reaction (2), then $R_p = (k_i k_p / k_t)[\mathrm{AA}]^2$, predicting that R_p should be proportional to $[\mathrm{AA}]^2$ but independent of I_a. We have already seen that $R_p \propto [\mathrm{AA}]$ and $(I_a)^{1/2}$, showing that reaction (8) cannot be an important step in the overall mechanism.

5. Summary

$\mathrm{Co(NH_3)_5N_3}^{2+}$ is an efficient photosensitizer of acrylamide free-radical polymerization through the generation of $\mathrm{N_3}^\bullet$ upon excitation at long wavelengths; the initiation reaction of $\mathrm{N_3}^\bullet$ with acrylamide produces monomer radicals which propagate the formation of polymer. The termination of the free-radical chain reaction occurs primarily via the mutual annihilation of the macroradicals; the reaction of macroradicals with $\mathrm{N_3}^\bullet$ cannot be of any importance. The fall-off in R_p at the highest [Co(III)] in Fig. 4 can be attributed to the onset of the kinetically competitive reaction of the macroradicals with the complex. $\mathrm{Co(NH_3)_5N_3}^{2+}$ may prove to be an effective photosensitizer for free-radical polymerization with the 633 nm line of He–Ne lasers despite the low value of its molar absorptivity at that wavelength (20–30 M^{-1} cm^{-1}).

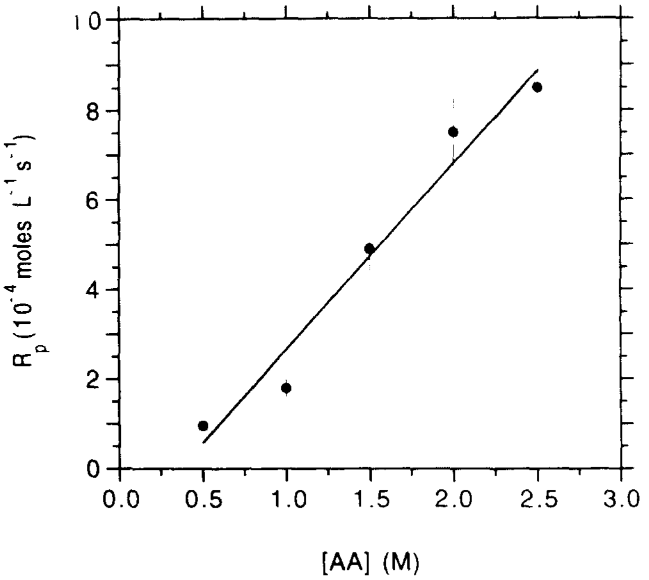


Fig. 6. R_p as a function of [AA] for $[\mathrm{Co(NH_3)_5N_3}^{2+}]$ = 0.25 mM at pH 2.5. Data are taken from Table 3.

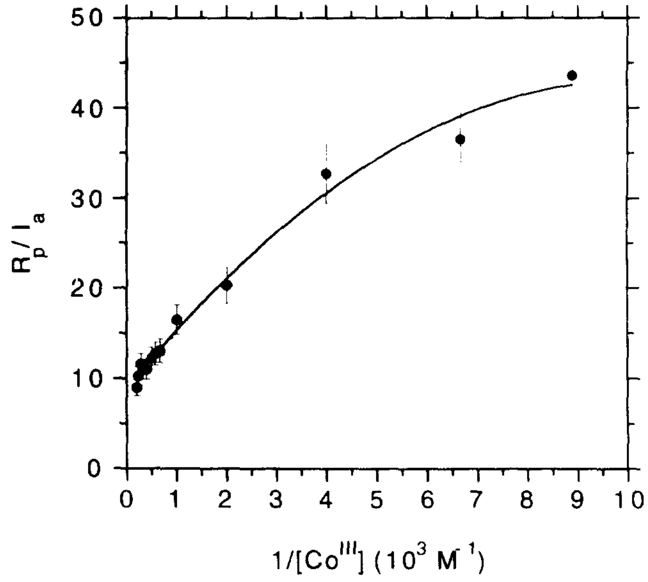


Fig. 7. R_p/I_a as a function of 1/[Co(III)] for [AA] = 1.0 M at pH 2.5.

Acknowledgments

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