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PHOTOSENSITIZED OXIDATION OF UNSATURATED POLYMERS
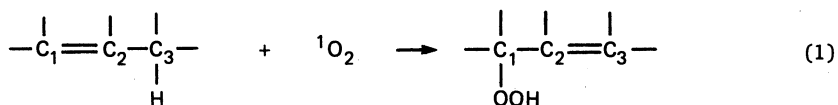
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Abstract - The photosensitized oxidation or singlet oxygenation of unsaturated hydrocarbon polymers and of their model compounds is reviewed. Emphasis is on work in this laboratory on cis and trans forms of 1,4-polyisoprene, 1,4-polybutadiene and 1,2-poly(1,4-hexadiene), and on 1,4-poly(2,3-dimethyl-1,3-butadiene) (cis/trans ratio ∿1:3). The microstructural changes which occur in these polymers on reaction with $^1O_2$ in solution were investigated by infrared, ^1H and ^{13}C NMR spectroscopy. The polymers were shown to yield allylic hydroperoxides with shifted double bonds according to the "ene" mechanism established for simple olefins. A convenient infrared measure of polymer hydroperoxidation was afforded by the absorbance ratio, $A_{2.9}/A_{6.9} \equiv A'$. Smooth correlations of A' with oxygen uptake were obtained with chlorophyll or methylene blue as photosensitizer, but Rose Bengal gave erratic A'-O_2 uptake data indicative of autoxidation accompanying the hydroperoxidation. The photosensitized oxidation of the above unsaturated polymers exhibited zero-order kinetics, the relative rates paralleling the reactivities of the corresponding simple olefins towards $^1O_2$. Two other polymers, 1,2-polybutadiene and 1,2-poly(trans-1,3-pentadiene), showed negligible reaction with $^1O_2$, reflecting the extremely low reactivities of their simple olefin analogs. This work demonstrated that singlet oxygenation of unsaturated polymers does not differ fundamentally from that of their low molecular weight analogs; such differences as do arise are due to secondary processes affecting the $^1O_2$-reacted polymers. The occurrence of degradation in singlet oxygenation of unsaturated polymers is discussed.
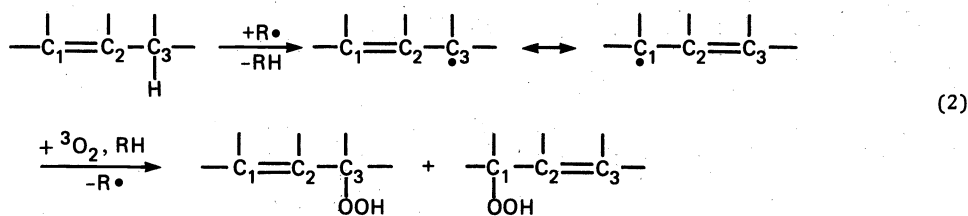
INTRODUCTION

During the past decade much interest has been shown in reactions of singlet oxygen ($^1O_2$) with a variety of compounds, including polymers, both saturated and unsaturated (1). In fact, two international conferences were held recently on this subject, one in Sweden in 1976 (2) and another in Canada in 1977 (3). Important papers bearing on the reaction of $^1O_2$ with unsaturated polymers or their model compounds were presented there by Rabek and Rånby (1,4,5), Ng and Guillet (6,7), and by Chaineaux and Tanielian (8,9). Concurrently, work in this laboratory on the photosensitized oxidation of 1,4-polyisoprene and 1,4-polybutadiene was reported at two meetings in the USA (10,11). Since then, additional related work has been performed by those researchers (12-16) and by us (17). The present paper surveys this literature, with emphasis on the spectroscopic analysis of various unsaturated polymers before and after reaction with $^1O_2$, and on the relative reactivities of such polymers towards $^1O_2$ vis-à-vis their simple olefinic analogs.

Interest in the photosensitized oxidation of unsaturated polymers arose from the realization that molecular oxygen in its lowest excited state ($^1\Delta_g$, $^1O_2$, with energy of 22.5 kcal/mol above the ground state, $^3\Sigma_g^-$, $^3O_2$), which is extremely reactive towards olefinic compounds (18,19), is implicated in the surface aging or oxidation of unsaturated polymeric materials exposed to air and sunlight. The topic of singlet oxygenation of such polymers is but one aspect of the larger subject of photodegradation, photooxidation and photostabilization of polymers (20) which is very important from the practical standpoint. The photosensitized oxidation of unsaturated polymers, to the extent that it involves $^1O_2$, is assumed to yield allylic hydroperoxides with shifted double bonds, according to the "ene" process:

$$-\underset{|}{\overset{|}{C_1}}=\underset{\underset{H}{|}}{\overset{|}{C_2}}-\overset{|}{\underset{|}{C_3}}- \quad + \quad {}^1O_2 \quad \longrightarrow \quad -\overset{|}{\underset{\underset{OOH}{|}}{C_1}}-\overset{|}{\underset{|}{C_2}}=\overset{|}{\underset{|}{C_3}}- \qquad (1)$$

established for simple olefins (18,19). Reaction 1 is to be distinguished from the autoxidation of olefins which involves $^3O_2$ and leads to the formation of allylic hydroperoxides with

both shifted and unshifted double bonds, according to the process:

$$-\overset{|}{C}_1=\overset{|}{C}_2-\underset{H}{\overset{|}{C}_3}- \quad \xrightarrow[-RH]{+R\bullet} \quad -\overset{|}{C}_1=\overset{|}{C}_2-\overset{|}{\underset{\bullet}{C}}_3- \quad \longleftrightarrow \quad -\overset{|}{\underset{\bullet}{C}}_1-\overset{|}{C}_2=\overset{|}{C}_3-$$

$$\xrightarrow[-R\bullet]{+{}^3O_2,\ RH} \quad -\overset{|}{C}_1=\overset{|}{C}_2-\underset{OOH}{\overset{|}{C}}_3- \quad + \quad -\underset{OOH}{\overset{|}{C}}_1-\overset{|}{C}_2=\overset{|}{C}_3-$$

(2)

Besides the ene reaction, there are two other reactions in which ${}^1O_2$ can take part: endoperoxide synthesis by 1,4 addition to cis-1,3 dienes (reaction 3), and dioxetane synthesis by 1,2 addition to an activated C=C double bond (reaction 4, where D = electron donor substituent); neither of these reactions has been observed in photosensitized oxidation of unsaturated polymers.

(3)

(4)
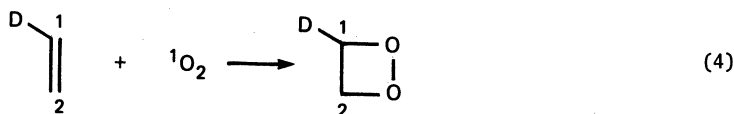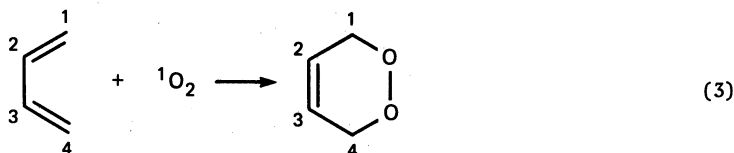
There has been controversy concerning the mechanism for reaction 1, whether it involves a perepoxide, dioxetane or an ene reaction, but the consensus now is that it involves a concerted "ene" process. The singlet oxygen may be generated by microwave discharge, photosensitization or by various chemical means in situ. Although singlet oxygen can also exist in a higher excited state (${}^1\Sigma_g^+$, with 37.5 kcal/mol), it is generally accepted that all of the chemistry induced by ${}^1O_2$ in solution, and essentially all that in the gas phase, is due to the ${}^1\Delta_g$, ${}^1O_2$ state; hence, the latter term (or simply ${}^1O_2$) and the term "singlet oxygen" have become synonymous (21).

1,4-POLYISOPRENE

Three double bond shifts are possible for the reaction of ${}^1O_2$ with 1,4-polyisoprene (PIP):

(5)
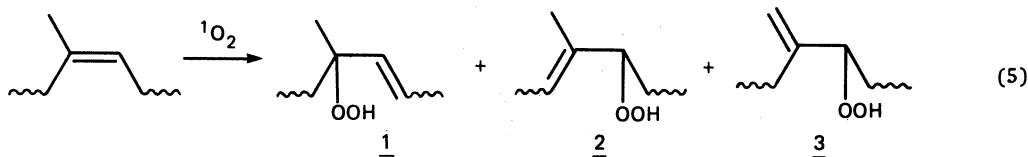
Kaplan and Kelleher (22) in 1972 presented evidence for one of those shifts, namely, to exomethylene groups (3) in the singlet oxygenation of squalene (SQ), a hexaisoprene with trans internal double bonds, which may be considered a model compound for PIP. Several years later, we showed that trans-PIP and SQ were alike in exhibiting the three possible double bond shifts, while cis-PIP gave mainly 1 and 2 and very little 3 (10). At about the same time, Chaineaux and Tanielian (8) presented evidence for all three double bond shifts in the reaction of ${}^1O_2$ with 4-methyl-4-octene and 4,8-dimethyl-4,8-dodecadiene, compounds which are mono- and di-isoprenic models of PIP. Still later, Ng and Guillet (7) obtained comparable results for 4-methyl-4-octene.

Figure 1 shows the IR changes accompanying the singlet oxygenation of cis-PIP, with chlorophyll (CL) as photosensitizer (10). The major changes are development of strong bands at 2.9 μm (OOH) and 10.3 μm (trans -CH=CH-, as in 1), and net decrease of the 12.0-μm band (-C(CH₃)=CH-, as in unreacted units and in 2). The broad but weak absorption at 11.3 μm (-C(=CH₂)-, as in 3) suggests that exomethylene groups, though present, are not important;
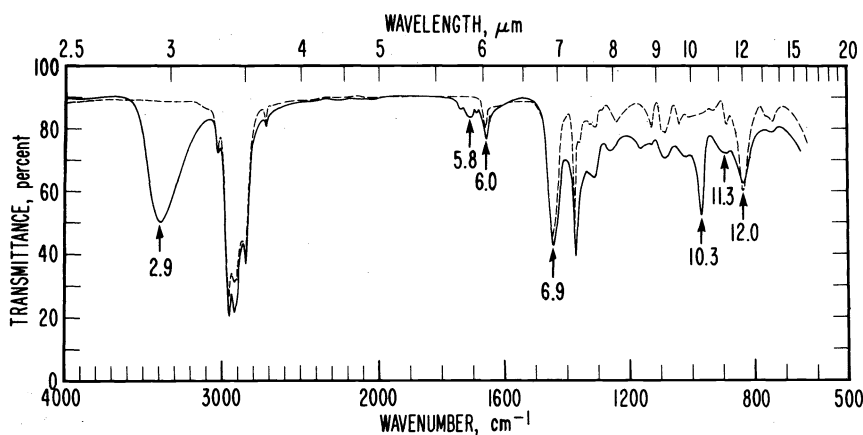
Fig. 1.   IR spectra of cis-PIP before (---) and after (——) CL-photosensitized oxidation.

this is consistent with the fact that the 6.0-μm peak (internal C=C) lacks a shoulder at
6.1 μm (external C=C). The shift to 2, although masked at 12.0 μm by the loss of original
-C(CH₃)=CH- units, is definitely indicated by ¹H NMR, as discussed below. The weak absorp-
tion at 5.8 μm is due to residual CL in the cast film of ¹O₂-reacted cis-PIP. When methylene
blue (MB) was used as photosensitizer, the 5.8-μm peak was absent and another peak appeared
instead at 6.27 μm which could be removed by washing the film with methanol. Otherwise, the
IR spectra obtained with MB were essentially the same as that shown in Fig. 1 for CL photo-
sensitization. Rose Bengal (RB), on the other hand, gave rise to extraneous absorptions at
9.3 and 9.9 μm (cyclic peroxides), indicating that sensitizer-induced autoxidation occurred
alongside the singlet oxygenation.

It should be stressed that the IR spectrum of ¹O₂-reacted cis-PIP typified by Fig. 1 is fun-
damentally different from the spectra of thermally or photochemically oxidized cis-PIP (23,24),
which show broad intense absorption throughout the 7-12 μm region (due to C-O groups) which
masks the unsaturation bands of interest.

As shown in Fig. 2, trans-PIP and SQ exhibit very similar IR changes as a result of MB-photo-
sensitized oxidation (10). Similar spectra were obtained with CL photosensitization, while
RB again gave indications of autoxidative side-reactions with trans-PIP but not with SQ. The
two trans isoprenic compounds show not only the development of strong bands at 2.9 and 10.3 μm
and the diminution of the 11.9-μm band, by analogy to cis-PIP, they also show important ab-
sorption at 11.1 and 6.1 μm, indicative of structure 3. These last two bands were previously
noted by Kaplan and Kelleher (22) and, in fact, the ¹O₂-reacted SQ shown in Fig. 2 is effec-
tively the hydroperoxide counterpart of their SQ-monoalcohol obtained through singlet oxygen-
ation followed by reduction.

Rabek and Rånby (13) recently presented an IR spectrum of cis-PIP after MB-photosensitized
oxidation which, although similar to Fig. 1, shows a more definite 11.3-μm band, and hence a
relatively larger amount of 3. Whatever the explanation for this difference, the IR spectra
for ¹O₂-reacted cis-PIP point to 1 as the major and 2 and 3 as the minor products, a qualita-
tive distribution suggested also by Ng and Guillet (7) by analogy to 4-methyl-4-octene.

A convenient measure of the degree of hydroperoxidation is given by the ratio, $A_{2.9}/A_{6.9} \equiv A'$,
where the 6.9-μm band (CH₂ bending vibration) is an internal standard. The ¹O₂-reacted cis-
PIP in Fig. 1, with A' = 0.76, was obtained for an oxygen uptake of 0.27 O₂/monomer unit. As
shown in Fig. 3, a smooth plot of A' versus O₂ uptake was obtained for cis-PIP with MB or CL
as photosensitizer (10), and similar plots were obtained for trans-PIP and SQ. Data for RB
were erratic, often falling to the right of the curve in Fig. 3 due to autoxidative effects,
and were therefore omitted. The single data point for tetraphenylporphine as sensitizer,
which fell nicely on the A'-O₂ uptake plot, was obtained in a different laboratory (25). An
obvious advantage of this plot is that, once obtained, it affords an estimate of the hydroper-
oxide content without recourse to chemical methods such as iodometry.

A sample of polystyrene-bound RB (26), in common with free RB, gave rise to concurrent autoxi-
dation and singlet oxygenation when used as photosensitizer for cis- and trans-PIP. Moreover,
the rates of O₂ uptake by PIP in the case of polymer-bound RB were much lower than expected
(10); on the other hand, the free and polymer-bound RB dyes gave normal singlet oxygenation
of SQ, unattended by autoxidation, and at comparable rates. Evidently, RB, free or polymer-
bound, reacts with PIP to produce polymeric radicals which, in turn, yield peroxy radicals
and ensuant autoxidation. The rather low efficiency of the bound RB for photosensitized oxi-
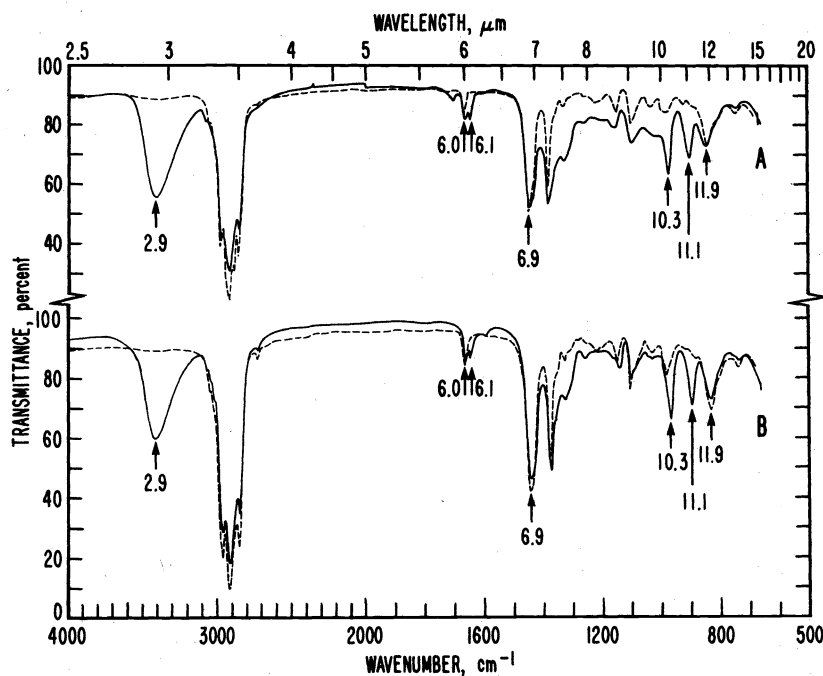dation of PIP, in contrast to that for SQ and other low molecular weight olefins (26), is

Fig. 2.   IR spectra of (A) trans-PIP and (B) SQ before (---) and after (——)
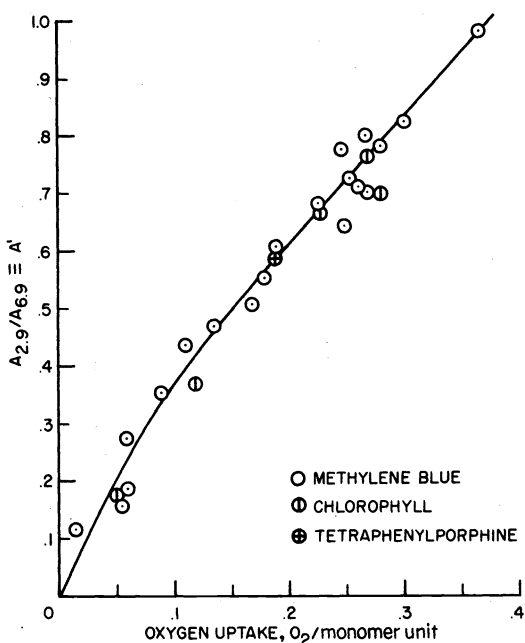MB-photosensitized oxidation.

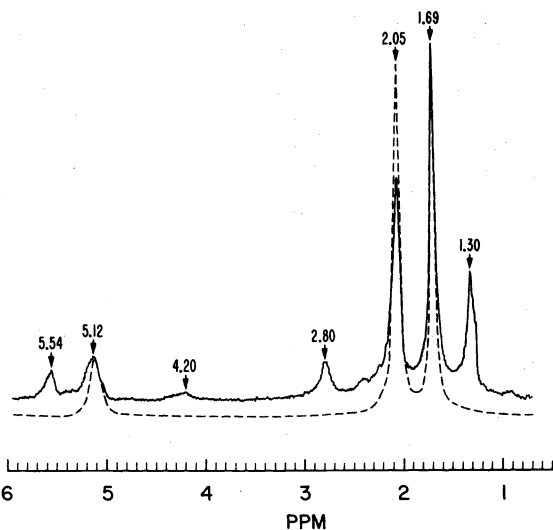Fig. 3.   IR measure of hydroperoxidation
in cis-PIP.

Fig. 4. ^{1}H NMR spectra of cis-PIP before (---)
and after (——) CL-photosensitized
oxidation, corresponding to Fig. 1.

apparently due to the need for the substrate to diffuse into the insoluble sensitizer bead,
which is much more difficult for a macromolecule than for a small molecule.

Figure 4 shows the ^{1}H NMR spectrum of $^1O_2$-reacted cis-PIP corresponding to the IR spectrum
in Fig. 1.   New resonances appear at 1.30 (CH$_3$-C-O-), 2.80 (=C-CH$_2$-C=), 4.20 (-CH-O-) and
5.54 ppm (-CH=CH-), while the original resonances at 2.05 (-CH$_2$C=) and 5.12 ppm (-C=CH-) are
correspondingly decreased.   Analogous NMR changes were observed for trans-PIP and SQ, except

that the latter compounds also showed new resonances at 4.8-4.9 ppm (-C(=CH$_2$)-). These ^{1}H
NMR data support the IR indications of double bond shifts (to $\underline{1}$ in cis-PIP, and to $\underline{1}$ and $\underline{3}$ in
trans-PIP and SQ), and establish the formation of $\underline{2}$ in all three compounds: the 5.54 and 4.8-
4.9 ppm resonances signify $\underline{1}$ and $\underline{3}$, respectively, and the 2.80 ppm resonance corresponds to
"skipped" methylenes resulting from shifts to $\underline{1}$ or $\underline{2}$ (as in $\underline{1}$' or $\underline{2}$'). The ^{1}O$_2$-reacted cis-

$$\text{(6)}$$
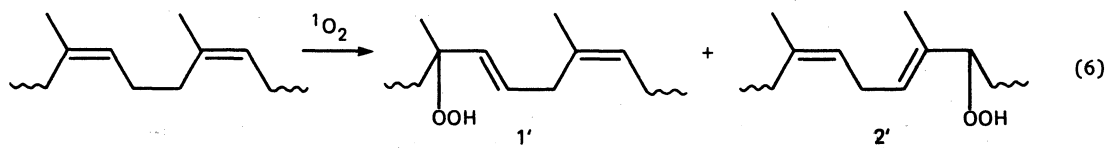
PIP (Figs. 1 and 4) was originally estimated to have about equal amounts of $\underline{1}$ and $\underline{2}$ with neg-
ligible $\underline{3}$, while the ^{1}O$_2$-reacted trans-PIP (Fig. 2) was estimated to have ∿48% $\underline{1}$, 26% $\underline{2}$ and
26% $\underline{3}$ (10). Recently, Ng and Guillet (7,16) presented a ^{1}H NMR spectrum of ^{1}O$_2$-reacted cis-
PIP (obtained with polystyrene-bound RB) which, although otherwise similar to Fig. 4, dis-
played a definite additional peak at 4.8-4.9 ppm indicative of some $\underline{3}$ formed in their hydro-
peroxidized cis-PIP.

Typical ^{13}C spectra of ^{1}O$_2$-reacted cis-PIP, before and after reduction, are shown in Fig. 5.
These spectra were obtained with CL or MB as photosensitizer, but not RB. The latter dye pro-
duces extraneous resonances at ∿60-85 ppm reminiscent of the peroxide/hydroperoxide/alcohol
resonances at ∿70-90 ppm in the ^{13}C spectrum of thermally oxidized cis-PIP (27). Figure 5 is
consistent with Figs. 1 and 4 in showing very little double bond shift to $\underline{3}$ in cis-PIP com-
pared to trans-PIP or SQ. Thus, the 113-110 ppm resonances are markedly weaker in cis-PIP
(Fig. 5) than in trans-PIP or SQ (Figs. 6 and 7). Figures 5-7 are interesting also in pro-
viding ^{13}C data on the effect of converting a hydroperoxide to an alcohol group in isoprenic
compounds: there is an upfield shift of 3 ppm for exomethylene carbon resonances in PIP and
SQ; and an upfield shift of 12 ppm in cis-PIP and 14 ppm in both trans-PIP and SQ, for the
oxygen-bearing carbon resonances. Similar upfield shifts of ∿12-13 ppm were observed for the
-$\overset{|}{\underset{|}{\text{C}}}$-O- resonances in various $\underline{t}$-alkyl hydroperoxides on reduction to the corresponding alco-
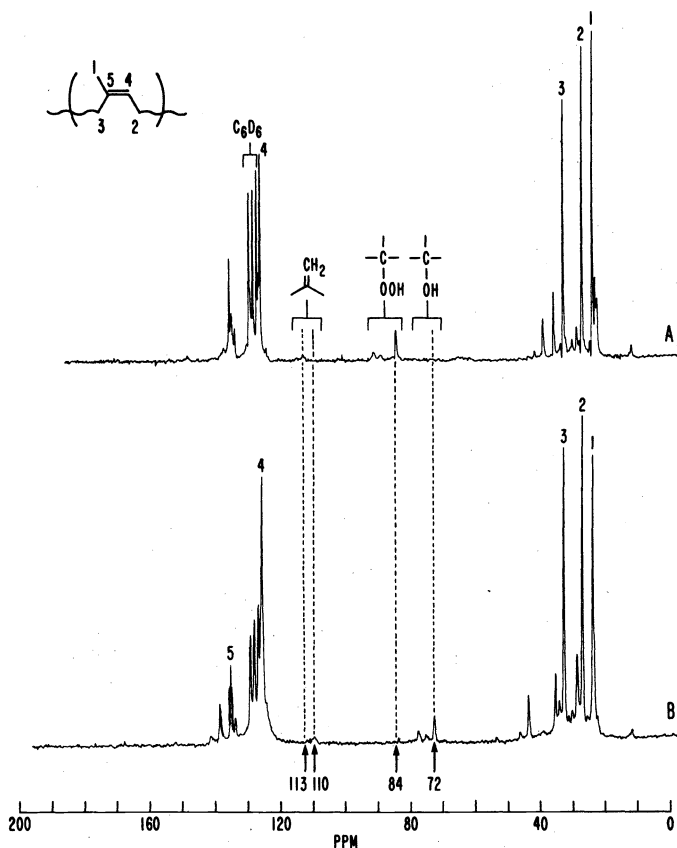hols (28).

Fig. 5. ^{13}C NMR spectra of ^{1}O$_2$-reacted cis-PIP before (A) and after (B) reduction
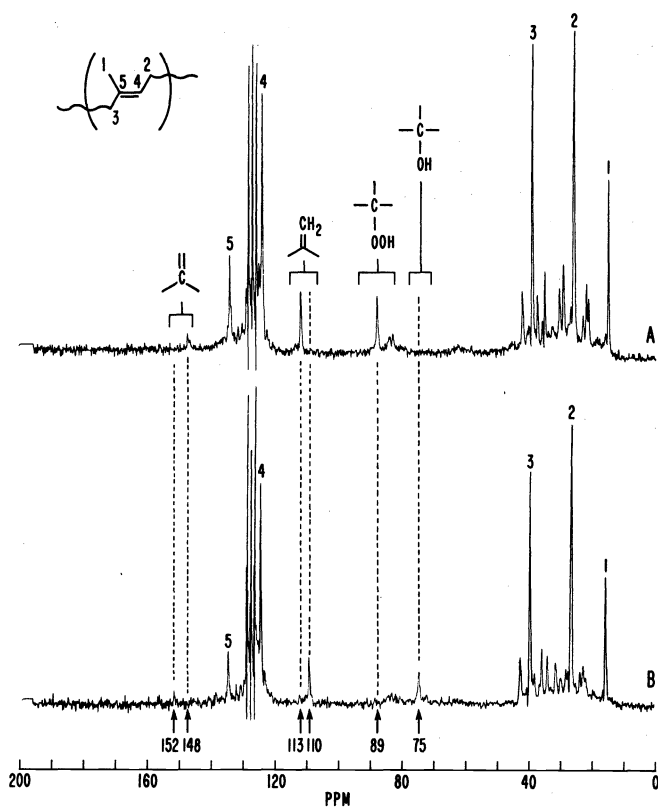with NaBH$_4$. Spectrum A corresponds to Figs. 1 and 4.

Fig. 6. ^{13}C NMR spectra of $^1O_2$-reacted trans-PIP before (A) and after (B) reduction with $NaBH_4$. Spectrum A corresponds to upper solid spectrum in Fig. 2.
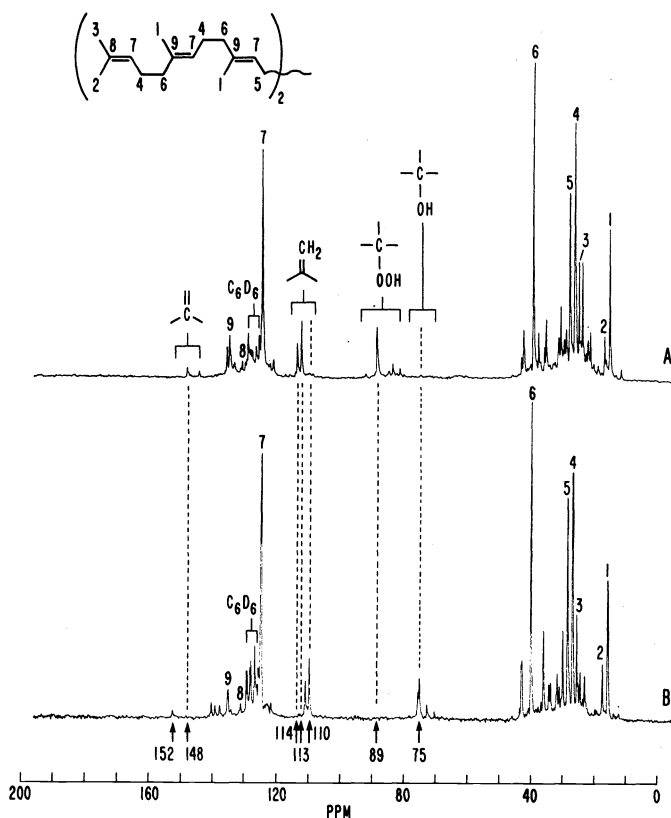

Fig. 7. ^{13}C NMR spectra of $^1O_2$-reacted SQ before (A) and after (B) reduction with $NaBH_4$. Spectrum A corresponds to lower solid spectrum in Fig. 2.

The ^{13}C spectra in Figs. 6 and 7 reinforce the similarity of trans-PIP and SQ in their reactions with $^1O_2$. Moreover, the resonances at 113 ppm can be assigned to the exomethylene carbon in an internal isoprene unit, while the resonance at 114 ppm is assignable to the corresponding carbon in a terminal isoprene unit (as in SQ). Also, the resonance at 148 ppm,

associated with the carbon attached to the exomethylene carbon, is shifted downfield by 4 ppm in both trans-PIP and SQ upon reducing the hydroperoxide to the alcohol.

MODEL COMPOUNDS OF 1,4-POLYISOPRENE

Tanielian and Chaineaux (8,9,14,15) carried out an extensive study of the RB-photosensitized oxidation in methanolic solution of 4-methyl-4-octene (MO), 4,8-dimethyl-4,8-dodecadiene (DMDD), 2,6-dimethyl-2,6-octadiene (DHM) and 2,7-dimethyl-2,6-octadiene (DMOD), as PIP model compounds containing one isoprene unit or two such units in head-to-tail or head-to-head arrangement. Their study provided further insight into the singlet oxygenation of PIP monomer units that could not be readily obtained from work on the polymers themselves. For the MO-$^1O_2$ reaction:

$$\text{MO} \xrightarrow{{}^1O_2} \underset{4}{\text{(OOH)}} + \underset{5}{\text{(OOH)}} + \underset{6}{\text{(OOH)}} \tag{7}$$
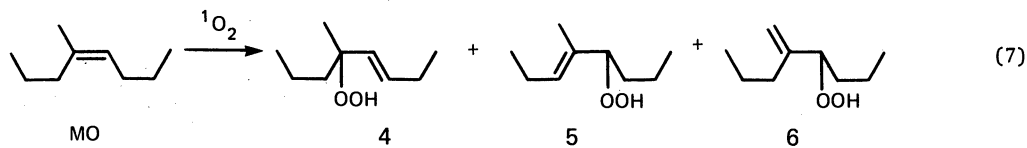
the distribution of shifted double bonds varied with the stereochemistry of the starting olefin (Table 1). The tendency for the relative yield of the exomethylene structure 6 to decrease with increasing cis content of the initial olefin parallels the situation with cis- and trans-PIP concerning the corresponding structures 3. However, the comparison breaks down with regard to the corresponding structures 5 and 2 (or 4 and 1), and this is perhaps a reflection of the different solvents used for the MO and PIP studies. On the other hand, the distribution obtained by Ng and Guillet (7,16) for the singlet oxygenation of MO with unspecified cis-trans content is almost identical to that obtained by us (10) for trans-PIP, but quite different from the distribution obtained by Tanielian and Chaineaux. It should be added that the latter workers (15) found the relative reactivities of trans- and cis-MO towards $^1O_2$ to be ∿1.7:1.0, which agrees very well with the corresponding ratio of ∿1.5:1.0 obtained by us for trans- and cis-PIP (10).

TABLE 1. Distribution of Shifted Double Bonds in Various Isoprenic Compounds on Reaction with $^1O_2$

| Compound	Percent Distribution			Ref.
	Di- (4 or 1)	Tri- (5 or 2)	Exo- (6 or 3)	
100% trans-MO	41	11	48	8
46% trans, 54% cis-MO	53	9	38	8
25% trans, 75% cis-MO	60	7	33	8
100% cis-MO	66	6	28	15
cis- + trans-MO	46	26	28	7, 16
trans-PIP	48	26	26	10
cis-PIP	47	47	6*	10
	major	minor	minor	7, 16

*New estimate made for this work.

Tanielian and Chaineaux (8,15) showed that a second addition of $^1O_2$ can occur in MO, but only through the intermediacy of the monohydroperoxide having the trisubstituted double bond (5), inasmuch as the disubstituted and exomethylene double bonds (in 4 and 6) are considerably less reactive:

$$\underset{5}{\text{(OOH)}} \xrightarrow{{}^1O_2} \underset{7}{\text{(OOH, OOH)}} + \underset{8}{\text{(OOH, OOH)}} \tag{8}$$
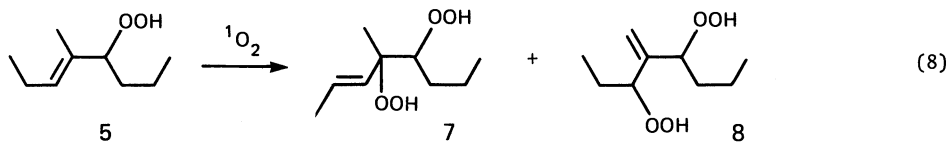
They also found that the trisubstituted double bond in 5 was deactivated by the allylic OOH group such that reaction 8 (yielding 7 and 8 in the ratio of 1:4) was about 1/20 times as fast as reaction 7.

The diisoprenic model compound, DMDD, was shown to yield on singlet oxygenation all six possible monohydroperoxides (9 through 14) (8). Furthermore, on the assumption that the trisubstituted double bonds in these products are the only ones likely to react with additional $^1O_2$, there are nine possible dihydroperoxides from DMDD, of which four were positively identified

(15 through 18) and three were presumed to have been formed (19, 20 and 21) on the basis that the trihydroperoxides 24, 25 and 26 were recovered from extended photosensitized oxidation of DMDD (8).


(9)

(10a)

(10b)

(10c)
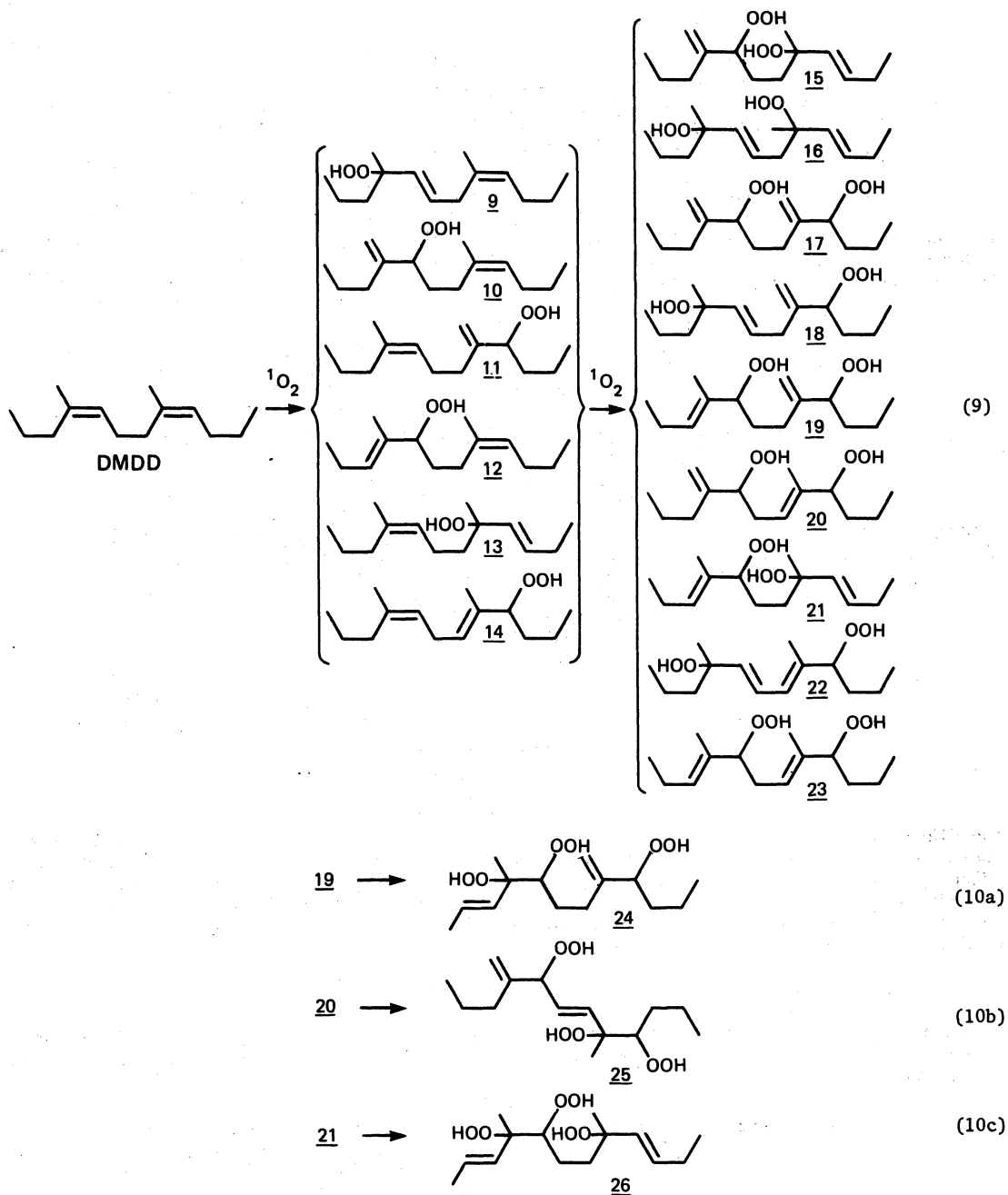
In every one of the hydroperoxidized products identified, the new disubstituted double bonds, where present, were in the trans configuration. Reactions 10a-c showed that diaddition of $^1O_2$ to the same isoprene unit is possible but only to a hydroperoxidized monomer unit that contains a trisubstituted double bond. However, no dihydroperoxides were obtained from DMDD in which the diaddition of $^1O_2$ occurred in the same isoprene unit while the other unit was left unreacted. This result is in keeping with the deactivation of a double bond by an allylic OOH group.

Tanielian and Chaineaux also showed, using DMDD (8) and DMOD (9), that the mechanism proposed by Kaplan and Kelleher (29) for singlet oxygenation of 1,4-polybutadiene (reaction 11) was

(11)
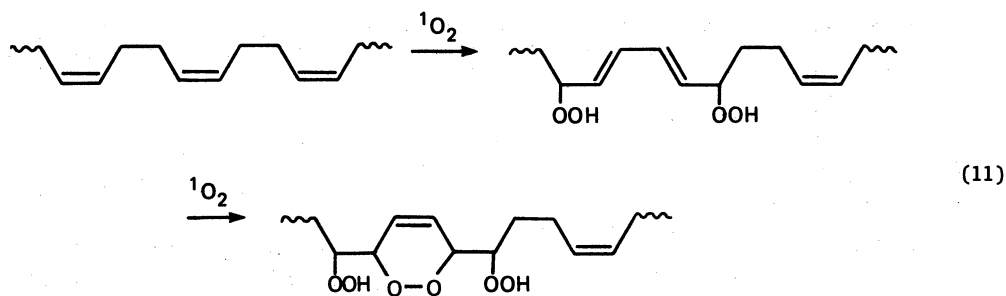
very unlikely. Thus, the dihydroperoxide 22 has a conjugated diene structure appropriate for undergoing reaction 11, but no dihydroperoxyendoperoxide of DMDD was detected. Likewise, in the singlet oxygenation of DMOD:

(12)
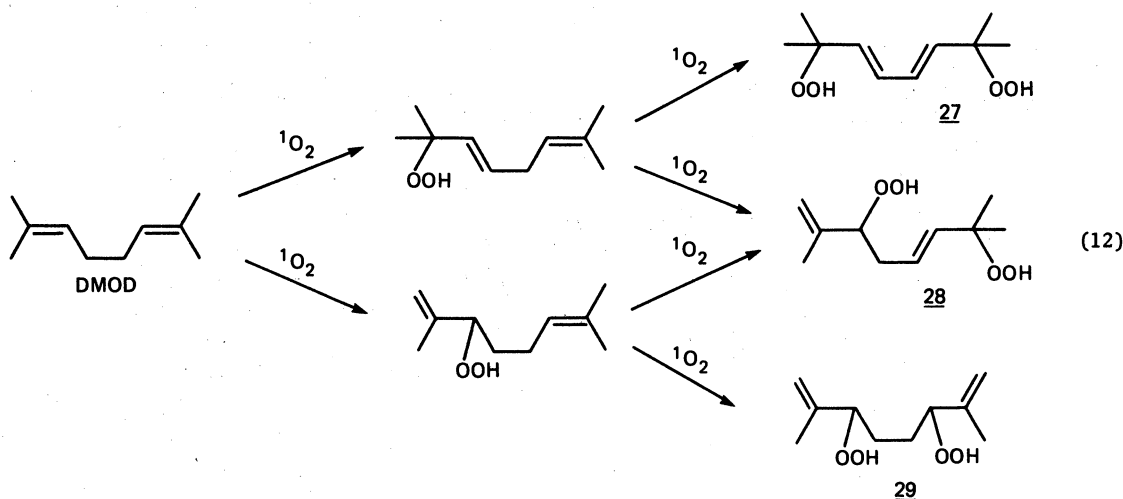
the dihydroperoxide 27 (with a conjugated diene structure) was obtained in fair yield, yet it could not be further singlet oxygenated to an endoperoxide. The failure of the dihydroperoxides 22 and 27 to form endoperoxides (despite the well-known tendency for $^1O_2$ to react with a conjugated diene by 1,4-cycloaddition (21)) was attributed to their acyclic structure and to the deactivating effect of the allylic OOH groups (9). Results analogous to those of DMDD and DMOD were also reported for DHM (14).

1,4-POLYBUTADIENE

Returning to the unsaturated polymers, we note that because of symmetry in the 1,4-polybutadiene (PBD) structure, only one double bond shift is possible for the $^1O_2$ reaction with cis-(or trans-) PBD:

(13)
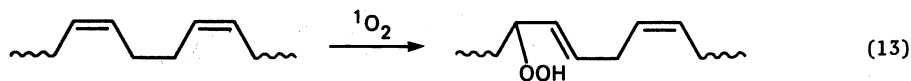
A number of papers have been concerned with this reaction, and many of them (1,4,22,29-33) have noted formation of hydroperoxide groups (revealed by new absorption at 2.9 μm in the ATR or transmission IR spectra of $^1O_2$-reacted PBD), but presented no evidence for the concomitant double bond shift. With the aid of IR and ^1H and ^{13}C NMR spectroscopy, we showed that reaction 13 indeed described the photosensitized oxidation of PBD and, moreover, that the shifted double bonds are virtually all-trans (11).

As indicated in Fig. 8, the singlet oxygenation of cis-PBD, with MB as photosensitizer, gave rise to new strong bands at 2.9 (OOH) and 10.3 μm (trans -CH=CH-) and a decrease of the 13.6-μm band (cis -CH=CH-). CL photosensitization gave similar spectra, but RB again gave extraneous bands due to autoxidative side-reactions (11). IR spectra of cis-PBD, after MB-photosensitized oxidation, were also presented elsewhere (12,13), but these do not show the
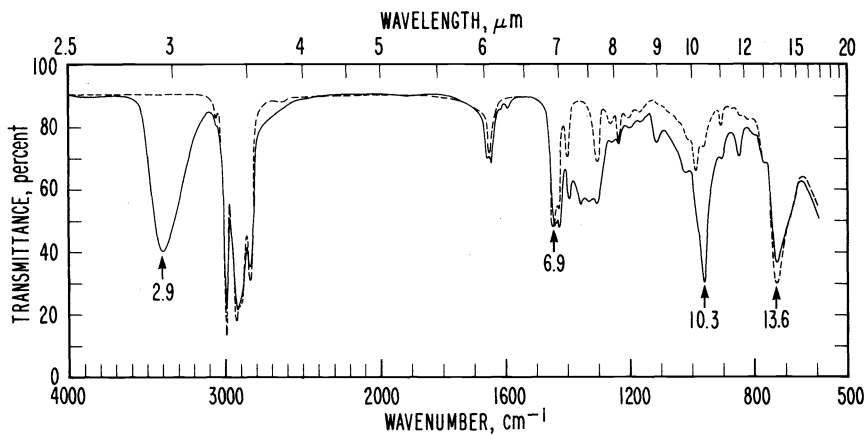
Fig. 8.   IR spectra of cis-PBD before (---) and after (——) MB-photosensitized oxidation.

large amount of double bond shift evident in Fig. 8.

Although the IR spectrum of trans-PBD after MB-photosensitized oxidation (Fig. 9) likewise displays the 2.9-μm band, there is no change in intensity of the 10.3-μm trans band nor growth of a 14.0-μm cis band. This is in accord with reaction 13 where the shifted double bonds have only the trans configuration. The 6.0-μm absorption is due to the C=C stretch of trans -CH=CH-, the symmetry of which is perturbed by the allylic OOH groups. The 6.2-μm peak corresponds to residual MB. Spectra similar to Fig. 9 were also presented by Rabek and Rånby (4,32, 33).
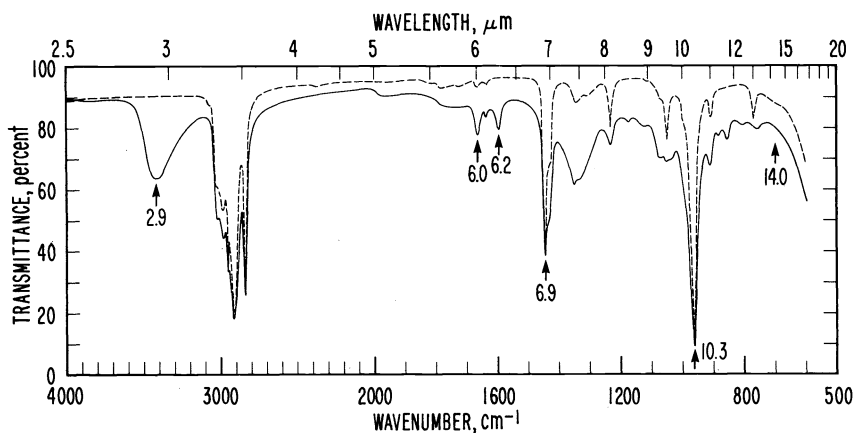

Fig. 9.   IR spectra of trans-PBD before (---) and after (——) MB-photosensitized oxidation.

That the new disubstituted double bonds formed in reaction 13, starting with either cis- or trans-PBD, are all-trans is in keeping with the results indicated earlier for singlet oxygenation of DMDD (8) as well as those for other isoprenic model compounds (9,14,15) and various simple low molecular weight olefins (34).

As with cis-PIP (Fig. 3), the degree of hydroperoxidation in cis-PBD is easily followed by means of the parameter $A' \equiv A_{2.9}/A_{6.9}$ (Fig. 10). Good correlations of A' with O_2 uptake were obtained with MB and CL, but not RB (11). The single data point for tetraphenylporphine was again based on an experiment performed in a different laboratory (25).

The ^{1}H NMR spectrum of $^1O_2$-reacted cis-PBD (Fig. 11) offers additional microstructural information. Besides the 2.1 (-CH$_2$=) and 5.4 ppm (-CH=) resonances of the unreacted cis-PBD, the spectrum shows a broad resonance centered at 1.7 ppm (-CH$_2$-C-O-) and other new resonances at 2.8 (=C-CH$_2$-C=), 4.3 (-CH-O-), and 7.8 ppm (-C-OOH). Characteristically, the 7.8 ppm peak can be removed by washing the ^{1}H NMR sample with D$_2$O.

Typical ^{13}C NMR spectra of $^1O_2$-reacted cis-PBD, before and after reduction, are shown in Fig. 12 (35). Substitution of -OH for -OOH shifts the δ peak at 86 ppm upfield by 13 ppm (to δ'), and the γ peak at 34 ppm downfield by 5 ppm (to γ'), displacements which reinforce the assignments given. Similar upfield shifts of ∿12-14 ppm were noted earlier for the analogous
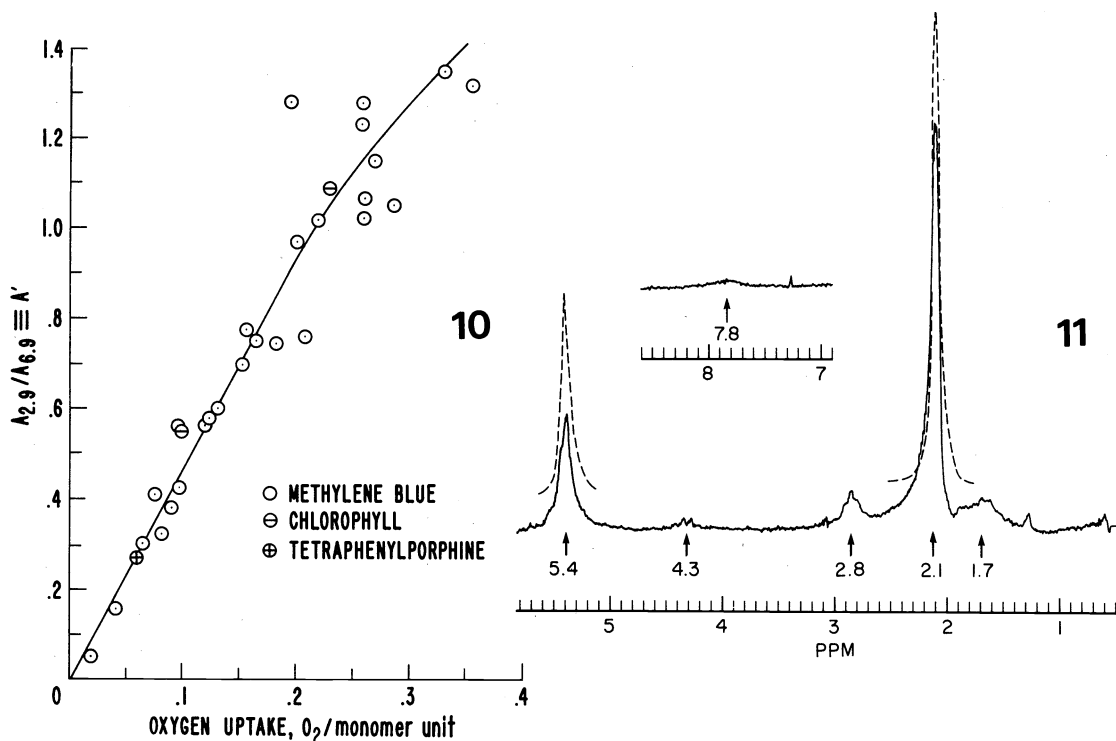
Fig. 10. IR measure of hydroper-
oxidation in cis-PBD.

Fig. 11. ^{1}H NMR spectra of cis-
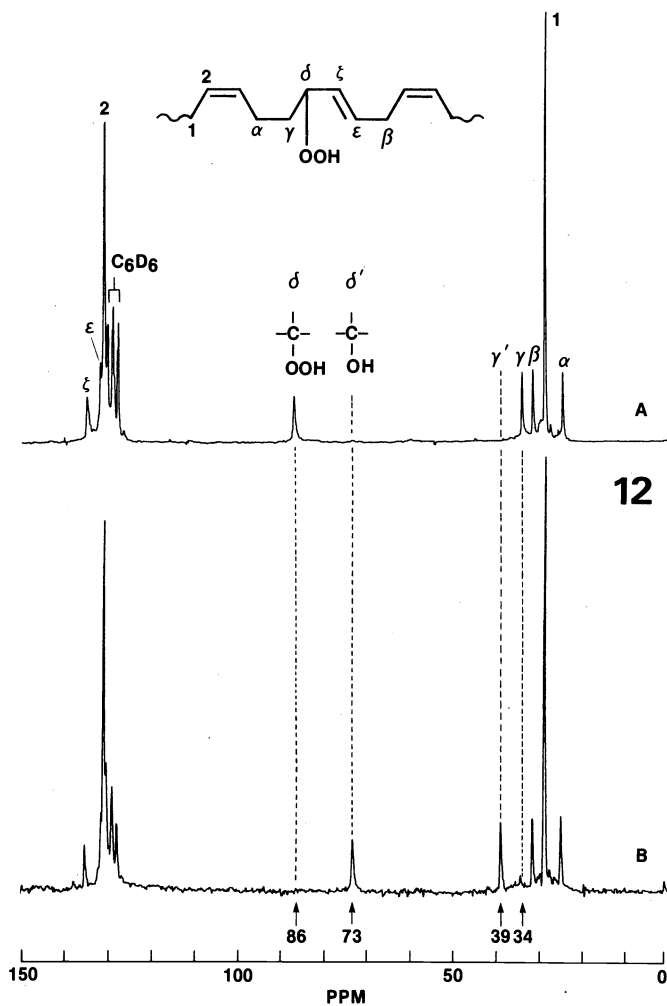PBD before (---) and after (———)
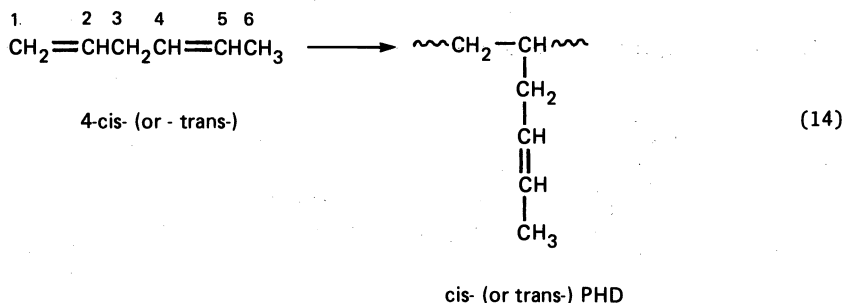MB-photosensitized oxidation.

Fig. 12. ^{13}C NMR spectra of $^1O_2$-
reacted cis-PBD before (A) and
after (B) reduction with $NaBH_4$.

$-\overset{\mid}{\underset{\mid}{C}}-O-$ resonances in $^1O_2$-reacted PIP (Figs. 5 and 6) or SQ (Fig. 7). Not surprisingly, Fig. 12 shows only one resonance for $-\overset{\mid}{C}-OOH$ and only one for $-\overset{\mid}{C}-OH$, not two resonances (∿5 ppm apart) for each of these carbons; this is in line with our observation that the shifted double bonds in reaction 13 have but one isomeric form, namely, trans. Likewise, the ^{13}C spectra of $^1O_2$-reacted trans-PBD, before and after reduction (11), displayed a single δ peak (at 86 ppm) and a single δ' peak (at 72 ppm), in accordance with the trans-only nature of the shifted double bond. Furthermore, Fig. 12 contains no unassigned resonances indicative of the endoperoxides (reaction 11) proposed by Kaplan and Kelleher (29) for $^1O_2$-reacted PBD; as we saw earlier, such structures were dismissed on the basis of model compounds (8,9,14,15).

1,2-POLY(1,4-HEXADIENE)S

Having examined the singlet oxygenation of PIP and PBD, polymers with C=C bonds inside the main chain, we now consider two polymers, with C=C bonds outside the main chain, which are quite reactive towards $^1O_2$ (17). These are cis and trans forms of 1,2-poly(1,4-hexadiene) (PHD) derived from stereospecific 1,2-polymerization of cis- or trans-1,4-hexadiene:

$$\underset{1}{CH_2}\!=\!\underset{2}{CH}\underset{3}{CH_2}\underset{4}{CH}\!=\!\underset{5}{CH}\underset{6}{CH_3} \longrightarrow \text{∿∿}CH_2\!-\!CH\text{∿∿} \atop {\overset{\mid}{CH_2} \atop \overset{\mid}{CH} \atop \overset{\parallel}{CH} \atop \overset{\mid}{CH_3}}$$

(14)

4-cis- (or - trans-)

cis- (or trans-) PHD

The cis contents in these polymers were initially 90.2% and 3.8%, respectively. On MB-photosensitized oxidation, cis- and trans-PHD yielded allylic hydroperoxides accompanied by double bond shifts to new vinyl and trans vinylene units via reaction 1.

The important IR changes observed for the cis-PHD-$^1O_2$ reaction (Fig. 13) are decreases of the 14.4- and 6.1-μm bands (both due to cis -CH=CH-), increase of the 10.4-μm band (trans -CH=CH-), growth of the 10.9-μm band (-CH=CH$_2$), and development of the strong 2.9-μm band (OOH). The product shown in Fig. 13 contained 0.32 O$_2$/monomer unit and had an A' = 0.78.

The IR spectrum of $^1O_2$-reacted trans-PHD (Fig. 14) similarly shows new bands at 2.9 and 10.9 μm, but no change in intensity of the 10.4-μm band nor a new peak at 14.4 μm. Thus, once again, the shifted vinylene double bonds are virtually all-trans. The product shown in Fig. 14 contained 0.30 O$_2$/monomer unit and had an A' = 0.34.

Figures 15 and 16 show the ^{13}C spectra of $^1O_2$-reacted cis- and trans-PHD with assignments of the important peaks (17). The two peaks labelled 1_C and 1_T in Fig. 15 (cis and trans $\underline{C}H_3$-CH=CH-, respectively) were present in the spectrum of the initial cis-PHD where they had the same ratio of intensities as indicated here; no 1_C peak is present in Fig. 16 but it was barely detectable in the spectrum of the initial trans-PHD. These ^{13}C NMR results conform to the expected absence of cis-trans isomerization of the original -CH=CH- double bonds on
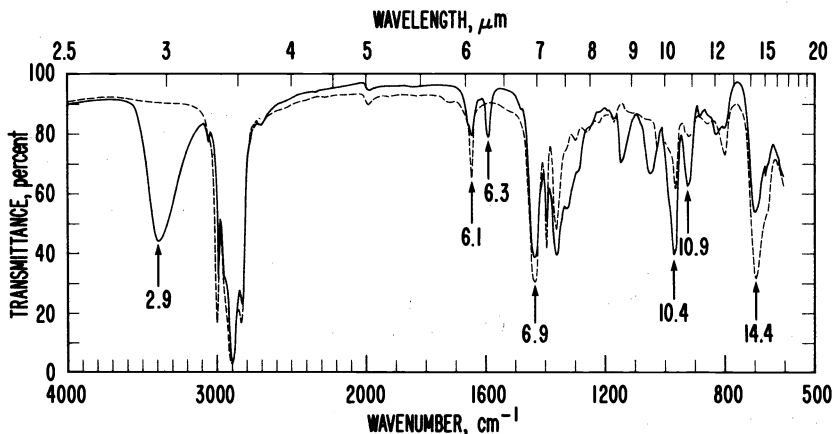

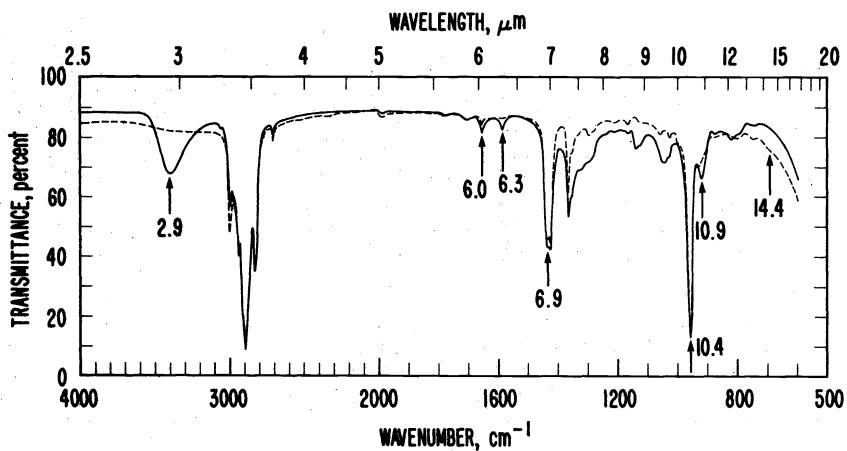Fig. 13. IR spectra of cis-PHD before (---) and after (——) MB-photosensitized oxidation.

Fig. 14. IR spectra of trans-PHD before (---) and after (——) MB-photosensitized oxidation.
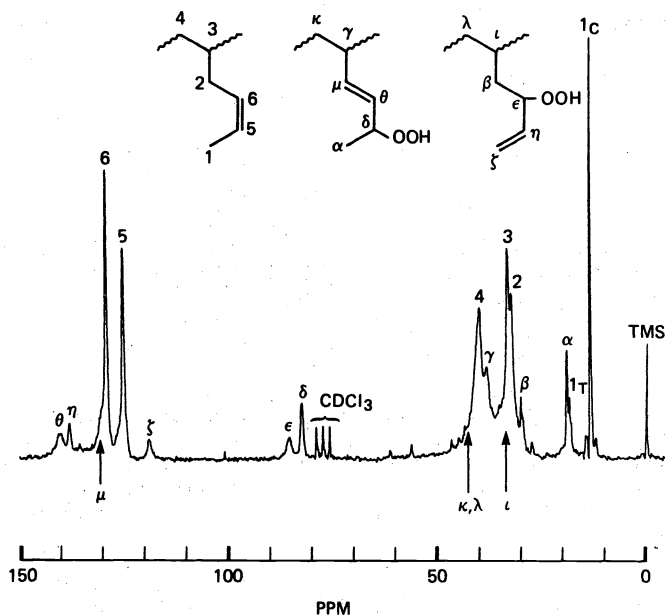

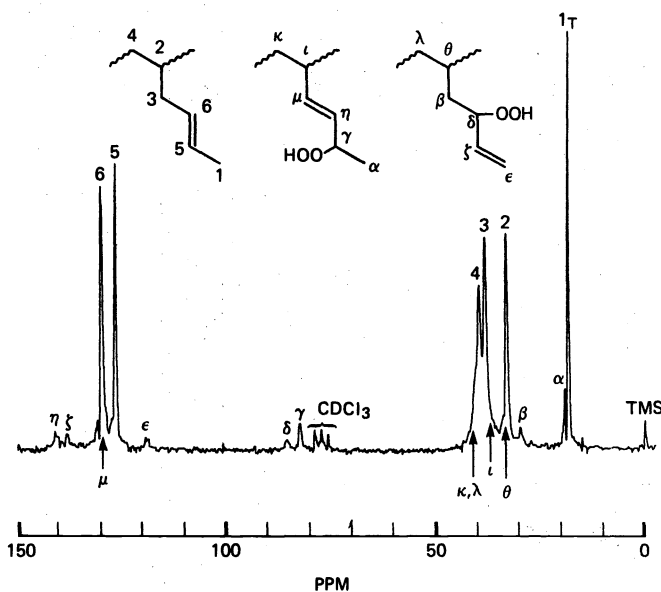Fig. 15. ^{13}C NMR spectrum of $^1O_2$-reacted cis-PHD corresponding to Fig. 13.

Fig. 16. ^{13}C NMR spectrum of $^1O_2$-reacted trans-PHD corresponding to Fig. 14.

reaction with $^1O_2$ (36). Since Figs. 15 and 16 show the same two $-\overset{|}{C}-OOH$ resonances at 82 and
85 ppm (δ,ε and γ,δ, respectively) and the same three olefinic carbon resonances (ζ,η,θ;
ε,ζ,η), it follows that cis- and trans-PHD must yield the same two hydroperoxidized products,
as shown on the figures. The ratios of new vinyl to new trans vinylene double bonds in $^1O_2$-
reacted cis- and trans-PHD were estimated, from the areas under the 82- and 85-ppm peaks, as
1.0:1.9 and 1.0:2.3, respectively.

A comparative kinetic study of the MB-photosensitized oxidation of PHD, PBD and its homolog,
polypentenamer, revealed a consistent tendency for $^1O_2$ to react much faster with cis than with
trans -CH=CH- double bonds whether the unsaturation is in the polymer backbone or located in
the pendent group (17). Thus, the relative rates for singlet oxygenation of cis- and trans-
PHD had a ratio of $\sim$3.8:1.0, while the corresponding ratios for PBD and polypentenamer were
$\sim$6:1 and $\sim$5:1, respectively. Moreover, cis-PHD, cis polypentenamer and cis-PBD were found to
have approximately the same singlet oxygenation rates, these being in the order of
$\sim$1.3:1.2:1.0.

1,2-POLYBUTADIENE; 1,2-POLY(TRANS-1,3-PENTADIENE)

Unlike cis- and trans-PHD, two other polymers with pendent double bonds were quite unreactive
towards $^1O_2$; these were 1,2 polybutadiene (VBD) and 1,2-poly(trans-1,3-pentadiene) (TPD):
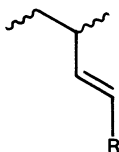
where R = H or CH_3, respectively. VBD had previously been reported to be inert towards $^1O_2$
(29), but IR evidence was offered recently for an extremely slow reaction: The spectrum of
$^1O_2$-reacted VBD, with <0.02 O_2/monomer unit, showed a very weak OOH absorption at 2.9 μm (12).
However, there were no IR changes indicative of the trisubstituted double bonds expected from
reaction 1. The very low O_2 uptake, together with the relatively low extinction coefficient
for the 12-μm band ($-\overset{|}{C}=CH-$), doubtless militated against direct IR evidence for shifted double
bonds. We obtained a spectrum for VBD after prolonged treatment with $^1O_2$ which was similar to
that of Fig. 4 in Ref. 12, but were unable to detect $-\overset{|}{C}-OOH$ resonances in the corresponding
^{13}C spectrum. We therefore concluded that there was negligible VBD-$^1O_2$ reaction (37). The
same conclusion was reached for TPD: the IR spectrum of this polymer, after extended exposure
to $^1O_2$, likewise displayed a very weak 2.9-μm band, but gave no indications of new vinyl or
trisubstituted double bonds in line with reaction 1; furthermore, the corresponding ^{13}C
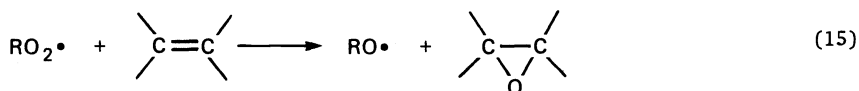spectrum lacked the characteristic $-\overset{|}{C}-OOH$ resonances (37).

Since the relative reactivities of simple olefins towards $^1O_2$ are in the order, tetra- > tri- >
disubstituted, with vinyl or monosubstituted double bonds being essentially unreactive (34,38,
39), it is not surprising that VBD showed negligible singlet oxygenation. In fact, Rabek and
Ranby (12) even suggested that the observed O_2 uptake by their VBD might have been due to the
1,4 double bonds present as a minor structural impurity, rather than to the 1,2 double bonds.

The lack of reactivity of TPD towards $^1O_2$ parallels the extremely low reactivity noted for
trans-4-methyl-2-pentene (39), a low molecular weight analog of TPD.

1,4-POLY(2,3-DIMETHYL-1,3-BUTADIENE)

A polymer with tetrasubstituted double bonds, 1,4-poly(2,3-dimethyl-1,3-butadiene) (PDMB,
$-CH_2C(CH_3)=C(CH_3)CH_2-$, with cis/trans ratio $\sim$1:3), was found to react very rapidly with $^1O_2$
to yield new exomethylene and trisubstituted double bonds (37). This is shown by new bands
at 2.9 μm (OOH), 6.1 and 11.1 μm (both due to $-C(=CH_2)-$) and at 11.8 μm ($-\overset{|}{C}=CH-$) in the IR
spectrum of $^1O_2$-reacted PDMB (Fig. 17). The latter had an A' value of 0.96 and an oxygen up-
take of 0.36 O_2/monomer unit, coordinates which fortuitously fit the A'-O_2 uptake plot for
cis-PIP (Fig. 3). Once again, the 5.8-μm peak is due to residual CL.

Figure 18 shows the ^{13}C NMR spectrum of the $^1O_2$-reacted PDMB along with tentative assignments
of the major resonances. Unfortunately, a sample of PDMB with either a very high cis or a
high trans structure was not available; such a polymer could have yielded simpler ^{13}C spectra.
In any case, the $^1O_2$-PDMB reaction appears straightforward and leads to the expected products
in accordance with reaction 1. However, the hydroperoxidized PDMB was quite unstable. This
is shown by the peak around 65 ppm which increased in intensity as the sample accumulated
additional transients in the ^{13}C spectrometer. That peak presumably represents epoxides
which can form through the following process (27):

$$RO_2\bullet \; + \; \underset{/}{\overset{\backslash}{C}}{=}\underset{\backslash}{\overset{/}{C}} \; \longrightarrow \; RO\bullet \; + \; \underset{/}{\overset{\backslash}{C}}\underset{\backslash}{\overset{/}{-}}\underset{O}{C} \tag{15}$$

where the peroxy radical is generated in the decomposition of the hydroperoxide, RO_2H.
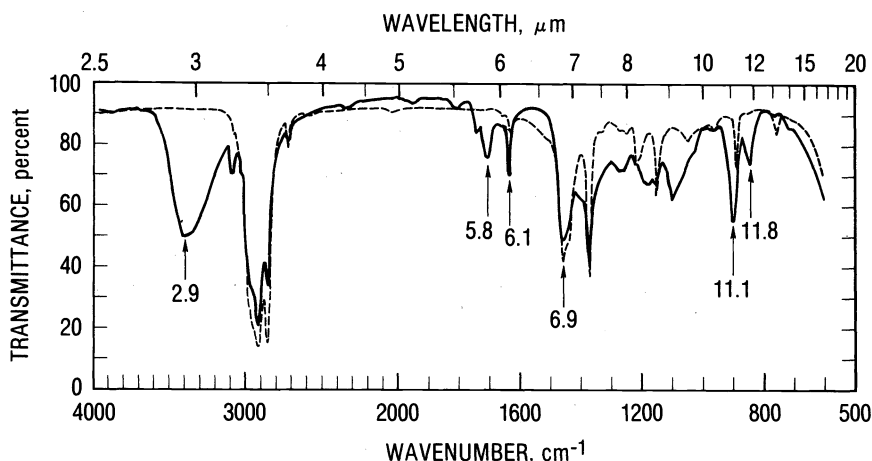
Fig. 17.   IR spectra of PDMB before (---) and after (——) CL-photosensitized oxidation.
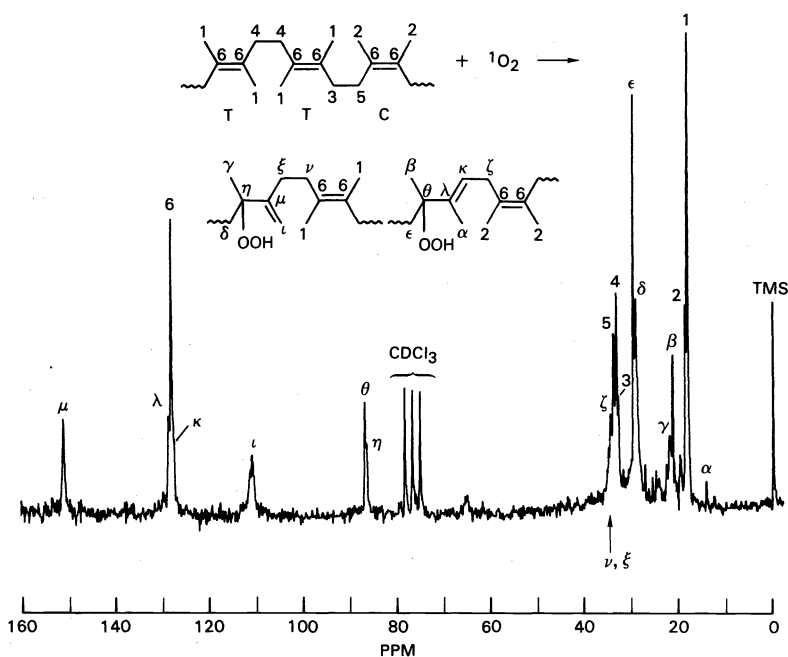
Fig. 18. ^{13}C NMR spectra of $^1O_2$-reacted PDMB corresponding to IR spectrum of Fig. 17.

OTHER POLYMERS WITH C=C BONDS

From the foregoing, it would be expected that nearly all hydrocarbon polymers containing di-, tri- or tetrasubstituted double bonds, either in the backbone or in sidechains, could react with $^1O_2$. Among the polymers which fall into this broad category are various butadiene or isoprene copolymers. Rabek and Rånby (1,12) recently reported on the dye-photosensitized oxidation of a butadiene-styrene copolymer (SBR) and a polystyrene-polybutadiene block copolymer (Solprene). The changes observed in the IR spectra of these copolymers after treatment with $^1O_2$ were attributed to changes associated with singlet oxygenation of the butadiene units, the styrene units being inert.

Finally, we may note that an EPDM synthetic rubber, comprising ethylene, propylene and
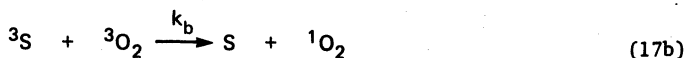
ethylidene norbornene, can also react with $^1O_2$ through the involvement of its pendent double
bonds (40):

$$\sim 2 \quad : \quad 1$$

$$\text{(16)}$$
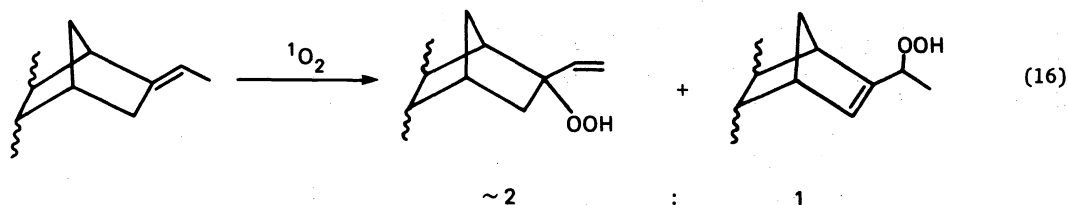
Reaction 16 is an interesting example of a singlet oxygenation of an unsaturated polymer which
may find practical application instead of being deleterious; in this case, treatment of EPDM
with $^1O_2$ causes this elastomer to have improved self-adhesion or tack, an important property
affecting its use in rubber technology (41).

KINETICS OF PHOTOSENSITIZED OXIDATION

The photosensitized oxidation of various unsaturated polymers can be described by the kinetic
scheme established for simple olefins (19,39,42):

$$S \xrightarrow{h\nu} {}^1S \xrightarrow{k_a} {}^3S \tag{17a}$$

$$^3S + {}^3O_2 \xrightarrow{k_b} S + {}^1O_2 \tag{17b}$$

$$^1O_2 + A \xrightarrow{k_c} AO_2 \tag{17c}$$

$$^1O_2 \xrightarrow{k_d} {}^3O_2 \tag{17d}$$

where S is sensitizer and A is acceptor. For sensitizers with triplet energy in excess of
22.5 kcal/mole, such as CL (32.0), MB (32.0) or RB (42.0 kcal/mole), the energy transfer
reaction 17b is very efficient. Steady-state treatment of reactions 17a-d leads to

$$\Phi_{(AO_2)} = \Phi_{({}^1O_2)} \left(\frac{k_c[A]}{k_d + k_c[A]} \right) \tag{18}$$

where Φ denotes quantum yield. For an acceptor which is sufficiently reactive and/or is at
high enough concentration to quench or react with all the $^1O_2$ before it decays to the ground
state, $k_c[A] \gg k_d$, and the reaction is zero order in acceptor. This situation obtains with
MB-photosensitized oxidations of cis and trans forms of PIP, PBD and PHD, as evidenced by the
typical straight line plots shown in Fig. 19. The comparative kinetic runs were carried out
under identical conditions of visible light irradiation, and of sensitizer and polymer con-
centration, in 25:1 benzene-methanol solution, using the procedure described (10,17).

A number of kinetic plots similar to those in Fig. 19 were obtained for each of the unsatu-
rated polymers studied in this laboratory; the average values of the slopes of such plots
were used to obtain relative rate constants for their reactions with $^1O_2$, as summarized in
Table 2. This table also contains corresponding literature data for various simple olefinic
analogs, and for several polymers studied elsewhere. The rate constants, k_r, are expressed
relative to that for cis-PIP ($k_r = 1.0$), while the k_r' values are relative to that for
cis-3-methyl-2-pentene ($k_r' = 1.0$).

As may be seen from Table 2, the relative reactivities towards $^1O_2$ for the unsaturated poly-
mers are similar to those for their simple mono-olefinic counterparts. This reinforces the
view developed on spectroscopic grounds that the mechanisms for singlet oxygenation are fun-
damentally the same for the two classes of compounds. Where differences arise, these must be
due to secondary processes occurring in the hydroperoxidized polymers or to interactions
between polymer and sensitizer.

DEGRADATION ATTENDING SINGLET OXYGENATION OF UNSATURATED POLYMERS

Depending upon the reaction conditions, singlet oxygenation of unsaturated polymers may be
accompanied by either extensive degradation or scarcely any. Thus, dye-photosensitized oxida-
tion in solution, besides yielding allylic hydroperoxides with shifted double bonds according

TABLE 2. Relative Rate Constants for Singlet Oxygenation of Unsaturated Polymers and Simple Olefinic Analogs

Polymer[a]	k_r	Olefin	k_r'
PDMB[b]	3.3		36[c]
PIP	1.00[d]		1.00[c,e]
PBD	0.17[f,g] 0.09[h] 0.1[i]		0.058[j]
PHD	0.20[k]		0.18[l]
TPD	m		0.0017[c,n]
VBD	m		0.0007$_3$[j]

(a) Work in this Laboratory except where noted. (b) cis/trans $\sim$ 1:3. (c) Ref. 39. (d) $k_{trans}/k_{cis} \sim$ 1.5.
(e) $k_{trans}/k_{cis} \sim$ 1.5[c]. (f) $k_{cis}/k_{trans} \sim$ 6.3. (g) $k_{cis}/k_{trans} \sim$ 4.7 for [structure] (h) Ref. 43. (i) Ref. 44; corresponding k_r values for butadiene-styrene and butadiene-acrylonitrile copolymers are 0.2 and 0.1, respectively, relative to cis-PIP ($k_r = 1$). (j) Ref. 38; derived value based on [structure] ($k_r' = 1$). (k) $k_{cis}/k_{trans} \sim$ 3.8.
(l) Ref. 43; calculated value relative to [structure] ($k_r' = 1$). (m) Too slow for accurate measurement.
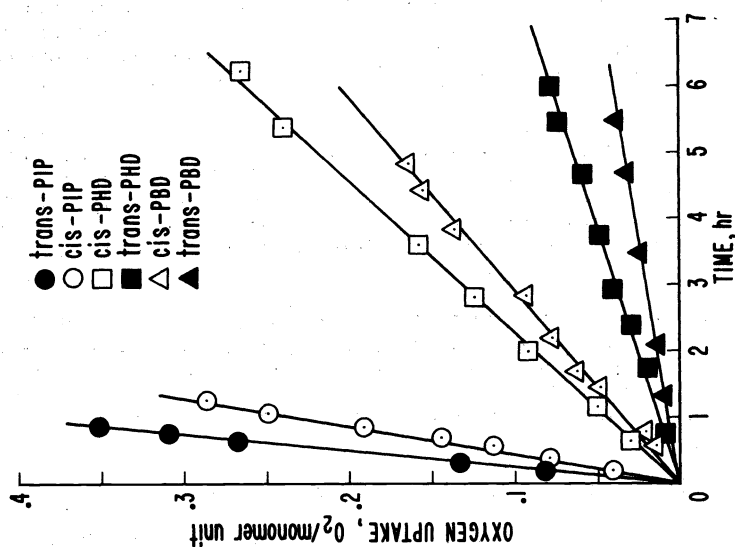(n) $k_{cis}/k_{trans} \sim$ 5.6[c].

Fig. 19. Comparative kinetic plots for the MB-photosensitized oxidation of various unsaturated polymers.

to reaction 1, was found to cause sharp decreases in viscosity or molecular weight of PBD (1,4,12,32,33), butadiene-styrene copolymers (1,12) and PIP (16). On the other hand, hydroperoxidation of cis- and trans-PBD in solution, with $^1O_2$ produced in situ from thermal decomposition of triphenylphosphite ozonide, gave rise to gelled polymers, more so in cis- than in trans-PBD, but in neither polymer was there chain scission (22,29). The gelation was ascribed to formation of peroxide bridges resulting from partial decomposition of the hydroperoxides. In contrast to singlet oxygenation in solution, thin films of PBD (22,30,32,33) and PIP (6,7,16) exposed to $^1O_2$ generated in the gas phase by microwave discharge, are hydroperoxidized at the surface only and experience no degradation. However, the $^1O_2$-treated films are unstable and display pronounced autoxidation when heated in air above ∿100°C (22,30,32,33); these same films, in the absence of air and put into solution, undergo chain scission when irradiated with near UV light (6,7,16,45). These effects, which are also observed for $^1O_2$-reacted polymers obtained by dye photosensitization (7,16,37), are a consequence of the facile thermal or photochemical decomposition of the polymer-OOH group.

The sharp decrease in viscosity of cis- and trans-PBD with time of dye-photosensitized oxidation in benzene-methanol solution (see Fig. 2 in Ref. 1) involved concomitant chain scission and crosslinking (1,12). The chain scission was due neither to direct action of $^1O_2$ on the polymer nor to photodecomposition of the hydroperoxides since the latter do not absorb the visible light used in dye photosensitization. Instead, on the basis of an ESR and UV spectroscopic study of the photoinduced bleaching of MB, Rabek and Rånby (1,13) concluded that chain scission was due to free radicals formed in the UV-irradiated MB-methanol-benzene photosensitizing system. Such radicals, of course, could abstract hydrogen from the polymers, thereby rendering them open to autoxidative chain scission in the presence of ground state oxygen (27). However, even with a decrease in intrinsic viscosity of PBD by a factor of ∿10-15 (1,4,32,33), the resulting hydroperoxidized polymer chains would still be sufficiently 'macromolecular' to make it difficult, if not impossible, to detect autoxidized end groups in the IR, ^1H or ^{13}C NMR spectra.

We also observed a sharp decrease in viscosity of PBD (or PIP) during singlet oxygenation in benzene-methanol solution using MB or RB as photosensitizer (37). On the other hand, when benzene-soluble CL was used, obviating the need for methanol in the polymer-sensitizer solutions, no decrease in viscosity occurred; instead PBD or PIP became somewhat gelled after extensive oxygen uptake (37). However, the products obtained with CL or MB photosensitization, despite the different viscosity effects, were spectroscopically indistinguishable, and we chose not to pursue the question of molecular weight changes attending the photosensitized oxidation.

Although hydroperoxides are the main carriers of the photooxidative chain, their decomposition does not represent an efficient mechanism for main chain scission (45). This was demonstrated by Ng and Guillet (6,7,16) in the near-UV photolysis of cis-PIP hydroperoxide (PIPH) in solution in the absence of oxygen. PIPH was prepared with different OOH contents by reacting cis-PIP with $^1O_2$ produced by microwave discharge or dye-photosensitization. The quantum yields for hydroperoxide decomposition and chain scission, Φ_{OOH} and Φ_S, respectively, were found to depend on OOH content, solvent, and wavelength and intensity of UV radiation, but the Φ_S/Φ_{OOH} ratio maintained an approximately constant value of 0.014. This rather low value was in accord with the proposed mechanism involving photoinduced rupture of the RO-OH bond (with primary quantum yield ∿0.8), free-radical induced chain decomposition of the ROOH groups (with overall Φ_{OOH} of the order of 3 to 8), and subsequent β-scission of the macroalkoxy radical intermediate, RO· (with Φ_S of the order of 0.03 to 0.1), in competition with hydrogen abstraction by that radical. These results indicate that $^1O_2$ plays a minor role in the photooxidation of polymers, limited mainly to the initiation process and contributing only indirectly to the chain scission.

CONCLUSION

The photosensitized oxidation or singlet oxygenation of various unsaturated hydrocarbon polymers follows the same ene-type reaction, leading to allylic hydroperoxides and shifted double bonds, as do their simple olefinic counterparts. Although the polymer-$^1O_2$ reaction does not directly cause degradation (chain scission and/or crosslinking), the resulting polymeric hydroperoxides are unstable, especially when dried, and can degrade as a consequence of incidental thermal or photochemical decomposition of ROOH groups. Degradation may also accompany the dye-photosensitized oxidation in solution to the extent that the irradiated dye, or radicals generated from it, can attack the dissolved polymer.

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