

Influence of the Experimental Conditions on the Photooxidation of Poly(vinyl chloride)

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SYNOPSIS

The photooxidation of poly(vinyl chloride) involves complex reactions in which photooxidation and photodiscoloration by the formation of polyenes compete. These reactions are now fairly well understood, and on the basis of the mechanisms formerly reported, it appears possible to investigate the influence of irradiation parameters such as the thickness of the samples, the temperature, or the external pressure of oxygen. This objective requires the distribution of the photoproducts through the irradiated polymer matrix to be analyzed at the microscopic level. The shapes of the profiles that are determined show that the overall behavior of the polymer results from oxygen-starvation effects. The diffusion of oxygen controls the rate of the photooxidation of the matrix, the rate of the photooxidative bleaching of the polyenes, and the rate of absorption of the light by the residual polyenes that have not been oxidized. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The photooxidation of poly(vinyl chloride) is known to cause a detrimental discoloration of the exposed materials. The reasons for this evolution have been studied, and the overall process that leads to this discoloration can be considered as fairly well understood: The discoloration is attributed to the formation of polyenic sequences with different lengths of conjugation, some of them being oxidized.¹⁻³ Former investigations concerning the mechanism of their formation have shown that these polyenes were formed by a multistep photochemical reaction.⁴ Consequently, the distribution of these polyenes following their conjugation length is dependent on the spectral distribution of the light source.⁵ It has been shown that once formed the polyenes were readily photooxidized,^{6,7} which provoked a deconjugation of the polyenic sequences and led to a photobleaching. The overall discoloration observed when poly(vinyl chloride) is photooxidized is then the result of the competition between a photodis-

coloration (by formation of polyenes from a non-oxidative photochemical reaction) and a photobleaching (by photooxidation of these polyenes).

Obviously, it is anticipated that among the many parameters that control the extent of the discoloration, the rate of photooxidation of the polyenes is of prime importance. Since poly(vinyl chloride) is not very permeable to oxygen, oxygen starvation effects are expected to occur and, then, the photooxidation of the polyenes to be controlled by the oxygen diffusion. Results reported formerly⁸ have shown that severe diffusion limitations were observed on the photooxidation of poly(vinyl chloride) measured by the formation of IR-absorbing photoproducts. These photoproducts that are detected by their IR absorption result from an oxidation of the polymer matrix itself and are formed in a relatively important concentration. On the contrary, the polyenes and their oxidation products are formed in very low concentrations that are not detected by IR spectroscopy, and, therefore, no direct experimental evidence of the control of the photooxidation of polyenes by the physical diffusion of molecular oxygen has been published.

The aim of this paper is to study the link between the distribution of the residual polyenes and the ox-

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idation photoproducts, on the basis of the mechanisms formerly proposed. This paper reports on measurements of the distribution of the photoproducts by micro (FTIR) spectroscopy or by analysis of multilayer samples irradiated in conditions of accelerated artificial aging. The influence of the pressure of oxygen on both the photooxidation and the discoloration of poly(vinyl chloride) is also reported.

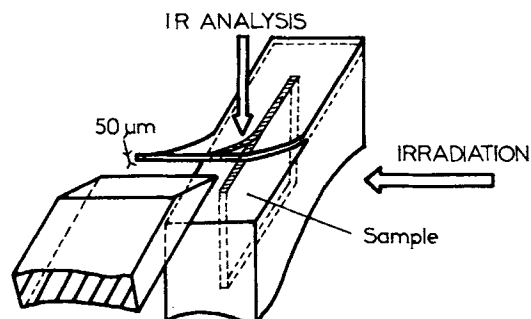
EXPERIMENTAL

Commercial poly(vinyl chloride) powder (Lucovyl BB 9010 obtained by mass polymerization) was supplied by ATOCHEM-France. The powder was purified by CHCl_3 (Uvasol, Merck) extraction and approximately 1% of a dibutylmaleate stabilizer (Irgastab T9) was mixed with the powder. The powder blend was finally pressed into thin films at 20 bars and 190°C for 45 s. The films so obtained were extracted by CHCl_3 to eliminate the stabilizer and were then irradiated.

The studies of the spatial distribution of the oxidation photoproducts have been realized on samples irradiated in accelerated photoaging units SEPAP 12-24 and SEPAP 30-24 at temperatures, respectively, of 60 and 35°C . These apparatus have been described formerly (see, e.g., Refs. 9 and 10). They are equipped with medium-pressure mercury lamps filtered by a Pyrex envelope. Although the designs of the units are different, the irradiated samples receive the same light intensities, and it has been determined that at the same temperature of irradiation the rate of evolution of standard samples are identical in both units.

A special apparatus has been designed to study the influence of the oxygen pressure: The PVC sample is set in a Pyrex tube located at one focal axis of an elliptic reactor. A medium-pressure mercury lamp (similar to those used in the SEPAP units) is set at the second focal axis of the reactor. The temperature of the sample is measured and regulated by a thermocouple in contact with the surface of the sample. At first, vacuum is made in the Pyrex tube and then oxygen is introduced. A manometric tube permits one to measure and to keep constant the pressure during irradiation.

UV-visible absorption spectra were recorded with a Perkin-Elmer UV 554 equipped with an integrating sphere. Micro(FTIR) spectrophotometric measurements were carried out following a procedure formerly described.¹¹ This procedure can be briefly described as follows: After irradiation, the sample was embedded in an epoxy resin and the whole sys-



Scheme 1 Principle for analyzing thin films using micro(FTIR) spectrophotometry.

tem was sliced with a Reichert and Jung microtome. A film with a thickness of approximately 50 microns was obtained and was examined through a Spectroscope (Spectra-Tech) IR microscope (see Scheme 1). Using this technique, the distributions of the photoproducts can be directly measured with a fairly good accuracy.

The IR microscope was attached to an FTIR spectrophotometer Nicolet 5 SX. IR spectra of the multilayers samples were recorded either with the Nicolet 5 SX or with a Nicolet 20 SX.

RESULTS

Determination of the Concentration Profiles by MicroFTIR Spectroscopy

Several films with a constant thickness of 385 microns were exposed in the SEPAP 12-24 unit (temperature 60°C) for various irradiation times from 10 to 76 h. The rear side of the films were masked with absorbing cardboards. After irradiation, the samples were sliced following the experimental procedures described above, and thin films with a thickness around 50 microns were obtained and analyzed by microFTIR spectroscopy. IR spectra were recorded every 14 microns in the external layers and every 30 microns in the core of the samples. The evolutions of absorbance measured at 1718 cm^{-1} were then measured and plotted against the deepness at which the spectra were recorded. Figure 1 shows the curves that were obtained for the five samples so analyzed. It is observed in the figure that the oxidation photoproducts were localized in the front and back surfaces while almost no oxidation was detected in the core of the sample. Even for the longest irradiation times, only the external layers revealed the presence of oxidation photoproducts. Moreover, it has to be noted that the profiles were

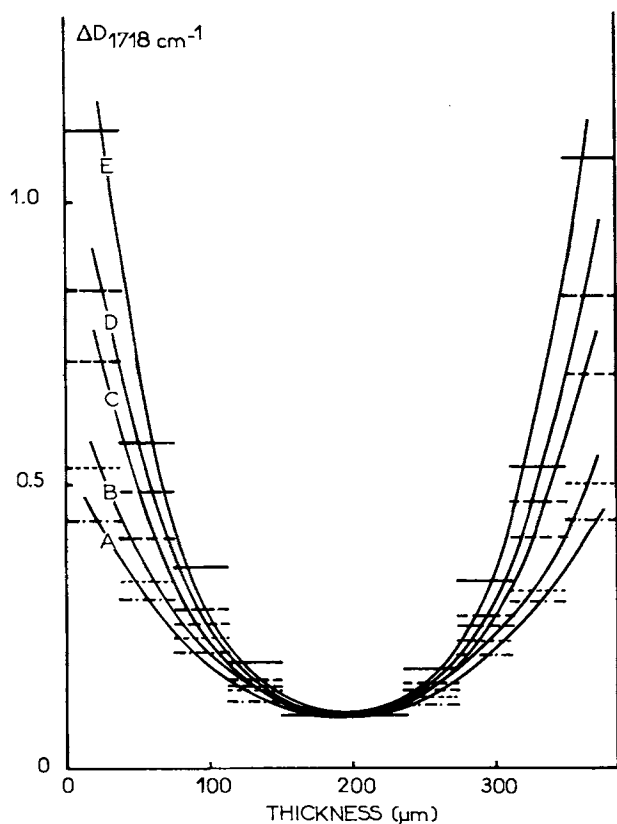


Figure 1 Evolutions of the oxidation profiles $\Delta DO_{1718\text{cm}^{-1}}$ of films exposed in the SEPAP 12-24 unit (temperature 60°C) for (a) 10 h, (b) 24 h, (c) 45 h, (d) 64 h, and (e) 76 h.

symmetrical for the short irradiation times but tended to become unsymmetrical for longer irradiation times: The irradiated front layers revealed, then, a more important concentration of oxidation photoproducts.

Determination of the Concentration Profiles by the "Multilayers" Method

The microFTIR spectroscopy permits measurement of the oxidation photoproducts formed in very small areas with a width of approximately 14 microns. Since no similar analytical method was available to measure the UV-visible absorption of the polyenes formed in such small areas, "multilayers" samples were irradiated. These samples were formed by several films placed in close contact side by side to prevent oxygen from diffusing between the different films. After irradiation, the films were peeled off and analyzed separately by UV-visible or IR transmission. The thickness of the different films was optimized to ensure an easy unsticking after irradiation.

A thickness of 125 microns was chosen and five films were placed carefully side by side to minimize the diffusion of oxygen between the sandwich layers. A sample with a total thickness of 625 microns was obtained.

The samples were irradiated in the two accelerated photoaging units, SEPAP 12-24 and SEPAP 14-24, that give similar intensities but permit one to carry out irradiations at different temperatures (60 and 35°C , respectively, for the 12-24 and 14-24 units).

Figure 2 shows the evolutions of absorbance at 1718 cm^{-1} for each film composing the multilayers samples exposed at 60°C in the SEPAP 12-24 unit. The samples were irradiated for 10, 20, 30, 40, and 56 h. It is observed that in these experimental conditions the oxidation occurred mainly in the front layers. The core and rear layers of the sample remained not very oxidized even for the longest irradiation time.

Similar experiments were carried out in the SEPAP 14-24 unit at 35°C and the results are shown

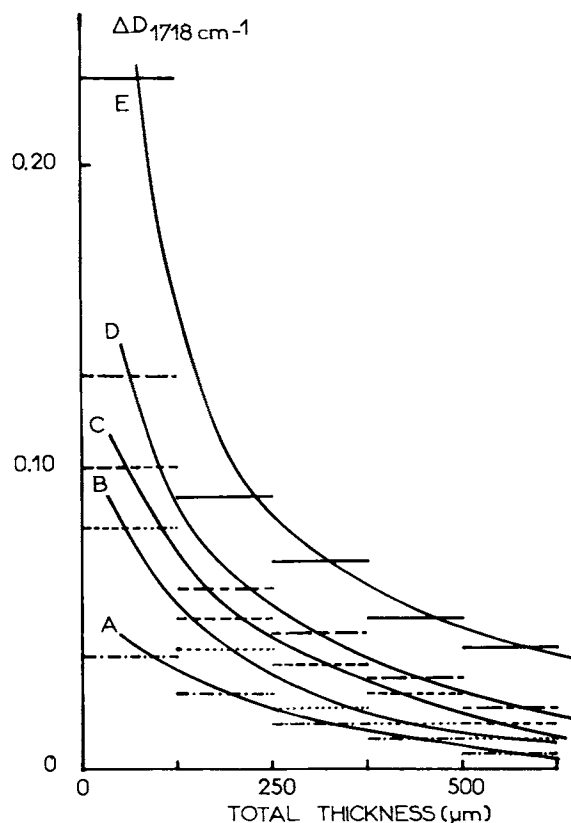


Figure 2 Evolutions of the oxidation profiles $\Delta DO_{1718\text{cm}^{-1}}$ of multilayer samples exposed in the SEPAP 12-24 unit (temperature 60°C) for (a) 10 h, (b) 20 h, (c) 30 h, (d) 40 h, and (e) 56 h.

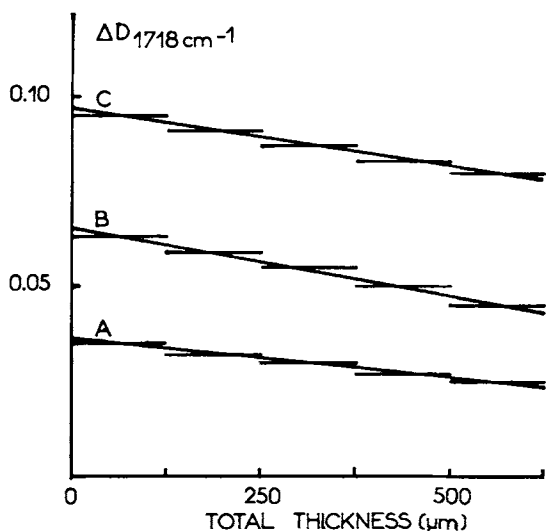


Figure 3 Evolutions of the oxidation profiles $\Delta DO_{1718\text{cm}^{-1}}$ of multilayer samples exposed in the SEPAP 12-24 unit (temperature 35°C) for (a) 68 h, (b) 120 h, and (c) 146 h.

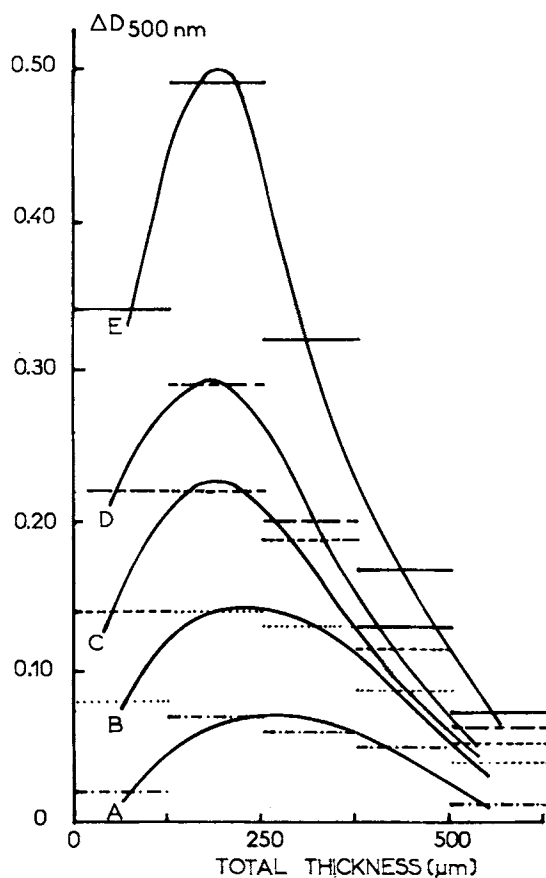


Figure 4 Evolutions of the absorbance at 400 nm of multilayer samples exposed in the SEPAP 12-24 unit (temperature 60°C) for (a) 10 h, (b) 20 h, (c) 30 h, (d) 40 h, and (e) 56 h.

on Figure 3. Since the temperature during irradiation was lower, longer irradiation times were required. Irradiations were performed for 68, 120, and 146 h, respectively. The shapes of the curves shown in Figure 3 are totally different: Quasi-linear variations were observed and the concentration gradients of the photooxidation products were not very pronounced.

As pointed out above, irradiation of multilayered samples were carried out to measure the distribution of the polyenes that could not be performed by other spectrophotometric methods. This distribution can be characterized by measuring the evolution of absorbance at 500 nm for each film making up the sample. Figure 4 shows the variations of optical density at 500 nm for the multilayered samples irradiated in the SEPAP 12-24 unit at 60°C in the same conditions as described above. For the lowest irradiation time, a symmetrical profile was observed: On the first and last films, almost no evolution of the absorbance at 500 nm was observed, whereas in the subsequent films, a weak increase of absorbance was measured. For higher irradiation times, a marked deformation of the shape of the profiles was observed: At the rear of the sample, no more significant increase of the absorbance was noticed, whereas an increase of absorbance was observed in

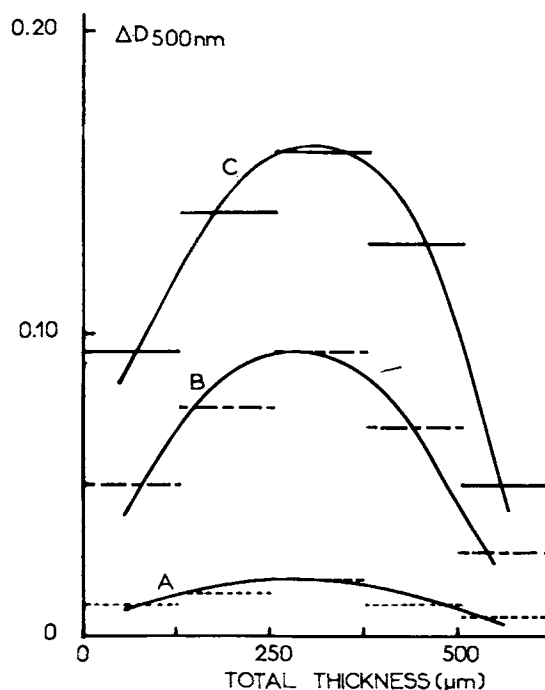


Figure 5 Evolutions of the absorbance at 400 nm of multilayer samples exposed in the SEPAP 14-24 unit (temperature 35°C) for (a) 68 h, (b) 120 h, and (c) 146 h.

the first film forming the multilayered sample and mainly in the films at the core of the sample. Moreover, the maximum of absorbance moved from the middle of the sample toward the front layers.

As shown in Figure 5, the results obtained for irradiations carried out in the SEPAP 30-24 unit at 35°C were slightly different: The difference in absorbance between the maximum observed in the core of the sample and the minima in the surface layers was smaller, and then the profiles appeared less pronounced.

Influence of the Oxygen Pressure

Poly(vinyl chloride) films with a thickness of 100 microns were irradiated under oxygen pressure

varying from 0 mm to 700 mmHg. The evolutions of the UV-visible and IR spectra were recorded for each condition of pressure, as a function of the irradiation times. Figures 6(a)-(d) show the evolutions of the UV-visible spectra for oxygen pressures of 0, 150, 400, and 750 mmHg, respectively. In Figure 6(a), the usual behavior of poly(vinyl chloride) irradiated in the absence of oxygen on polychromatic light is observed: The evolution that is observed corresponds to the formation and accumulation of polyenic sequences, $-(CH=CH)_n-$, with different lengths of conjugation. They correspond to the different maxima observed on the spectrum. Respective values of $n = 3, 4, 5, 7, 8,$ and 9 have been attributed to the absorption maxima at 286, 312, 328, 368, 394, and 421 nm.¹² When oxygen is present

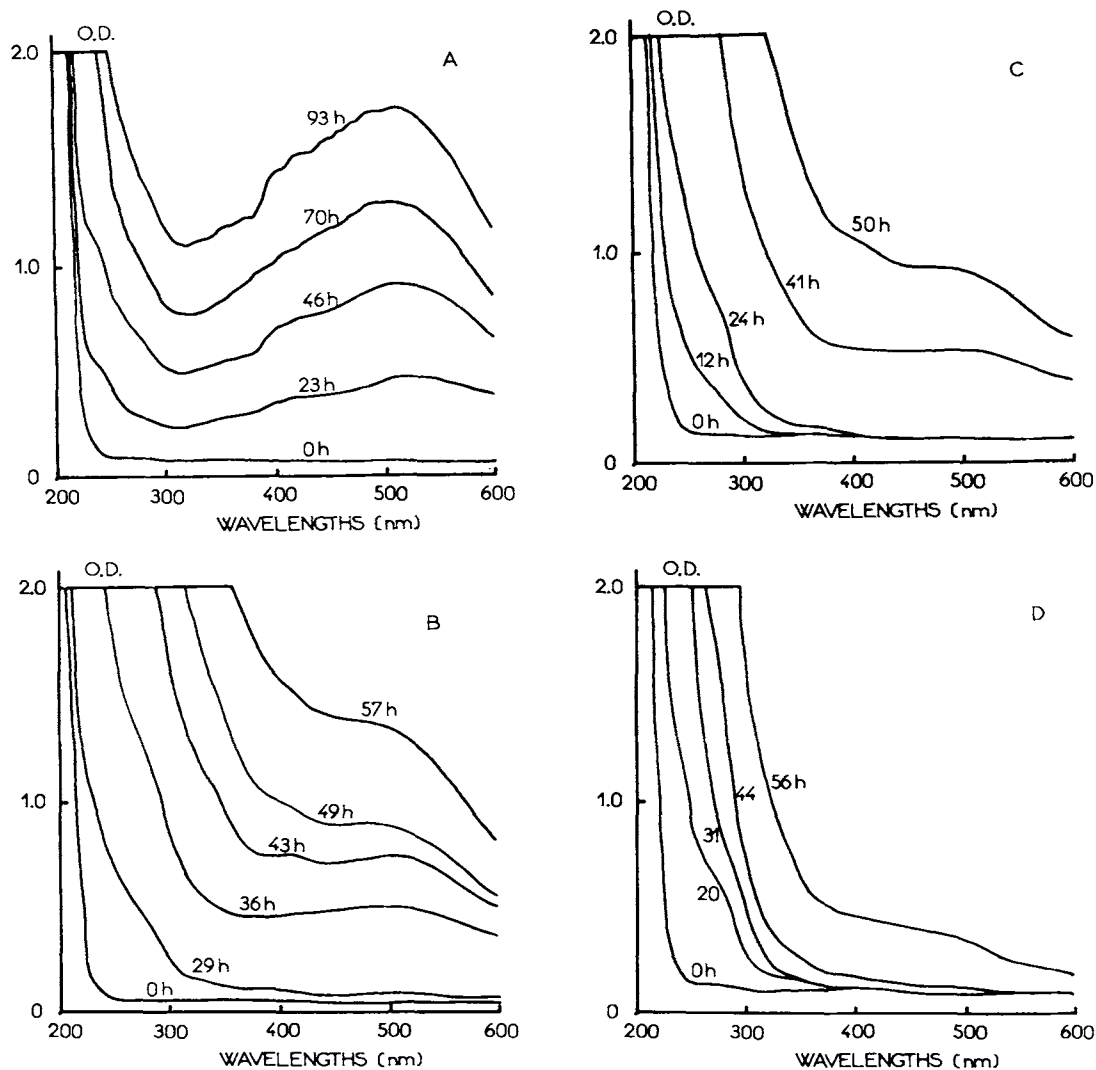


Figure 6 Evolutions of the UV-visible spectra of poly(vinyl chloride) films (thickness 100 microns) irradiated under various oxygen pressures: (a) in vacuum; (b) $PO_2 = 150$ mmHg; (c) $PO_2 = 400$ mmHg; (d) $PO_2 = 700$ mmHg.

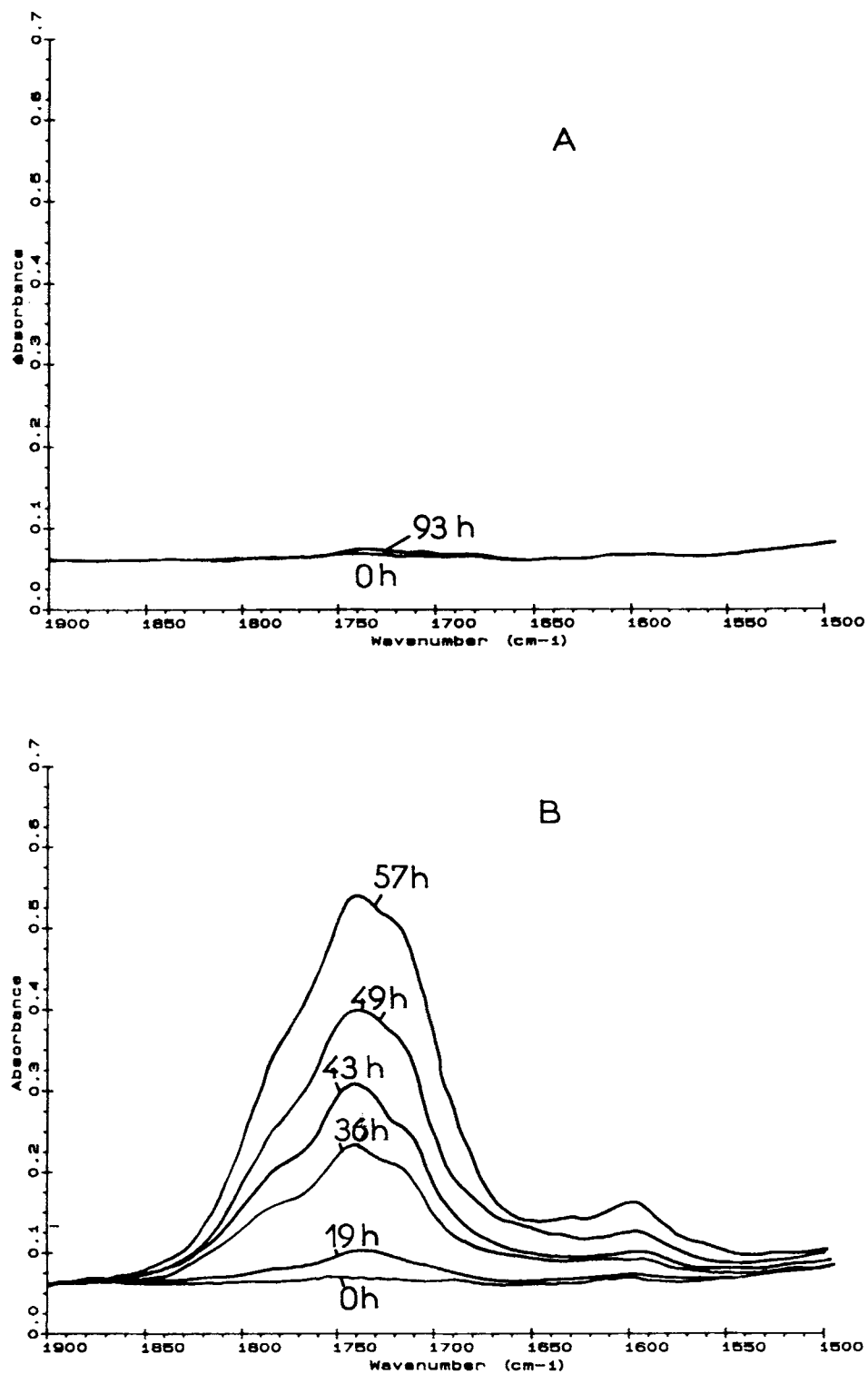


Figure 7 Evolutions of the IR spectra of poly(vinyl chloride) films (thickness 100 microns) irradiated under various oxygen pressures: (a) in vacuum; (b) PO₂ = 150 mmHg; (c) PO₂ = 400 mmHg; (d) PO₂ = 700 mmHg.

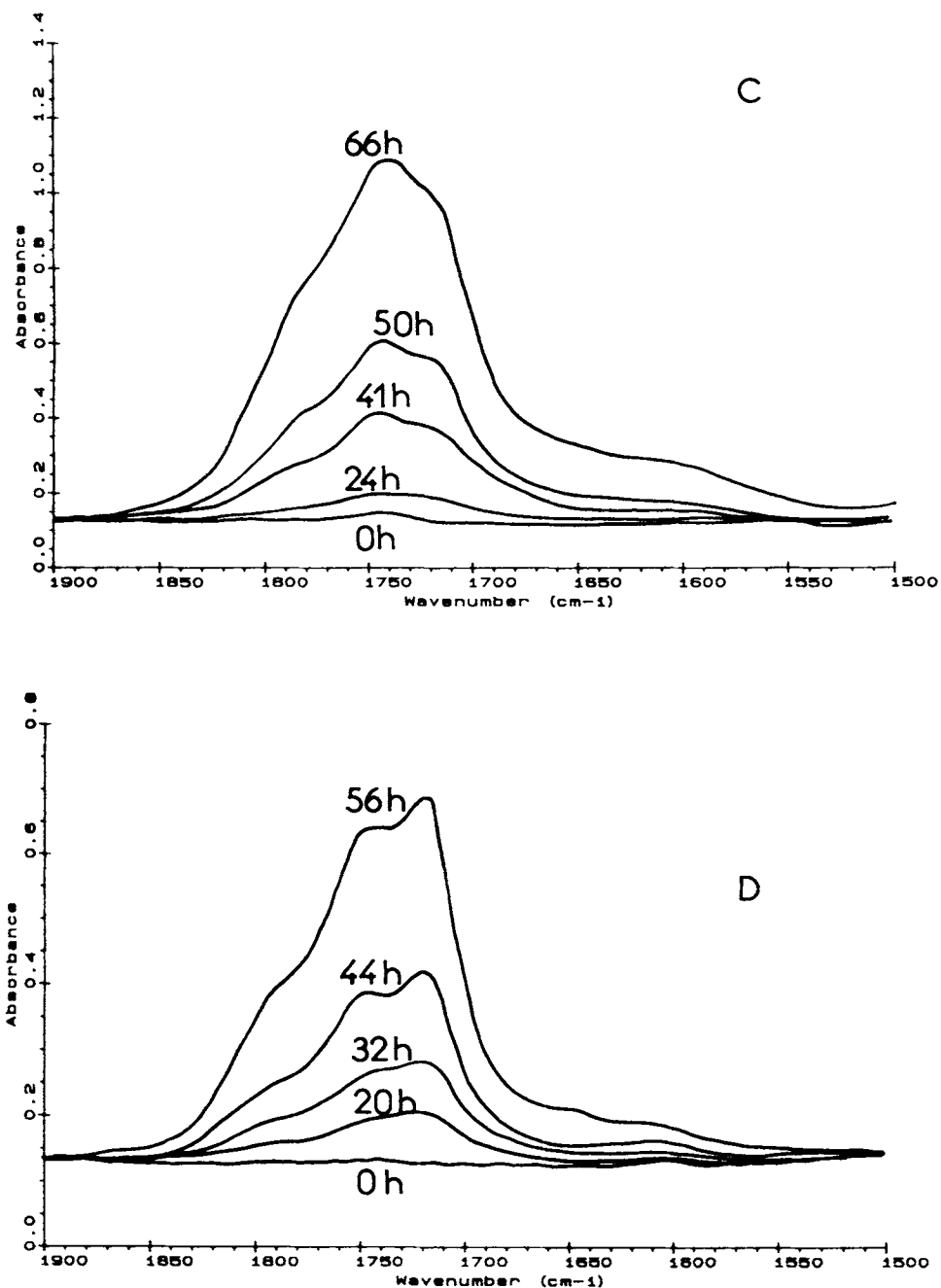


Figure 7 (continued from the previous page)

in the reactor at a pressure of 150 mmHg, the evolution of the spectra is rather different, as shown on Figure 6(b). The broad band between 380 and 600 nm is no longer observed distinctly, and the front of initial absorption moves toward the longer wavelengths. When the oxygen pressure increases [Fig. 6(c) and (d)], both evolutions become more and more important, and for the highest pressure (700 mmHg), the only effect observed is a shift of the

absorption front; the broad band in the visible range of the spectrum has almost disappeared.

The IR spectra of the samples on irradiation were also recorded. At first, it was determined that the spectra of the sample irradiated in vacuum showed no evolution [Fig. 7(a)]. The spectra of the samples irradiated under oxygen pressures of 150, 400, and 700 mmHg are presented in Figures 7(b)–(d). It is observed in these figures that the shapes of the car-

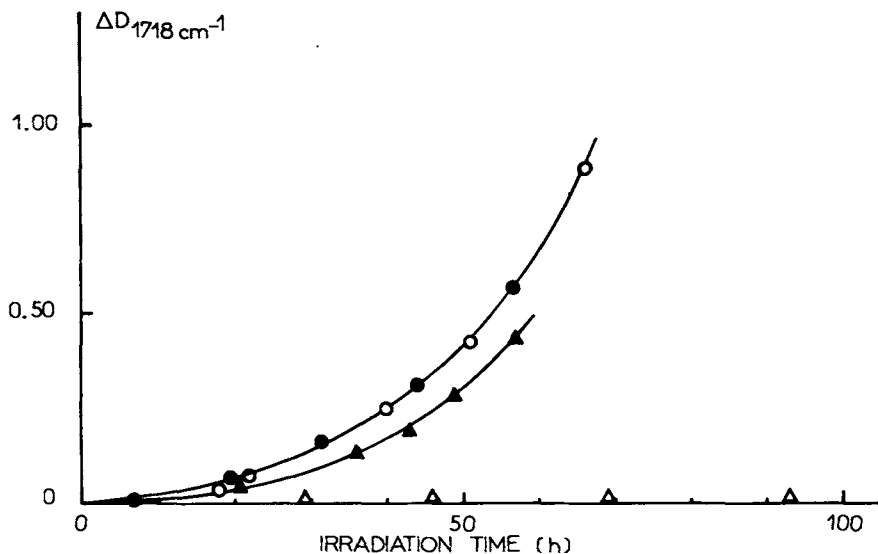


Figure 9 Variations of absorbance at 1718 cm^{-1} vs. irradiation time of poly(vinyl chloride) samples irradiated under various oxygen pressures: (Δ) in vacuum; (\blacktriangle) $\text{PO}_2 = 150\text{ mmHg}$; (\circ) $\text{PO}_2 = 400\text{ mmHg}$; (\bullet) $\text{PO}_2 = 700\text{ mmHg}$.

whereas the sources with a spectrum closest to the solar spectrum (xenon and mercury medium-high pressure sources) permit the formation of the whole range of polyenes.

The polyenic sequences are highly absorbing in the UV-visible range and are responsible for a marked discoloration. In the presence of oxygen, these polyenes are readily photooxidized. Their ox-

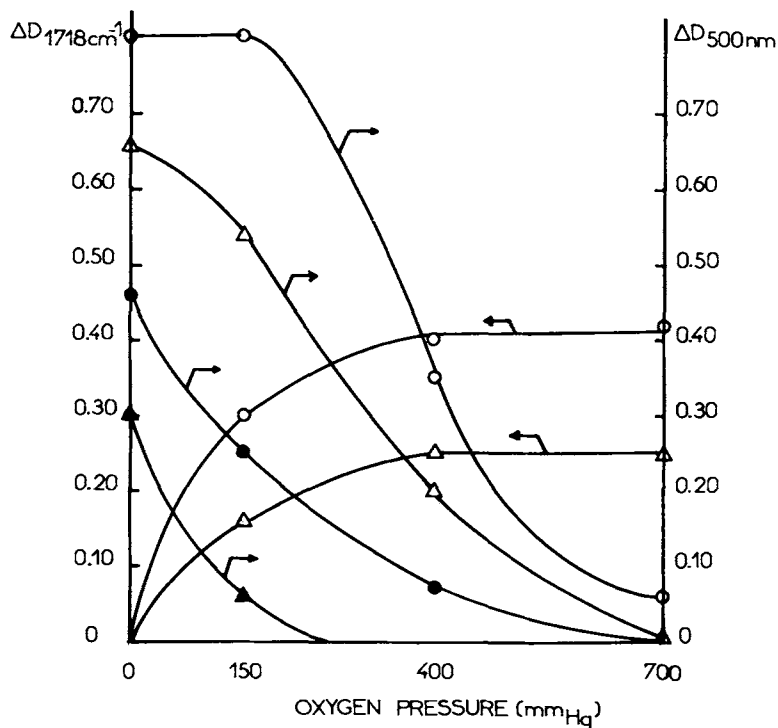
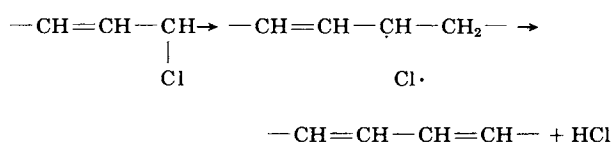


Figure 10 Variations of absorbance at 1718 cm^{-1} and 500 nm vs. oxygen pressure of poly(vinyl chloride) samples irradiated for (Δ) 20 h, (\bullet) 30 h, (\blacktriangle) 40 h, and (\circ) 50 h.

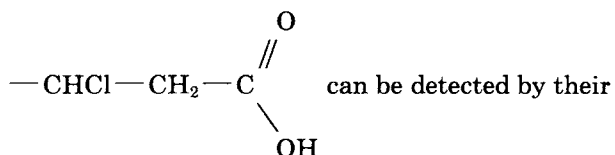
idation photoproducts absorb at shorter wavelengths since the photooxidation leads to a deconjugation of the system. As the extinction coefficients of the polyenes decrease drastically when the conjugation length is shortened, the photooxidation leads to an efficient photobleaching. The oxidation photoproducts of the polyenes accumulate in the polymer matrix and they are responsible for the UV absorption that corresponds to the shift of the initial absorption front toward the longer wavelengths.

The photochemical reactions that lead to the formation of polyenes involves the photolysis of C—Cl bonds next to the double bonds. Chlorine radicals, Cl·, that are obtained can abstract a hydrogen atom on the neighboring carbon:



An extension of the length of conjugation is obtained and hydrochloric acid is formed.

Chlorine radicals can also escape from the immediate surroundings, react with the “normal” structures, —CH₂CHCl—, and induce in the presence of oxygen the chain oxidation reaction of the matrix. The photoproducts have been identified¹³ and among them carboxylic acids with the structure



IR absorption at 1718 cm⁻¹ and used to follow the extent of the photooxidation.

It was shown previously that on irradiation in conditions of medium-accelerated photoaging of rigid PVC films the photooxidation rate became invariant for thicknesses higher than 100 microns. The determination of the oxidation photoproducts profiles of films with a thickness of 385 microns shows, indeed, a heterogeneous distribution of these photoproducts. This distribution is characterized by a one-dimensional gradient along the incident light axis. At this thickness level of 385 microns, and in these conditions of irradiations, oxygen diffusion is then the rate-controlling process. The shape of the profiles observed for the earliest irradiation times is nearly symmetrical. This result is in accordance with the models based on the general theory of Fick's laws and the profiles correspond to the Fickian diffusion profile of oxygen reported in the litera-

ture.¹⁴⁻¹⁸ Only the front and back surfaces where oxygen can diffuse are photooxidized. The oxidation concerns approximately the first 150 microns near the external surfaces of the sample, and practically no oxidation is detected in the bulk. When the irradiation time increases, the oxidation profiles tend to become unsymmetrical. This behavior results from the fact that in the bulk that remains unoxidized the polyenic sequences formed by a purely photolytic process can accumulate. This leads to the formation of a light-absorbing layer that prevents the light from reaching the back layers of the sample. The decrease in the rate of photooxidation in these layers is then the result of a decrease in the absorbed light intensity.

It appears then that two effects are conjugated, i.e., the control of the photooxidation rate by oxygen diffusion and the control of the photooxidation rate by the rate of light absorption. As a consequence, the shapes of the oxidation profiles will be totally dependent on the thickness of the exposed samples. For samples with a thickness of 625 microns, only the layers corresponding approximately to the first 150 microns near the front surface of the sample are oxidized and the concentration of the oxidation photoproducts decreases very fast from the front to the core of the samples. The fact that the rear layers of the sample remain unoxidized results from the screen effect played by the polyenes that can accumulate to an important concentration as diffusion of oxygen toward the core of the sample becomes more and more difficult when the thickness increases.

The shape of the profiles is deeply modified when the temperature of the samples during irradiation decreases from 60 to 35°C. The decrease in the temperature is responsible for a decrease in the rate of photooxidation (activation energy for PVC photooxidation has been formerly evaluated to 12–15 kcal mol⁻¹). The thickness of the photooxidized layer increases. The polyenic sequences can be oxidized even in the core of the sample, but as shown in Figure 5, the oxidation is not complete and a low concentration may be observed in the core layers. The screen effect played by these polyenes remains low, which permits the photoproducts to be formed quasi-homogeneously in the bulk of the sample.

Among the different experimental parameters that influence the photooxidative behavior of PVC, the external oxygen pressure during irradiation has an important effect on the competition between photooxidation and photolysis. The fate of the polyenic sequences obtained by photolysis is directly dependent on the concentration of oxygen in the poly-

mer matrix. At high oxygen pressures, an efficient oxidative photobleaching occurs and the evolution of the UV spectra of exposed samples has to be attributed to the accumulation of the photoproducts of oxidation of polyenes that absorb at short wavelengths. For irradiations in vacuum, the accumulation of polyenic sequences with different lengths of conjugation can occur. When the oxygen pressure varies from 0 to 700 mmHg, a progressive shift between these two cases is observed and the corresponding deformation of the UV-visible spectra is recorded.

From a kinetic point of view, it is observed that the rate of formation of the polyenic sequences is almost linear for irradiations in vacuum. This is the result of two antagonist behaviors: Since the fraction of light absorbed by the system increases, as a result of the accumulation of the polyenes, the rate of the photochemical reactions increases. However, this effect is compensated by the decrease of the path length of the photochemical reactor, since the absorption becomes more superficial.

When irradiations are carried out in the presence of oxygen, an induction period is observed. This induction time results from an efficient bleaching of the polyenes by photooxidation. The induction time increases significantly with the concentration of oxygen, i.e., with the oxygen pressure.

The rate of oxidation measured by the accumulation of the photoproducts at 1718 cm^{-1} becomes practically independent of the concentration of oxygen for pressures above 400 mmHg. The evolutions of the IR spectra in the carbonyl domain show that a different evolution of the relative concentration of oxidation photoproducts occurs when the pressure of oxygen increases. A similar evolution of the oxidation stoichiometries is observed currently with other polymers in conditions of photooxidation at various oxygen pressures (e.g., polypropylene, polyethylene) but no explanation has yet been given.

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