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Photosensitized Oxidation of Unsaturated Polymers

Morton A. Golub

June 1979
PHOTOSENSITIZED OXIDATION OF UNSATURATED POLYMERS

Morton A. Golub
Ames Research Center, National Aeronautics and Space Administration, Moffett Field, California 94035, USA

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-pentadiene), and on 1,4-poly(2,3-dimethyl-1,3-butadiene) (cis/trans ratio 9:1:3). The microstructural changes which occur in these polymers on reaction with \( ^1\text{O}_2 \) in solution were investigated by infrared, \( ^1\text{H} \) and \( ^1\text{C} \) 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, \( A_{298}/A_{293} \). Smooth correlations of \( A' \) with oxygen uptake were obtained with chlorophyll or methylene blue as photosensitizer, but Rose Bengal gave erratic \( A_{1\text{O}_2} \) uptake data indicative of autooxidation 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 \( ^1\text{O}_2 \). Two other polymers, 1,2-polybutadiene and 1,2-poly(trans-1,3-pentadiene), showed negligible reaction with \( ^1\text{O}_2 \), 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 \( ^1\text{O}_2 \)-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 (\( ^1\text{O}_2 \)) 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 \( ^1\text{O}_2 \) with unsaturated polymers or their model compounds were presented there by Rabek and Ranby (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 \( ^1\text{O}_2 \), and on the relative reactivities of such polymers towards \( ^1\text{O}_2 \) 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 (\( ^1\text{O}_2 \)), with energy of 22.5 kcal/mole above the ground state, \( ^3\text{E} \), 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 \( ^1\text{O}_2 \), is assumed to yield allylic hydroperoxides with shifted double bonds, according to the "ene" process:

\[
\begin{align*}
\text{H} & \quad \text{C}_1 \quad \text{C}_2 \quad \text{C}_3 \\
\uparrow & \quad \downarrow & \quad \downarrow \\
\text{C}_1 & \quad \text{C}_2 \quad \text{C}_3 \\
& & \text{COH}
\end{align*}
\]

established for simple olefins (18,19). Reaction 1 is to be distinguished from the autooxidation of olefins which involves \( ^3\text{O}_2 \) and leads to the formation of allylic hydroperoxides with
both shifted and unshifted double bonds, according to the process:

\[
\begin{align*}
\text{C}_1=\text{C}_2=\text{C}_3 + \text{RH} & \rightarrow \text{C}_1=\text{C}_2=\text{C}_3 + \text{C}_1=\text{C}_2=\text{C}_3 \\
\text{C}_1=\text{C}_2=\text{C}_3 + \text{O}_2 & \rightarrow \text{C}_1=\text{C}_2=\text{C}_3 + \text{O}_2 \\
\text{C}_1=\text{C}_2=\text{C}_3 + \text{O}_2 & \rightarrow \text{C}_1=\text{C}_2=\text{C}_3 + \text{O}_2
\end{align*}
\]

(2)

Besides the ene reaction, there are two other reactions in which \(^1\text{O}_2\) 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.

There has been controversy concerning the mechanism for reaction 1, whether it involves a peroxide, 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 \(^1\text{O}_2^*\), with 37,5 kcal/mole), it is generally accepted that all of the chemistry induced by \(^1\text{O}_2\) in solution, and essentially all that in the gas phase, is due to the \(^1\text{O}_2\) state; hence the latter term (or simply \(^1\text{O}_2\)) and the term "singlet oxygen" have become synonymous (21).

1,4-POLYISOPRENE

Three double bond shifts are possible for the reaction of \(^1\text{O}_2\) with 1,4-polyisoprene (PIP):

\[
\begin{align*}
\text{cis-PIP} + \text{O}_2 & \rightarrow \text{cis-PIP} \\
\text{trans-PIP} + \text{O}_2 & \rightarrow \text{trans-PIP} \\
\text{trans-PIP} + \text{O}_2 & \rightarrow \text{trans-PIP}
\end{align*}
\]

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 Tanjellan (8) presented evidence for all three double bond shifts in the reaction of \(^1\text{O}_2\) with 4-methyl-1-octene and 4,8-dimethyl-1,8-dodecadiene, compounds which are mono- and di-isoprenic models of PIP. Still later, Ng and Guillot (7) obtained comparable results for 4-methyl-1-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 \(\mu\)m (O=O) and 10.3 \(\mu\)m (trans -CH=CH-, as in 1), and net decrease of the 12.0-\(\mu\)m band (-C(CH)=CH-, as in unreacted units and in 2). The broad but weak absorption at 11.3 \(\mu\)m (-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(OH)=C=O groups, is definitely indicated by IR; and, as discussed below, the weak absorption at 5.8 µm is due to residual CL in the cast film of 102-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 photosensitization. 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 102-reacted cis-PIP typified by Fig. 1 is fundamentally 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-photosensitized 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 absorption 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 102-reacted SQ shown in Fig. 2 is effectively the hydroperoxide counterpart of their SQ-monoalcohol obtained through singlet oxygenation followed by reduction.

Rabek and Šaboty (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 102-reacted cis-PIP point to 1 as the major and 2 and 3 as the minor products, a qualitative distribution suggested also by Ng and Guillet (7) by analogy to 4-methyl-1-octene.

A convenient measure of the degree of hydroperoxidation is given by the ratio, \( \frac{A_{10.2}}{A_{9.9}} = A' \), where the 6.9-µm band (CH bending vibration) is an internal standard. The 103-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 hydroperoxide 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 autoxidation 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, unattenuated 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 ensuing autoxidation. The rather low efficiency of the bound RB for photosensitized oxidation of PIP, in contrast to that for SQ and other low molecular weight olefins (26), is...
Figure 2. IR spectra of (A) trans-PIP and (B) SQ before (---) and after (-----) MB-photosensitized oxidation.

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

Figure 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 $^1$O$_2$-reacted cis-PIP corresponding to the IR spectrum in Fig. 1. New resonances appear at 1.30 (CH$_3$-O-), 2.80 (-CH$_2$-C=), 4.20 (-CH=O-) and 5.54 ppm (-CH=CH-), while the original resonances at 2.05 (-CH=CN) and 5.12 ppm (-CH$_2$-) 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 (CH=CH2). These \(^1\)H NMR data support the IR indications of double bond shifts (to 1 in cis-PIP, and to 1 and 3 in trans-PIP and SQ), and establish the formation of 2 in all three compounds: the 5.54 and 4.8-4.9 ppm resonances signify 1 and 3, respectively, and the 2.80 ppm resonance corresponds to "skipped" methylenes resulting from shifts to 1 or 2 (as in 1' or 2'). The \(^1\)O\(_2\)-reacted cis-PIP (Figs. 1 and 4) was originally estimated to have about equal amounts of 1 and 2 with negligible 3, while the \(^1\)O\(_2\)-reacted trans-PIP (Fig. 2) was estimated to have \(\approx\)485 1, 26% 2 and 25% 3 (10). Recently, Nag and Golitzen (7,16) presented a \(^1\)H NMR spectrum of \(^1\)O\(_2\)-reacted cis-PIP (obtained with polystyrene-bound BB) which, although otherwise similar to Fig. 4, displayed a definite additional peak at 4.8-4.9 ppm indicative of some 3 formed in their hydroperoxidized 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 BB. The latter dye produces extraneous resonances at \(\approx\)60-85 ppm reminiscent of the peroxide/hydroperoxide/alcohol resonances at \(\approx\)60-80 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 3 in cis-PIP compared 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 providing \(^13\)C data on the effect of converting a hydroperoxide to an alcohol group in isoprenoid compounds: there is an upfield shift of 3 ppm for exomethylene carbon resonances in PIP and SQ; and a upfield shift of 12 ppm in cis-PIP and 14 ppm in both trans-PIP and SQ, for the A-O- resonances in various t-alkyl hydroperoxides on reduction to the corresponding alcohols (28).

![Fig. 5. \(^13\)C NMR spectra of \(^1\)O\(_2\)-reacted cis-PIP before (A) and after (B) reduction with NaBH₄. Spectrum A corresponds to Figs. 1 and 4.](image-url)
The $^{13}\text{C}$ spectra in Figs. 6 and 7 reinforce the similarity of trans-PIP and SQ in their reactions with $^{12}\text{O}_2$. 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 5O upon reducing the hydroperoxide to the alcohol.

**MODEL COMPOUNDS OF 1,4-POLYSOPRENE**

Tanielian and Chaineaux (8,9,14,15) carried out an extensive study of the RR-photosensitized oxidation in methanolic solution of 4-methyl-1-octene (MO), 4,8-dimethyl-1,4,8-dodecadiene (DMDOD), 2,6-dimethyl-2,6-octadiene (DMDOD) and 2,7-dimethyl-2,6-octadiene (DMDOD), 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-$O_2$ reaction:

\[
\begin{align*}
\text{MO} & \overset{1^O_2}{\rightarrow} 4 \\
& \overset{1^O_2}{\rightarrow} 5 \\
& \overset{1^O_2}{\rightarrow} 6
\end{align*}
\]

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 5. However, the comparison breaks down with regard to the corresponding structures 5 and 6 (or 4 and 5), 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 Guillot (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 $O_2$ to be 4:1:7:1:0, which agrees very well with the corresponding ratio of 4:1:5:1:0 obtained by us for trans- and cis-PIP (10).

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Di- (4 or 1)</th>
<th>Tri- (5 or 7)</th>
<th>Exo- (6 or 3)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% trans MO</td>
<td>41</td>
<td>11</td>
<td>48</td>
<td>8</td>
</tr>
<tr>
<td>46% trans, 54% cis MO</td>
<td>53</td>
<td>9</td>
<td>38</td>
<td>8</td>
</tr>
<tr>
<td>25% trans, 75% cis MO</td>
<td>60</td>
<td>7</td>
<td>33</td>
<td>8</td>
</tr>
<tr>
<td>100% cis MO</td>
<td>66</td>
<td>6</td>
<td>28</td>
<td>15</td>
</tr>
<tr>
<td>cis + trans MO</td>
<td>46</td>
<td>26</td>
<td>28</td>
<td>7,16</td>
</tr>
<tr>
<td>trans PIP</td>
<td>48</td>
<td>26</td>
<td>26</td>
<td>10</td>
</tr>
<tr>
<td>cis PIP</td>
<td>major</td>
<td>minor</td>
<td>minor</td>
<td>7,16</td>
</tr>
</tbody>
</table>

*New estimate made for this work.*

Tanielian and Chaineaux (8,15) showed that a second addition of $O_2$ 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:

\[
\begin{align*}
\text{5} & \overset{1^O_2}{\rightarrow} 7 \\
\text{5} & \overset{1^O_2}{\rightarrow} 8
\end{align*}
\]

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, DMDOD, 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 $O_2$, there are nine possible dihydroperoxides from DMDOD, 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).

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 $^{1}O_2$ 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 $^{1}O_2$ 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 EDMD (9), that the mechanism proposed by Kaplan and Kelleher (29) for singlet oxygenation of 1,4-polybutadiene (reaction 11) was
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:

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 DMOD and DMOD were also reported for BBM (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:

A number of papers have been concerned with this reaction, and many of them (1,4,22,29-35) have noted formation of hydroperoxide groups (revealed by new absorption at 2.9 \( \mu m \) 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 \( ^13C \) 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 \( \mu m \) (trans -CH=CH-) and a decrease of the 13.6-\( \mu m \) 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
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 Ranby (4,32, 33).

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 DMDO (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' = A2.9/A6.9 (Fig. 10). Good correlations of A' with O2 uptake were obtained with MB and CL, but not RR (11). The single data point for tetraphenylporphine was again based on an experiment performed in a different laboratory (25).

The 1H NMR spectrum of 1O2-reacted cis-PBD (Fig. 11) offers additional microstructural information. Besides the 2.1 (-CH2C=) and 5.4 ppm (-CH=) resonances of the unreacted cis-PBD, the spectrum shows a broad resonance centered at 1.7 ppm (-CH2-O- and other new resonances at 2.8 (-CH2-C=), 4.3 (-CH-O-), and 7.8 ppm (-C-OOH). Characteristically, the 7.8 ppm peak can be removed by washing the 1H NMR sample with 1D2O.

Typical 13C NMR spectra of 1O2-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 y peak at 34 ppm downfield by 5 ppm (to y'), displacements which reinforce the assignments given. Similar upfield shifts of 812-14 ppm were noted earlier for the analogous
Fig. 10. IR measure of hydroperoxidation 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 $^1$O$_2$-reacted cis-PBD before (A) and after (B) reduction with NaBH$_4$. 
Resonances in O₂-reacted PIP (Figs. 5 and 6) or SQ (Fig. 7). Not surprisingly, Fig. 12 shows only one resonance for ^-011 and only one for ^-011, 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 ^13C spectra of O₂-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 O₂-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)

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 O₂ (17). These 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:

\[
\begin{align*}
1 & \quad 2 \quad 3 \quad 4 \quad 5 \quad 6 \\
\text{CH}_2=CH\text{CH}_2\text{CH} & \quad \longrightarrow \quad \text{CH} \quad \text{CH} \\
\text{CH} & \\
\text{CH} & \\
\text{CH} & \\
\text{CH}_3 & \\
\end{align*}
\]

(14)

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-O₂ 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=CH₂), and development of the strong 2.9-µm band (O=O). The product shown in Fig. 13 contained 0.32 O₂/monomer unit and had an \( \Delta' = 0.78 \).

The IR spectrum of O₂-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 O₂/monomer unit and had an \( \Delta' = 0.34 \).

Figures 15 and 16 show the ^13C spectra of O₂-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-CH₂=CH-CH=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 ^13C 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-PHE before (---) and after (——) MB-photosensitized oxidation.

Fig. 15. $^{13}$C NMR spectrum of $^{18}$O-reacted cis-PHE corresponding to Fig. 13.

Fig. 16. $^{13}$C NMR spectrum of $^{18}$O-reacted trans-PHE corresponding to Fig. 14.
reaction with \(^{1}O_2\) (36). Since Figs. 15 and 16 show the same two \(^{1}O_2\) resonances at 82 and 85 ppm (\(\delta_{c}\) and \(\delta_{\alpha}\), respectively) and the same three olefinic carbon resonances (\(\delta_{c},\delta_{\alpha},\delta_{\beta}\); \(\delta_{c},\delta_{\alpha},\delta_{\beta}\)), it follows that cis- and trans-PBD must yield the same two hydroperoxided products, as shown on the figures. The ratios of new vinyl to new trans-vinylene double bonds in \(^{1}O_2\)-reacted cis- and trans-PBD were estimated, from the areas under the 82- and 85-ppm peaks, as 1:0.1:0.9 and 1:0.2:3, respectively.

A comparative kinetic study of the MB-photosensitized oxidation of PBD, PBD and its homolog, polyethylene, revealed a consistent tendency for \(^{1}O_2\) to react much faster with cis than with trans- \(\cdot\text{CH}-\text{CH}_2\)-double bonds whether the unsaturation is in the polymer backbone or located in the pendant group (17). Thus, the relative rates for singlet oxygenation of cis- and trans-PBD had a ratio of \(<3:8:1\:0\), while the corresponding ratios for PBD and polyethylene were \(<0:1\) and \(<5:1\), respectively. Moreover, cis-PBD, cis polyethylene and cis-PBD were found to have approximately the same singlet oxygenation rates, these being in the order of \(1.3:1.2:1.0\).

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

Unlike cis- and trans-PBD, two other polymers with pendant double bonds were quite unreactive towards \(^{1}O_2\): these were 1,2 polybutadiene (VBD) and 1,2-poly(trans-1,3-pentadiene) (TPD);

where \(R = H\) or \(\text{CH}_2\), respectively. VBD had previously been reported to be inert towards \(^{1}O_2\) (29), but IR evidence was offered recently for an extremely slow reaction: The spectrum of \(^{1}O_2\)-reacted VBD, with \(\text{CH}_2\)O2\text{Ter}nmomer unit, showed a very weak \(^{1}O_2\) absorption at 2.9 \(\mu\m\) (12). However, there were no IR changes indicative of the trisubstituted double bonds expected from reaction 1. The very low \(^{1}O_2\) uptake, together with the relatively low extinction coefficient for the 12-\(\mu\m\) band (\(\text{CH}_2\)), doubtless militated against direct IR evidence for shifted double bonds. We obtained spectra for VBD after prolonged treatment with \(^{1}O_2\), which was similar to that of Fig. 4 in Ref. 12, but were unable to detect \(^{1}O_2\) resonances in the corresponding \(^{13}C\) spectrum. We therefore concluded that there was negligible VBD-\(^{1}O_2\) reaction (37). The same conclusion was reached for TPD: the IR spectrum of thier polymer after extended exposure to \(^{1}O_2\), likewise displayed a very weak 2.9-\(\mu\m\) 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 \(^{1}O_2\) resonances (37).

Since the relative reactivities of simple olefins towards \(^{1}O_2\) 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, Babek and Röthy (12) even suggested that the observed \(^{1}O_2\) 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 \(^{1}O_2\) 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-PIMETHYL-1,3-BUTADIENE)

A polymer with tetrasubstituted double bonds, 1,4-poly(2,3-dimethyl-1,3-butadiene) (PMB, \(\text{CH}_2\text{C}(-\text{CH}_3)\text{C}(-\text{CH}_3)\text{CH}_2\_\_\_\_\_, with cis/trans ratio \(<1:3\)), was found to react very rapidly with \(^{1}O_2\) to yield new exomethylene and trisubstituted double bonds (37). This is shown by new bands at 2.9 \(\mu\m\) (\(^{1}O_2\)) and 11.1 \(\mu\m\) (both due to \(-\text{CH}(-\text{CH}_3)\)) and at 11.8 \(\mu\m\) (\(-\text{CH}(-\text{CH}_3)\)) in the IR spectrum of \(^{1}O_2\)-reacted PMB (Fig. 17). The latter had an \(A^*\) value of 0.96 and an oxygen uptake of 0.36 \(\text{O}_2\) per monomer unit, coordinates which fortuitously fit the \(A^*\)-\(^{1}O_2\) uptake plot for cis-PIP (Fig. 3). Once again, the 5.8-\(\mu\m\) peak is due to residual \(\text{Cl}\).

Figure 18 shows the \(^{13}C\) NMR spectrum of the \(^{1}O_2\)-reacted PMB along with tentative assignments of the major resonances. Unfortunately, a sample of PMB 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 \(^{1}O_2\)-PMB reaction appears straightforward and leads to the expected products in accordance with reaction 1. However, the hydroperoxided PMB 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):
where the perox radical is generated in the decomposition of the hydroperoxide, RO₂H.

\[
\text{RO}_2^+ + \text{C} = \text{C} \rightarrow \text{RO}^+ + \text{C} = \text{C}
\]

Fig. 17. IR spectra of PDMS before (----) and after (---) CL-photosensitized oxidation.

Fig. 18. \(^{13}C\) NMR spectra of \(^{1}O_2\)-reacted PDMS 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 Kimby (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
ethyliuc norbornene, can also react with $^{1}$O$_2$ through the involvement of its pendent double bonds (40):

\[
\begin{align*}
\text{S} & \xrightarrow{k_s} \text{S}_1 \quad (17a) \\
\text{S}_1 + ^{3}$O$_2 & \xrightarrow{k_h} \text{S} + ^{1}$O$_2 \quad (17b) \\
^{1}$O$_2 + A & \xrightarrow{k_r} \text{AO}_2 \quad (17c) \\
^{1}$O$_2 & \xrightarrow{k_d} ^{3}$O$_2 \quad (17d)
\end{align*}
\]

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

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

where $\Phi$ denotes quantum yield. For an acceptor which is sufficiently reactive and/or is at high enough concentration to quench or react with all the $^{1}$O$_2$ before it decays to the ground state, $k_d[A] \gg k_d$, 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 concentration, 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 unsaturated 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 $^{1}$O$_2$, as summarized in Table 2. This table also contains corresponding literature data for various simple olefin 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 $^{1}$O$_2$ 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 funda-

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

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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$k_e$</th>
<th>Olefin</th>
<th>$k_e'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMB</td>
<td>3.3</td>
<td></td>
<td>10.5</td>
</tr>
<tr>
<td>PIP</td>
<td>1.06</td>
<td></td>
<td>1.00</td>
</tr>
<tr>
<td>PBD</td>
<td>0.17</td>
<td></td>
<td>0.058</td>
</tr>
<tr>
<td>PHD</td>
<td>0.20</td>
<td></td>
<td>0.18</td>
</tr>
<tr>
<td>TPD</td>
<td>m</td>
<td></td>
<td>0.0007</td>
</tr>
<tr>
<td>VBD</td>
<td>m</td>
<td></td>
<td>0.0007</td>
</tr>
</tbody>
</table>

(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) $k_{trans}/k_{cis} \sim 15$. (f) $k_{cis}/k_{trans} \sim 6.3$. (g) $k_{cis}/k_{trans} \sim 4.7$ for $\sim$. (h) Ref. 43. (i) Ref. 44. Corresponding $k_e$ values for butadiene-styrene and butadiene-acrylonitrile copolymers are 0.2 and 0.1, respectively, relative to cis-PIP ($k_e = 1$). (j) Ref. 38; derived value based on $\sim$. (k) $k_{cis}/k_{trans} \sim 3.8$. (l) Ref. 43; calculated value relative to $\sim$. (m) $k_e = 1$. (n) Too slow for accurate measurement.

$\sim k_{cis}/k_{trans} \sim 5.6$. 

$\sim k_{cis}/k_{trans} \sim 5.6$.
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 \( \text{O}_2 \) produced in situ from thermal decomposition of triphenylmethoxide, 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 peroxycarbonate bridges resulting from partial decomposition of the hydroperoxide oxygen atom to singlet oxygenation in solution, thin films of PBD (22,28,32,33) and PIP (6,7,16) exposed to \( \text{O}_2 \) generated in the gas phase by microwave discharge, are hydroperoxidized at the surface only and experience no degradation. However, the \( \text{O}_2 \)-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 \( \text{O}_2 \)-reacted polymers obtained by dye photosensitization (7,16,37), are a consequence of the facile thermal or photochemical decomposition of the polymer-\( \text{O}_2 \)H group.

The sharp decrease in viscosity of cis- and trans-PBD with time of dye-photo sensitization oxidation in benzene-methanol solution (see Fig. 2 in Ref. 1) involved concomitant chain scission (1,12). The chain scission was due neither to direct action of \( \text{O}_2 \) 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, Babek and Kann (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 unreactive 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, H or \(^1\text{H}\) NMR spectra.

We also observed a sharp decrease in viscosity of PBD (or PIP) during singlet oxygenation in benzene-methanol solution using MB or BB as photosensitizer (37). On the other hand, when benzene-soluble CI was used, obviating the need for methanol in the polymer-sensitizer solutions, no decrease in viscosity occurred; instead PBD or PIP became somewhat gel-like after prolonged irradiation with CI or BB photosensitizers. The results obtained with CI or BB photosensitizers, 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 \( \gamma \) and Guillet (6,7,16) in the near-IR photolysis of cis-PIP hydroperoxide (PIPH) in solution in the absence of oxygen. PIPH was prepared with different \( \text{O}_2 \)-H contents by reacting cis-PIP with \( \text{O}_2 \) produced by microwave discharge or dye-photosensitization. The quantum yields for hydroperoxide decomposition and chain scission, \( \gamma_{\text{O}_2} \) and \( \gamma_{\text{\text{O}_2}} \), respectively, were found to depend on \( \text{O}_2 \)-H content, solvent, and wavelength and intensity of IR radiation, but the \( \gamma_{\text{O}_2} \) value for the different \( \text{O}_2 \)-H 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 \( \text{O}_2\-\text{O}_2 \) bond (with primary quantum yield \( \gamma_{\text{O}_2} \)), free-radical induced chain decomposition of the \( \text{O}_2\-\text{O}_2 \) groups (with overall \( \gamma_{\text{O}_2} \) of the order of 3 to 8), and subsequent \( \gamma_{\text{\text{O}_2}} \) of the macroalkoxy radical intermediate, \( \text{O}_2^* \) (with \( \gamma_{\text{\text{O}_2}} \) of the order of 0.03 to 0.1), in competition with hydrogen abstraction by that radical. These results indicate that \( \text{O}_2 \) 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 one-step reaction, leading to allylic hydroperoxides and shifted double bonds, as do their simple olefinic counterparts. Although the polymer-\( \text{O}_2 \) 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 \( \text{O}_2\-\text{O}_2 \) 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.

Acknowledgment - The author expresses his appreciation to Dr. R. V. Genner and Mr. M. L. Rosenberg for their valuable contributions to the singlet oxygenation studies carried out in this laboratory and cited in the references.
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