The Photolysis of Polyvinylpyrrolidone in Aqueous Solutions in the Presence of Oxygen and Cupric Ions

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SUMMARY

The oxidative photolysis of polyvinylpyrrolidone with light of $\lambda = 2537$ Å has been studied over a range of oxygen pressures and polymer concentrations. The results show that chain scission and cross linking take place simultaneously. In the range where cross linking is a negligible component, a mechanism based on chain scission due to components which lead to chain scission without intervention of oxygen, and a component which leads to chain scission via hydroperoxide side groups, has been proposed. This mechanism accounts satisfactorily for all observed features of the reaction. The degree of degradation at any one time decreases with oxygen pressure. Cupric ions, with or without oxygen present, have very little influence on the degradation process. However, the UV spectra of PVP in the presence of cupric ions are different from those without them.

The photolysis of polyvinylpyrrolidone (PVP) in oxygen-free aqueous solutions was investigated recently [1]. It was ascertained that the process is initiated to a large extent by a Norrish type II cleavage with a much smaller component of type I cleavage. Recombination between double-bonded chain ends and polymer radicals takes place subsequently. The very initial photolysis is independent of chain length and polymer concentration but subsequently branches out for different concentrations of polymer, the degradation decreasing with concentration. The quantum yield for chain scission is small (10^{-5} to 10^{-6}).

The investigation was extended to photolysis in aqueous polymer solutions in the presence of oxygen, and some experiments were also performed in the presence of cupric ions. The reaction in the presence of oxygen proceeds via chain scission and some simultaneous cross linking. The latter increases with oxygen pressure. The evaluation of intrinsic viscosity data in terms of number-average chain lengths has to be treated with caution, as the shape of the polymer molecules changes with branching and cross linking. A mechanism for the photolysis at oxygen pressures where cross linking is negligible is proposed in the present paper.

Cupric ions have very little effect on the photolysis, whether it takes place in the presence or absence of oxygen. This is understandable, as PVP is a very weak base. In contrast, the photolysis of isotactic polymethacrylic acid in the presence of cupric ions is very much more susceptible to degradation than in their absence[2].

EXPERIMENTAL

Materials

The same samples of PVP (General Aniline and Film Corp., New York) were used as in the previous work [1]: (1) fraction P_I, $[\eta] = 3.42$ dl/g, $\overline{M}_{v \cong n} = 4.77 \times 10^6$, and $DP_{v \cong n} = 4.3 \times 10^4$, and (2) fraction P'_{II}, $[\eta] = 3.62$ dl/g, $\overline{M}_{v \cong n} = 5.24 \times 10^6$, and $DP_{v \cong n} = 4.71 \times 10^4$. Intrinsic viscosities were converted to viscosity average chain lengths, using a relationship as follows [3]: $[\eta] = 3.93 \times 10^{-4} \overline{M}_v^{0.59}$ dl/g. Purification and fractionation procedures were described previously [1]. Oxygen was obtained from the Linde Company and was dried before being passed into the apparatus. Water was double distilled. All other chemicals were of AR grade.

Apparatus and Procedure

The photolysis apparatus was the same as before [1]. The light intensity was kept constant during any one series of experiments but not necessarily for different series of experiments. A vacuum system, which permitted one to maintain a constant oxygen pressure, was attached to the reaction cell during any one experiment. It is shown in Fig. 1. The empty reaction vessel was first attached at D. The system was then evacuated by opening all stopcocks except E_3. Oxygen was introduced via E_3, followed by complete evacuation (E_3 closed) to remove all residual air. The system was then filled with oxygen to a pressure of about 110 cm Hg. E_2 was closed and the system evacuated except for flask B. The reaction vessel was then removed and filled with 10 ml of the appropriate polymer solution. The solution was frozen with liquid nitrogen and again attached to the system. This was evacuated and the air from the
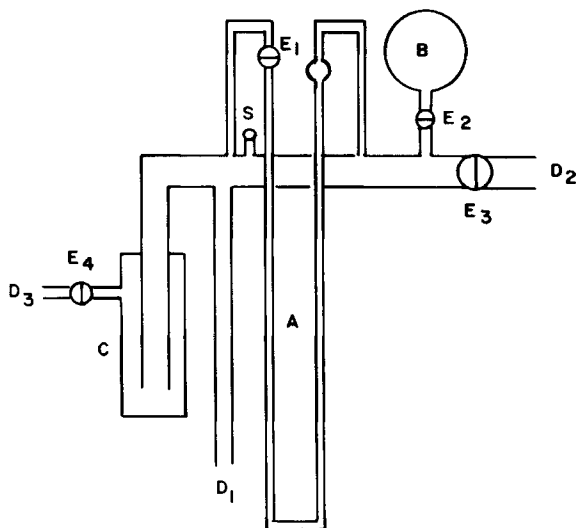
Fig. 1. Oxygen pressure system: A, manometer; B, one-liter flask; C, condenser; D_1, connection to reaction vessel; D_2, connection to oxygen cylinder; D_3, connection to vacuum pump; E_1, E_2, E_3, and E_4, stopcocks; S, safety outlet.

solution was removed by repeated thawing, pumping, and freezing. Eventually oxygen from flask B was introduced up to the desired pressure. Any evaporation of water from the polymer solution during this procedure was taken into account.

RESULTS

Photolysis in the Presence of Oxygen

Aqueous solutions of P_I were irradiated while in equilibrium with oxygen over a range of pressures (25°C, constant light intensity, 0.1% w/v, $\lambda \cong 2537$ Å). Figure 2 shows $[\eta]_t / [\eta]_{t=0}$ plotted as a function of irradiation time for various oxygen pressures (12, 24, 48, 76, and 90 cm Hg). The degree of degradation,

$$\alpha = (1/\overline{DP}_{n,t}) - (1/DP_{n,0})$$

plotted versus irradiation time is shown in Fig. 3. The viscosity average chain lengths were transformed into number-average chain length via the random chain scission theory. This is permissible as long as cross linking is a very small component of the total process. The types of curves in the presence of oxygen are quite dif-
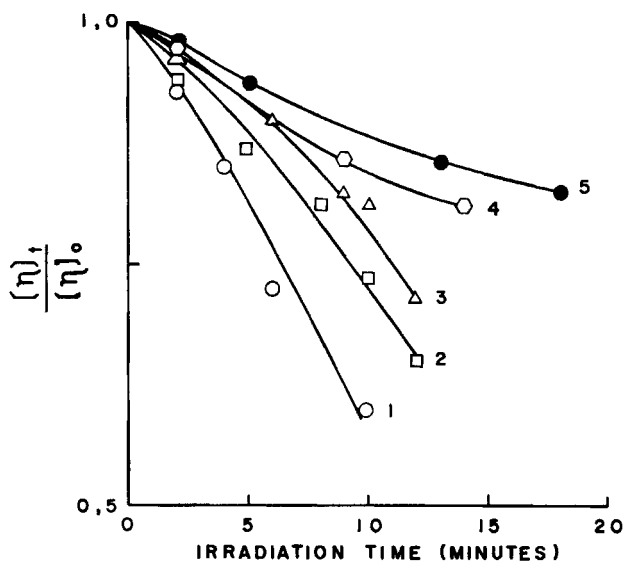
Fig. 2. Ratio of intrinsic viscosities after irradiation time t to
t = 0, respectively: 1, 12 cm Hg; 2, 24 cm Hg; 3, 48 cm Hg; 4, 76 cm
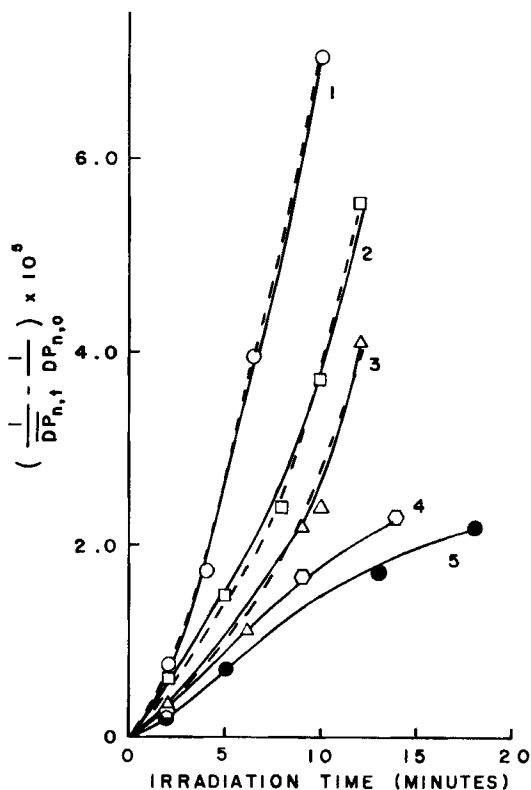Hg; 5, 90 cm Hg.

ferent from those obtained in its absence. It is noteworthy that the
degree of degradation for a given reaction time decreases with in-
creasing oxygen pressure.

Figure 4 shows the results of photolyses for various polymer
concentrations for 12 cm Hg at 25°C (P_I, 0.1, 0.2, 0.3% w/v). Here
the degree of degradation decreases with increasing polymer con-
centration. The degree of degradation as a function of degradation
time for three temperatures (25, 45, and 55°C, P_I 0.1% w/v, 48 cm
Hg of O_2) gives an Arrhenius equation $k_{exp} = 8.8 \times 10^{-2}$
$e^{-6000/RT}$ (min^{-1}) for the first 2 min of the reaction.

The optical absorbances (1 cm) for the absorption maxima
($\lambda = 1970$ Å) of 0.1% w/v solutions of P_I irradiation in the presence
of 12 cm Hg of oxygen at 25°C decrease with time. The solutions
were diluted to 0.002% w/v for measurement of the UV spectra. In
the absence of oxygen the absorbances increase with time [1].

Photolysis in the Presence of Cu^{2+}

Fraction P_I was photolyzed (0.1% w/v, 25°C) in the absence of
oxygen but in the presence of various amounts of cupric ions ($CuCl_2$).
The ratios of moles of Cu^{2+} to monomeric unit moles were 0, 7/100,
14/100, and 42/100, respectively. The results are given in Fig. 5.

Fig. 3. Degree of degradation as a function of irradiation time for various pressures. 1, 12 cm Hg; 2, 24 cm Hg; 3, 48 cm Hg; 76 cm Hg; 5, 90 cm Hg.

Copper ions in this range of concentractions do not influence the photolysis. The slight decrease in the degree of degradation with increasing copper concentration is due to slight changes in conformation of the polymer molecules in the presence of electrolyte. This was shown by plots of intrinsic viscosities for a number of fractions of different chain length versus intrinsic viscosities obtained in the presence of copper ions.

Photolyses in the presence of cupric ions and air show some minor differences from those carried out in the presence of air or oxygen alone. The type of curve is quite similar to those obtained without cupric ions; however, the degree of degradation first decreases with increasing Cu^{2+} ion concentration, but if the latter is further increased, the degree of degradation starts to increase again

(see Fig. 6, molar ratios Cu^{2+}/monomeric unit moles: 2/1000, 7/100, and 14/100; 0.1% w/v of P'_{II} at 25°C). The intrinsic viscosities were corrected for the effect of electrolyte concentration.

DISCUSSION

The degradation curves (see Fig. 3) in the presence of oxygen are quite different from those obtained in its absence (see Fig. 1 of [1]). Figure 2 shows the typical characteristics of a polymer, which undergoes chain scission and cross linking simultaneously. (PVP in bulk, exposed to oxygen and UV light ($\lambda > 2800$ Å), almost com-
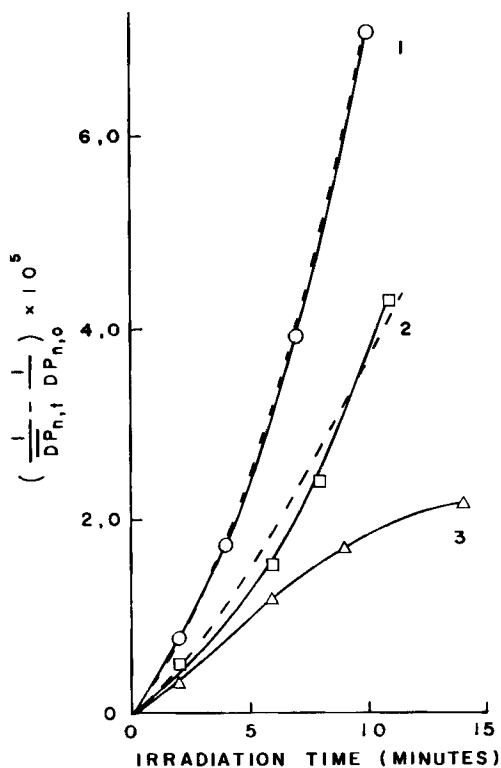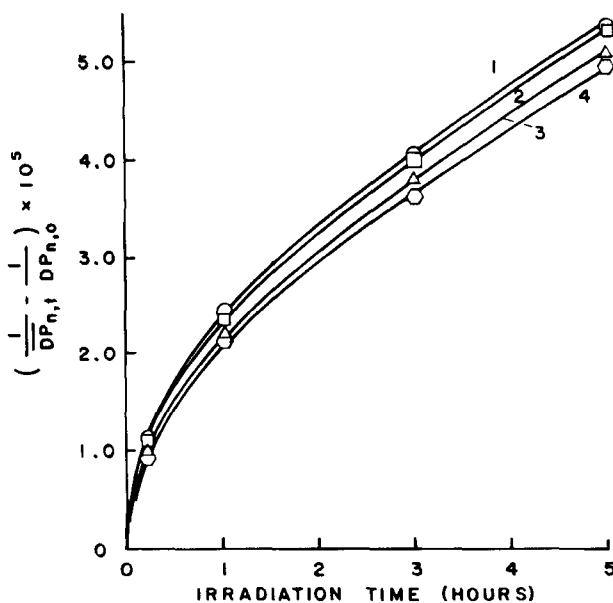

Fig. 4. Degree of degradation as function of irradiation time for various polymer concentrations. 1, 0.1% w/v; 2, 0.2% w/v; 3, 0.3% w/v.
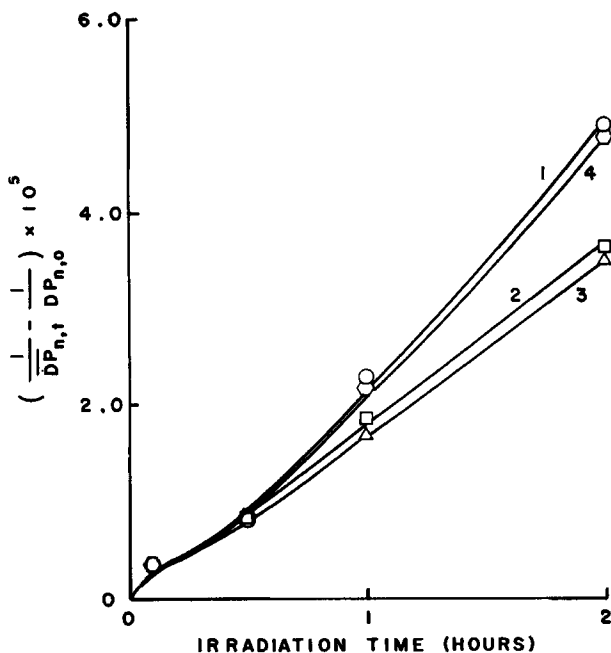
Fig. 5. Degree of degradation as function of irradiation time for the photolysis of PVP (P I 0.1%, 25°C) in the presence of cupric ions. 1, without cupric ions; 2, molar ratio† 7/100; 3, molar ratio† 14/100; 4, molar ratio† 42/100. †Cu^{2+}/monomeric units of PVP.

pletely cross links [4].) According to Shultz et al. [5], the following relationship should hold in such a case:

$$([\eta]/[\eta]_0)^{1/\alpha} = (1 - R/R^*)^{-1} = \overline{M}_w/M_{w,0} \tag{1}$$

Here α is the exponential constant in the Mark-Houwink equation for the system under discussion, R and R^* the radiation dose before the gel point is reached and the radiation dose required just to reach the gel point, respectively, and $M_{w,0} \cong n$ and $\overline{M}_w$ are weight-average molecular weights at times t = 0 and t, respectively. R can be expressed by R = Kt, where t is the irradiation time and K a constant of proportionality, provided the polymer and oxygen concentrations are kept constant. Equation (1) has been derived for polymer samples, which have a random molecular size distribution. Fraction P_I will fairly rapidly approach such a distribution, while degrading. Thus it is expected that the plot of $[(M_{w,0}/M_w) - 1]$ versus irradiation time t will give fairly good straight lines, as long as chain scission is predominant for various oxygen pressures and

Fig. 6. Degree of degradation as function of irradiation time for photolysis of PVP (P'I 0.1% w/v, 25°C) in the presence of cupric ions and air. 1, without cupic ions; 2, molar ratio 2/100; 3, 7/100; 4, 14/100.

constant polymer concentration. The weight-average molecular weights were obtained by doubling the corresponding number-average molecular weights. Actually, fairly good straight lines are obtained up to about 10 min of the reaction. The slope $= -1/R^*$; as the experimental slope is positive, R^* must have a negative value. According to Shultz et al.[5], this is only possible if $\beta/\alpha' > 2$, where β is the total number of chain scissions and α' the total number of cross links at time t or R, respectively. This result indicates that the number of chain scissions is at least double the number of cross links.

If the cross-linking component of the reaction is very small, intrinsic viscosity values can still be transformed into number-average chain lengths with sufficient accuracy. This seems to be the case for the photolyses carried out under 12, 24, and 48 cm Hg of oxygen pressure (P_I 0.1% w/v, 25°C). Actually, the oxygen pressure or its concentration in the solution is given by Henry's law:

$$P_{O_2 \, solution} = K_4 P_{O_2 \, gas}.$$

The photolysis curves shown in Fig. 3 for 12, 24, and 48 cm Hg (P_I 0.1% w/v, 25°C) and the one for double the polymer concentration (P_I 0.2% w/v, 25°C) and 12 cm Hg of oxygen pressure can be fitted (Fig. 3, dashed lines) by an empirical equation as follows:

$$\frac{[\eta]_0 - [n]}{[n]_0} = \alpha = \frac{1}{\overline{DP}_{n,t}} - \frac{1}{\overline{DP}_{n,o}} = K_I t + (K_{II}/b)(e^{-bt} - 1) \qquad (2)$$

where $[n]_0$ and $[n]$ are the concentrations of main chain links at times $t = 0$ and t, respectively, and α is the degree of degradation. K_I, K_{II}, and b are constants, whose values are given in Table 1.
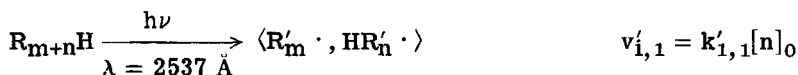
Table 1. Parameters for Empirical Equation (2) for the Photolysis of PVP (P_I) at 25°C

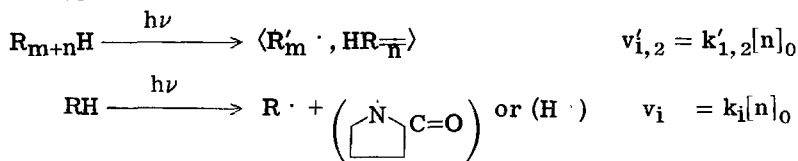| P_{O_2}, cm Hg	Polymer concentration, % w/v	$10^5 K_I$, min^{-1}	$10^5 K_{II}$, min^{-1}	$\Delta 10^5 K$, min^{-1}	b, min^{-1}
12	0.1	1.26	1.00	0.26	0.13
24	0.1	1.42	1.25	0.17	0.043
48	0.1	1.98	1.90	0.11	0.025
12	0.2	1.22	1.00	0.22	0.041

The experimental results can be accounted for by a chain scission reaction component of type I, producing, via cages, polymer radicals, and one of the Norrish type II cleavages, one double-ended chain and one polymer radical, as was the case for the reaction in the absence of oxygen [1]. This photolysis was previously formulated without cages; this does not alter the kinetics but gives a different meaning to some of the rate constants. Repolymerization does not occur as the radical chain ends rapidly react with oxygen. The main reaction, however, is a chain reaction, which leads via hydroperoxides to main chain scission. The whole photolysis process can be formulated as follows.
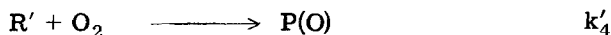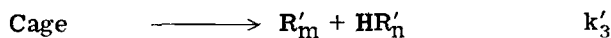
Initiation:

Type 1:

$$R_{m+n}H \xrightarrow[\lambda = 2537 \text{ Å}]{h\nu} \langle R'_m \cdot, HR'_n \cdot \rangle \qquad\qquad v'_{i,1} = k'_{1,1}[n]_0$$

Type 2:

$$R_{m+n}H \xrightarrow{h\nu} \langle R'_m \cdot , HR_{\overline{n}} \rangle \qquad\qquad v'_{i,2} = k'_{1,2}[n]_0$$

$$RH \xrightarrow{h\nu} R \cdot + \left(\underset{\square}{\dot{N}} C{=}O \right) \text{ or } (H \cdot) \quad v_i = k_i[n]_0$$

RH stands here for main chain links; R · for polymer radicals, which have their radical nature somewhere along the chain backbone: and R′ for a polymer radical, which has its radical nature at the chain end. ⟨ ⟩ signifies solvent cages containing polymer radicals and $R_{\overline{n}}$ signifies a polymer chain with a double-bond end. Further,

$$\text{Cage} + O_2 \longrightarrow RH + O_2 \qquad\qquad k'_2$$

Chain scissions:

$$\text{Cage} \longrightarrow R'_m + HR'_n \qquad\qquad k'_3$$

$$R' + O_2 \longrightarrow P(O) \qquad\qquad k'_4$$
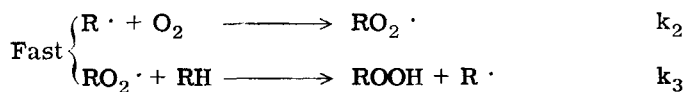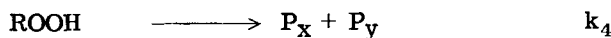
P(O) signifies a "dead" polymer molecule, which has an oxygen containing end group.

Propagation:

$$\text{Fast}\begin{cases} R \cdot + O_2 \longrightarrow RO_2 \cdot & k_2 \\ RO_2 \cdot + RH \longrightarrow ROOH + R \cdot & k_3 \end{cases}$$

Chain scission:

$$ROOH \longrightarrow P_x + P_y \qquad\qquad k_4$$

$$ROOH \xrightarrow{h\nu} ROOH^* \qquad\qquad k_5$$
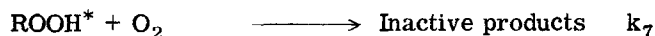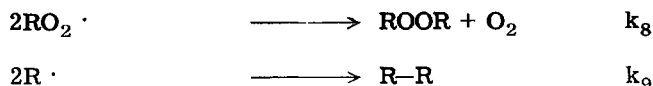
ROOH* stands for an energy-rich (activated) hydroperoxide molecule. The chain scission reaction does not need to be formulated with cages here, as no polymer radicals are involved. Equilibrium is always maintained between 5 and 6.

$$ROOH^* + RH + O_2 \longrightarrow ROOH + \text{products} \quad k_6$$

$$ROOH^* + O_2 \longrightarrow \text{Inactive products} \qquad k_7$$

Termination (cross linking):

$$2RO_2 \cdot \quad\longrightarrow\quad ROOR + O_2 \qquad k_8$$

$$2R \cdot \quad\longrightarrow\quad R{-}R \qquad k_9$$

This mechanism leads to the following equations and relationships. For details, see the Appendix.

The total rate of chain scission is given by

$$-\frac{d[n]}{dt} = -\left\{ \left(\frac{d[n]}{dt}\right)_I + \left(\frac{d[n]}{dt}\right)_{II} \right\} = k_3' \frac{(k_{1,1}' + k_{1,2}')[n]_0}{k_2'[O_2]} + k_4 \frac{a}{b} (1 - e^{-bt})$$

$$(3)$$

Here

$$a = k_3[n]_0[RO_2 \cdot] = \frac{k_i^{1/2} k_2 k_3 [O_2][n_0]^{3/2}}{(k_9 k_3^2 [n_0]^2 + k_2^2 k_8 [O_2]2)^{1/2}} \qquad (4)$$

and

$$b = \frac{k_7 k_5}{k_6 [O_2][n_0] + k_7} \qquad (5)$$

Integration of Eq. (3) yields

$$\frac{[n] - [n]_0}{[n]_0} = \alpha = \frac{1}{\overline{DP}_{n,t}} - \frac{1}{\overline{DP}_{n,0}} = k_3' \frac{k_{1,1}' + k_{1,2}'}{k_2'} \frac{t}{[O_2]} +$$

$$k_4 \frac{a}{b[n]_0} \left[t + \frac{1}{b}(e^{-bt} - 1) \right] \qquad (6)$$

Equation (6) can be written in the form

$$\alpha = (K_I' + K_{II}) t + (K_{II}/b)(e^{-bt} - 1) \qquad (7)$$

or

$$\alpha = K_I t + (K_{II}/b)(e^{-bt} - 1) \qquad (8)$$

Equation (8) is identical with the empirical equation (1).

The constant b should have a positive numerical value and should be proportional to the reciprocal oxygen pressure and decrease with polymer concentration. This is actually the case (see Table 1). $\Delta K = K_I - K_{II}$ should be proportional to the reciprocal oxygen pressure and to the square root of the polymer concentration. This

is also approximately the case (see Table 1). The constant K_{II}
should be approximately proportional to the square of the oxygen
pressure and independent of polymer concentration. This is also
the case (see Table 1). Thus the mechanism proposed fits all ex-
perimental facts.

The photolysis of PVP in the presence of cupric ions, but in the
absence of oxygen, gives identical curves to those in the absence of
cupric ions. In the presence of air and cupric ions, curves similar
to those in the presence of oxygen or air only are obtained. However,
there is one peculiar feature inasmuch as small copper ion/mono-
meric unit molar ratios show less degradation than is observed in
the absence of cupric ions. However, when the molar ratio is further
increased, the degradation also increases. The reason for this be-
havior is not understood.

The UV spectra of PVP in the presence of cupric ions (no oxygen)
are quite different from those in their absence (see Fig. 7). The
optical densities increase with time of irradiation. This is the oppo-
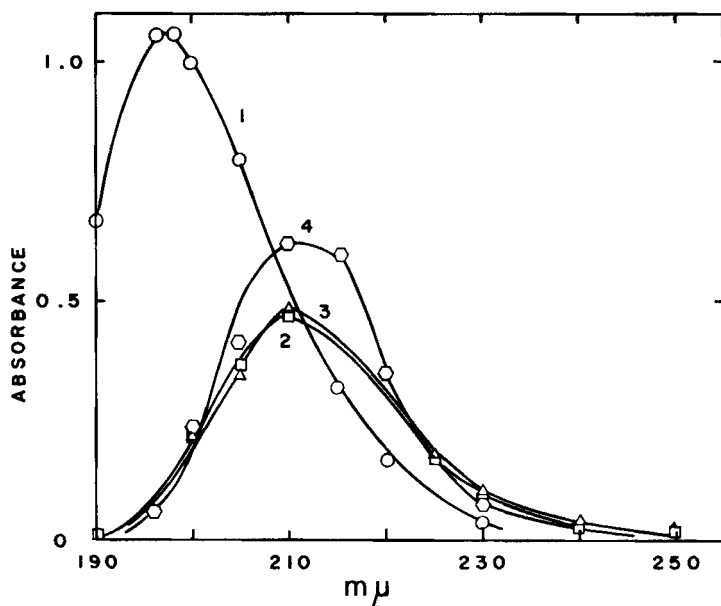site trend as that found for the photolysis without cupric ions and
oxygen.

Fig. 7. Oxidative photolysis of PVP fraction P_I' (concn. 0.002% w/v)
UV spectra in the presence of cupric ions. 1, PVP fraction P'I (t = 0);
2, PVP with cupric ions (t = 0); 3, 0.5 hr; 4, 3.0 hr.

ACKNOWLEDGMENT

APPENDIX

Only initial stages of the whole degradation process are considered. The rate of direct photolytic chain scission is

$$- (d[n]/dt)_I = k'_3 [cage] \tag{1'}$$

The steady-state concentration of cages amounts to

$$[cage] = \frac{(k'_{1,1} + k'_{1,2})[n]_0}{k'_2[O_2] + k'_3} \cong \frac{(k'_{1,1} + k'_{1,2})[n]_0}{k'_2[O_2]} \tag{2'}$$

$[n]_0 \cong [n]$ stands for main chain link concentrations at times $t = 0$ and t, respectively. The total links broken is quite small, less than 1%. Hence

$$- \left(\frac{d[n]}{dt}\right)_I = k'_3 \frac{(k'_{1,1} + k'_{1,2})[n]_0}{k'_2[O_2]} \tag{3'}$$

The mechanism for the process leading to chain scission via hydroperoxide side groups is as follows. For steady-state conditions one has

$$k_i[n]_0 = v_i = k_8[RO_2 \cdot]^2 + k_9[R \cdot]^2 = fv_i + (1 - f)v_i = \text{constant}$$

Hence

$$[R \cdot] = \left(\frac{k_i[n_0] - k_8[RO_2 \cdot]}{k_9}\right)^{1/2} \tag{1}$$

The rate of formation of $[RO_2 \cdot]$ radicals is

$$d[RO_2 \cdot]/dt = k_2[R \cdot][O_2] - k_3[n_0][RO_2 \cdot] - k_8[RO_2 \cdot]^2 = 0 \tag{2}$$

Assuming $[RO_2 \cdot]$ to be very small, its steady-state concentration is given by

$$[RO_2 \cdot] = k_2[R \cdot][O_2]/k_3[n_0] \tag{3}$$

Substituting $[R\cdot]$ from Eq. (1) into Eq. (2) gives

$$[RO_2\cdot] = \frac{k_i^{1/2}k_2[n_0]^{1/2}[O_2]}{(k_9 k_3^2[n_0]^2 + k_2^2 k_8[O_2]^2)^{1/2}} \tag{4}$$

The rate of chain scission is given by

$$\left(\frac{d[n]}{dt}\right)_{II} = k_4[ROOH] \tag{5}$$

Further,

$$\frac{d[ROOH]}{dt} = \frac{k_3 k_i^{1/2}[n_0]^{3/2} k_2[O_2]}{(k_9 k_3^2[n_0]^2 + k_2^2 k_8[O_2]^2)^{1/2}} - k_7[ROOH^*] - k_4[ROOH] \tag{6}$$

The steady-state concentration of $[ROOH^*]$ is

$$[ROOH^*] = \frac{k_5[ROOH]}{k_6[n_0][O_2] + k_7} \tag{7}$$

Introducing Eq. (7) into (6) gives [if $k_4(ROOH)$ is very small]

$$\frac{d[ROOH]}{dt} = \frac{k_i^{1/2}k_2 k_3[n_0]^{3/2}[O_2]}{(k_9 k_3^2[n_0]^2 + k_2^2 k_8[O_2]^2)^{1/2}} - \frac{k_7 k_5[ROOH]}{k_6[n_0][O_2] + k_7} \tag{8}$$

Equation (8) can be written in the form

$$d[ROOH]/dt = a - b[ROOH] \tag{9}$$

a and b are given by Eqs. (4) and (5) in the main part of this paper.

Integration of Eq. (9) gives

$$[ROOH] = a/b \, (1 - e^{-bt}) \tag{10}$$

Introducing Eq. (10) into (5) and adding (3′) gives, on integration,

$$\frac{[n]_0 - [n]}{[n]_0} = \alpha = \frac{1}{\overline{DP}_{n,t}} - \frac{1}{DP_{n,0}}$$

$$= \frac{k_3'(k_{1,1}' + k_{1,2}')t}{k_2'[O_2]} + k_4\frac{1}{b[n]_0}t + k_4\frac{a}{b^2[n]_0}(e^{-bt}-1) \tag{11}$$

or

$$\alpha = (K_I' + K_{II})t + (K_{II}/b)(e^{-bt} - 1)$$
$$= K_I t + (K_{II}/b)(e^{-bt} - 1) \tag{12}$$

REFERENCES

[1] H. H. G. Jellinek and L. C. Wang, *J. Macromol. Sci.*, **A2, 781** (1968).
[2] H. H. G. Jellinek and S. N. Lipovac, IUPAC Meeting, Brussels, June 1967, *J. Polymer Sci. Symp.*, in press.
[3] L. C. Cerny, T. E. Hermniak, and J. F. Meier, *J. Polymer Sci.*, **44,** 539 (1960).
[4] H. H. G. Jellinek and F. Kryman, unpublished results.
[5] A. R. Shultz, P. I. Roth, and G. B. Rathmann, *J. Polymer Sci.*, **22,** 495 (1956).