

NOTES

Oxidation of Polyene Structures in Poly(vinyl Chloride) by Molecular Oxygen and Singlet Oxygen

INTRODUCTION

It is well known that polyene sequences are formed during thermal,¹⁻⁴ photochemical,⁵⁻⁷ and chemical⁸⁻¹⁰ dehydrochlorination of poly(vinyl chloride) (PVC). Conjugated polyenes are colored if the chains contain sequences of at least eight conjugated double bonds. In oxidative atmospheres bleaching reactions occur because of attack of oxygen on long polyenes, which reduces the length of conjugation. We have observed that singlet oxygen $^1\text{O}_2(^1\Delta_g)$ produced in a dye-photosensitized reaction reacts much faster with polyene sequences than molecular oxygen in its triplet ground state $^3\text{O}_2(^3\Sigma_g^-)$.

For better understanding of the bleaching mechanism by $^3\text{O}_2$ and $^1\text{O}_2$, efforts have been made to estimate type and concentration of the polyenes present from the absorption spectrum of dechlorinated PVC during the oxidation processes and correlate this information with IR spectra, molecular weight distribution, and average molecular weight.

RESULTS AND DISCUSSION

Strongly colored polyene structures were prepared as described previously⁸ by dehydrochlorination of PVC (Pevikon S-655, Kema Nord AB, Fikentscher *K* value 65, $\overline{M}_n = 39,000$, $\overline{M}_w = 74,000$, and polydispersity factor 1.9) in KOH/EtOH solution. The absorption spectra of dehydrochlorinated PVC were measured using a Perkin-Elmer 575 UV-VIS spectrometer, and they are shown in Figures 1 and 2. The spectra were analyzed considering their complexity due to overlap of spectra of individual polyenes. As an example, trienes usually have three main maxima and higher polyenes usually have four. The extinction coefficient of a polyene at a certain wavelength increases linearly with the *n* number for all polyenes.^{11,12} The effect of an increase in *n* of conjugated double bonds is to displace the spectrum to longer wavelengths. Individual peaks obtained in a spectrum (Fig. 1 or Fig. 2) may be attributed to different *n* of conjugated double bonds. Below 300 nm, the spectrum becomes complicated because of formation of PVC charge-transfer complexes (CT complexes) with tetrahydrofuran used here as solvent. The polyenes absorbing in the region of 300 to 450 nm have *n* values of 3 to 10.

The absorption spectra of polyenes show changes during exposure to $^3\text{O}_2$ (Fig. 1) and $^1\text{O}_2$ (Fig. 2) in THF solution (1 wt %) during irradiation with a 500-W tungsten lamp ($\lambda > 400$ nm). $^1\text{O}_2$ was generated in solution using a polymer-based Rose Bengal dye (Polyscience Inc., U.S.A.) (0.5 g/50 ml solution). Analysis of the spectra shows that long sequences (*n* = 10-6) disappear first. The rate constants of the disappearances differ for different *n* values (Fig. 3).

The first-order rate of polyene consumption by $^3\text{O}_2$ increases proportional to the length of polyenes. This behavior was observed in all experiments where oxidation was carried out by $^3\text{O}_2$. The consumption rate of short polyenes (*n* = 4) is much lower than the rate obtained for long polyenes (*n* = 10).

The pseudo-second-order rate of polyene consumption in the case of $^1\text{O}_2$ decreases proportional to the length of the polyene. The consumption rate of short polyenes (*n* = 4) is higher than the rates for *n* = 10. The rate of reaction increases also during the course of the reaction. It is concluded that the polyene-singlet oxygen reaction is different from the polyene- $^3\text{O}_2$ reaction.

The IR spectra were obtained from films cast from 0.5-1.0 wt % polymer solutions using a Perkin-Elmer 257 IR spectrometer. Depending on type of solvent used during oxidation, the formation of new absorption bands was observed: (i) $^1\text{O}_2$ oxidation in THF solution, [Figure 4(c)]: 3400-3440 cm^{-1} band attributed to OOH and/or OH groups and 1800-1700 cm^{-1} attributed to CO groups. (ii) $^1\text{O}_2$ oxidation in $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$, only the 3400-3440 cm^{-1} band is formed.

During the oxidation of pure THF by $^3\text{O}_2$, Figure 4(a), and $^1\text{O}_2$, Figure 4(b), the formation of the

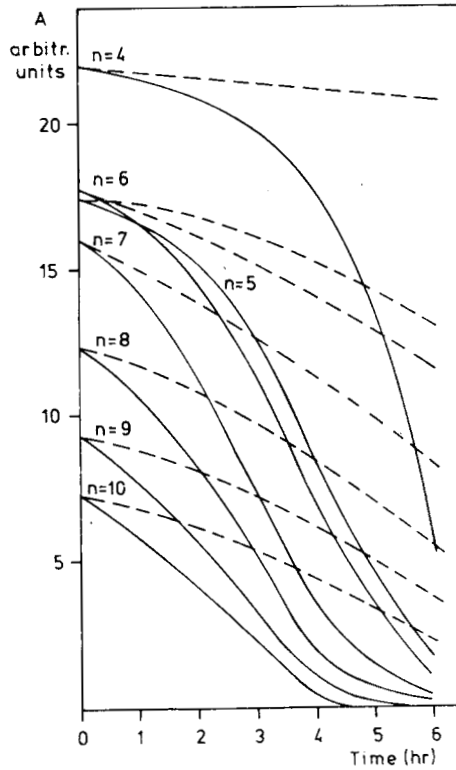


Fig. 3. Kinetic curves of disappearance of polyene structures with different n values during: (---) oxidation with $^3\text{O}_2$; and (—) oxidation with $^1\text{O}_2$.

and several peaks in this region have very strong absorptions. Normally, the C–O–C stretching vibrations in a six-membered ring absorb at the frequency of $1185\text{--}1085\text{ cm}^{-1}$. As the ring becomes smaller, the asymmetric C–O–C stretching vibrations move progressively to lower wave numbers (longer wavelengths), whereas the symmetrical C–O–C stretching vibration (ring breathing frequency) moves to shorter wavelengths. Another band should appear in the region of $950\text{--}800\text{ cm}^{-1}$ attributed

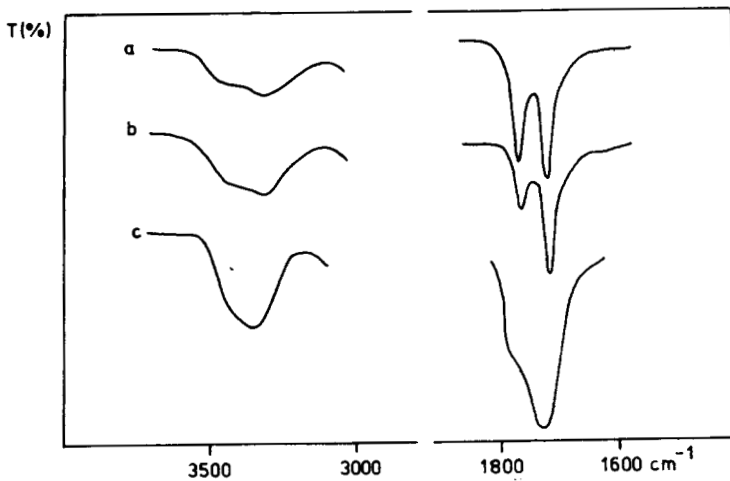
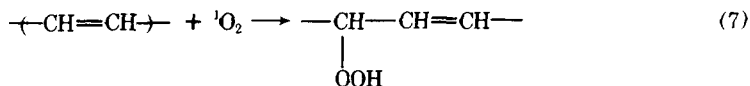
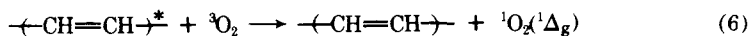
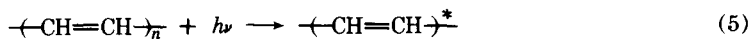


Fig. 4. IR spectra of: (a) THF only oxidized with $^3\text{O}_2$ for 6 hr; (b) THF only oxidized with $^1\text{O}_2$ for 6 hr; (c) PVC contained polyene structures oxidized in THF solution with $^1\text{O}_2$ for 6 hr.

to asymmetric ring stretching in which the C-C bond is stretching during contraction of the C-O bond.

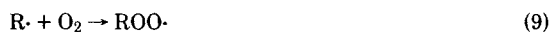
It has also been proposed⁵ that singlet oxygen may be formed directly in the energy transfer reaction between photoexcited polyene structures and $^3\text{O}_2$. The following mechanism was proposed:



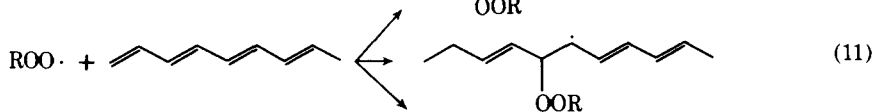
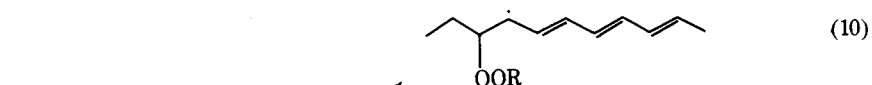
The energies of polyene singlet excited states are as follows: 107 kcal/mole for triene, 94 kcal/mole for tetracene, and 84 kcal/mole for pentene.²⁵ The efficiency of singlet-triplet energy is rather low, probably because of the short lifetime of the excited singlet state (ca. 10^{-9} sec).

Free Radicals Formed During Oxidation of THF both by $^3\text{O}_2$ and $^1\text{O}_2$

These may react with oxygen by addition and form peroxy radicals (ROO·):



Some possible reactions of THF-peroxy radicals (ROO·) with polyene structures are



The addition of a α -hydroperoxide tetrahydrofuran fragment across a double bond may reduce the extent of conjugation.¹² The double bond which is attacked by peroxide is likely to be in one of the following positions in the conjugated chain: the end, next to the end, the middle, or a random position.

The hydroperoxide concentration measured during oxidation of pure THF by $^3\text{O}_2$ after 60 min of oxygen flow of 60 ml/min during visible light irradiation was 0.012M, whereas in the presence of polymer-based Rose Bengal ($^1\text{O}_2$ oxidation) under the same experimental conditions was 0.068M.

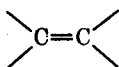
Considering the kinetics of the disappearance of different n polyene structures in the presence of $^3\text{O}_2$ and $^1\text{O}_2$ (Figs. 1 and 2, respectively), it is difficult to assume that only THF-peroxy radicals are responsible for the observed reactions. THF-peroxy radicals or other types of free radicals formed during THF oxidation have to play a considerable role in the termination of macroradicals which are formed during oxidation of polyene structures. As a result of these reactions, we never observed crosslinking reaction in THF solution, whereas oxidation of polyene structures in $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ under the same conditions as in THF causes crosslinking.

Molecular weight distributions (MWD) were measured by gel permeation chromatography (Waters Ass. Instrument, model ALC/GPC 201) with THF as solvent. After oxidation by $^3\text{O}_2$ and $^1\text{O}_2$, the MWD curves are shifted toward lower molecular weights. The \bar{M}_w/\bar{M}_n ratios calculated from MWD curves show that chain scission is greater for oxidation with singlet oxygen. Random scission of a most probable distribution with the \bar{M}_w/\bar{M}_n ratio equal to two would keep the ratio approximately the same, regardless of the extent of scission.

TABLE I
Change in Molecular Weights Observed during Oxidation and Ozonization of PVC Samples
Containing Polyene Structures

Sample	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
Polyene-PCV sample before oxidation	32,900	67,000	2.03
Polyene-PVC oxidized 6 hr with $^3\text{O}_2$	14,000	32,000	2.31
Polyene-PVC oxidized 6 hr with $^1\text{O}_2$	11,000	22,500	2.04
Polyene-PVC sample before oxidation and after ozonization	2,300	4,600	1.96
Polyene-PVC oxidized 6 hr with $^3\text{O}_2$ and after ozonization	4,300	6,700	1.56
Polyene-PCV oxidized 6 hr with $^1\text{O}_2$ and after ozonization	2,400	5,000	2.10

Oxidative chain scission by ozone oxidation followed by GPC analysis shows that the distribution of internal bonds in the oxidized macromolecules differ for the oxidation experiments studied (Table



I). In the presence of hydroperoxy groups, an ozonization reaction cannot give a definite account of the distribution of internal double bonds because a β -scission process^{26,27} may occur simultaneously with decomposition of the ozonides.²⁸

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