LASER-INDUCED DEGRADATION OF POLYVINYL CHLORIDE II: OXYGEN BLEACHING OF POLYENES

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Summary

The reaction of oxygen with polyenes of polyvinyl chloride was shown to proceed effectively under irradiation by the 514.5 nm emission line of an argon ion laser. The quantum yield of this photobleaching was estimated to be 0.015. A mechanism is suggested for the oxygen bleaching reaction both in the dark and under laser irradiation. The polyenyl radicals $-(CH=CH)_n-\overset{\cdot}{C}H-CH_2-CHCl-$, resulting from chlorine β-scission of excited singlet polyenes, are assumed to play a predominant role by reacting with $^3O_2$ to form allylic hydroperoxides or cyclic peroxides by an intramolecular process.

1. Introduction

In the preceding paper [1] we have reported some quantitative investigations on the laser-induced degradation of polyvinyl chloride (PVC) films and have shown that visible light is still efficient in promoting the dehydrochlorination process in this polymer. The quantum yield of hydrogen chloride (HCl) formation was found to be increased by the presence of oxygen in spite of an effective bleaching of the conjugated polyenes by atmospheric oxygen.

In the present paper we have tried to estimate the quantum yield of this photobleaching reaction and we suggest a possible mechanism which would account for our experimental observations.

2. Quantum yield of photobleaching of PVC polyenes by oxygen

During the UV photolysis of PVC the absorbance of the film increases with irradiation time in the presence of both nitrogen and pure oxygen (Fig. 1). During the laser photolysis of the UV-degraded polymer the ab-
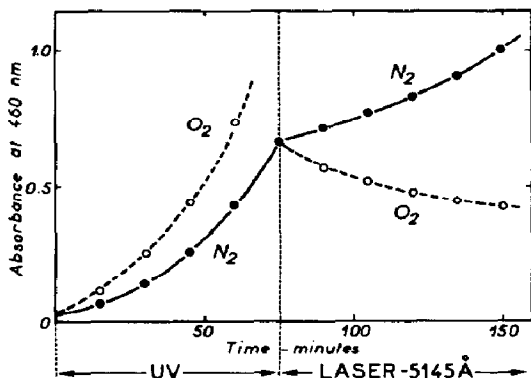
Fig. 1. The variation in the absorbance at 460 nm of the PVC film with the irradiation time in the UV and 514.5 nm photolysis in the presence of nitrogen (●) or oxygen (○).
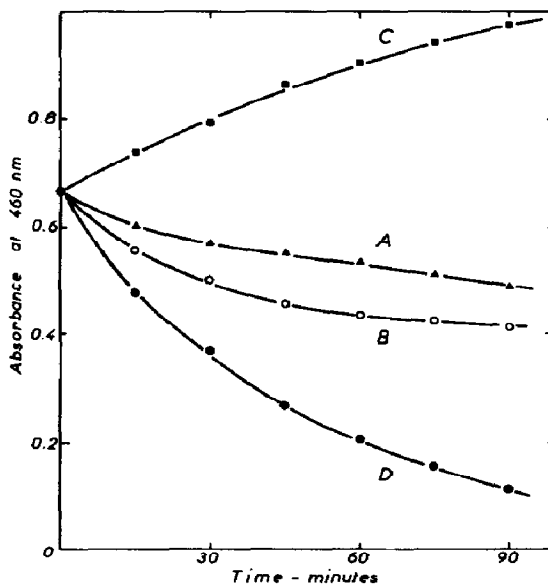
Fig. 2. Kinetics of oxygen bleaching of UV-degraded PVC film: curve A, dark bleaching; curve B, photobleaching by the 514.5 nm photolysis in oxygen; curve C, calculated increase in the absorbance at 460 nm due to polyene formation in the laser-induced oxidation of PVC; curve D, calculated photobleaching of polyenes (curve B — increase in curve C).

sorbance in the range 250 - 600 nm continues to increase for the experiments carried out in nitrogen whereas it decreases in the presence of oxygen. This decrease is expected to result from two opposing effects: (1) an increase in the absorbance due to the formation of conjugated polyenes since HCl is still evolved during the laser-induced oxidation of PVC (ref. 1, Fig. 1); (2) a very efficient photobleaching reaction caused by the attack by oxygen of these polyenes, a process which apparently more than offsets effect (1). The bleaching of polyenes by molecular oxygen occurs even in the dark (Fig. 2, curve A) but at a slower rate than that under laser irradiation (Fig. 2, curve B).

In order to determine the quantum yield of this bleaching reaction it was necessary to evaluate the amount of polyenes formed by the laser-induced dehydrochlorination of PVC in the presence of oxygen. This can be done by measuring the optical density of the PVC film at different wavelengths as a function of the HCl evolved during the laser photolysis of PVC in nitrogen. A linear relationship is obtained (Fig. 3). Knowing the amounts of HCl evolved during the laser-induced oxidation of PVC it is then possible from these curves to evaluate what would be the increase in the optical density, for instance at 460 nm, if there were no bleaching reaction (Fig. 2, curve C). By subtracting this increase from the bleaching curve B, curve D is obtained which represents the decrease in the absorbance if no dehydro-
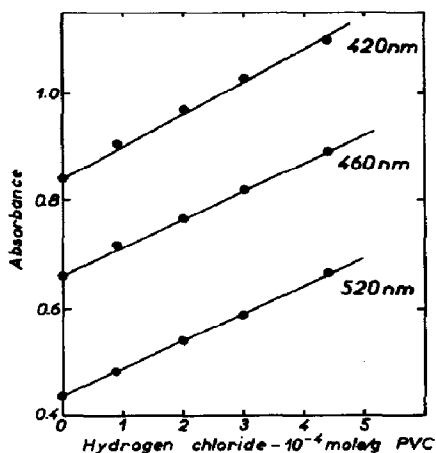
Fig. 3. Visible absorbance of degraded PVC film as a function of the amount of HCl evolved during the 514.5 nm photolysis in nitrogen.
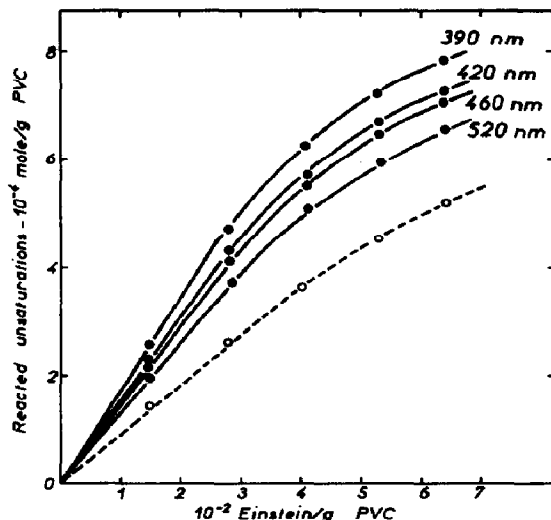
Fig. 4. The amount of double bonds reacting photochemically with oxygen, determined from the absorbance at various wavelengths (Fig. 3), as a function of the number of photons absorbed by the polymer in the 514.5 nm photolysis of PVC in the presence of oxygen (- - -, ○, HCl evolved).
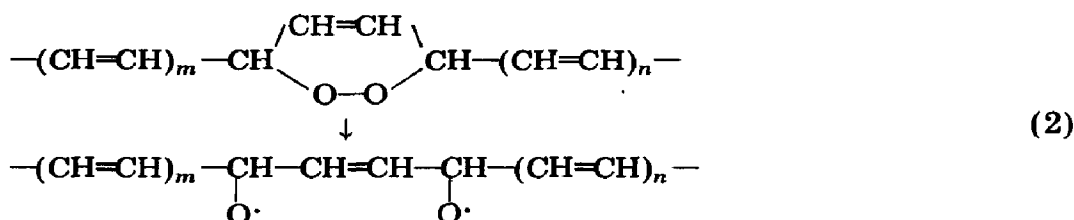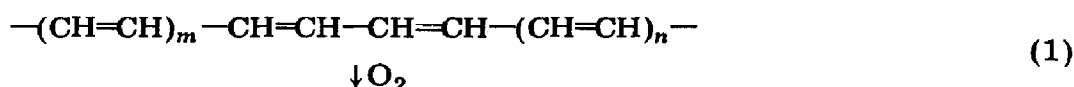
chlorination process were to occur and thus corresponds to the true consumption of the polyenes during the laser-induced oxidation of PVC. Since there is a contribution of the dark bleaching process (curve A), the difference between curves A and D will finally correspond to the amount of polyenes which has reacted with oxygen in a purely photochemical process. Under our experimental conditions the photobleaching of conjugated polyenes by oxygen appears to be about twice as fast as the bleaching in the dark.

Using the absorbance *versus* [HCl] curves of Fig. 3 it is then possible to evaluate from the difference between curves A and D of Fig. 2 the total amount of double bonds which has disappeared, assuming that each HCl molecule corresponds to one double bond. We have shown recently [2] that the major route of production of HCl in the photooxidation of PVC films is indeed the "zip" dehydrochlorination which generates one double bond for each HCl molecule evolved. Figure 4 shows that the amount of double bonds which has reacted with oxygen by a photochemical reaction increases linearly with the number of photons absorbed, at least in the first part of the irradiation. The slope of this straight line is the quantum yield of the photobleaching by oxygen of PVC polyenes. Its value is relatively high (1.5 X 10^{-2}) compared with the quantum yield of dehydrochlorination (0.9 X 10^{-2}) [1] and is not very dependent on the wavelength used in this calculation, *i.e.* the photobleaching efficiency is essentially the same regardless of the length of the conjugated polyene sequence.
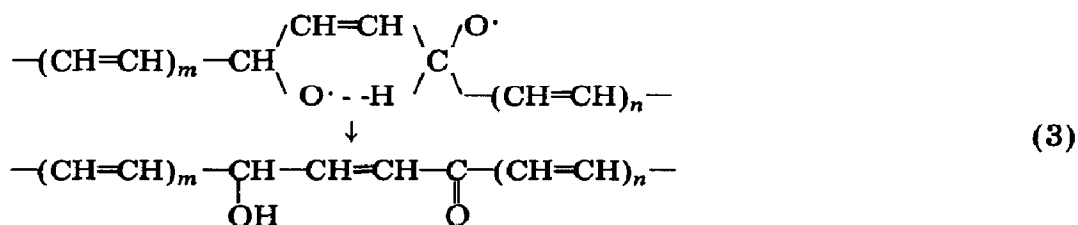
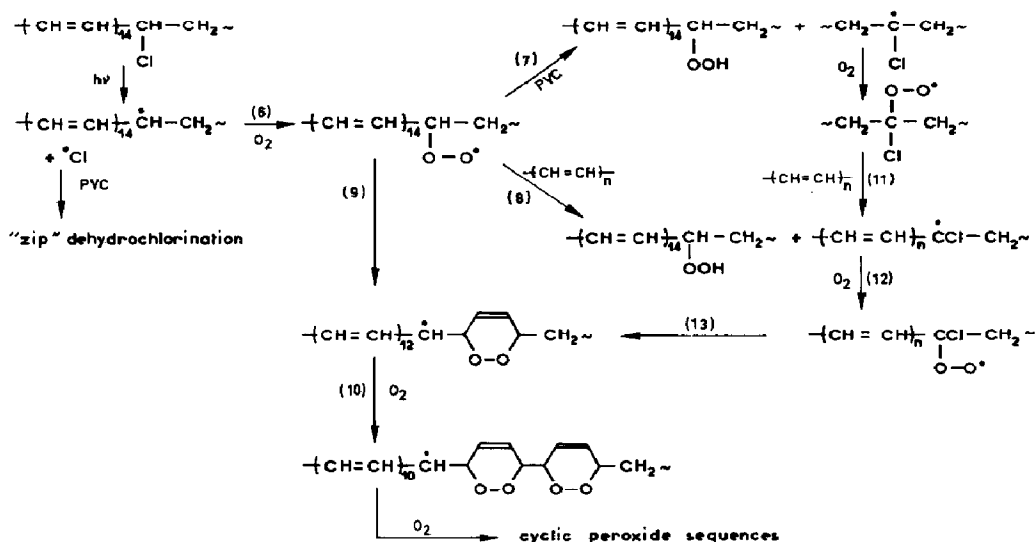## 3. Mechanism of the oxygen bleaching reaction

3.1. Dark bleaching

Ground state oxygen is known to react slowly with conjugated polyene systems, probably through a charge transfer complex [3, 4], thus reducing the length of the sequences (reaction (1)). The resulting cyclic peroxide may then decompose and create new propagating radicals as suggested by Druesdow and Gibbs [5].

$$-(CH=CH)_m-CH=CH-CH=CH-(CH=CH)_n-$$
$$\downarrow O_2 \tag{1}$$

$$-(CH=CH)_m-CH\overset{/CH=CH\diagdown}{\underset{\diagdown O-O\diagup}{}}CH-(CH=CH)_n- $$

$$\downarrow$$

$$-(CH=CH)_m-\underset{\underset{O\cdot}{|}}{CH}-CH=CH-\underset{\underset{O\cdot}{|}}{CH}-(CH=CH)_n- \tag{2}$$

The alkoxy radicals produced in reaction (2) have been assumed to initiate some new degradation chains in order to account for the faster rate of thermal dehydrochlorination observed when oxygen is passed over partly degraded PVC [6]. However, since in our case very little HCl was evolved during the oxygen bleaching in the dark, we have to consider either that these cyclic peroxides are stable under our experimental conditions or that they decompose without generating propagating radicals. A possible reaction would be an internal rearrangement of the alkoxy biradical leading to the formation of $\alpha-\beta$ unsaturated ketones and alcohols:

$$-(CH=CH)_m-CH\overset{/CH=CH\diagdown}{\underset{\diagdown O\cdot--H}{}}\overset{/O\cdot}{\underset{\diagdown}{C}}-(CH=CH)_n- $$

$$\downarrow$$

$$-(CH=CH)_m-\underset{\underset{OH}{|}}{CH}-CH=CH-\underset{\underset{O}{\|}}{C}-(CH=CH)_n- \tag{3}$$

The IR spectrum of the PVC film irradiated for 75 min in a nitrogen atmosphere exhibits indeed, after 1 h of oxygen bleaching in the dark, a broad carbonyl absorption centred at 1720 cm^{-1}, in agreement with previous observations on the reaction of oxygen with polyacetylene [7]. By taking an average extinction coefficient of $400 \text{ l mol}^{-1} \text{ cm}^{-1}$ for these ketone groups, their rate of formation was estimated to be approximately 2×10^{-5} mol $g^{-1} h^{-1}$, i.e. about one-tenth of the rate of disappearance of the unsaturations, thus indicating that the cyclic peroxides formed in reaction (1) are essentially stable at room temperature.
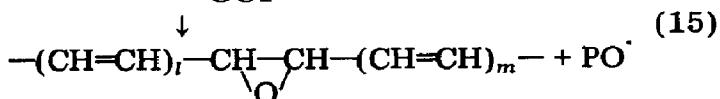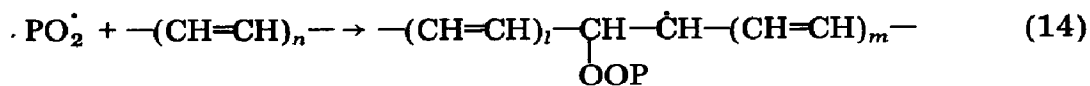
As expected from this dark bleaching mechanism, the consumption of polyenes is faster for long conjugated sequences since the probability of the oxygen attack is enhanced as the sequence length increases.

3.2. Photobleaching

In addition to this dark bleaching reaction, a photobleaching process develops efficiently during the laser-induced oxidation of degraded PVC: $\Phi_{bleaching} = 1.5 \times 10^{-2}$. The 514.5 nm photons which are absorbed by polyenes with sequence lengths above 14 lead to the formation of polyenyl free radicals with delocalized unpaired electrons [8]. These radicals were assumed to react easily with oxygen to give polyenyl peroxy radicals, the second unpaired electron resulting from the opening of the double bond being probably delocalized in a resonance structure [9].

$$-(CH\!=\!CH)_{14}- \xrightarrow{\text{514.5 nm}} -(CH\!=\!CH)_{14}-^{*} \to -CH\!\cdots\!CH\!\cdots\!CH\!\cdots\!CH\!\cdots\!CH-$$

$$\downarrow O_2$$

$$-CH\!=\!CH\!-\!\underset{\underset{O\!-\!O\cdot}{|}}{C}H\!-\!CH\!=\!CH-$$

$$(4)$$

If reaction (4) were the main route of polyene consumption, we would expect the photobleaching efficiency to be much higher for the polyenes which absorb the laser emission, *i.e.* with sequence lengths above 14. In fact the quantum yield of the consumption of polyenes is similar for short and long sequences (Fig. 4), thus indicating that another oxygen bleaching mechanism takes place.

The excited singlet polyenes (or the polyenyl biradicals) formed by irradiation have a short lifetime (approximately 10^{-9} s) [9, 10] and should thus disappear before reacting with oxygen, mostly by splitting off the labile allylic chlorine:

$$\left[-(CH\!=\!CH)_{14}-\underset{\underset{Cl}{|}}{C}H\!-\!CH_2-\right]^{*} \to -(CH\!=\!CH)_{14}-\dot{C}H\!-\!CH_2- + \dot{C}l \qquad (5)$$

i.e. reaction (5) should be highly favoured over reaction (4). Since the chlorine radical evolved will initiate a new degradation chain, this reaction might explain why dehydrochlorination still proceeds in the laser photolysis of PVC in the presence of oxygen, even more efficiently than in a nitrogen atmosphere [1], in spite of the bleaching reaction. Moreover, the formation of singlet oxygen by energy transfer from the excited polyene structures to ground state oxygen, which has been suggested in PVC photooxidation [11], seems to be very unlikely because of both the short lifetime of the excited singlet state of these structures and the lack of any oxygen inhibition effect on the dehydrochlorination process which should have occurred if $^{1}O_2$ were to react with polyenes to give allylic hydroperoxides.

Scheme 1. Photobleaching by oxygen of PVC polyenes.

Since the polyenyl radical $-(CH{=}CH)_{14}{-}\dot{C}H{-}CH_2{-}$ resulting from reaction (5) is not likely to undergo a chlorine β-scission process, it should live long enough to react with surrounding oxygen (Scheme 1, reaction (6)). The resulting polyenyl peroxy radical may then either abstract a tertiary or allylic hydrogen from the polymer with the formation of an allylic hydroperoxide (reactions (7) and (8)) or undergo an intramolecular process with the formation of cyclic peroxides (reaction (10)) as suggested by Nagy *et al.* [12] in their recent study of the thermal oxidation of PVC.

If the polyenyl radical formed in reaction (9) reacts again with oxygen, it will lead to a step-by-step shortening of the polyene sequence and the formation of adjacent cyclic peroxide structures (reaction (10)). Such an intramolecular chain reaction might explain why we observed no conversion of long sequences into shorter sequences during the photooxidation of PVC. Reactions (9) and (10) should also apply to the shorter polyene peroxy radicals resulting from reactions (8) or (11) and (12), thus accounting for the bleaching of polyenes with $n < 14$ which do not absorb the 514.5 nm radiation (reaction (13)).
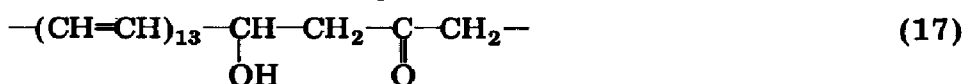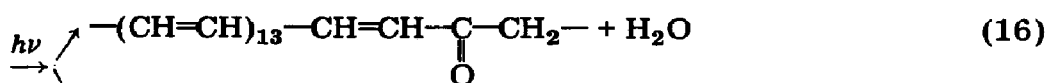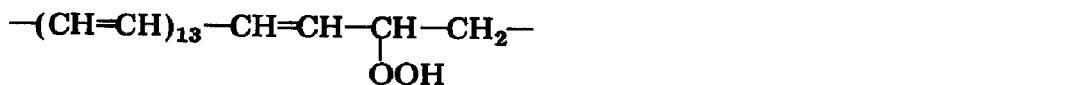
Another possible bleaching process would be the addition of a polymer peroxy radical ($PO_2^\bullet$) to a conjugated polyene [12, 13]:

$$. PO_2^\bullet + {-}(CH{=}CH)_n{-} \rightarrow {-}(CH{=}CH)_l{-}\underset{\displaystyle OOP}{CH}{-}\dot{C}H{-}(CH{=}CH)_m{-} \qquad (14)$$

$$\downarrow \qquad\qquad (15)$$

$${-}(CH{=}CH)_l{-}\underset{\displaystyle \diagdown O \diagup}{CH{-}CH}{-}(CH{=}CH)_m{-} + PO^\bullet$$

with $n = l + m + 1$.

If reactions (14) and (15) were to contribute substantially to the shortening of the polyene sequence length during the laser-induced oxidation of PVC, we would expect the rate of polyene consumption to be proportional to the polyene sequence length. In fact the quantum yield of the photobleaching process was found to be almost independent of the polyene sequence length in the range that could be investigated ($n > 6$) (Fig. 4). This suggests that the main bleaching route goes through the allylic hydrogen abstraction by peroxy radicals (reactions (8) and (11), which are not dependent on the polyene sequence length), followed by the intramolecular chain reaction of the resulting polyene peroxy radical (reactions (13) and (10)).

Finally, in order to account for the formation of carbonyl groups observed during the oxygen photobleaching of PVC at a rate of approximately 5×10^{-5} mol g^{-1} h^{-1}, we may consider that they result either from termination reactions of peroxy radicals or from a polyene-sensitized decomposition of the allylic hydroperoxides formed in reactions (7) and (8) according to the following scheme:

$$\text{—(CH=CH)}_{13}\text{—CH=CH—CH—CH}_2\text{—}$$
$$\underset{\text{OOH}}{\mid}$$

$$\xrightarrow[\text{hv}]{} \begin{cases} \text{—(CH=CH)}_{13}\text{—CH=CH—C—CH}_2\text{— + H}_2\text{O} \\ \qquad\qquad\qquad\qquad\quad \underset{\text{O}}{\parallel} \end{cases} \tag{16}$$

$$\text{—(CH=CH)}_{13}\text{—CH—CH}_2\text{—C—CH}_2\text{—} \tag{17}$$
$$\qquad\qquad\qquad\underset{\text{OH}}{\mid}\qquad\underset{\text{O}}{\parallel}$$

These reactions would also account for the relatively low hydroperoxide content observed in the photooxidation of PVC films [14].

From the relative values of Φ_{HCl} (0.9×10^{-2}) and $\Phi_{bleaching}$ (1.5×10^{-2}) determined in the laser-induced oxidation of PVC, it can be concluded that, for each HCl molecule evolved and for each unsaturation formed by the chain dehydrochlorination process, 1.7 unsaturations are consumed by a photochemical reaction with oxygen. Under the conditions of oxygen pressure, light intensity and wavelength selected the oxygen photobleaching of UV-degraded PVC appears thus to compete effectively with the "zip" dehydrochlorination process which is responsible for the poor photostability of PVC.

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