still quite efficient in the long chains, one may conclude that single-step Förster transfer is not an appropriate explanation, and one must postulate some kind of energy migration between naphthalene groups before the final transfer to anthracene. Whether or not this occurs by a "hopping" mechanism between adjacent naphthalenes or across loops in the chain cannot be established from these data, and a final resolution must await further experimental studies.

In conclusion it is evident from these results that the solvent exerts a significant effect on the energy transfer process from the naphthyl chromophores to the 9-VA trap in the PNMA–VA copolymer. This solvent effect cannot be attributed to dielectric or polar changes in the medium since addition of methanol (polar) or cyclohexane (nonpolar) to a solution of PNMA in $CHCl_3$ (a good solvent) decreases the excimer emission equally. Incorporation of a 9-VA trap into the naphthyl methacrylate polymer results in a very rapid (<1 ns) transfer or localization of energy on this chromophore, even when present at very low concentration (<0.06 mol %). The temperature dependence of the PNMA–VA fluorescence suggests a transfer of energy from the naphthyl monomer rather than the excimer. This rapid and efficient localization of energy from a network of absorbing naphthyl chromophores to a small concentration of low-energy traps is similar in many respects to the process of the energy localization process in aggregated systems and may simulate some of the aspects of photosynthesis.

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Singlet Oxygen Initiation of Polymer Photooxidation: Photolysis of *cis*-1,4-Poly(isoprene hydroperoxide)[1]

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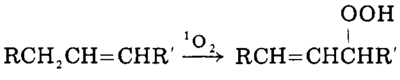
ABSTRACT: Reaction of singlet oxygen with *cis*-1,4-polyisoprene gives *cis*-1,4-poly(isoprene hydroperoxide). The kinetics and mechanism of the photolysis of this polymer–singlet oxygen adduct have been studied at 313 nm in solution in the absence of oxygen. The primary quantum yield for photolysis of the polymer hydroperoxide was 0.8. The subsequent radical-induced chain decomposition of the hydroperoxide results in a high overall quantum yield for hydroperoxide decomposition (Φ_{OOH}). The chain propagation reaction rate constant is estimated as 9×10^4 M^{-1} s^{-1}. The polymer degradation kinetics was studied and the rate constant for the β scission of the polymeric alkoxy radical (generated from primary hydroperoxide decomposition) is estimated as 2.7×10^4 s^{-1}. The quantum yield of polymer chain scission (Φ_S) is of the order of 0.1. From the experimental values of Φ_{OOH} and Φ_S, the ratio Φ_S/Φ_{OOH} can be approximated as a constant of 0.014. This agrees remarkably well with the theoretical value of 0.01 derived from the mechanism proposed in this study.

The detailed mechanism and kinetics of the initiation of elastomer photooxidation is still an open question.[2] One proposed mechanism involves the addition of singlet molecular oxygen to form an allylic hydroperoxide in general polymers as a key preinitiation step.[3] The subsequent photodecomposition of this hydroperoxide would initiate an autocatalytic chain reaction.[4] The reaction of singlet oxygen with olefinic acceptor systems has been studied extensively.[5-9] The addition of singlet oxygen to the double bonds of an unsaturated polymer to give an allylic hydroperoxide attached to the polymer chain proceeds via the well-known "ene" reaction mechanism:[10]



$$\mathrm{RCH_2CH{=}CHR'} \xrightarrow{{}^1O_2} \mathrm{RCH{=}CH\overset{\displaystyle OOH}{\overset{|}{C}}HR'} \qquad (1)$$

In order to understand the detailed mechanism of the photooxidation of elastomers in general, and the role of singlet oxygen in the initiation step in particular, it is important to investigate the kinetics and mechanism of

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the photochemical degradation process resulting from the introduction of such groups into a polymer chain. This paper reports a kinetic investigation on the photolysis of the *cis*-1,4-polyisoprene (natural rubber) and its singlet oxygen adduct in solution. The reaction can be followed conveniently and with great precision by automatic viscometry and hydroperoxide analysis. Oxygen was excluded in order to avoid the complexity of concurrent photooxidation steps.

Experimental Section

Generation of Singlet Oxygen. Singlet oxygen was generated both by the microwave discharge method[11] and the dye-photosensitization method.[12] In the former procedure, oxygen at 5 Torr was led over a mercury droplet and through an EMS 200 microwave discharge apparatus (2450 MHz, 100 W) in a quartz tube, where the energy from the wave guide was coupled with the gas stream. Singlet oxygen, oxygen atoms, and ozone were generated. The latter two species were removed by reaction with traces of mercury vapor and formed a mercury oxide ring inside the quartz tube. The singlet oxygen stream was then passed through a cold trap (−78 °C) and led into the reaction vessel containing freeze-dried polymer in the dark. The path length from the discharge zone to the reaction cell was about 1 m, which is short enough for the singlet oxygen to survive at the pumping rate used (30 L/min). Hydroperoxide was formed after the singlet oxygen reaction. The amount of OOH formed was linear with the time of reaction, as reported previously,[10a,11b] although the yield was low.

In the second method, the polymer-bound sensitizer, Rose Bengal covalently bonded on polystyrene (tradename Photox, Hydron Laboratories, Inc., New Brunswick, N.J.), was used. The solution to be oxidized was irradiated by a GE sun lamp with a Schott 530 nm cutoff filter in front of the irradiation cell to give incident light with λ >530 nm. This wavelength excites the dye but causes little photodecomposition of the resulting hydroperoxide. The heterogeneous solution was 1 wt % in the sensitizer and about 5 wt % in the olefin substrate. Oxygen was bubbled slowly through the cooled solution during irradiation. Singlet oxygen, which was generated by energy transfer from the excited dye triplet to ground state molecular oxygen, was added subsequently to the olefin double bond to yield the allylic hydroperoxide product. After reaction, the insoluble polymer-bound sensitizer was filtered off and the clear resultant solution of the oxidized product was analyzed.

A commercial sample of masticated natural rubber (*cis*-1,4-polyisoprene) was purified by dissolving it three times in spectroscopic grade benzene and precipitating with reagent grade methanol. The precipitated rubber was dried 48 h under vacuum at room temperature. The sample was dissolved in spectral grade benzene and stored in the dark under nitrogen atmosphere. No trace of antioxidants or other additives could be detected (IR and UV) for samples after this treatment. The polymer was characterized by spectroscopic methods (IR, UV, and NMR). All data showed the polymer was pure *cis*-1,4-polyisoprene (*cis*-pip).

The viscosity average molecular weight ($\bar{M}_v$) of the polymer was determined in toluene at 25 °C using an Ubbelohde viscometer. The Mark–Houwink constants (K and a) for *cis*-pip in toluene, benzene, and cyclohexane are available in the "Polymer Handbook".[13] The number average molecular weight ($\bar{M}_n$) of the polymer in toluene at 25 °C was determined by osmometry. The $\bar{M}_v$ and $\bar{M}_n$ for the *cis*-pip sample were 2.96×10^5 and 1.26×10^5, respectively. The viscosity–molecular weight relationship for *cis*-1,4-polyisoprene in 1,2-dichloroethane was determined using the rapid method described by Kilp and Guillet,[14] which used the random scission of polymer chains to produce samples of known polydispersity. In this case the polymeric hydroperoxide was photolyzed to various extents and single point determinations of osmotic pressure and viscosity were made. From the data shown in Figure 1, the relationship obtained was

$$[\eta] = 8.22 \times 10^{-5}\bar{M}_v^{0.77} \text{ at } 30\ °\text{C} \qquad (2)$$

Since 1,2-dichloroethane is an ideal solvent for the polymer and for photochemical studies, this relationship was utilized extensively in subsequent work. The excellent linearity of the experimental curve is probably a reflection of the fact that the starting dispersity of the polymer was close to 2.[14]

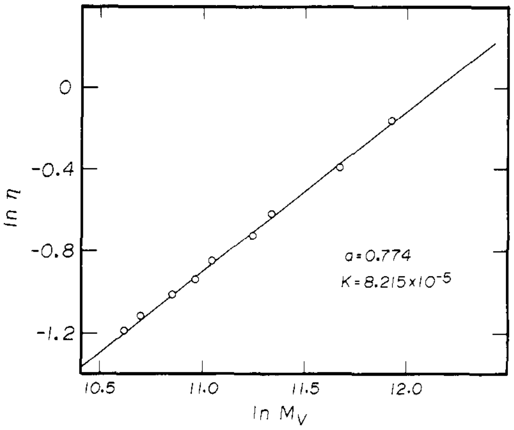


Figure 1. Plot of log η vs. log M_v for *cis*-1,4-polyisoprene in dichloroethane at 30 °C.

Singlet Oxygen–Polymer Reaction and Hydroperoxide Analysis. A measured amount of stock polymer in benzene solution (1.2 wt %) was freeze-dried overnight under vacuum. For microwave discharge treatment, the freeze-dried porous film was introduced to the reaction vessel and treated with singlet oxygen. After 2 to 20 h of treatment, the polymer was dissolved in purified solvent and kept in a refrigerator. This method gives a low concentration of hydroperoxide formation in the polymer chain (<0.5%). For higher contents of hydroperoxide in the polymer, the Rose Bengal sensitization method was used. The freeze-dried polymer was dissolved in 1,2-dichloroethane and oxidized in the presence of the dye, as described previously.

Two methods were used for hydroperoxide analysis. The first was by iodometry,[15] using a combination of titration and colormetric determination good to ca. 10^{-4} M. A value of 2.5×10^4 M^{-1} for the molar extinction coefficient of I_3^- at 360 nm[16] was adopted. Alternatively, the triphenylphosphine method[17] was used for determination of hydroperoxide. Triphenylphosphine (TPP) was quantitatively oxidized by OOH to form triphenylphosphine oxide (TPPO)

$$Ph_3P + ROOH \rightarrow Ph_3P{=}O + ROH \qquad (3)$$

The decrease of TPP was measured by monitoring the UV absorbance at 260 nm. With the known extinction coefficient of TPP and TPPO at 260 nm, the amount of hydroperoxide can be determined. This method allows the determination of OOH concentrations to a lower limit of 10^{-6} M and gives more consistent results than those from iodometry.

All chemicals used were purified by conventional methods (e.g., distillation and/or recrystallization before use). 2-Methyl-2-hexene (Pfaltz and Bauer) was oxidized without further purification. The isomeric 4-methyl-4-octene was synthesized by a Wittig reaction.[10b]

Photolysis of the Singlet Oxygen–Polymer Adduct. The automatic viscometer for photolysis and viscosity measurements has been described by Kilp and co-workers.[18] An optical train was equipped with an AEI medium pressure mercury arc and a Jena 313 interference filter to isolate a monochromatic parallel light beam of wavelength 313 nm. The intensity of the incident beam was determined by ferrioxalate actinometry. Variation of light intensity was achieved by placing darkened screens in front of the irradiation cell. The light transmitted was measured by a pyroelectric radiometer (PR 200, Molectron Corp.) at the end of the optical train. The Teflon sample tubing between the irradiation cell and the viscometer was connected to a flow-through cell in a Unicam SP 500 UV spectrometer. Thus the absorbance of the polymer solution during photolysis could also be monitored. Samples were saturated with nitrogen during photolysis. Periodically the viscosity and absorbance were determined and a known amount (0.1 mL) of solution was pipetted out for hydroperoxide determination. The temperature of the irradiation cell and the viscometer was controlled within ±0.1 °C by a Tamson circulating water bath. For variation of incident light wavelength, a Bausch and Lomb super pressure mercury arc connected with

Table I
Hydroperoxide Content of *cis*-Polyisoprene after Various Singlet Oxygen Treatments

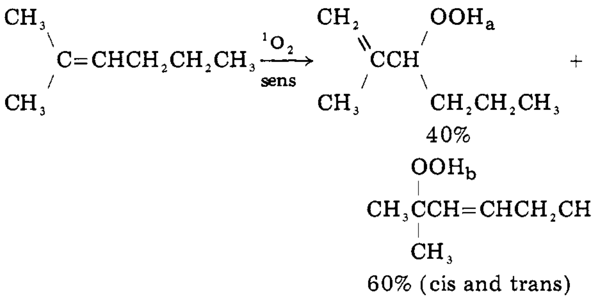
method of $^1O_2$ generation	time of $^1O_2$ treatment, h	hydroperoxide content in polymer		
		mol %[a]	mol/L[b]	$[\eta]$[c]
control sample	0	$<5 \times 10^{-3}$	$<5.0 \times 10^{-6}$	2.24
discharge[d]	4	0.05	4.8×10^{-5}	2.10
discharge[d]	6	0.07	6.6×10^{-5}	2.05
discharge[d]	10	0.10	8.8×10^{-5}	1.99
discharge[d]	20	0.15	1.4×10^{-4}	2.04
sensitization[e]	2	1.2	1.04×10^{-3}	2.12
sensitization[e]	5	2.7	2.50×10^{-3}	0.82
sensitization[e]	overnight	6.4	6.01×10^{-3}	0.12

[a] OOH to monomer mol %. [b] 0.6 g of polymer in 50 mL of solution. [c] $[\eta]$ in CH_2ClCH_2Cl at 30 °C. [d] Microwave discharge method; oxidized film redissolved in cyclohexane for analysis. [e] Dye sensitization method; 1,2-dichloroethane used as solvent during oxidation. Polymer freeze-dried.

a high intensity monochromator was used in the optical train.

Results

Reaction of Singlet Oxygen with *cis*-1,4-Polyisoprene. Addition of singlet oxygen to olefinic double bonds to give an allylic hydroperoxide proceeds via a well-documented "ene" reaction mechanism. 2-Methyl-2-hexene, which may serve as an approximate model compound for 1,4-polyisoprene, reacts with $^1O_2$ to give a mixture of hydroperoxides in the following isomeric distribution (measured by NMR: H_a, δ 7.60; H_b, δ 8.10):

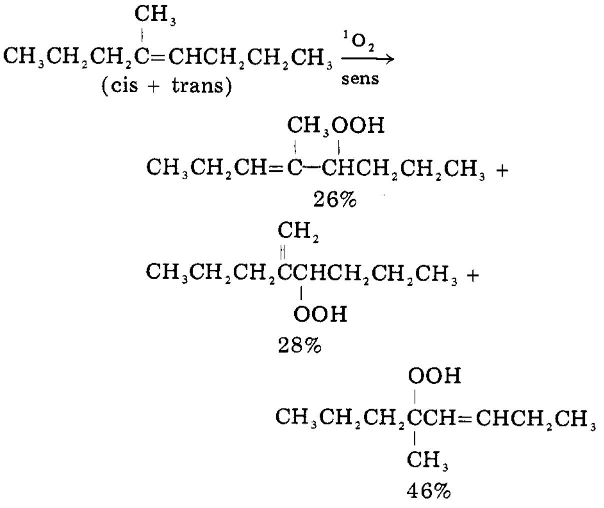


$$(CH_3)_2C{=}CHCH_2CH_2CH_3 \xrightarrow[\text{sens}]{^1O_2} \underset{40\%}{CH_2{=}C(CH_3)CH(OOH_a)CH_2CH_2CH_3} + \underset{60\%\ \text{(cis and trans)}}{CH_3C(OOH_b)(CH_3)CH{=}CHCH_2CH_3} \quad (4)$$

Addition of $^1O_2$ to 4-methyl-4-octene, a closer model compound for 1,4-polyisoprene, gives the products shown in Scheme I.[10b,19]

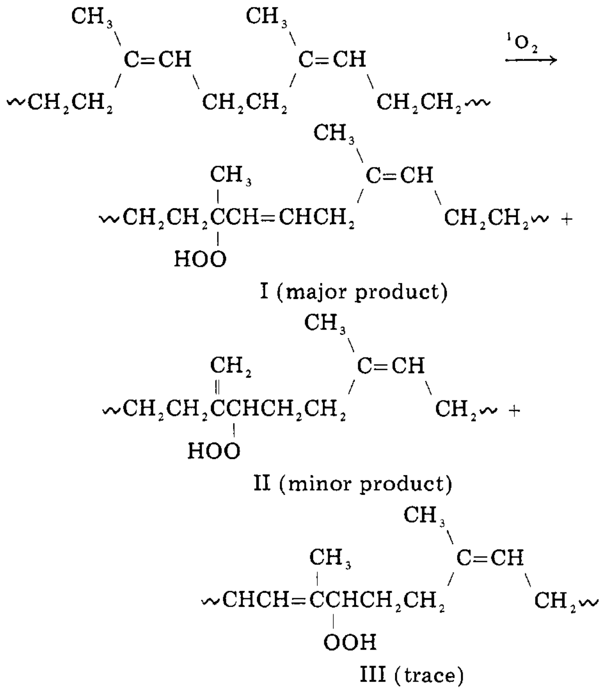
The products were in cis–trans isomeric forms. In these reactions the probability of a second addition of singlet oxygen to the adjacent double bond is low and is only possible if the monohydroperoxide has a trisubstituted double bond.

Scheme I



$$\underset{\text{(cis + trans)}}{CH_3CH_2CH_2C(CH_3){=}CHCH_2CH_2CH_3} \xrightarrow[\text{sens}]{^1O_2} \underset{26\%}{CH_3CH_2CH{=}C(CH_3){-}CH(OOH)CH_2CH_2CH_3} + \underset{28\%}{CH_3CH_2CH_2C({=}CH_2)CH(OOH)CH_2CH_2CH_3} + \underset{46\%}{CH_3CH_2CH_2C(OOH)(CH_3)CH{=}CHCH_2CH_3} \quad (5)$$

Scheme II



$$\sim CH_2CH_2C(CH_3){=}CHCH_2CH_2C(CH_3){=}CHCH_2CH_2\sim \xrightarrow{^1O_2} \underset{\text{I (major product)}}{\sim CH_2CH_2C(CH_3)(OOH)CH{=}CHCH_2C(CH_3){=}CHCH_2CH_2\sim} + \underset{\text{II (minor product)}}{\sim CH_2CH_2C({=}CH_2)CH(OOH)CH_2CH_2C(CH_3){=}CHCH_2\sim} + \underset{\text{III (trace)}}{\sim CHCH{=}C(CH_3)CH(OOH)CH_2CH_2C(CH_3){=}CHCH_2\sim} \quad (6)$$

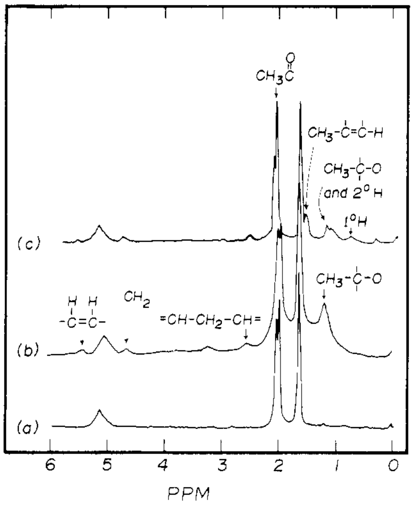


Figure 2. H^1 NMR of (a) *cis*-polyisoprene, (b) its singlet oxygen adduct, and (c) the photolyzed adduct.

Reactions of *cis*-1,4-polyisoprene and singlet oxygen and yields of hydroperoxide are shown in Table I. No change in molecular weight of the polymer was observed when the hydroperoxide content was below 1 mol % in the polymer. However, in the dye-sensitization method, a high hydroperoxide concentration occurred with a concomitant decrease in polymer molecular weight. By analogy of eq

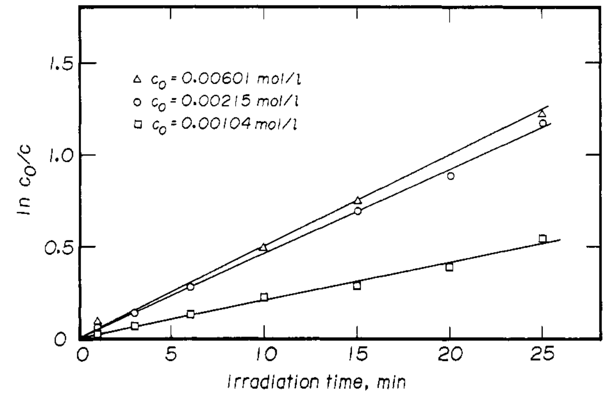


Figure 3. Photodecomposition of *cis*-poly(isoprene hydroperoxide) in cyclohexane: 30 °C at 313 nm; $I_A{}^0 = 7.2 \times 10^{-7}$ einsteins/min.

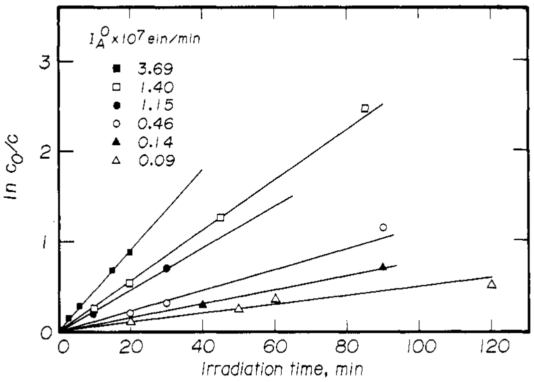


Figure 4. Photodecomposition of *cis*-poly(isoprene hydroperoxide) at various incident light intensities: [OOH] = 2.5×10^{-3} mol/L; in 1,2-dichloroethane; 30 °C at 313 nm.

4 and eq 5 for the model compounds, the reaction scheme for $^1O_2$ polymer is considered to be as shown in Scheme II.

The formation of the major product (I) is in structural consistency with the stereospecificity of the "ene" reaction[20] and the electrophilic nature of the singlet oxygen.[7] The ^1H NMR spectrum (Figure 2) of the $^1O_2$–*cis*-pip adduct lends support to eq 6. New NMR resonance peaks appear at δ 1.30 ($H_3CC(O)$–), 2.60 ($=CHCH_2C=$), and 5.50 ($-CH=CH-$), which were derived from the major product (I). Similar results have been reported by Golub et al.[21a,b] Appearance of a resonance at δ 4.8 to 4.9 ($-C=CH_2$) indicated a considerable amount of minor product (II) present. This is consistent with the product distribution in the model compounds studied. Thus it is reasonable to consider that addition of singlet oxygen to polyisoprene yields poly(isoprene hydroperoxide) (pip-OOH) with structures I, II, and III, but with I as the predominant product. Products II and III should be present in roughly equal amounts if analogies to eq 4 and 5 are valid.

Photolysis of the Poly(isoprene hydroperoxide). Photodecomposition of the poly(isoprene hydroperoxide) was performed in 1,2-dichloroethane and cyclohexane. The reaction kinetics were monitored by measuring the change in hydroperoxide and the absorbance of the solution. The initial amount of hydroperoxide in the polymer was controlled by the time of singlet oxygen oxidation treatment. An apparent first-order kinetics with respect to the hydroperoxide concentration for the rate of photodecomposition of hydroperoxide is observed. The photodecomposition rate is a function of initial hydroperoxide concentration in the polymer and intensity of the incident light, but apparently independent of the temperature of the solution. Figures 3 and 4 depict the rate of photodecomposition of poly(isoprene hydroperoxide) with different original OOH content and at differing light intensities.

Table II
Quantum Yields for Photodecomposition of *cis*-Poly(isoprene hydroperoxide) at 313 nm

sample no.	[OOH] × 10^3, mol/L	temp, °C	intensity $I_A{}^0 \times 10^7$, einsteins/min	Φ_{OOH}[a]
3-4	1.04	30.0	1.41	3.2[b]
3-6	6.01	30.0	6.70	8.4[b]
3-13	2.15	30.0	3.69	5.4[b]
3-15	2.15	40.0	3.69	5.4[b]
3-16	2.15	22.3	3.69	5.3[b]
3-17	2.05	12.9	3.70	5.7[b]
3-36	2.50	30.0	1.15	10.3[c]
3-37	2.50	30.0	1.40	9.8[c]
3-38	2.50	30.0	0.46	14.4[c]
3-40	2.50	30.0	0.14	28.0[c]
3-42	2.50	30.0	0.095	30.0[c]

[a] Relative error estimated at ±6%. [b] In cyclohexane. [c] In 1,2-dichloroethane.

The apparent quantum yield for hydroperoxide decomposition (Φ_{OOH}) was obtained using the following expression:

$$\Phi_{OOH} = (Vc_0/I_A{}^0\Delta t)\ \ln\ (c_0/c) \qquad (7)$$

where c_0 and c are the molar concentrations of hydroperoxide at $t = 0$ and time t, V is the volume of the solution, and $I_A{}^0$ is the absorbed light intensity at 313 nm and $t = 0$. The term $(1/\Delta t)\ \ln\ (c_0/c)$ is obtained from the slope of the ln (c_0/c) vs. time plots in Figures 3 and 4. V is nearly constant since the total amount of solution removed for analysis is only about 3% of the total. Since there is no a priori information on the extinction coefficient of the polymeric hydroperoxide, the measured absorbance of the sample at 313 nm was used for calculation of $I_A{}^0$. This will overestimate the real $I_A{}^0$ value and give a lower value of Φ_{OOH}, since there could possibly be trace amounts of carbonyl groups present in the polymer which could contribute to the 313-nm absorption.

The Φ_{OOH} values determined are listed in Table II for different reaction conditions. The error associated with the value is the standard deviation determined by least-squares analysis of the data.

Degradation of the *cis*-Polyisoprene Chain. The kinetics of polymer chain degradation was measured by monitoring the flow-time change of the solution with the automatic viscometer using the viscosity–molecular weight relationship for *cis*-polyisoprene in 1,2-dichloroethane determined previously. With the viscosity and absorbance data, the number of chain scissions (S) and quantum yield of polymer chain scission (Φ_S) were calculated by the following expressions: $S = (\bar{M}_v{}^0/\bar{M}_v) - 1$ and $\Phi_S = (w/\bar{M}_n{}^0)(S/I_At)$ where $\bar{M}_v{}^0$ and $\bar{M}_v$ are determined by a measurement at the intrinsic viscosity of the solution,[22a,b] w is the weight of the polymer, I_A is the number of moles of photons (einsteins) absorbed by the polymer per unit time, and t is the period of irradiation. Blank experiments showed that pure *cis*-1,4-polyisoprene does not degrade under the irradiation of near-UV light in the absence of oxygen. The poly(isoprene hydroperoxide), however, showed a significant decrease in molecular weight upon irradiation at 313 nm. The molecular weight changes for different samples under irradiation are shown in Figure 5.

Table III
Quantum Yield of Polymer Chain Scission in Photolysis of *cis*-Poly(isoprene hydroperoxide) at 313 nm

sample no.	incident light wavelength, nm	[OOH] × 10^3, mol/L	temp, °C	intensity $I_A{}^0$ × 10^7, einsteins/min	$\overline{M}_n{}^0$	$\Phi_S{}^a$
3-4	313	1.04	30	1.41	126 000	0.04^b
3-13	313	2.15	30	3.69	40 000	0.11^b
3-15	313	2.15	40	3.69	40 000	0.12^b
3-16	313	2.15	22.3	3.69	40 000	0.11^b
3-17	313	2.05	12.9	3.70	40 000	0.12^b
3-36	313	2.50	30.0	1.15	29 000	0.11^c
3-37	313	2.50	30.0	1.40	29 000	0.12^c
3-38	313	2.50	30.0	0.46	29 000	0.20^c
3-40	313	2.50	30.0	0.14	29 000	0.45^c
3-42	313	2.50	30.0	0.095	29 000	0.16^c
3-41	313	2.50	30.0	0.41	29 000	0.36^c
3-6	313	6.01	30.0	6.70	3 000	0.11^b
2-110	340	0.01	30.0	0.40	126 000	0.03^c
2-109	313	0.01	30.0	3.71	126 000	0.05^c
2-108	295	0.01	30.0	4.00	126 000	0.06^c
2-107	280	0.01	30.0	0.66	126 000	0.11^c

[a] Relative error ±10%. [b] In cyclohexane. [c] In 1,2-dichloroethane.

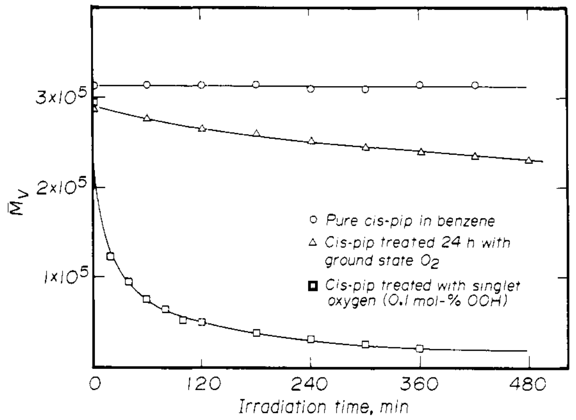


Figure 5. Molecular weight change for pure and oxidized *cis*-1,4-polyisoprene on photolysis at 313 nm.

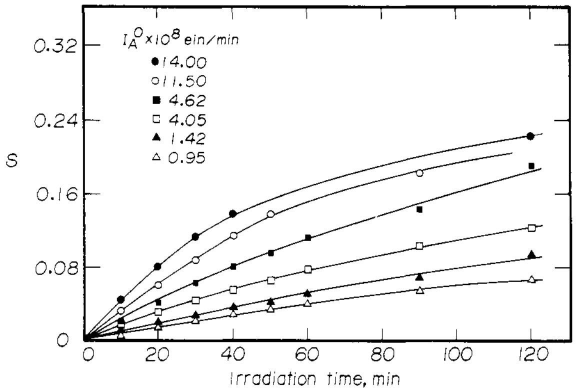
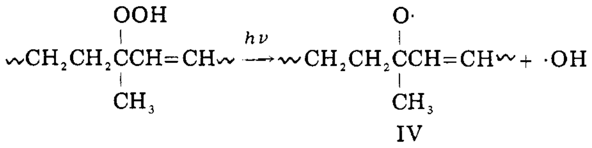


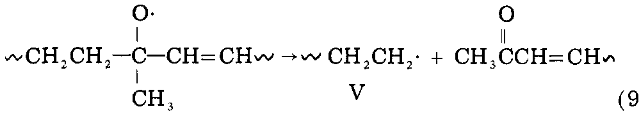
Figure 6. Polymer photoscission of poly(isoprene hydroperoxide) at various incident light intensities: [OOH] = 2.5 × 10^{-3} mol/L; in 1,2-dichloroethane; 30 °C at 313 nm; $\overline{M}_n{}^0$ = 29 000.

Upon photolysis, the hydroperoxide group decomposes to give a polymeric alkoxy radical and one OH radical, and chain scission presumably occurs as a result of the subsequent β cleavage of the macromolecular alkoxy radical:



$$\sim CH_2CH_2\underset{CH_3}{\overset{OOH}{C}}CH{=}CH\sim \xrightarrow{h\nu} \sim CH_2CH_2\underset{CH_3}{\overset{O\cdot}{C}}CH{=}CH\sim + \cdot OH \quad (8)$$

IV



$$\sim CH_2CH_2\underset{CH_3}{\overset{O\cdot}{C}}-CH{=}CH\sim \rightarrow \sim CH_2CH_2\cdot + CH_3\overset{O}{\overset{\|}{C}}CH{=}CH\sim \quad (9)$$

V

The NMR spectral data of the photolyzed *cis*-pip OOH shown in Figure 2 are consistent with this scheme. The increase in intensity of δ 1.98 signal is due to the formation of the terminal methyl ketone.

The rate of chain scission is a function of factors such as polymer molecular weight, incident light intensity, and the concentration of hydroperoxide groups in the polymer chain. Figure 6 shows the photodegradation rate as a function of incident light intensity. Table III lists the quantum yields of chain scission (Φ_S) under a variety of experimental conditions. It is important to note that whereas the quantum yields for hydroperoxide decomposition all range from 3 to 30, that for chain scission is consistently less than unity and usually about 0.1. Since β scission of alkoxy radicals of the structure shown in eq 9 is expected to be favored, it seems likely that either only a small proportion of the total hydroperoxide decomposition leads to alkoxy radicals, or some other process, e.g., hydrogen abstraction, competes effectively with β scission. The effect of wavelengths on Φ_S, as shown in Table III, has been discussed by Ng and Guillet.[10b]

Discussion

Reaction of singlet oxygen with *cis*-1,4-polyisoprene gives allylic tertiary and secondary hydroperoxides I and II according to reaction 6. This is supported by the NMR spectral data of the oxidized product and is in accordance with the results from model compound studies. Spectroscopic data on the dye-sensitized oxidized polyisoprene reported by Golub et al.[21a,b] also agree with the proposed scheme. Since hydroperoxide formation is generally considered as the precursor step in the photooxidation and photodegradation of hydrocarbon polymers (especially in the diene polymers with unsaturation along the chain backbone), and the singlet oxygen involved "ene" reaction is regarded as a key step in the hydroperoxide formation, reaction 8 has fundamental importance as an initiation step for the photooxidation of elastomers.

Near-ultraviolet radiation (91 kcal/einstein at 313 nm) has sufficient energy to cleave the RO–OH bond (bond energy 42 kcal/mol).[23] Initial fission occurs at the oxygen–oxygen bond of the hydroperoxide in near-UV photolysis and has been confirmed both for small molecules[4,24] and polymeric hydroperoxides.[25] Upon photolysis, the

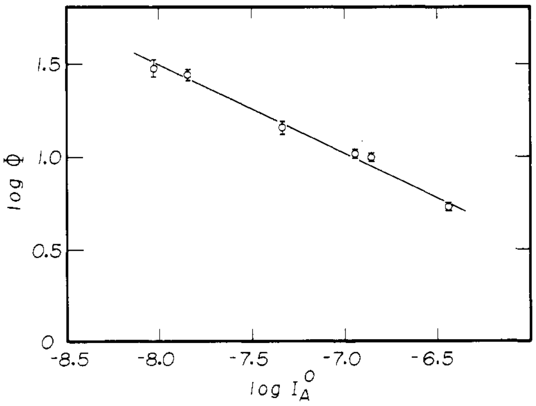
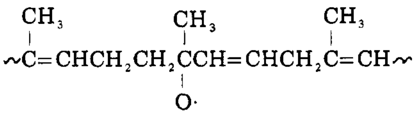


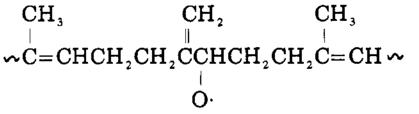
Figure 7. Dependence of poly(isoprene hydroperoxide) photodecomposition quantum yield on absorbed light intensity: [OOH] = 2.5 × 10^{-3} mol/L; 30 °C at 313 nm; in 1,2-dichloroethane.

poly(isoprene hydroperoxides) I and II decompose into the macroalkoxy radicals Ia and IIa and the hydroxy radical



$$\sim\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_2CH_2\underset{\underset{\displaystyle O\cdot}{|}}{\overset{\displaystyle CH_3}{\overset{|}{C}}}CH{=}CHCH_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH\sim$$

Ia



$$\sim\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_2CH_2\underset{\underset{\displaystyle O\cdot}{|}}{\overset{\displaystyle CH_2}{\overset{\|}{C}}}CHCH_2CH_2\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH\sim$$

IIa

in the primary step; subsequent reaction of these radicals may result in radical-induced decomposition of the hydroperoxide and polymer chain scission via β scission of Ia and IIa. The high overall quantum yield of hydroperoxide photodecomposition (Φ_{OOH}) listed in Table II, and its dependence on the concentration of hydroperoxide in the polymer, suggest the presence of a significant radical-induced decomposition path for the R'OOH:

$$\begin{matrix} HO\cdot & & H_2O \\ R'O\cdot & + R'OOH \rightarrow & R'OH + R'OO\cdot \\ R\cdot & & RH \end{matrix} \qquad (10)$$

where R' is the polymer and R the solvent. Martin and Norrish[4] have shown that the photodecomposition of *tert*-butyl hydroperoxide proceeded via a radical induced chain with relatively high quantum yields. Carlsson and Wiles,[25] in analytical studies of photolysis of poly(propylene hydroperoxide) in a solid film, found a higher overall quantum yield, although they did not favor radical-induced decomposition as a possible mechanism. In solution, the mobility of the macroradicals IV and V and the diffusion rate of the small molecule radical (·OH and R·) are high, thus a high probability of chain propagation might be expected. The quantum yield is nearly independent of temperature, as shown by data in Table II. This is in agreement with the findings of Martin and Norrish[4] and suggests that the activation energy for the primary (direct cleavage) and secondary (chain reaction) process of OOH decomposition is low. As pointed out by Reinisch and Gloria, it is only ca. 5% of the dissociation energy of the bond which is cleaved.[26] Indeed the photon energy at 313 nm is much higher than the RO–OH bond energy, so that the radicals produced from the primary step will be "hot" and might react before their excess energy is reduced by collisions with the surroundings. The quantum yield of the overall OOH decomposition is markedly dependent on the amount of light absorbed (Figure 6). A log–log plot for Φ_{OOH} and the amount of light absorbed, as shown in Figure 7, show that the rate of R'OOH decomposition is proportional to $I_A^{-1/2}$. This strongly favors the conclusion that bimolecular termination by a reaction involving a free-radical chain-carrying species is predominant in the induced chain process.[27] A tentative mechanism for the radical-induced chain decomposition of poly(isoprene hydroperoxide) is given in eq 11a–j.

initiation

$$R'OOH + h\nu \rightarrow R'O\cdot + \cdot OH \qquad \phi I_A \qquad (11a)$$

$$R'O\cdot + RH \rightarrow R'OH + R\cdot \qquad K_2[RH][RO\cdot] \qquad (11b)$$

$$HO\cdot + RH \rightarrow HOH + R\cdot \qquad K_3[RH][HO\cdot] \qquad (11c)$$

propagation

$$R\cdot + R'OOH \rightarrow RH + R'OO\cdot \qquad K_p[R\cdot][R'OOH] \qquad (11d)$$

$$2R'OO\cdot \rightarrow 2R'O\cdot + O_2 \qquad K_5[R'OO\cdot]^2 \qquad (11e)$$

rearrangement

$$R'O\cdot \rightarrow \cdot R'OH \qquad K_6[R'O\cdot] \qquad (11f)$$

β scission

$$R'O\cdot \rightarrow \beta\text{-scission product} + R'\cdot \qquad K_s[R'O\cdot] \qquad (11g)$$

$$\cdot R'OH + RH \rightarrow \cdot R'HOH + R\cdot \qquad K_8[\cdot R'OH][RH] \qquad (11h)$$

termination

$$2R'OO\cdot \rightarrow R'OOR' + O_2 \qquad K_9[R'OO\cdot]^2 \qquad (11i)$$

and

$$R\cdot + R\cdot \rightarrow 2R \qquad K_t[R\cdot]^2 \qquad (11j)$$

In this scheme R' denotes the polymeric species and R is the small solvent molecule. Considering the low concentration of hydroperoxide and the relatively low mobility of the polymeric radicals compared to the diffusion rate of the hydroxyl and solvent free radical in solution, the active chain carrying species should be R· and ·OH and the predominant termination is by recombination of solvent radicals. An important concept in the above scheme is that the macroalkoxy radical intermediate decays via β scission, or inter- and intramolecular hydrogen abstraction, much faster than via recombination with another radical. The reverse reaction to eq 11d to regenerate the polymeric hydroperoxide is neglected considering the large values of the quantum yield for hydroperoxide decomposition observed. Presumably this reaction is much less rapid than eq 11d. The recombination of peroxy radicals R'OO· either gives two new alkoxy radicals[28] or a diamagnetic termination product R'OOR'[29] via a tetraoxide intermediate [R'OOOOR'].

Assuming that $k_t[R\cdot]^2 \gg k_9[R'OO\cdot]^2$ and $k_p[R\cdot][ROOH]$, the rate of loss of hydroperoxide is expressed by:

$$-d[R'OOH]/dt = k_p[R\cdot][R'OOH] + 2\phi I_A \qquad (12)$$

Rearrangement of eq 12 gives an expression for the quantum yield of hydroperoxide decomposition.

$$\Phi_{OOH} = -d[R'OOH]/dt/I_A = k_p(2\phi/k_t)^{1/2}I_A^{-1/2}[R'OOH] + 2\phi \qquad (13)$$

In eq 13, I_A is the amount of light absorbed and ϕ is the primary quantum yield for the photolytic decomposition of R'OOH. If the above mechanism is correct, a plot of $I_A^{-1/2}$[R'OOH] vs. Φ_{OOH} gives a straight line, thus sup-

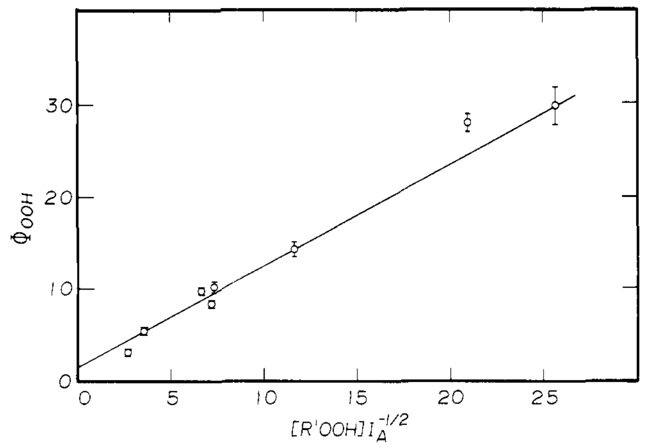


Figure 8. Quantum yield of poly(isoprene hydroperoxide) photodecomposition vs. $[R'OOH]I_A^{-1/2}$.

porting the arguments presented above.

From Figure 8 a best-fitted straight line gives an intercept $2\phi = 1.6$, thus the primary quantum yield for RO–OH is $\phi = 0.8$. This is in good agreement with the approximate theoretical primary quantum yield value of 0.7 for hydroperoxide photolysis, predicted by the method of Reinisch and Gloria based on an O–O bond strength of 42 kcal/mol.[26] From the intercept and the slope of Figure 8, a relation between k_p and k_t can be formulated:

$$k_1 = 0.89k_t^{1/2} \qquad (14)$$

The rate of termination of 2R· radicals should have a rate constant approximately that of a diffusion-controlled process (i.e., $k_t \doteq 10^{10}$),[30] thus the propagation step should have a rate constant

$$k_p \doteq 9 \times 10^4\ M^{-1}\ s^{-1} \qquad (15)$$

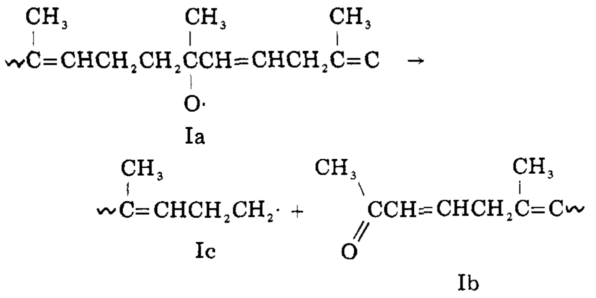
which is of the right order of magnitude for the rate constant of hydrogen abstraction for alkyl radicals in solution.

Equation 12 can be rearranged to the following form, given that the light absorption of the hydroperoxide is weak:

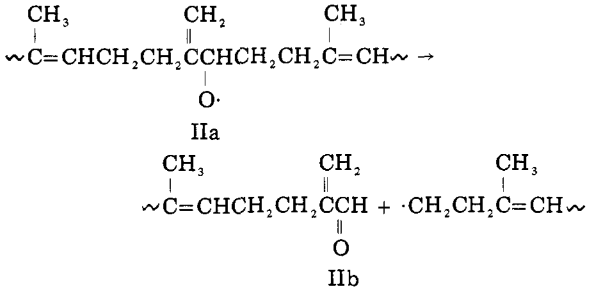
$$-d[R'OOH]/dt = (aI_A^{1/2} + b)[R'OOH] \qquad (16)$$

where a and b are constants. Since the change in I_A during the course of photolysis is small, the term $(aI_A^{1/2} + b)$ should be nearly constant, thus leading to an apparent first-order decomposition kinetics for [R'OOH], as observed.

Since the primary photochemical process involves the photolysis of the hydroperoxide to give hydroxy and macroalkoxy radicals, chain scission of the polymer must occur at a subsequent step. The most likely process is β cleavage of alkoxy radicals Ia and IIa, both of which lead to chain scission, although formation of product IIb is less probable because it originates from minor hydroperoxide II (eq 6). β cleavage of Ia to give a methyl radical without main chain scission is expected to proceed with negligible efficiency based on the chemistry of small molecule analogues. The quantum yields of polymer chain scission shown in Table III are quite low, suggesting that other competing reactions involving the macroalkoxy radical are efficient.


$$\sim C(CH_3){=}CHCH_2CH_2C(CH_3)(O\cdot)CH{=}CHCH_2C(CH_3){=}C \rightarrow \sim C(CH_3){=}CHCH_2CH_2\cdot + (CH_3)C({=}O)CH{=}CHCH_2C(CH_3){=}C\sim \qquad (17)$$

Ia, Ic, Ib

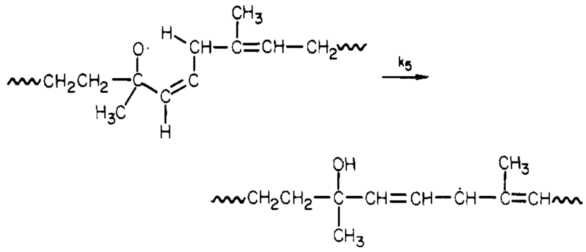

$$\sim C(CH_3){=}CHCH_2CH_2C({=}CH_2)CH(O\cdot)CH_2CH_2C(CH_3){=}CH\sim \rightarrow \sim C(CH_3){=}CHCH_2CH_2C({=}CH_2)CH{=}O + \cdot CH_2CH_2C(CH_3){=}CH\sim \qquad (18)$$

IIa, IIb

Intermolecular hydrogen abstraction by tertiary alkoxy radicals is a well-characterized reaction. For the *tert*-butyl alkoxy radical in hydrocarbon solvents, a rate constant of $8 \times 10^4\ M^{-1}\ s^{-1}$ was found for proton abstraction.[30] The reactivity of the macroalkoxy radical Ia and IIa toward H abstraction is expected to be similar, therefore a value of about $10^5\ M^{-1}\ s^{-1}$ can be reasonably assumed for k_2 for the reaction[11b]

$$R'O\cdot + RH \xrightarrow{k_2} R'OH + R\cdot \qquad (19)$$

Intramolecular hydrogen abstraction of the alkoxy radical is also significant if a δ hydrogen is present in the radical[30] because the formation of a quasi-six-membered cyclic transition state is possible. For polyisoprene alkoxy radicals Ia and IIa this intramolecular H abstraction causing radical rearrangement is strongly favored due to the presence of the δ allylic hydrogen. Particularly for Ia, the δ hydrogens are "activated" by being flanked by two allylic double bonds and the resulting "diallylic" radical is strongly stabilized:



(20)

This reaction could very well compete with β scission and would not result in chain scission since this stabilized radical would probably terminate by combination with a solvent radical R·.

Addition of the macroalkoxy radical to the olefinic system in the polyisoprene chain is expected to be nonefficient. For example, Walling[30] observed that β cleavage of *t*-BuO· was enhanced in the presence of an olefin and that no addition reaction occurred. Furthermore, addition of the macroradical to the hindered double bonds in *cis*-pip (inter or intra) may also have unfavorable stereochemical requirements.

A steady-state treatment of the kinetics of polymer chain scission according to our proposed mechanistic scheme gives an expression for the rate of polymer chain scission

$$\frac{d\bar{S}}{dt} = k_s[R'O\cdot] = \frac{k_s\phi I_A}{(k_5 + k_6 + k_2[RH])} + \left(\frac{2k_5k_p[R'OOH]}{(k_5 + k_9)(k_5 + k_6 + k_2[RH])}\right)\left(\frac{2\phi I_A}{k_t}\right)^{1/2} \qquad (21)$$

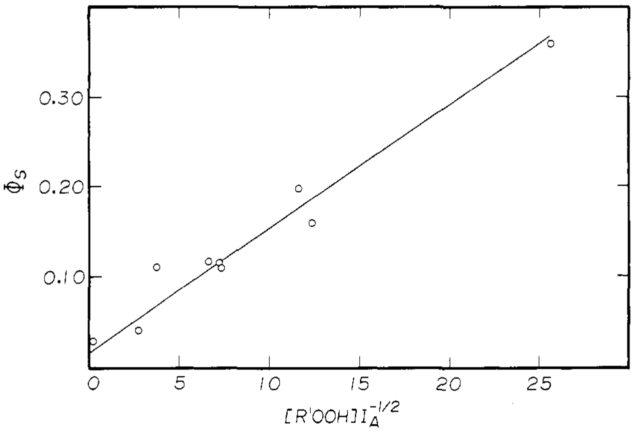


Figure 9. Quantum yield of poly(isoprene hydroperoxide) chain scission vs. $[R'OOH]I_A^{-1/2}$.

where $\bar{S}$ is the number of moles of scissions. Therefore, the quantum yield of polymer chain scission is expressed as

$$\Phi_S = \frac{(d\bar{S}/dt)}{I_A} = \frac{k_S\phi}{(k_S + k_6 + k_2[RH])} + \left(\frac{2k_5k_Sk_p(2\phi/k_t)^{1/2}}{(k_5 + k_9)(k_S + k_6 + k_2[RH])}\right)([R'OOH]I_A^{-1/2}) \quad (22)$$

A plot of $[R'OOH]I_A^{-1/2}$ vs. Φ_S is shown in Figure 9. The approximately linear relationship observed lends support to the proposed mechanism. In 1,2-dichloroethane solution, the concentration of the solvent is about 13 M, thus $k_2[RH] = 10^6\ M^{-1}\ s^{-1}$. If the rate of intramolecular hydrogen abstraction is about equal to that of the intermolecular process, then $k_6 \approx k_2[RH] = 10^6\ s^{-1}$. From the intercept in Figure 8 and the observed value of the primary quantum yield for hydroperoxide photolysis, $\phi = 0.8$, k_S, the polymer chain scission rate constant for the polyisoprene alkoxy radical, is found to be $2.7 \times 10^4\ s^{-1}$. This is in good agreement with the rate constant of ca. $2 \times 10^4\ s^{-1}$ for the elimination of $(CH_3)_2CHCH_2\cdot$ by β scission of tertiary alkoxy radicals in solution[31,32] and confirms that $k_5 \ll k_6$ or $k_2[RH]$. From the slope in Figure 8, together with the information obtained from Figure 7, it is found that $k_5 = 0.3k_9$, although for small molecules, ROO· terminates with a rate constant of $9.5 \times 10^5\ M^{-1}\ s^{-1}$.[33] Polymeric peroxy radicals may terminate more slowly so that $k_9 \leq 9.5 \times 10^5\ M^{-1}\ s^{-1}$.

It is worth noting that the ratio Φ_S/Φ_{OOH} should be approximately a constant if the amount of light absorbed is low:

$$\frac{\Phi_S}{\Phi_{OOH}} = \frac{2k_5k_S}{(k_5 + k_9)(k_S + k_6 + k_2[RH])} \approx 0.01 \quad (23)$$

A plot of Φ_{OOH} vs. Φ_S is depicted in Figure 9; a straight line relationship with a slope (constant ratio of Φ_S/Φ_{OOH}) of 0.014 is in fair agreement with the theoretical value of 0.01 considering the approximations made. This also gives a strong support to the proposed mechanism involving free radical induced hydroperoxide decomposition and subsequent β scission of the alkoxy radical.

Our proposed mechanism for the photolysis of poly(isoprene hydroperoxide) in solution, i.e., eq 11a–j, requires a small molecule solvent free radical to propagate the chain reaction. Therefore the nature of solvents plays a decisive role on the overall rate of reactions and variations of both quantum yields of hydroperoxide loss and polymer chain scission should result in different solvents.[10a] This is shown in Table IV. When benzene is used as solvent, abstraction of the aryl hydrogen by the radicals generated in primary photolytic cleavage of the polymer hydroperoxide (eq 11b and 11c) is very difficult, due to the much higher bond energy of phenyl hydrogen than those of alkyl hydrogens. This leads to a very low concentration of radical chain carrier R· and thus results in the very low value of Φ_S shown in Table IV.

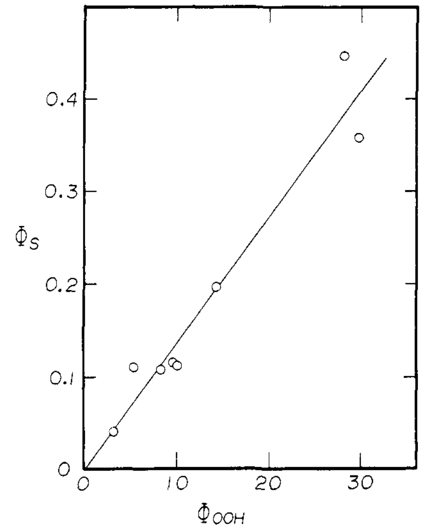


Figure 10. Relation between Φ_{OOH} and Φ_S for *cis*-poly(isoprene hydroperoxide).

Table IV
Effect of Solvent on Quantum Yield of Chain Scission (Φ_S) for Poly(isoprene hydroperoxide)[a]

solvent	Φ_S
dichloroethane	0.051
cyclohexane	0.031
benzene	0.004

[a] Irradiated at 313 nm, 30 °C, [OOH] < 0.06%.

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Photochemistry of Ketone Polymers. 13. Quenching of Excited Ketone Carbonyls by Hydroperoxides and Peroxides[1]

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ABSTRACT: Studies of the photolysis of ketone-containing polymers such as poly(styrene-*co*-phenyl vinyl ketone) and poly(styrene-*co*-methyl isopropenyl ketone) in the presence of di-*tert*-butyl peroxide and *tert*-butyl hydroperoxide show that both the singlet and triplet n–π^* state of the ketones are quenched by the peroxides at diffusion-controlled rates. The energy transfer results in the ketone-sensitized decomposition of the hydroperoxides and is best explained by proposing the formation of an intermediate exciplex between the excited state of the ketone and the ground state of the peroxide. In view of the simultaneous presence of keto, hydroperoxy, and peroxy groups in the photooxidation of hydrocarbons generally, and hydrocarbon polymers in particular, this phenomenon should be considered in all attempts to establish detailed mechanisms of photodegradation.

Photooxidation of hydrocarbon polymers yields oxygenated species such as hydroperoxide, peroxide, and ketones, usually with a concomitant deterioration of polymer physical properties.[2,3] In view of the intense activity in the study of the mechanism and kinetics of the photooxidation of polymers, it is surprising that there are few reports in the literature concerning the mutual interactions of these key species in photooxidation. Acyl peroxides and benzoyl peroxides, for example, are known to undergo photosensitized decomposition sensitized by polynuclear hydrocarbons such as anthracene and toluene.[4,5] Walling and Gibian showed that the decomposition of benzoyl peroxide and *tert*-butyl hydroperoxide (*t*-BuOOH) could also be photosensitized by aromatic ketones such as acetophenone and benzophenone.[6] Überreiter and Bruns[7] have reported that tetralin hydroperoxide undergoes photosensitized decomposition in the presence of fluorenone, and Nakata and Tokumaru[8] reported the singlet sensitized decomposition of benzoyl peroxide by aromatic hydrocarbons such as chrysene, anthracene, and naphthalene.

This paper concerns the quantitative study of energy transfer from polymeric ketones (aromatic and aliphatic) to hydroperoxides and peroxides, and from small molecular ketones to polymeric hydroperoxides. It serves to demonstrate that interaction between these species is significant and may be expected during the photooxidation of many polymers.

Experimental Section

Polymers. Three polymers were used in this study. *cis*-1,4-Polyisoprene hydroperoxide was prepared by singlet-oxygen oxidation by the microwave discharge method and characterized by the method described previously.[9] The resultant polymer is of low hydroperoxide content (ca. 0.1%) and is unchanged in molecular weight. Poly(styrene-*co*-phenyl vinyl ketone) with 7.6 mol % ketone (PS–PVK, 7.6%) and poly(styrene-*co*-methyl isopropenyl ketone) (PS–MIPK, 6%) were prepared by emulsion polymerization as described previously.[10] The ketone content of the copolymers was determined by measuring the absorbance of the copolymer at 313 nm, adopting an extinction coefficient of the ketone chromophore measured from the corresponding vinyl ketone homopolymers. The polymers were reprecipitated three times into cool methanol and freeze–dried before use. The purified polymers were characterized by spectroscopic methods such as UV, IR, and NMR. The number average molecular weight, $\bar{M}_n$, was determined by osmometry, and the viscosity average molecular weight, $\bar{M}_v$, was determined using the corresponding Mark–Houwink constants for polystyrene[11] and *cis*-1,4-polyisoprene (*cis*-PIP).[12] The molecular weights of these polymers are summarized in Table I.

Chemicals. *tert*-Butyl hydroperoxide (Lucidol, 90%) was purified using Piette's procedure[13] to a purity of >99%. Recrystallized Luperox 2.5, 2.5 crystal (2,5-dimethyl-, 2,5-dihydroperoxyhexane) was obtained as a research sample from Lucidol Corp. and further purified to >99 mol % by Professor T. Tidwell. Di-*tert*-butyl peroxide (D-*t*-BuP) (MC & B practical grade) was vacuum distilled twice (30 °C (12 mm)). Decanoyl peroxide was recrystallized from a 3:1 mixture of methanol and chloroform and vacuum dried for 48 h. Spectroscopic grade acetone (Fisher) was used without further purification. 3,3-Dimethyl-2-butanone (pinacolone) (Baker, practical grade) was distilled before use. Spectroscopic grade benzene (Fisher) was used as solvent without further purification. Reagent grade 1,2-dichloroethane (Fisher) was dried over $CaCl_2$ and freshly distilled before use. The molar absorptivity of the ketone copolymers and the small molecules determined using a Cary 14

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