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The Photolysis of Polyvinylpyrrolidone in Oxygen-Free Aqueous Solutions*

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SUMMARY

The photolysis of polyvinylpyrrolidone in oxygen-free aqueous solutions has been investigated as a function of polymer concentration, chain length, light intensity, and temperature. Ultraviolet spectra at various degrees of degradation have been measured. The experimental data can be satisfactorily accounted for by a Norrish type II cleavage of main chain links for ketones in conjunction with a small component of type I chain scission yielding polymer radicals. Recombination of double-bond-ended chains with polymer radicals takes place.

Investigations of the photolysis of water-soluble synthetic polymers in the absence of oxygen are quite rare [1]. The rate of photodegradation is usually a function of light intensity, pH, and ionic strength. Photolysis generally leads to a random degradation process. Such a photolysis process should be independent of polymer concentration for small light absorption [2]. If a concentration dependence is found, this is an indication that either the solvent participates in the degradation process or that another reaction in addition to the chain scission is operative, such as repolymerization or cross-linking.

The present work is concerned with the photolysis of polyvinylpyrrolidone (PVP) in aqueous solution in the absence of oxygen, as a function of polymer concentration, chain length, light intensity, and temperature. pH values apparently do not influence this reaction. If extremely high or low pH values were chosen, there might be an

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effect, as this polymer is a weak base; the intrinsic viscosities, for instance, change at these extreme pH values, indicating a change in conformation of the chain molecules.

The photolysis of PVP was found to be dependent on its concentration in water. This can be accounted for quantitatively by assuming random chain scission with subsequent recombination of polymer fragments (repolymerization). This process is similar to the type II mechanism proposed for poly(methyl vinyl ketone) by Guillet and Norrish [3]. Type I is also operative for this polymer but only to a small extent. The problem, whether singlet or triplet excited states are involved, is controversial and will not be discussed in this paper [4]. Wissbrun [5] also investigated the photolysis of poly(methyl vinyl ketone) and of poly(methyl isoprenyl ketone). The first polymer showed a type II cleavage, whereas the second produced monomer by unzipping, also involving a type II process. David et al. [6] studied the photolysis of poly(phenyl vinly ketone); the type II reaction is operative in this case.

Materials

Unfractionated PVP (K90), obtained from General Aniline and Film Corporation, New York, N. Y., was purified by precipitation with acetone from aqueous solution. It was, subsequently, dried at 60°C in a vacuum oven until constant weight was obtained. Nitrogen, from the Linde Company, was freed of residual oxygen by passing it through alkaline pyrogallol solution, water, and a drying tower (Drierite). All other chemicals were of AR grade.

Apparatus

The photolysis apparatus was similar to one used prevously [7]; the light source was a low-pressure mercury lamp emitting more than 95% of its light at 2537 Å (Englehard, Hanovia, N.J., No. 735-A-7). An ultrasil cylindrical quartz tube of 3.2 cm O.D. and 18 cm length was used as the reaction vessel, located in a water bath, thermostated at 25 ± 0.05°C. The light transmission of ultrasil quartz is practically 100% for a 1 cm thickness in the wavelength range 2500-3000 Å.

Procedure

Before and during light exposure, oxygen-free nitrogen was passed through the polymer solution. Ten milliliters of PVP solution was used for each experiment. Intrinsic viscosities, $(g/dl)^{-1}$, were measured in Ostwald-Fenske viscometers at 25 ± 0.05°C.

Eighty grams of PVP (K90) was dissolved in 1 liter of H_2O and acetone was slowly added at room temperature to the stirred solution. The precipate was allowed to settle after 3.5 liters of acetone had been added. The supernatant liquid was discarded. The precipitate was dissolved in 2 liters of H_2O and fractionated into six fractions by adding acetone dropwise and stirring the solution. The fractions were dried to constant weight in a vacuum oven at 60°C.

Three of the fractions were taken for the photolysis experiments. The viscosity average molecular weight was evaluated as follows [8]:

$$[\eta] = 3.93 \times 10^{-4} M_v^{0.59} (g/dl)^{-1}$$

The intrinsic viscosities, molecular weights, and chain lengths of the three fractions and of the unfractionated samples are given in Table 1. As the polymer samples are fractions, their chain lengths obtained from Eq. (1) can be taken as approximately equal to their number average chain lengths. Thus the number-average chain length for any degree of degradation can be obtained by means of the theory of random chain scission [2]. The random nature of the process will still be preserved if polymer with double-bond chain ends combine at random with polymer radicals, as is the case with PVP.

Table 1

Fraction	$[\eta]$, $(g/dl)^{-1}$	$10^{-6} MW_{v \cong n}$	$10^{-4} DP_{v \cong n}$
P I	3.42	4.77	4.29
P II	2.38	2.59	2.32
P V	1.50	1.18	1.02
Unfractionated sample	1.98	$\overline{DP}_v = 1.69 \times 10^4$	

EXPERIMENTAL RESULTS

Polymer Concentration; Initial Chain Length

The three fractions were irradiated with light of $\lambda = 2537$ Å and constant intensity as a function of concentration [0.1% (w/v), 0.2% (w/v), and 0.5% (w/v)]. Figure 1 shows degradation curves for fraction P I. The photolysis rate is independent of concentration in its very initial stages, but decreases rapidly afterward with concentration. The degradation is independent of chain length for any one polymer concentration (range $DP_{n,0}$ 1.02×10^{-4} to 4.3×10^{-4}).

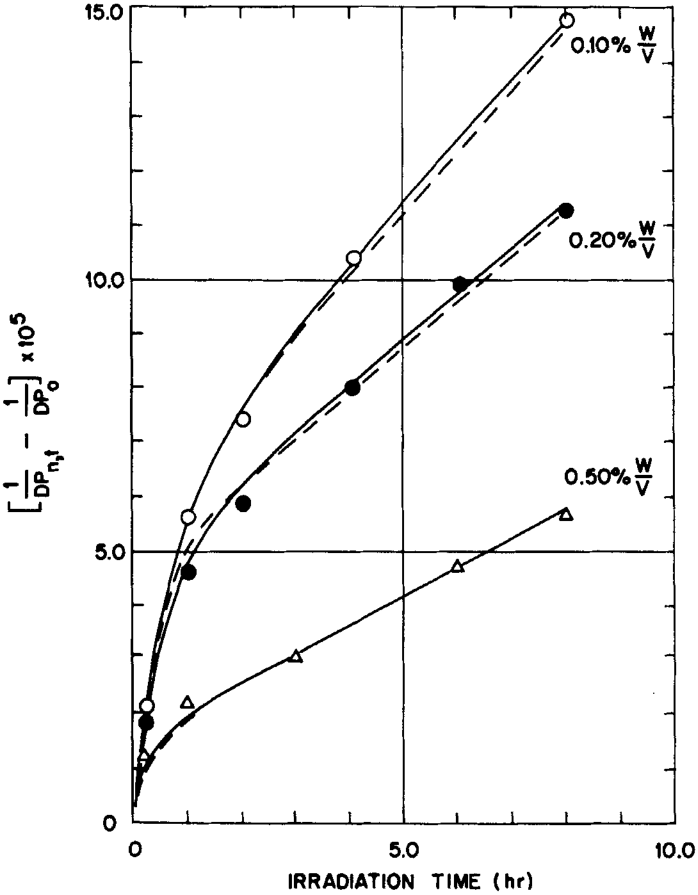


Fig. 1. Photolysis of fraction P I ($DP_{n,0} = 4.3 \times 10^4$) as a function of polymer concentration at 25°C.

Light Intensity

Figure 2 shows the effect of light intensity (100, 73, and 51% transmission; filter: nickel sulfate solutions) for fraction P I [0.1% (w/v)]. The rate decreases with decreasing light transmission. This will be discussed below.

Temperature

Figure 3 shows results for fraction P II [0.1%(w/v)] degraded at 25, 50, and 65°C. The initial part of the reaction is independent of

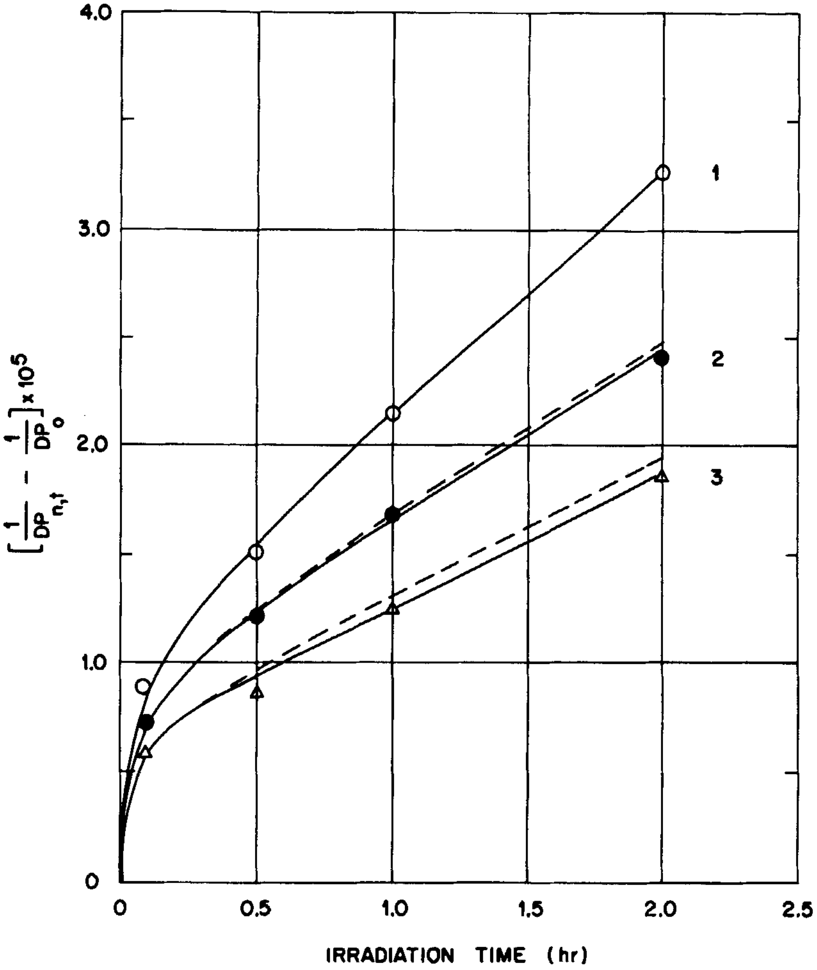


Fig. 2. Photolysis of P I [0.1%(w/v)] as a function of relative light intensity: (1) 100%, (2) 73%, (3) 51% light transmission; 25°C.

temperature. However, this initial part branches out into three curves, one for each temperature. (Light intensity was different from that in previous experiments.)

Ultraviolet Spectra

Ultraviolet spectra of P I [diluted from 0.1% (w/v), at which photolysis was carried out, to 2×10^{-3} %(w/v) for absorption

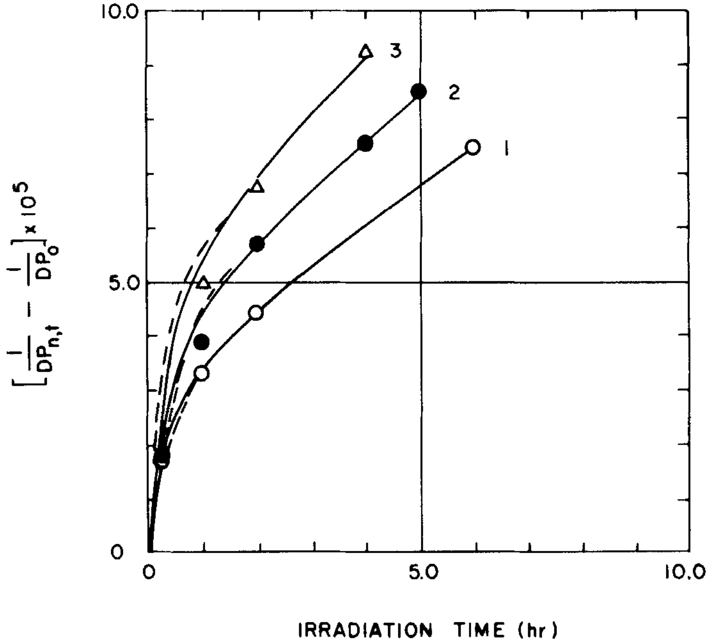


Fig. 3. Photolysis of fraction P II [0.1%(w/v)] as a function of temperature: (1) 25°C, (2) 50°C, (3) 65°C.

measurements] were determined with a Beckman DBG spectrophotometer at various stages of the degradation process (Fig. 4). The extinctions (1-cm cell) increase with increasing photolysis time. The absorption maxima at 1950 Å increase linearly with time. Infrared spectra of unexposed and moderately exposed samples did not show any difference (Beckman Microspec).

Chain-Scission Quantum Yield

The chain-scission quantum yield was determined for fraction P I ($DP_{n,0} = 4.3 \times 10^{-4}$). Actinometry was carried out using $K_3Fe(C_2O_4)_3 \cdot 3H_2O$. The light intensity I_0, passed through 1 cm² of the reaction vessel, was 2.16×10^{15} quanta/sec/cm². The quantum yield for chain scission amounted to

$$\phi_s = \frac{s \cdot cN_A}{2.303E_{1cm}I_0DPn,_0M_1t} \qquad (1)$$

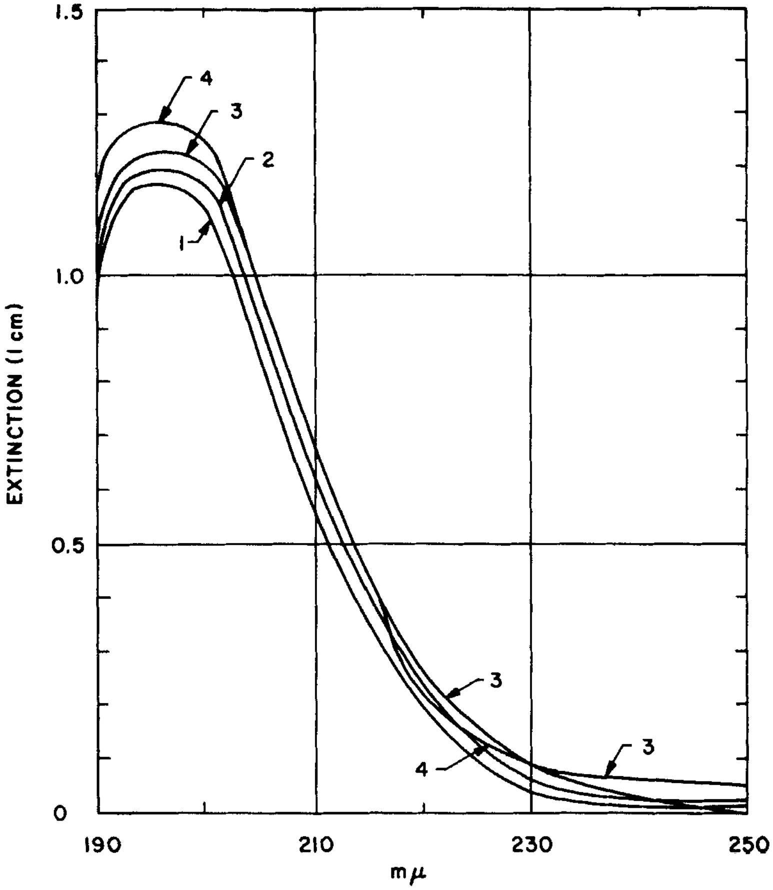


Fig. 4. Ultraviolet spectra of P I (extinctions, 1 cm) photolyzed in 0.1%(w/v) solution, spectra obtained with 2 × 10^{-3} %(w/v) solutions, as a function of photolysis time: (1) 0, (2) 1 hr, (3) 4 hr, (4) 8 hr.

s, the average number of breaks in each original chain, is obtained from chain-scission experiments for a period of time t, c is the polymer concentration in g/cm^3, N_A Avogadro's number, E_{1cm} the extinction of the solution, I_0 the incident light intensity in quanta sec/cm^2, $DP_{n,0}$ the initial polymer chain length, and M_1 the monomer molecular weight. The results for 25°C are given in Table 2; extinctions increased with reaction time.

The quantum yield decreases with increasing concentration and also with degradation time. The latter is understandable as the extinctions of the solutions increase with reaction time.

Table 2

Concn., g/cm^3	$\frac{1}{\overline{DP}_t} - \frac{1}{DP_0}$	s	t, sec	E, 1 cm	ϕ_s, chain scissions/quanta
0.001	2.02×10^{-5}	0.867	720	2.25	1.4×10^{-5}
0.001	5.55×10^{-5}	2.38	3600	2.50	6.7×10^{-6}
0.002	1.82×10^{-5}	0.781	720	4.50	1.2×10^{-5}
0.002	4.61×10^{-5}	1.98	3600	4.50	5.6×10^{-6}
0.005	1.08×10^{-5}	0.463	720	11.25	7.3×10^{-6}
0.005	2.35×10^{-5}	1.01	3600	11.50	2.9×10^{-6}

DISCUSSION

The very initial straight-line part of the photolysis reaction shows the characteristics of a pure random process: independence of chain length and concentration. For weak light absorption and for polymer solutions, which obey Beer's law, a relationship is obeyed as follows:

$$\frac{1}{\overline{DP}_{n,t}} - \frac{1}{DP_{n,o}} = k_{ir}t = \phi_s k I_0 t \qquad (2)$$

Here k_{ir} is the random scission-rate constant, which is independent of the geometry of the reaction vessel, chain length, and polymer concentration. $DP_{n,o}$ and $\overline{DP}_{n,t}$ are the chain lengths at t = 0 and t, respectively; ϕ_s is the quantum yield for chain scission (ϕ_s = moles of broken main chain links per mole of quanta absorbed); k is an optical constant (molar absorptivity based on monomeric unit moles); and I_0 is the incident light intensity.

The photolysis of PVP quickly slows down after its initial stages, indicating that the process becomes more complicated. Guillet and Norrish [3] found a similar slowing down for the photolysis of poly(methyl vinyl ketone) in dioxane solution. They could account for their results by a so-called type II mechanism for ketones. However, in the present instance, it was assumed that type II cleavage and, to a smaller extent, type I cleavage, which provides polymer radicals, are operative at the same time.

The photolysis curves can, in principle, also be fitted by a degradation process for a polymer with weak links. However, in this case, the degradation should remain independent of polymer concentration and chain length in its initial and subsequent stages, unless the solvent takes part in the reaction. It seems unlikely that the solvent would not participate in the early stages, but would do so during the subsequent stages, as one would have to conclude from the experimental data. In addition, Guillet and Norrish [3] have pointed out that the quantum efficiency for the weak-link photolysis would have to be abnormally high, as the number of weak links is usually quite small. An alternative to the magnitude of the quantum yield would be that the excitation would travel along the polymer chains quite efficiently. This is unlikely.

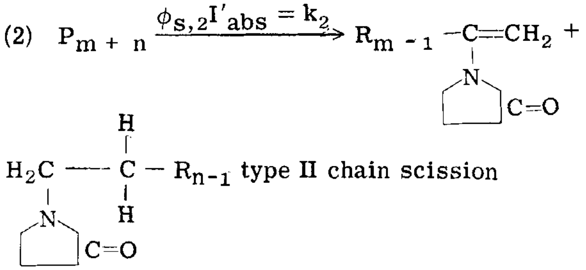
Mechanism; Kinetics: Rate Constants as a Function of Chain Length and Concentration

The assumed mechanism consists of two simultaneous initiation reactions. One produces polymer chains by chain scission with double bonds at one of the chain ends and single bonds at the other chain end; the other scission reaction forms only polymer radicals. Initiation is followed by recombination (repolymerization) of the double-bond chain ends with polymer radicals; termination is affected by disproportionation of polymer radicals.

It is not unlikely that a depropagation reaction forming some monomer takes place, especially at elevated temperatures.

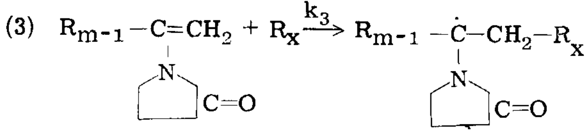
Initiation:

$$(1)\quad P_m + n \xrightarrow{\phi_{s,1}I'_{abs} = k_1} R_m + R_n \quad \text{type I chain scission}$$



$$(2)\quad P_m + n \xrightarrow{\phi_{s,2}I'_{abs} = k_2} R_{m-1}-C{=}CH_2 + H_2C-CH_2-R_{n-1} \quad \text{type II chain scission}$$

Recombination ("repolymerization")



$$(3)\quad R_{m-1}-C{=}CH_2 + R_x \xrightarrow{k_3} R_{m-1}-\dot{C}-CH_2-R_x$$

Second-order termination (disproportionation):

$$(4)\quad R_x + R_y \xrightarrow{k_{4,d}} P_x + P_y$$

Here $\phi_{s,1}$ and $\phi_{s,2}$ are the chain-scission quantum yields for reactions (1) and (2), respectively; I'_{abs} is the light intensity (in einsteins) absorbed on the average by one volume unit of polymer;

k_1 and k_2 are rate constants for initiation; and k_3 and $k_{4,d}$ are rate constants for recombination (repolymerization) and disproportionation, respectively. R and P stand for polymer radicals and "dead" polymer, respectively.

The rate of breaking main chain links is given by

$$-d[n]/dt = (k_1 + k_2)[n] - k_3[Z][R] = k[n_0] - k_3[Z][R] \tag{3}$$

$k_1 + k_2 = k$ and [n] is the concentration of main chain links. As only a small percentage of main chain links are broken during photolysis, [n] is practically equal to $[n_0]$, the initial concentration of main chain links; [Z] is the concentration of double-bond chain ends at time t.

The rate of polymer radical production is

$$d[R]/dt = 2\,k_1[n_0] - 2k_{4,d}[R]^2 \tag{4}$$

Recombination is not included in Eq. (4), because one radical is consumed while another one is formed.

One has for steady-state conditions,

$$[R] = \left(\frac{k_1}{k_{4,d}}\,[n_0]\right)^{1/2} \tag{5}$$

The rate of formation of double bonds, Z, is given by

$$d[Z]/dt = k_2[n_0] + k_{4,d}[R]^2 - k_3[Z][R] \tag{6}$$

Here the second term can be neglected, as the main termination step is assumed to be $k_3[Z][R]$; hence Eq. (6) reduces to

$$\frac{d[Z]}{dt} = k_2\,[n_0] - k_3\,[Z]\left(\frac{k_1}{k_{4,d}}\,[n_0]\right)^{1/2} = k_2\,[n_0] - k'\,[Z] \tag{7}$$

where

$$k' = \left(k_3\frac{k_1}{k_{4,d}}\,[n_0]\right)^{1/2}$$

Integration of Eq. (7) gives

$$[Z] = \frac{k_2[n_0]}{k'}\,(1 - e^{-k't}) \tag{8}$$

Introducing Eqs. (5) and (8) into Eq. (3) yields

$$-\,d[n]/dt = k[n_0] - k_2[n_0]\,(1 - e^{-k't}) \tag{9}$$

Equation (9) gives, on integration,

$$[n_0] - [n] = [N_0]s = [k_1t - \frac{k_2}{k'}\,(e^{-k't} - 1)][n_0] \tag{10}$$

s is the average number of main chain breaks in each original chain at time t; $s = (DP_{n,0}/\overline{DP}_{n,t}) - 1$; and $[N_0] = [n_0]/DP_{n,0}$, the initial concentration of polymer chains in the monodisperse sample. Hence one finally obtains:

$$\frac{1}{\overline{DP}_{n,t}} - \frac{1}{DP_{n,0}} = k_1t - \frac{k_2}{k'}\,(e^{-k't} - 1) \tag{11}$$

The experimental results can be fitted to Eq. (11). The procedure is as follows. For relatively large times, t, Eq. (11) reduces to

$$\frac{1}{DP_{n,t}} - \frac{1}{DP_{n,0}} = k_1t + \frac{k_2}{k'} \tag{11a}$$

Hence k_1 can be obtained from the slope of the straight line at relatively large t values. The intercept of this straight line with the ordinate at t = 0 then gives k_2/k'. Thus these two values are quite unambiguous. k′ can then be calculated from Eq. (11) by choosing a $(1/\overline{DP}_{n,t}) - (1/DP_{n,0})$ value belonging to a short reaction time from the experimental curve. Undue weight is usually placed on the first point of the experimental curve by this procedure and its value frequently has to be adjusted, as it obviously does not accurately fit the whole experimental curve. However, this adjustment does not exceed about 10% of the value. Once k′ is obtained, k_2 is also known. The relevant values are given in Table 3.

Table 3 shows that the sum of the rate constants for chain scission, $k = k_1 + k_2$, remains practically independent of polymer concentration and chain length, except for a very small trend to smaller values with increasing concentration (see average). This independence of k is in agreement with a random chain-scission process. The rate constant, k_1, for chain scission leading to radicals (type I cleavage for ketones) is independent of chain length but dependent on concentration. The chain-scission constant, k_2 (type II cleavage), producing single-ended and double-bonded chain ends, is independent of polymer concentration and practically independent of chain length, except for a small tendency to increase with chain length. These

Table 3. Photolysis Rate Constants of PVP (K90) Fractions ($\lambda = 2537$ Å) for Different Concentrations on Oxygen-Free Water at 25°C [Eq. (11)]

Fraction	Concn., %(w/v)	$10^5 k_1$, hr^{-1}	$10^5 \frac{k_2}{k'}$	$10^5 k_2$, hr^{-1}	k', hr^{-1}	$10^5 k = (k_1 + k_2)10^5$, hr^{-1}	$10^{-2} k'/k_1{}^{1/2} = k_3 \left(\frac{[n_0]}{k_{4,d}}\right)^{1/2}$ $hr^{-1/2}$
P I	0.1	1.12	5.6	10.0	1.8	11.1	5.3
P II	0.1	1.11	6.3	12.6	2.0	13.7	6.0
P V	0.1	1.13	6.7	11.5	1.7	12.6	5.0
Av.[a]	0.1	1.12 ±1.0 × 10⁻²	6.2 ±0.57	11.4 ±1.7	1.8 ±0.15	12.5 ±1.3	5.3 ±0.78
P I	0.2	0.83	4.7	10.4	2.2	11.2	7.6
P II	0.2	0.82	4.7	11.4	2.2	12.2	7.7
P V	0.2	0.84	5.0	13.1	2.6	13.9	7.8
Av.[a]	0.2	0.83 ±1.0 × 10⁻²	4.8 ±0.19	11.6 ±1.1	2.5 ±0.23	12.4 ±1.4	7.7 ±0.07
P I	0.5	0.54	1.5	10.8	7.2	11.3	31.0
P II	0.5	0.55	1.6	11.5	7.3	12.0	31.0
P V	0.5	0.56	1.5	11.2	7.3	11.8	31.0
Av.[a]	0.5	0.55 ±1.0 × 10⁻²	1.5 ±0.06	11.2 ±0.35	7.3 ±0.06	11.7 ±0.36	31.0 ± 0.16
Overall av.				11.4 ±0.2		12.2 ±0.44	

[a] The ± values are standard deviations = $(\text{variance}/n - 1)^{1/2}$.

characteristics of k_1 and k_2 make their sums, i.e., the k values, practically independent of chain length and concentration, as pointed out above. The composite rate constant

$$k' = k_3 \left(\frac{k_1}{k_{4,d}} [n_0]\right)^{1/2}$$

is independent of chain length but increases with concentration. A plot of $k_1/k^{1/2}$ versus $[n_0]^{1/2}$ increases faster than linearly; hence $k_3/k_{4,d}^{1/2}$ must increase with polymer concentration but is independent of chain length. This, of course, is reflected in the behavior of k_2 and k'. All these results, including the small quantum yield for chain scission, are in satisfactory agreement with the postulated mechanism.

Light Intensity

Figure 2 was evaluated as described above. The rate constants as a function of relative light intensity are given in Table 4.

The light intensity was altered by means of nickel sulfate solutions. Table 4 shows that the constants for the two primary processes, k_1 and k_2, and consequently also k, are dependent on the incident light intensity, decreasing with decreasing light intensity;

$$k' = k_3 \left(\frac{k_1[n_0]}{k_{4,d}}\right)^{1/2}$$

is practically independent of light intensity, as $k_1^{1/2}$ is only a small factor, so that its variation is too small to affect k' appreciably; k_2/k' is dependent on light intensity, since k_2 is. Straight lines are obtained by plotting k_1, k_2, k', k, and k_2/k', respectively, against the

Table 4. Photoylsis Rate Constants as Function of Relative Light Intensity; Fraction P I [0.1%(w/v)]; λ = 2537 Å; 25°C

Rate constants	Transmission, %		
	100	73	51
$10^5 k_1$ hr^{-1}	1.09	0.79	0.57
$10^5 k_2/k'$	1.08	0.90	0.75
$10^5 k_2$ hr^{-1}	10.0	8.1	6.9
k'hr^{-1}	9.3	9.0	9.2
$10^5 k$ hr^{-1}	11.1	8.9	7.5

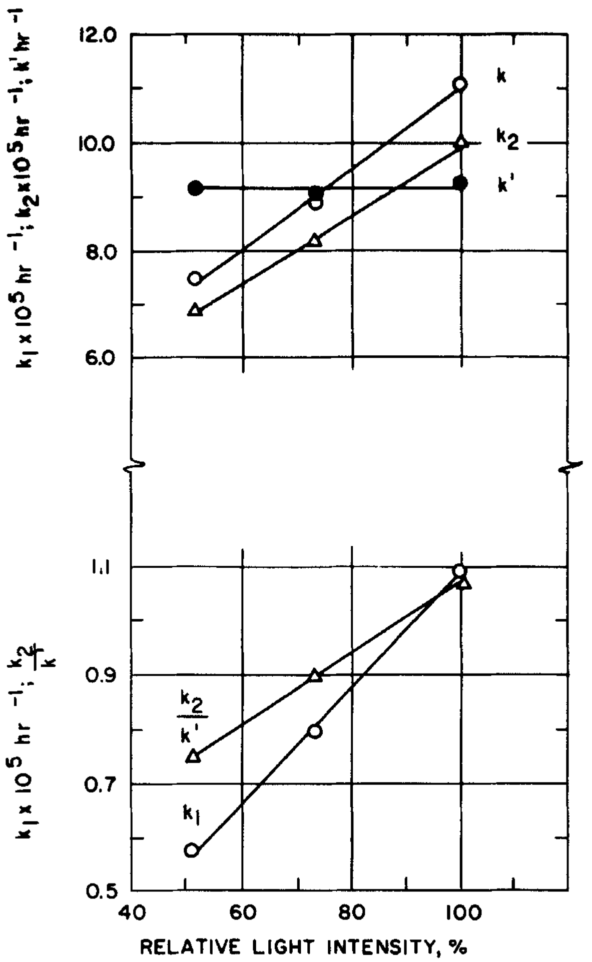


Fig. 5. Rate constants k_1, k_2, k, k', and k_2/k' as functions of the first power of the relative light intensity.

relative light intensity (see Fig. 5). This first power dependence of the rate constants on light intensity is in agreement with the proposed mechanism, if the termination rate by disproportionation is much smaller than the "repolymerization" rate, as was assumed here.

Table 5. Photolysis Rate Constants as a Function of Temperature; P II, 0.1%(w/v); λ = 2537 Å

Temperature °C	25	50	65
$10^5 k_1$ hr.$^{-1}$	0.79	0.93	1.18
$10^5 k_2/k'$	2.8	3.8	4.3
k'hr.$^{-1}$	3.1	2.4	2.1
$10^5 k_2$ hr.$^{-1}$	8.5	8.1	9.0
$10^5 k$ hr.$^{-1}$	9.3	9.0	10.2

Temperature

The rate constants as a function of temperature are given in Table 5 (compare Fig. 3). $k = k_1 + k_2$ is practically independent of temperature, keeping in mind that there is a change of 40°C in temperature. This agrees with the mechanism, as k is a rate constant for primary photoprocesses. There seems to be a slight variation in the proportions of k_1 to k_2 with change in temperature. k_1 has a small trend to increase with temperature; this may be due to an increase in quantum yield with temperature. The decrease of k' with temperature is believed to be significant, as this rate constant is a composite one, i.e.,

$$k' = k_3 \left(\frac{k_1 [n_0]}{k_{4,d}} \right)^{1/2}$$

containing the rate constants k_3 and $k_{4,d}$, which should have energies of activation (termination is always diffusion-controlled in solution or bulk). Log k' plotted versus 1/T gives a straight line (see Fig. 6), yielding an energy of activation for $k_3/k_{4,d}{}^{1/2}$ of −2.0 kcal/mole or $-2.0 = \Delta E_{k_3} - \frac{1}{2}\Delta E_{k_4}$. If it is assumed that the energy of activation for the diffusion-controlled termination is in the range 20-30 kcal/mole, then E_{k_3} ranges from 8.0 to 13.0 kcal/mole.

UV Absorption

The increase in extinction (1 cm) with time for the wavelengths at maximum absorption (1970 Å) follows a zero-order law. This increase probably has some connection with the rate of double-bond formation.

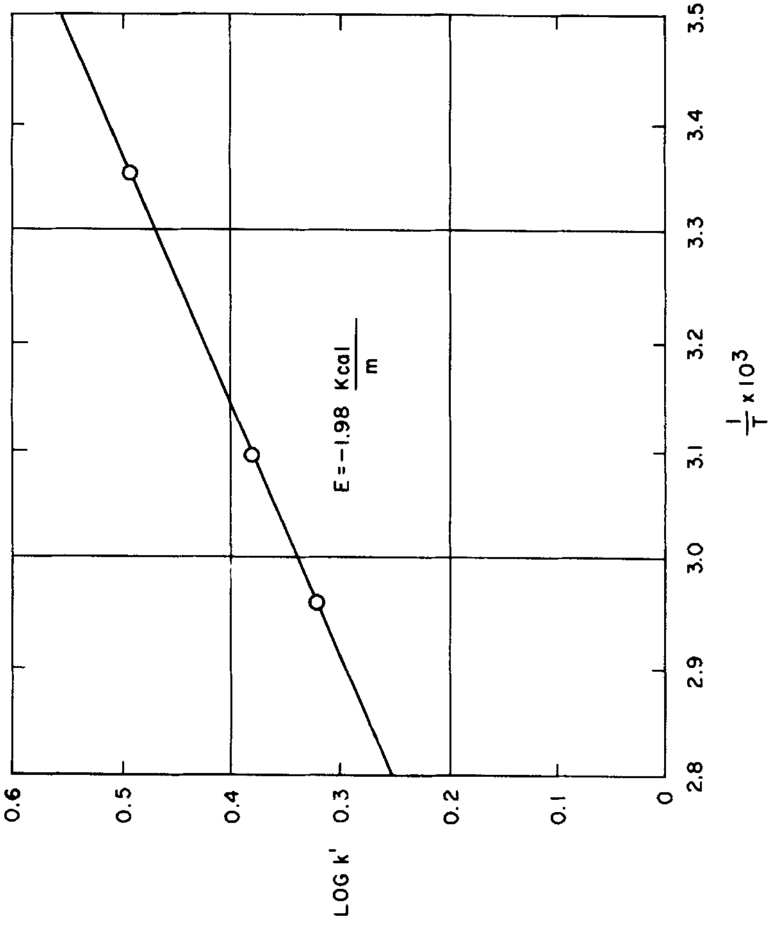


Fig. 6. Arrhenius plot for the composite rate constant $k' = k_3(k_1[n_0]/k_{4,d})^{1/2}$.

CONCLUSION

The general conclusion which can be drawn from this work is that all experimental data are in agreement with the proposed mechanism. Thus this mechanism (simultaneous type I—small percentage of the total scission reaction—and type II chain scission and "repolymerization") seems likely to be realized. This statement has, of course, the limitations of all proposed reaction mechanisms based mainly on kinetic considerations (i.e., there is always a possibility of an alternative kinetic scheme fitting the experimental data).

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