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Photochemistry of Ketone Polymers. 17. Photodegradation of an Amorphous Ethylene–Propylene Copolymer

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ABSTRACT: Samples of an amorphous ethylene–propylene (78:22 mol %) copolymer were thermally oxidized to produce polymers with varying amounts of keto and hydroperoxy groups. Additional samples were prepared in which the hydroperoxy groups were removed by thermal decomposition under vacuum. Studies were then made of the quantum yields of chain scission (Φ_s), carbonyl loss (Φ_{-CO}), and terminal vinyl formation (Φ_{II}) in solution and in solid films. Samples containing both carbonyl and hydroperoxide showed much higher values of Φ_s (0.2–1.3) than those containing only ketones ($\Phi_s = 0.036$). Furthermore the results could not be explained by direct absorption of light by the hydroperoxide groups, since in all cases more than 87% of the light was absorbed by the ketone structures. The results are consistent with a relatively efficient transfer of excitation energy from the keto group to hydroperoxide, possibly by the exciplex mechanism recently proposed by Ng and Guillet. At 250 and 276 nm, where strong primary absorption by hydroperoxide occurs, a dark scission reaction was observed, which is attributed to the bimolecular reaction of two peroxy radicals on the polymer chain followed by β scission of the resulting macroalkoxy radical. The significance of these results to the mechanism of polyolefin photooxidation is discussed.

Many studies of the oxidative degradation of polyolefinic materials by ultraviolet or visible light[1-8] or heat[9-13] have been published during the past decade. It has been recognized that the basic reactions in the photooxidation of polyolefins are similar to those occurring in thermal oxidation. The two chemical species believed to be important in causing the thermal degradation and photodegradation of polyolefins are hydroperoxide groups and ketone or aldehyde carbonyls. There has been some controversy in the literature as to whether the hydroperoxide groups or the ketone groups are more effective sensitizers in photooxidation and in maintaining the oxidative chain reactions that lead to polymer degradation.[14-17]

Hydroperoxides are produced in aliphatic or aromatic polymers from polymer radicals formed mechanically or chemically. In the presence of air, these radicals react to give peroxy radicals that are stabilized by hydrogen atom abstraction to give hydroperoxy groups. In cases where the polymer contains relatively large concentrations of double bonds, such as in polyisoprene or polybutadiene, hydroperoxides can also occur by addition of singlet oxygen to form an allylic hydroperoxide,[5,15] although it is unlikely that this reaction is important in the oxidation of saturated aliphatic or aromatic polymers.

Guillet has pointed out that after the initial stages of photooxidation, the accumulation of carbonyl groups will cause the light excitation to be overwhelmingly concentrated on the carbonyl chromophores.[17] Chain scission would then occur via the Norrish type I and II reactions characteristic of ketone compounds as well as those involved in the oxidation process per se. It is, therefore, important to understand the photodegradation of ketone polymers in the presence of hydroperoxide groups on the polymer backbone. It is well established that photooxidation of polyolefins takes place primarily in the amorphous phase. Copolymers of ethylene and propylene

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Table I
Characterization of PEP Samples Thermally Oxidized at 125 °C

sample	oxidation time, min	$\overline{M}_n$[a]	$\overline{M}_v$[b]	carbonyl conc × 10^5, mol g^{-1}	OOH conc × 10^5, mol g^{-1}	$\overline{M}_w$[d]	$\overline{M}_w/\overline{M}_n$
I	0	76 400	128 000			139 000	1.82
II	1400	67 300	116 000	0.23	0.46	126 000	1.87
III	1800	60 100	110 000	1.02	0.95	119 000	1.99
IV	3300[c]	30 400	116 000	2.24	1.13	126 000	1.79
V	2600	53 500	83 700	3.55	1.4	90 900	1.70
VI	2800	49 400	69 000	5.76	1.8	75 000	1.52
VII	3100	43 000	54 000	11.3	2.5	58 700	1.36

[a] From osmometry in toluene. [b] From viscometric data, $K = 9.4 \times 10^{-4}$ dL/g and $\alpha = 0.657$ in the Mark-Houwink equation, at 25 °C in toluene. [c] Oxidation carried out at a lower temperature (120 °C). [d] Calculated from $\overline{M}_v$, assuming most probable distribution.

are now available that are substantially amorphous and can be considered to represent a reasonable model for the amorphous regions in low-density polyethylene. In this study several samples of an ethylene–propylene copolymer (PEP) were thermally oxidized in order to introduce different amounts of hydroperoxides and carbonyls into the polymer. The effect of the concentrations of hydroperoxides and carbonyls on the rate of photodegradation can thus be investigated. This can then be compared with the photodegradation of oxidized PEP samples that have been dehydroperoxidized by vacuum heating. PEP (Vistalon 702) is completely amorphous and, unlike most other saturated aliphatic polyolefins, is soluble in various solvents at room temperature. This allows the polymer to be easily studied by the highly precise automatic viscometer developed in these laboratories for polymer solution degradation.

Experimental Section

The PEP copolymer rubber was obtained from Esso Chemical Canada under the commercial name of Vistalon 702 with an ethylene:propylene weight ratio of 70:30 (mole ratio 78:22). It was prepared with a vanadium catalyst, which suggests that the polymer is substantially linear. It has a density of 0.86 and contains 0.1 wt % stabilizers. The polymer is soluble in toluene, benzene, and carbon tetrachloride on heating to 50 °C and a true solution remains at 25 °C. A batch of the original polymer was dissolved in toluene at 60 °C, and the small amount of insoluble gel was filtered off and precipitated with cold methanol. The reprecipitation was repeated twice to eliminate the stabilizer. Films of approximately 0.5-mm thickness were pressed between then Teflon sheets at 100 °C for 0.5 min on a Carver press and then quenched quickly with cold water. Translucent films were obtained, which could be easily peeled off from the Teflon sheets. All solvents and reagents used in the experiment were Fisher ACS or reagent grade.

Thermal Oxidation and Functional Group Analysis. PEP films were thermally oxidized in an air oven at 125 °C in Teflon supports that fit directly onto the sample holder of a Perkin-Elmer Model 337 IR spectrophotometer. At different times of thermal oxidation, the mounted films were withdrawn from the oven and their IR spectra were taken. The extent of the oxidation was followed by noting the development of hydroperoxide and carbonyl absorption regions in the spectra at 3550 and 1720 cm^{-1}, respectively.

The oxidized films were then dissolved in toluene, and a small amount of insoluble, cross-linked products was filtered off and precipitated with methanol. The purified samples of oxidized PEP were pressed between Teflon sheets into thin films of ~ 0.15-mm thickness. The amount of hydroperoxides in oxidized samples was analyzed quantitatively by the method of Mitchel and Perkins,[18] which involves taking the IR spectra of oxidized films before and after exposure to sulfur dioxide for 30 min. The characteristic sulfate band at 1190 cm^{-1} was used to determine the amount of hydroperoxide present in the original sample, using dimethyl sulfate and diethyl sulfate in carbon tetrachloride as calibration standards. Analyses on different films of the same oxidized sample agreed to within 10%.

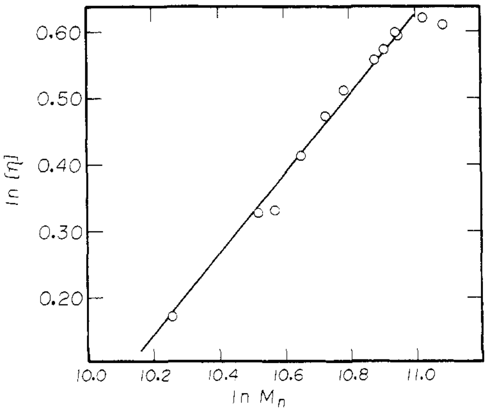


Figure 1. Double-logarithmic plot of [η] vs. M_n for PEP in toluene at 25 °C.

Dehydroperoxidized samples were obtained by placing the thermally oxidized films between Teflon sheets and heating to 125 °C in vacuo (10^{-4} torr) for 8 h. The dehydroperoxidized samples show increased absorption in the carbonyl region, but terminal vinyl bonds were absent from the infrared spectra. The number of ketone chromophores present was estimated by assuming that the IR extinction coefficient of the model ketone 1,1-dioctadecylacetone ($C_{18}H_{37}CH(COCH_3)C_{18}H_{37}$) is similar to the average ϵ of the carbonyl group in the oxidized samples. The justification of such a treatment will be considered later. Results of these experiments are summarized in Table I.

Photolysis. Solution photolysis studies were carried out at 313 nm in nitrogen at 25 °C. The change in viscosity with the irradiation time was followed by automatic viscometry in an instrument previously described.[19] The polymer concentration was kept low at about 0.25 w/w %. This ensures that intermolecular processes such as cross-linking would be minimal under the irradiation conditions. The incident light intensity was estimated by potassium ferrioxalate actinometry. For the wavelength studies, a Bausch and Lomb SP 200 mercury lamp was used in conjunction with a Bausch and Lomb high-intensity monochromator.

Molecular Weight Determination. All number-average molecular weights, $\overline{M}_n$, were measured in toluene in a Mechrolab Model 500 high-speed membrane osmometer. The changes in intrinsic viscosity [η] during irradiation were converted into viscosity-average molecular weights, $\overline{M}_v$, by applying the Mark–Houwink equation:

$$[\eta] = K\overline{M}_v^{\alpha} \qquad (1)$$

Values of K and α were determined by the method of Kilp and Guillet.[20] Polymer degradation was effected by photolyzing an unoxidized PEP sample under oxygenated conditions with the full arc of a medium-pressure mercury lamp in toluene solution.

A double-logarithmic plot of [η] vs. $\overline{M}_n$ for the PEP copolymer is shown in Figure 1. It is obvious that the plot exhibits considerable curvature in the early stage (upper right portion) but becomes linear at the later stages of the photoscission process when the molecular weight distribution approaches the most probable polydispersity of 2.[20] From the slope and intercept of the double-logarithmic plot, K and α for the PEP copolymer in toluene at 25 °C in eq 1 were found to be 9.4×10^{-4} dL/g and 0.657, respectively.

It is worth pointing out that it is not essential to incorporate a small amount of vinyl ketone in the polymer whose K and α values are to be determined before one can use the method of Kilp and Guillet. The present data demonstrate that the degradation can be carried out by simply photolyzing a polymer sample in an oxygenated solution. It is possible that the method of Kilp et al. may have a greater versatility than realized and may be extended to the determination of K and α for polymers that do not copolymerize easily with vinyl ketone monomers. Whether oxidative degradation always leads to the most probable molecular weight distribution resulting from random scission remains to be determined.

Quantum Yield Calculations. The quantum yield of scission Φ_s in the solution studies was calculated according to

$$\Phi_s = \frac{W}{I_a \bar{M}_n^{\,0}}[(\bar{M}_v^{\,0}/\bar{M}_v) - 1] \tag{2}$$

where W is the concentration of the polymer in solution, I_a is the amount of light absorbed, and $\bar{M}_n^{\,0}$ and $\bar{M}_v^{\,0}$ are the initial and $\bar{M}_n$ and $\bar{M}_v$ the final number- and viscosity-average molecular weights, respectively. The validity of using such an equation in the evaluation of Φ_s has been discussed elsewhere.[21]

The quantum yield of disappearance of the carbonyl peak Φ_{-CO} and the concomitant development of double bonds in the photolysis of film samples were calculated by using eq 3 and 4.[22] K_0

$$\ln (K_0/K) = 2.3\Phi_{-CO} I_0^{\,i} \epsilon t \tag{3}$$

$$K_{II} = \frac{Z\Phi_{II}C_0}{\Phi_{-CO}}(1 - \exp(-2.3 I_0^{\,i} \Phi_{-CO} \epsilon t)) \tag{4}$$

and K represent the IR carbonyl intensity at irradiation time zero and t, respectively, $I_0^{\,i}$ is the incident light intensity in quanta s^{-1} cm^{-2}, and ϵ is the UV extinction coefficient at the wavelength of excitation. In this case, it was taken to be 13 100 mol^{-1} cm^2, the same as that for a poly(ethylene + 1% carbon monoxide, copolymer at 313 nm. K_{II} is the IR absorbance at 909 cm^{-1} for vinyl double-bond formation. Z is a calibration factor equal to 1.0×10^5 mol^{-1} cm^2 for vinyl absorption, and C_0 is the initial amount of carbonyl chromophores present.

The quantum yield for the decomposition of hydroperoxide, Φ_{-OOH} can be calculated by using an equation similar to (3) except that the IR absorbance at 3350 cm^{-1} was followed and ϵ was taken to be 260 mol^{-1} cm^2 at 313 nm, the same as that for di-*tert*-butyl peroxide in dichloroethane.

Results and Discussion

Thermal Oxidation. The PEP copolymer showed an induction period of about 23 h at 125 °C, after which hydroperoxide and carbonyl groups began to accumulate. The IR spectra of oxidized PEP samples bear much resemblance to those of oxidized polyethylene.[23] The hydroperoxide region shows one sharp peak at 3550 cm^{-1}, indicating the presence of free OH stretching, and a broader peak centered at 3400 cm^{-1} from hydrogen-bonded OH groups.[24] It was concluded that these OH absorptions were due predominantly to hydroperoxides, since the hydroxyl region in an oxidized PEP sample that had been dehydroperoxidized by vacuum heat treatment is almost identical with that of an unoxidized sample.

The carbonyl region was composed of one sharp peak at 1720 cm^{-1} and a well-defined smaller peak at 1785 cm^{-1}. The latter has been identified to be due to γ-lactones in the oxidation of polyethylene and polypropylene.[23] Adams undertook chemical analyses on the functional group content in thermally oxidized polypropylenes and polyethylenes. His results ruled out the presence of significant amounts of aldehyde groups since the C–H stretching frequency at 2730 cm^{-1} was absent. It was also shown that about 35% of the IR carbonyl absorption was due to ketone groups, and the distribution of various carbonyls was the same for samples oxidized at slightly different temperatures.[23] In the current work, it was therefore assumed that one-third of the carbonyl region in oxidized PEP samples was due to ketonic absorption. This assumption allows one to calculate the amount of light absorbed at 313 nm (the irradiation wavelength used in the present photolysis studies) by the ketone chromophores, since other carbonyls such as acids, esters, or γ-lactones do not absorb at 313 nm.

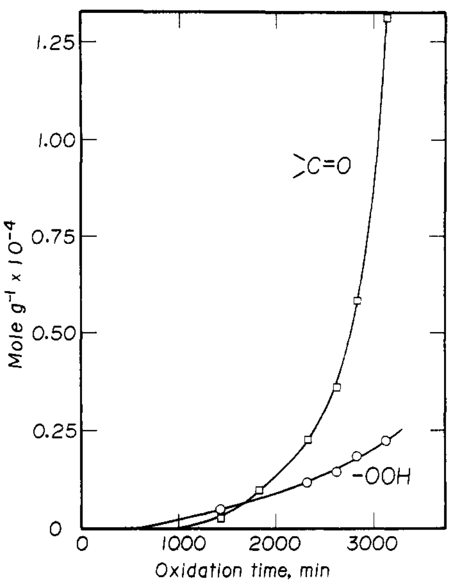


Figure 2. Amount of carbonyl and hydroperoxide groups during the thermal oxidation of PEP at 125 °C.

Table II
Characterization of Dehydroperoxidized PEP Samples

sample	$\bar{M}_n$[a]	M_v[b]	carbonyl conc × 10^5, mol g^{-1}	$\bar{M}_w$[c]	$\bar{M}_w/\bar{M}_n$
IIa	63 000	106 000	0.29	115 000	1.83
IIIa	48 400	72 500	1.31	78 800	1.63
IVa	46 900	68 400	2.7	74 300	1.58
Va	39 300	61 300	6.1	66 600	1.69
VIa	29 800	38 600	9.6	41 900	1.41

[a] From osmometry in toluene. [b] From viscometry, $K = 9.4 \times 10^{-4}$ and $\alpha = 0.657$ in the Mark-Houwink equation, at 25 °C in toluene. [c] Calculated from $\bar{M}_v$, assuming most probable distribution.

Table I shows the $\bar{M}_v$, $\bar{M}_n$, and concentration of hydroperoxide and carbonyl groups at different time periods of thermal oxidation of PEP. Figure 2 shows the plot of the amount of hydroperoxides and carbonyls in the oxidized sample with the oxidation time. At the initial stage of thermal oxidation, the amount of hydroperoxides was higher than that of ketones. However, the amount of carbonyl quickly builds up after the initial period, while the level of hydroperoxide concentration remains relatively low. It should also be pointed out that samples II–VII were still in an early stage of oxidation and the variation of hydroperoxide concentration with oxidation time did not go through a maximum as in heavily oxidized low-density polyethylene.[14,25] At such an early stage of thermal oxidation, it is generally recognized that the proportions of different carbonyls do not differ much at different oxidation times.[23]

Table II shows the $\bar{M}_n$, $\bar{M}_v$, the polydispersity, and the concentration of carbonyl groups in the dehydroper-

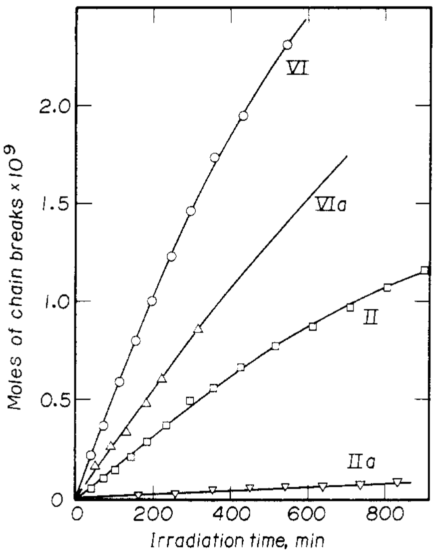


Figure 3. Plot of the number of chain scissions with time during the irradiation of PEP samples in toluene in N_2 at 313 nm at 25 °C.

oxidized samples IIa–VIa, which were obtained from the vacuum heat treatment of thermally oxidized samples II–VI, respectively. The dehydroperoxidized samples show a decrease in $\bar{M}_n$, an increase in carbonyl absorption at 1720 cm^{-1}, and complete disappearance of hydroperoxide absorption at 3550 cm^{-1} compared to the corresponding thermally oxidized samples.

The γ-lactone peak at 1785 cm^{-1} of dehydroperoxide samples showed a small but definite increment. It was found that the amount of γ-lactone formed during thermal oxidation is negligible in polyethylene but significant in polypropylene.[23] Adams proposed that γ-lactones or other cyclic carboxylates were formed from a reaction of peroxy acids, which are present in polyolefin samples oxidized at lower temperature.[23]

Comparison of results in Tables I and II shows that only the PEP samples that contain high hydroperoxide concentrations give significant increases in carbonyl concentration on heating under high vacuum (~10^{-4} torr). In the dehydroperoxidization of sample II, not every hydroperoxide group decomposed led to the formation of a carbonyl. However, in the same treatment of VI, the decomposition of one hydroperoxide group was found to give rise to more than one carbonyl group. This observation demonstrates that the thermal decomposition of hydroperoxides in the PEP films is concentration dependent and that hydroperoxide acts as an "autocatalyst" during thermal oxidation. Recent results by Iring et al. showed that the rate of thermal decomposition of polyethylene hydroperoxides did not follow unimolecular or pseudounimolecular kinetics and was a function of the carbonyl content of the polymer.[26] These results were interpreted as evidence for a synergistic effect between carbonyls and hydroperoxides during the thermal oxidation of polyolefins.[26] The present results also indicate that there is some sort of correlation between the decomposition of the hydroperoxide and the carbonyl content of the oxidized samples.

Solution Photolysis of Thermally Oxidized PEP Samples. Figure 3 shows the plot of the number of moles of chain scission against the irradiation time in the photolysis of four of the oxidized PEP samples, viz., II, IIa, VI, and VIa, in toluene at 313 nm in nitrogen. Both the sample with hydroperoxides an those which had been dehydroperoxidized showed well-correlated linear graphs during the initial conditions. The initial rates of chain scission and the apparent quantum yields of scission Φ_s for various samples were calculated and entered in Table III. A control experiment with an unoxidized PEP sample showed no decrease in solution viscosity up to more than 300 min of irradiation, although irradiation in air produced a small but significant decrease in viscosity.

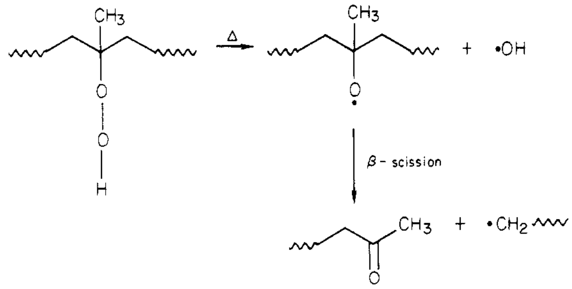
Table III
Photolysis of Oxidized PEP Samples in Toluene at 313 nm in Nitrogen

sample	OOH conc × 10^5, mol L^{-1}	ketone conc × 10^5, mol L^{-1}	initial scission rate × 10^{10}, mol min^{-1}		ϕ_s[a]
II	1.1	0.19[b]	1.7[c]		1.3
III	2.2	0.83[b]	3.9[c]		0.74
IV	2.7	1.8[b]	1.4[c]		0.12
V	3.5	2.9[b]	2.5[d]		0.17
VI	4.4	4.7[b]	5.3[d]		0.23
IIa		0.52[e]	0.10[c]		0.034
IIIa		2.4[e]	0.56[c]		0.039
IVa		4.9[e]	0.82[c]		0.028
Va		9.7[e]	2.4[d]		0.044
VIa		17.8[e]	3.0[d]		0.035
				av	0.36

[a] I_A calculated using ϵ_{313} nm = 13.1 M^{-1} cm^{-1}, same as that for the PE-1% CO copolymer in dodecane. [b] Assuming one-third of total carbonyls due to ketone. [c] $I_0{}^i$ = ~7.8 × 10^{15} quanta s^{-1}. [d] $I_0{}^i$ = 6.5 × 10^{15} quanta s^{-1}. [e] Assuming 75% of carbonyls due to ketone (see later discussion).

Table III shows that the Φ_s values in II–VI are consistently much larger than those found in their corresponding dehydroperoxidized samples. It is obvious that the removal of hydroperoxides by vacuum heat treatment, although increasing the carbonyl concentration, markedly decreased the rate of photodegradation in PEP samples. Part of this increased photosensitivty of II–VI over the dehydroperoxidized samples is possibly due to the fact that less of the functional groups in the former series were located on chain ends.

Dehydroperoxidization under vacuum led to chain scission with the conversion of hydroperoxide groups on the backbone to ketone groups at the chain end (eq 5). Thus



(5)

with the formation of a terminal ketone and a macroalkyl radical. Only the hydroperoxide formed at a propylene center was included since thermal oxidation at a tertiary center on a polypropylene chain is expected to be many times faster than that at the methylene carbon of polyethylene.[27] However, the main source of this increased photodegradability must be due to the presence of the hydroperoxides in the former samples. Quantum yield values are usually independent of the number of chromophores present, unless the photoprocess involved is not a unimolecular reaction, or when the overall reaction involves a chain mechanism. It is known that the quantum yields of the Norrish type I and II processes are inde-

Table IV
Relative Amounts of Incident Light at 313 nm Absorbed by Hydroperoxide and Ketone Groups during the Irradiation of Samples II–VI in Table III[a, b]

sample	% of total incident light absorbed by sample solution (I_A)	% of I_A absorbed by ketone[c] (A)	% of I_A absorbed by hydroperoxide[d] (B)	ratio A/B
II	0.016	87	13	7
III	0.067	94	6	16
IV	0.145	97	3.4	29
V	0.226	97.3	2.7	37
VI	0.358	97.9	2.1	46

[a] Polymer concentration ~0.24 g dL^{-1}. [b] Path length of irradiation cell is 2.5 cm. [c] Assuming one-third of carbonyls due to ketone, with ϵ_{313} ~ 13.1 M^{-1} cm^{-1}, same as that for an ethylene–1% CO copolymer. [d] ϵ_{313} (OOH) assumed to be 0.3 M^{-1} cm^{-1}, same as that for low molecular weight hydroperoxides.

pendent of the amount of light absorbed or the amount of chromophores present. However, this is not the case for hydroperoxides. For example, in the photolysis of polyisoprene hydroperoxide, it was found that the quantum yield for photodecomposition of the hydroperoxide group, $\Phi_{\text{-OOH}}$ is significantly larger than unity and is also a function of the amount of light absorbed and the concentration of hydroperoxide.[28] Quantum yields of chain scission, Φ_s, were also much lower than $\Phi_{\text{-OOH}}$, usually around 0.1 or lower, only a small fraction of $\Phi_{\text{-OOH}}$. The quantum yields of chain scission as measured by type II products during the irradiation of low molecular weight long-chain alkanones are usually around 0.05 or lower.[29] These facts suggest that the high Φ_s values obtained in samples II–VI are due to synergistic interaction between the hydroperoxide and ketone chromophores, although the nature of this synergism is far from clear.

Early studies by Walling and Gibian indicated that the photodecomposition of hydroperoxides was sensitized by ketones,[30] although no mention was made of the mechanism of interaction. More recently, it has been shown that the photodecomposition of polyisoprene hydroperoxide was also sensitized by small-molecule ketones.[31] Ng and Guillet demonstrated that the photodegradation of styrene–vinyl ketone copolymers could be quenched by hydroperoxides and peroxides.[31,32] These results were interpreted in terms of an "exciplex" mechanism by which excited ketone molecules interact with ground-state hydroperoxides or peroxides to form an excited-state charge-transfer complex.[31,32]

The Φ_s values for the samples with both hydroperoxide and ketone groups showed large variations, depending on the hydroperoxide and ketone contents of individual samples (Table III). This is in contrast to the almost constant Φ_s values in the series of dehydroperoxidized samples and points again to the importance of interactions between the hydroperoxide and ketone groups during photodegradation. Table IV shows the amount of light absorbed by hydroperoxide and ketone groups during the irradiation of samples II–VI described in Table III. The data indicate that the amount of light absorbed by the ketone groups is many times greater than that by the hydroperoxide groups, even for the least oxidized sample II, and becomes increasingly more important as the oxidation proceeds. Furthermore, it is not possible to explain the relatively high quantum yields for chain scission on the basis of adding up the contributions of chain scission from direct absorption by the two components separately using reasonable values for Φ_s for the hydroperoxy and keto groups, respectively. Thus, it seems probable that the light initially absorbed by the ketones is transferred to hydroperoxides, which subsequently decompose to give the observed decrease in molecular weight. This synergistic interaction between hydroperoxide and ketones is consistent with several observations: (i) the much larger Φ_s values in samples with both ketone and hydroperoxide groups, (ii) the dependence of Φ_s on ketone and hydroperoxide concentrations, and (iii) the relative amount of light absorbed by the two chromophores. Further consideration of this effect will be discussed in a later section.

The average Φ_s value of 0.036 in the dehydroperoxidized sample is lower than, but comparable to, the type II quantum yield of ~0.06 in a long-chain linear alkanone (C_{43}), which can be used as a model compound for poly(methylene) having ketone groups on its main chain.[29] The lower value is expected because some of the ketone groups will be at chain ends and therefore will not be detected viscometrically. Considering the assumptions made in calculating the ketone contents of the dehydroperoxidized samples, the similar Φ_s values obtained are quite remarkable and indicate that the quantum yield of scission (directly proportional to ds/dt) is independent of the ketone content and molecular weight of the dehydroperoxidized PEP samples. The almost constant Φ_s values indicate that some carbonyl groups are distributed randomly on the PEP chain and lend support to the assumption that the proportion of ketone in the total carbonyl content of the oxidized samples was approximately constant. Apparently, the decrease in molecular weight observed with dehydroperoxidized PEP samples is predominantly due to the type I and II reactions characteristic of ketone compounds.

Irradiation in the Solid Phase. The energy of the incident radiation used (91 kcal/einstein at 313 nm) is high enough to cleave the RO–OH bond (bond energy 42 kcal mol). It is well-known that hydroperoxides undergo photodecomposition into alkoxy and hydroxy radicals, similar to the thermal decomposition represented by eq 5. In polymeric systems, subsequent β scission of the macroalkoxy radical leads to a decrease in molecular weight.

The rate constants for β scission of alkoxy radicals in small molecules[33] and macromolecular systems[31] are usually of the order of 10^4 s^{-1}, whereas that for bimolecular hydrogen abstraction lies in the range 10^5–10^6 M^{-1} s^{-1}.[34] Assuming similar rate constants can be applied to the photolysis of oxidized PEP samples with hydroperoxides, one could conclude that β scission of the macroalkoxy radical will only be a minor process in comparison to hydrogen abstraction to give an alcohol group attached to the chain. This speculation can be tested by measuring the quantum yield of photodecomposition of PEP hydroperoxides and comparing these to the values of Φ_s determined earlier. The low concentration of hydroperoxide in the oxidized PEP samples renders solution studies very difficult to perform; therefore irradiations were carried out in the solid phase.

(a) Irradiation of Oxidized PEP Samples Containing both Ketone and Hydroperoxide Groups. Figure

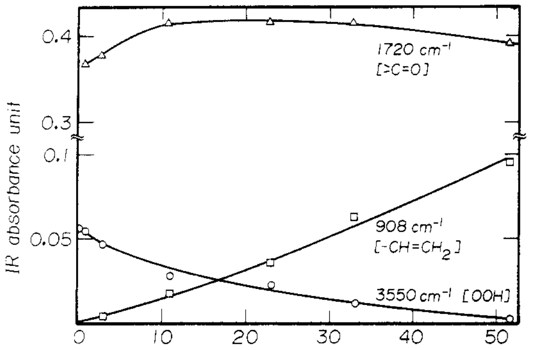


Figure 4. Changes in IR absorbance during the irradiation of PEP sample VI film at 313 nm at 23 °C in N_2.

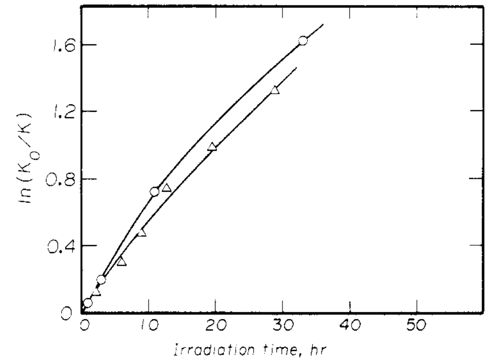


Figure 5. Photolysis of oxidized PEP films with different amounts of hydroperoxides and carbonyls (λ = 313 nm, 23 °C, in N_2). Hydroperoxide IR absorbance plotted according to eq 3. (○) Sample VI, 1.8×10^{-5} mol/g -OOH, 5.8×10^{-5} mol/g >C=O; (△) sample IV, 1.1×10^{-5} mol/g -OOH, 2.2×10^{-5} mol/g >C=O.

4 shows the change in IR absorbance of carbonyl, hydroperoxide and vinyl groups during the irradiation of oxidized PEP (sample VI). The carbonyl absorbance shows an initial rise, becomes steady, and then decreases slowly with the time of irradiation. This behavior can be explained by the net conversion of hydroperoxide to ketonic compounds during the initial period of photolysis, followed by a steady-state conversion of hydroperoxide to ketones and loss of ketones via the Norrish type I and type II processes. At the later stage, when photolysis of the smaller amount of hydroperoxides present may no longer refurnish the amount of ketone groups lost, the IR absorbance at 1720 cm^{-1} decreases. The decrease in IR absorbance at 3550 cm^{-1} is expected because of the decomposition of the hydroperoxide group, whereas the increase at 908 cm^{-1} is due to the formation of vinyl groups via the Norrish type II process.

When the hydroperoxide disappearance was plotted according to eq 3, the nonlinear behavior at long irradiation times (Figure 5) suggests that the decomposition of hydroperoxide groups is not characterized by a unimolecular or pseudounimolecular rate parameter. The sample containing a higher concentration of hydroperoxide groups shows a somewhat larger initial slope, showing the dependence of $\Phi_{\text{-OOH}}$ on hydroperoxide concentrations. $\Phi_{\text{-OOH}}$ values for samples IV and VI were calculated from the observed rates and the calculated absorbance to be 11 and 9.2, respectively, considerably larger than unity. These facts suggest that photodecomposition of PEP hydroperoxide follows a radical chain mechanism (Scheme I), similar to that proposed by Ng and Guillet for polyisoprene hydroperoxide.[28,31] In Scheme I, R′ and R represent the polymeric species and solvent molecules, respectively. In view of the low concentration of polymeric hydroperoxide groups and the relatively low mobility of the polymeric radicals compared to the diffusion of hydroxyl and solvent radicals, it was suggested that the active chain-carrying species are R· and ·OH radicals.[31] Ng and Guillet found that $\Phi_{\text{-OOH}}$ of polyisoprene hydroperoxide ranged from 5 to 30, depending on the concentration of hydroperoxides and the incident light intensity. Their results are consistent with such a radical chain mechanism. Present results for the photodecomposition of PEP hydroperoxide in solid films follow a similar pattern.

Scheme I

Initiation	
$R'OOH + h\nu \rightarrow R'O\cdot + \cdot OH$	ϕI_A
$R'O\cdot + RH \rightarrow R'OH + R\cdot$	$K_2[RH][RO\cdot]$
$HO\cdot + RH \rightarrow HOH + R\cdot$	$K_3[RH][HO\cdot]$
Propagation	
$R\cdot + R'OOH \rightarrow RH + R'OO\cdot$	$K_p[R\cdot][R'OOH]$
$2R'OO\cdot \rightarrow 2R'O\cdot + O_2$	$K_5[R'OO\cdot]^2$
Rearrangement	
$R'O\cdot \rightarrow \cdot R'OH$	$K_6[R'O\cdot]$
β Scission	
$R'O\cdot \rightarrow \beta\text{-scission product} + R'\cdot$	$K_s[R'O\cdot]$
$\cdot R'OH + RH \rightarrow \cdot R'HOH + R\cdot$	$K_8[\cdot R'OH][RH]$
Termination	
$2R'OO\cdot \rightarrow R'OOR' + O_2$	$K_9[R'OO\cdot]^2$
$R\cdot + R\cdot \rightarrow 2R$	$K_t[R\cdot]^2$

Sample VI contains more than twice the amount of carbonyls as IV. If the ketone groups were to act as a light screen for the radiation, the rate for sample VI would have been lower than for sample IV (Figure 5). The higher rate is consistent with the transfer of excitation energy from the ketones to the hydroperoxides to induce subsequent decomposition. The higher value of $\Phi_{\text{-OOH}}$ for VI can thus be explained by its higher carbonyl content. Such a consideration is reasonable since the ketone group in this sample absorbs at least 30 times more 313-nm light than the hydroperoxide.

These results lead to the conclusion that although the presence of hydroperoxide groups is necessary for the accelerated photodegradation of oxidized PEP samples, the importance of ketones cannot be neglected because of their much higher concentrations and UV absorption coefficents. Hence the importance of ketone groups during photodegradation of oxidized polyolefins may lie not so much in their role as reactive chromophores leading to direct chain scission but in their role as the primary absorber of the incident light.

(b) Irradiation of Dehydroperoxidized Samples. Since the exact amount of IR absorbance at 1720 cm^{-1} attributable to ketone and aldehyde groups was not known in the dehydroperoxidized samples, it was necessary to plot the IR absorbance changes according to a modified equation.

$$\ln \{xK_0/[K - K_0(1 - x)]\} = 2.303\Phi_{\text{-CO}}I_0^{\text{i}}\epsilon t \qquad (6)$$

where x refers to the fraction IR absorbance due to ketone and aldehyde groups. The remaining fraction $(1 - x)$ due to ester or carboxylic groups is not expected to change with irradiation time because they do not undergo photolysis at 313 nm, the wavelength of excitation. It is possible to have an estimate of x by fitting various numerical values of x in eq 6 and looking for the value of x when the plot of $\ln \{xK_0/[K - K_0(1 - x)]\}$ vs. t (excluding the $t = 0$ point) gives the highest correlation coefficient and a y-intercept value closest to zero in the best fit of $y = mx + c$. It was found that $x = 0.75$ best satisfied the conditions during the irradiation of Va and $\Phi_{\text{-CO}}$ was calculated to be 0.047, which compares with a value of $\Phi_{\text{-CO}} = 0.073$ for the PE–

Table V
Effect of Wavelength of Excitation on Photoscission of Oxidized PEP, Sample VII[a]

irradiation wavelength, nm	$I_0^i \times 10^{-16}$, quanta s^{-1}	ϵ_{OOH},[b] M^{-1} cm^{-1}	ϵ_{ketone},[c] M^{-1} cm^{-1}	dS/dt × 10^3, scission/min	S' × 10^{20}, (scission/min)/quantum incident	ϕ_s[e]
250	0.15	10.5	43	2.5 26[d]	2.8 29[d]	0.83 8.8[d]
276	0.12	2.2	36	1.6 28[d]	2.1 37[d]	0.76 13[d]
288	0.32	1.06	36	2.2	1.0	0.41
300	1.3	0.48	2.6	4.9	0.62	0.31
313	2.1	0.21	13	3.5	0.27	0.27
323	0.71	0.06	5.0	0.65	0.15	0.39

[a] Irradiated at 313 nm in cyclohexane at 23 °C; PEP contains approximately 2.5 × 10^{-5} mol g^{-1} of hydroperoxide and 3.8 × 10^{-5} mol g^{-1} of ketone. [b] Calculated based on *tert*-butyl hydroperoxide in acetonitrile. [c] Calculated based on 3-*n*-propyl-2-heneicosanone in heptane. [d] From the "fast" component of the plot of S vs. irradiation time. [e] Calculated based on light absorbed by the ketone.

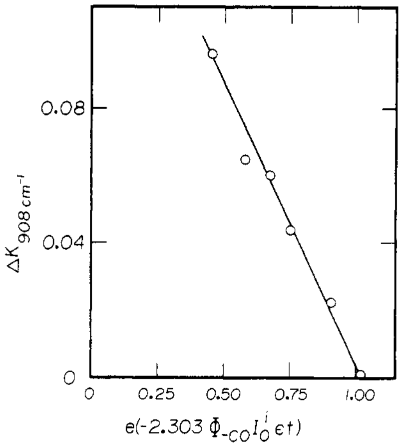


Figure 6. Irradiation of dehydroperoxidized sample Va showing change of vinyl absorbance at 908 cm^{-1} with irradiation time according to eq 4.

1% CO copolymer under similar irradiation conditions.[35] Figure 6 shows the plot of the IR absorbance of vinyl group formation according to eq 6 during the irradiation of a Va film. Φ_{II} was calculated to be 0.076, assuming 75% of the carbonyl groups are due to ketones and aldehyde groups. This is remarkably consistent with Φ_{II} = 0.074 in the PE–1% CO copolymer.[29,35] Comparison of this value of Φ_{II} with the observed value of Φ_s = 0.036 for the dehydroperoxidized PEP samples (Table III) leads to the conclusion that about half of the ketone groups are at the end of the polymer chain and hence do not contribute to main-chain scission.

The fraction of ketone and aldehyde groups in the total carbonyl content (x = 0.75) of the dehydroperoxidized samples is considerably higher than that assumed (x = $^1/_3$) in the oxidized PEP samples that had not been subjected to vacuum heating. This difference can be explained by the fact that hydroperoxide and other peroxy compounds decompose to form ketones and aldehyde groups predominantly, with no increase in the ester and carboxylic contents of the sample. This situation would be expected when the thermal decomposition is carried out under vacuum, where the low concentration of oxygen does not result in further oxidation of the primary products.

Effect of the Wavelength of Excitation. The UV spectrum of oxidized PEP samples often does not give sufficient resolution to determine whether the hydroperoxide or the ketonic compounds are the chief absorbing species that initiate the subsequent photochemistry. Although it is generally assumed that most incident radiation above 280 nm would be absorbed by the ketonic compounds, whether the photoscissioning process is due primarily to light absorbed by ketones or by hydroperoxides remains an open question. A highly oxidized sample VII was irradiated at different wavelengths in cyclohexane solution, and the initial rates of photoscission per quanta of incident light were estimated. The idea was to obtain an excitation spectrum using the rate of scission as the probe. Figure 7 shows the plot of the number of scissions, S, with irradiation time for a highly oxidized PEP sample VII in cyclohexane at 23 °C over the range 250–323 nm, which covers the entire n–π* band of aliphatic ketones and the tail of hydroperoxide absorption. Variation of S with irradiation time shows good linear plots at 323, 313, 300, and 288 nm. Irradiation at 276 and 250 nm showed two anomalies: first, a two-component variation of S with time, with the initial rise much larger (about 9–10 times) than the subsequent component, and second, the viscosity of the polymer solution irradiated for a short initial period (e.g., 3 min) continued to decrease over a matter of hours, even after the light had been cut off.

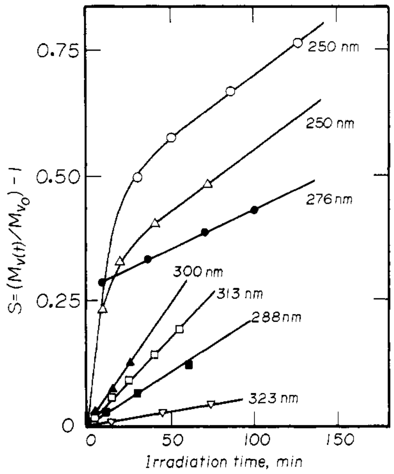


Figure 7. Irradiation of sample VII in cyclohexane at different wavelengths at 25 °C plotting the number of scissions for original polymer molecules, S, with irradiation time.

(a) Excitation Spectrum of Scission. Table V shows the effects of excitation wavelength on the photoscission process, where $S' = (\mathrm{d}S/\mathrm{d}t)/I_0^i$ represents the initial rate of scission per incident quantum and Φ_s is the quantum yield of scission calculated assuming the light absorbed was due entirely to ketone groups. The UV ϵ values for a typical hydroperoxide and ketone are also included in order to compare the relative amount of light absorbed by each at the particular wavelengths. The excitation spectrum (with S' plotted against the wavelength of excitation) and the absorption spectrum of the oxidized PEP sample in cyclohexane are shown in Figure 8. The data points

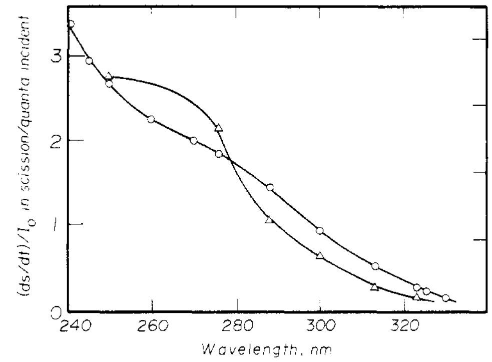
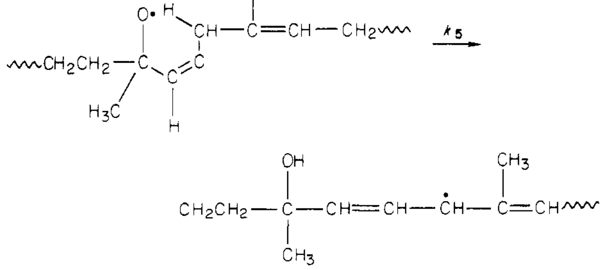


Figure 8. Excitation spectrum of PEP sample VII using the rate of scission as a probe. (○) Absorption of sample VII in cyclohexane; (△) excitation data for scission process.

at 276 and 250 nm were calculated based on the "slow component" of the observed rates of scission with irradiation time. Current data indicate that the absorption spectrum of the oxidized PEP sample correlates closely with the excitation spectrum, especially at wavelengths greater than 288 nm.

Comparison of the excitation data (S') of sample VII with the absorption data in typical model compounds of ketones and hydroperoxides in the region 288–323 nm shows that the excitation spectrum is more indicative of a ketone ($\epsilon_{288}/\epsilon_{323}$ for hydroperoxides and ketones are 1.06/0.06 and 35.6/5.0, respectively, i.e., 15 and 7, whereas S'_{288}/S'_{323} = 1.04/0.15 = 7). The present results seem to confirm that the absorbing species leading to the subsequent polymer scission is the ketone group. The small variation in the Φ_s values from 288 to 323 nm demonstrates the independence of Φ_s on excitation wavelength. This behavior is not expected if the photoscission had been due to a direct photolysis of the hydroperoxide, since a definite wavelength effect (larger $\Phi_{\text{-OOH}}$ at shorter wavelengths) was observed in the photolysis of both low molecular weight and polymeric hydroperoxides.[28,31]

The Φ_s values over the range from 288 to 323 nm are also much larger than those obtained in the photolysis of polyisoprene hydroperoxide, which were found to be 0.1 or lower in a wide variety of reactant concentrations, light intensities, and excitation wavelengths.[28,31] The relatively low Φ_s values were attributed to an intramolecular hydrogen abstraction (eq 7), which competes with β scission



(7)

of the polymeric alkoxy radical. This reaction was postulated to be highly efficient in polyisoprene because of the presence of two allylic hydrogens and the strongly stabilized "diallylic" radical that results.[28,31] The absence of allylic hydrogens in saturated PEP samples in the present work is therefore expected to increase the yield of β-scission products for the polymeric alkoxy radical since the intramolecular hydrogen abstraction is not as efficient as in unsaturated alkoxy radicals.

(b) Photolysis at 276 and 250 nm. Figure 9 shows the plot of the number of scissions S vs. time in the dark in toluene solution after different preirradiation time periods at 250 nm. The dark scission reaction appears to be partially quenched by oxygen and increases with the length of the preirradiation period. The initial slope of the S vs. time plot for the sample preirradiated for 3 min is about 100 times that for the sample preirradiated for 1 min. The variation of the extent of the dark reaction with the preirradiation period is obviously connected to the concentration of the intermediate reactant responsible for the dark reaction. Thus the reaction intermediate was formed in abundance when irradiated at 250 to 276 nm, but only in small concentrations when irradiated at 288 nm and higher. Therefore, attempts were made to fit the dark scission reaction to different rate equations.

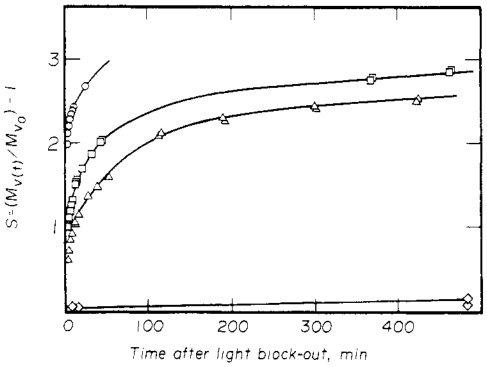


Figure 9. Scission of PEP sample VII in the dark in toluene at 250 nm at 25 °C after (□) preirradiation for 3 min in N_2, (△) preirradiation for 3 min in air, (○) preirradiation for 10 min in N_2, and (◇) preirradiation for 1 min in N_2.

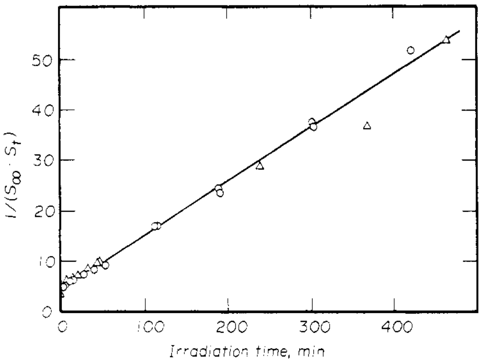


Figure 10. Second-order plot of the dark scission reaction according to eq 8: (△) in N_2; (○) in air.

(c) Kinetic Analysis of the Dark Scission Reaction. First-order plots of the scission process in the dark indicate that the dark reaction does not follow simple first-order or pseudo-first-order kinetics. Figure 10 shows the second-order plot of scission according to

$$1/(S_\infty - S_t) = k_s t + 1/S_\infty \qquad (8)$$

where S_∞ is the number of scissions at infinite time when all the reactants have been converted to scission products, which can be obtained from extrapolation to a very long reaction time, and k_s is the phenomenological rate constant of the scission reaction in the dark.

A well-correlated straight line with k_s of 41 $M^{-1}\ s^{-1}$ indicates that the scission process is second order with respect to the intermediate that gives rise to scission. The value of k_s is surprisingly low compared to the rate constants of β scission of free alkoxy radicals, which are usually of the order of 10^4–$10^5\ s^{-1}$.[33,36] The long reaction time for scission in the dark suggests that the intermediates giving rise to chain scission have lifetimes extending into minutes and even hours. Examination of the stability or organic reactive intermediates indicates that peroxy radicals are relatively stable and are readily detectable in solution, even at room temperature.[33] For example, the half-life of the peroxy radicals produced in the high-energy irradiation of polyethylene films in air has been estimated to be approximately 20 min at room temperature.[36] Moreover, peroxy species have been widely postulated as the main propagating agent in the autoxidation of small-molecule hydrocarbons and polymers. Hydrogen abstraction reactions and the bimolecular self-reactions of small-molecule peroxy radicals proceed with rate constants of the order of 10^0–10^{-2} and 10^3–10^6 M^{-1} s^{-1}, respectively.[33]

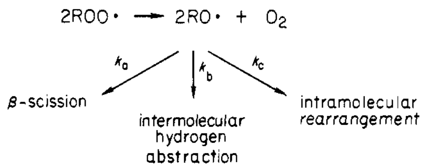
The present results suggest that the reaction intermediate in the dark reaction is likely to be a polymeric peroxy radical. The fact that the dark reaction was present only in samples irradiated at 250 and 276 nm indicates that polymeric peroxy radicals are produced in relatively high concentrations at these wavelengths ($\sim 10^5$–10^6 M). A tentative mechanism to explain the suspected high concentration of peroxy radicals is outlined in eq 9. At short

$$\text{ROOH} \xrightarrow{h\nu} \text{RO}\cdot + \cdot\text{OH} \tag{9a}$$

$$\text{RO}\cdot + \text{ROOH} \rightarrow \text{ROH} + \text{ROO}\cdot \tag{9b}$$

$$\text{HO}\cdot + \text{ROOH} \rightarrow \text{HOH} + \text{ROO}\cdot \tag{9c}$$

wavelengths, the UV absorption coefficients of hydroperoxides are significantly larger (Table V). Because of the much higher percentage of light absorbed by the hydroperoxide, direct photolysis of hydroperoxides would occur to form macroalkoxy radicals, which then abstract hydrogens from remaining hydroperoxides to produce peroxy radicals. Fission occurs predominantly at the oxygen–oxygen bond for irradiations in the near-UV range.[37] Wavelength studies on hydroperoxide decomposition extending into the 250-nm region are unavailable and it is uncertain whether irradiation at short wavelengths would favor photocleavage at the oxygen–hydrogen and carbon–oxygen bonds as well. In any event, a relatively high concentration of peroxy radicals is expected for irradiations at short wavelengths. The long lifetime of peroxy radicals facilitates the bimolecular reaction between them.



(10)

The observed decrease in molecular weight in the dark can thus be attributed to β scission of the alkoxy radicals. If one assumes that the rate-determining step of the dark scission is the bimolecular reaction of the polymeric peroxy radicals, then the dark scission reaction would appear to be second order with respect to [ROO·], as observed.

Assuming a simple reaction scheme, as in eq 10, one can write

$$-\frac{d[\text{RO}\cdot]}{dt} = \frac{1}{2}k_t[\text{ROO}\cdot]^2 - k_a[\text{RO}\cdot] + k_c[\text{RO}\cdot] + k_b[\text{RO}\cdot][\text{RH}] \tag{11}$$

where [RH] is the concentration of the solvent. Assuming steady-state conditions, eq 11 becomes after rearrangement

$$[\text{RO}\cdot] = \frac{1}{2}\left(\frac{k_t[\text{ROO}\cdot]^2}{k_a + k_c + k_b[\text{RH}]}\right) \tag{12}$$

But the rate of scission is given by

$$\frac{d[\text{S}]}{dt} = k_a[\text{RO}\cdot] \tag{13}$$

Combining eq 12 with 13 gives

$$\frac{d[\text{S}]}{dt} = \frac{k_a k_t[\text{ROO}\cdot]^2}{2(k_a + k_c + k_b[\text{RH}])} \tag{14}$$

consistent with the observed second-order behavior for the dark scission reaction. k_a is usually around 2×10^4 s^{-1}.[27,29,35] The termination rate constant, k_t, in small molecules is usually around 10^6 M^{-1} s^{-1}, probably 10^5 for polymeric peroxy radicals. k_b for hydroperoxy radicals is 10^5 M^{-1} s^{-1},[33] and [RH] = 15 for cyclohexane. Also, k_c should be much larger than k_t and of the order of 10^7–10^8. Substituting these numerical rate constants in eq 14, one can have a rough estimate of the phenomenological rate constant k_s. It was found to be 10–10^2, in reasonable agreement with the observed dark scission rate constant of 41 M^{-1} s^{-1}. These results are thus consistent with the proposal that polymeric peroxy radicals are responsible for the scission reaction in the dark.

The photoscission of oxidized PEP samples at 250 nm was partially quenched by oxygen. This observation can be accommodated in the above reaction scheme since solvent radicals may be oxidized to peroxy radicals by oxygen, which are less efficient chain-carrying agents than the solvent alkyl radicals. The amount of polymeric peroxy radicals is thus reduced, and hence the subsequent scission process.

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secondary and tertiary sites is about equal. This should not, however, affect the main thesis of this work, since β scission of secondary radicals is unlikely to occur. According to our mechanism the scission will occur primarily from attack at tertiary carbon atoms.
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Polymeric Photosensitizers: Effects of Intramolecular Energy Migration on Sensitization Efficiencies

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ABSTRACT: The occurrence of intramolecular energy migration was found to have no significant effect on the efficiency of ketyl radical formation via hydrogen abstraction from cumene by benzophenone (BP) or poly(vinylbenzophenone) (PVBP). Rate constants were found to be 1.1×10^6 and 0.81×10^6 M^{-1} s^{-1} for the small molecule and the polymer, respectively. The large difference in rate consants, 9.6×10^6 and 22.2×10^6 M^{-1} s^{-1} for BP and PVBP, respectively, when tetrahydrofuran was used as a quencher is probably attributable to preferential solvation. Conversely, intramolecular energy migration was found to significantly enhance the overall efficiency of triplet energy transfer to 1-methylnaphthalene (MeN). Rate constants for formation of ^{3}MeN were found to be 0.94×10^9 and 1.85×10^9 M^{-1} s^{-1} for BP and PVBP, respectively. An energy migration coefficient, Λ, of 3.28×10^{-5} cm^2 s^{-1} and a frequency of energy migration, ω, of 7.88×10^{10} s^{-1} were calculated for PVBP. For a series of copolymers of methyl methacrylate with vinylbenzophenone, values of Λ and ω were strongly dependent on the ketone content of the polymer and decreased sharply at 40 mol % VBP or less.

Introduction

While it is found that generally, the photoprocesses typical of a chromophore covalently linked to a polymer chain do not deviate remarkably from those in their small-molecule analogues, significant differences can and do occur quite regularly. These differences are usually a reflection of the somewhat unusual environment that the polymeric chromophores find themselves in. Their attachment at regular intervals to a long carbon–carbon chain leads to very high effective local concentrations and hence interactions that may be significantly larger than those seen in solutions of equimolar but isotropically distributed small molecules. A particularly striking example of this is the observation that for solutions of polystyrene and ethylbenzene, both 10^{-3} M in phenyl rings, the total emission spectrum for the former is dominated by excimer emission while the latter displays only normal fluorescence.[1,2]

Equally of interest, but more difficult to quantify, is the occurrence of intramolecular energy migration along the polymer chain. The first good evidence for this process was reported by Fox and Cozzens[3] through the observation of P-type delayed fluorescence resulting from triplet–triplet annihilation in dilute (10^{-3} M) solutions of poly(vinylnaphthalene). Since then, numerous systems have been investigated[4,5] and intramolecular energy migration seems to be the rule rather than the exception in polymers containing chromophores that absorb in the near UV.

If intramolecular energy migration is sufficiently facile, its migration distance may begin to approximate the polymer chain length. Since the entire macromolecule (rather than a single chromophore attached to it) can now be considered as the reactive species, the net result is an increase in the effective collisional radius for reactions with small-molecule substrates. In principle, this could lead to increased efficiencies in photosensitized reactions through the use of polymeric rather than small-molecule photosensitizers.

Attempts to demonstrate the feasibility of this approach have centered about the photosensitized isomerization of *cis*- and *trans*-stilbene. Moser and Cassidy[6] and Irie et al.[7] have shown that poly(phenyl vinyl ketone) is no more efficient as a sensitizer than are small-molecule triplet-energy donors such as acetophenone. Similar results were obtained by Serle et al.[8] and Hammond et al.[9] However, Irie et al.[7] have reported enhanced sensitization of stilbene isomerization when copolymers of phenyl vinyl ketone with a small amount of 2-vinyl naphthalene were used. Also of great interest, Kamachi et al.[10] have reported that the rate constant for hydrogen abstraction from tetrahydrofuran was roughly twice as large for poly(4-vinylbenzophenone) as for benzophenone itself. Both groups have proposed that intramolecular energy migration in the polymer chain plays an important role in the enhancement of photosensitization efficiencies.

In the course of parallel investigations, we have had cause to partially reexamine some of these interpretations. We report here results that strongly suggest the absence of any polymer effect when the sensitization step proceeds at rates that are considerably below the diffusion-controlled limit. Conversely, in donor–quencher interactions that begin to approach the diffusion-controlled limit, intramolecular energy migration does lead to an enhancement of photosensitization efficiencies.

Experimental Section

Benzene (Fisher Spectranalyzed Grade) was further purified by refluxing over P_2O_5 for several hours followed by distillation.

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