Anal. Calcd for $WC_{49}H_{72}O_3$: C, 65.91; H, 8.13. Found: C, 65.88; H, 8.08.

Acknowledgment. R.R.S. thanks the National Science Foundation for support through Grant DMR 84-17818. We thank Prof. R. E. Cohen for helpful discussions and for use of equipment.

Registry No. $W_2(O\text{-}t\text{-}Bu)_6$, 57125-20-9; $Mo(CPr)(O\text{-}t\text{-}Bu)_3$, 91780-93-7; $W(C\text{-}t\text{-}Bu)(DIPP)_3$, 91229-76-4; $W(CEt)(O\text{-}t\text{-}Bu)_3$, 82228-88-4; $(t\text{-}BuO)_3W{\equiv}C(CH_2)_6C{\equiv}W(O\text{-}t\text{-}Bu)_3$, 119272-25-2; $(t\text{-}BuO)_3W{\equiv}C(CH_2)_5C{\equiv}W(O\text{-}t\text{-}Bu)_3$, 119272-26-3; $(t\text{-}BuO)_3W{\equiv}C(CH_2)_4C{\equiv}W(O\text{-}t\text{-}Bu)_3$, 119272-27-4; $(t\text{-}BuO)_3W{\equiv}C(CH_2)_2C{\equiv}W(O\text{-}t\text{-}Bu)_3$, 119272-28-5; $(t\text{-}BuO)_3Mo{\equiv}C(CH_2)_2C{\equiv}Mo(O\text{-}t\text{-}Bu)_3$, 119272-29-6; $W[C(t\text{-}Bu)C(CH_2)_6C][O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2]_3$, 119272-30-9; $Mo(C\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_3$, 82209-30-1; polycyclooctyne, 106989-28-0; cyclooctyne, 1781-78-8; 2,10-dodecadiyne, 31699-38-4; 1,9-cyclohexadecadiyne, 1697-71-8; 1,8-cyclotetradecadiyne, 1540-80-3; 2,8-decadiyne, 4116-93-2; 2,6-octadiyne, 764-73-8; 1,5-hexadiyne, 628-16-0.

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Photooxidation of Poly(vinyl chloride). 1. A Reexamination of the Mechanism

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Received April 14, 1988; Revised Manuscript Received December 5, 1988

ABSTRACT: Oxidation photoproducts formed by irradiation of poly(vinyl chloride) in the presence of air were investigated by FTIR spectroscopy. Specific chemical treatments were developed in order to identify the photoproducts. It was shown that only a few compounds were formed, including hydroperoxides, chlorinated ketones, acid chlorides, and carboxylic acids. A general scheme accounting for the mechanism of photooxidation of poly(vinyl chloride) is proposed.

Introduction

Despite the large number of papers dealing with the photodegradation of poly(vinyl chloride), it remains true that the carbonylated photoproducts observed by IR spectroscopy of aged films have not been totally identified. As a consequence, the mechanism of photooxidation is not established. In contrast, the initiation step involving absorption of light by poly(vinyl chloride) (PVC) has been extensively investigated. Even if some disagreement still exists concerning the nature of the absorbing chromophores responsible for the initiation step,[1] good potential candidates are postulated, for example, α-chlorinated short conjugated polyenes.[2,3]

The nature of the photoproducts responsible for the discoloration of PVC exposed to UV light has also been determined, and it is unambiguously agreed that the growing polyene sequences resulting from the well-known dehydrochlorination of poly(vinyl chloride) cause this discoloration. The length of these polyenes is readily characterized by UV spectrometry.[4] The quantum yield of dehydrochlorination has been measured by Decker and was evaluated as $\Phi_{HCl} = 0.11$.[5] This author pointed out that the catalytic effect of HCl could be questioned and showed that the initially autoaccelerated shape of the kinetic curves of photodehydrochlorination of PVC was in fact the result of an increase in UV absorption resulting from the growth of the polyene sequences. This experimental observation was considered to be a strong argument in favor of an alkene-sensitized initiation process. As a matter of fact, we have proposed more recently[6] that the photodehydrochlorination of PVC involved a "multistep" excitation of polyene sequences. Each excitation leads to an increase of the length of conjugation:

$$—(CH{=}CH)_nCH(Cl)CH_2— \xrightarrow{h\nu} [—(CH{=}CH)_n\dot{C}HCH_2— + Cl^\bullet]$$

$$[—(CH{=}CH)_n\dot{C}HCH_2— + Cl^\bullet] \rightarrow —(CH{=}CH)_{n+1}— + HCl$$

Some of the chlorine atoms, $Cl^\bullet$, can escape from the immediate surroundings and initiate an oxidation chain:

$$[—(CH{=}CH)_n\dot{C}HCH_2— + Cl^\bullet] \rightarrow [—(CH{=}CH)_n\dot{C}H—] + Cl^\bullet$$

$$Cl^\bullet + —CH_2CHCl— \xrightarrow{O_2} \text{oxidation chain}$$

In the presence of oxygen, several photoproducts are obtained which are easily detected by their IR absorption. Difficulties in identifying the many potential photoproducts that appear in a composite carbonyl band centered around 1745 cm^{-1} are probably the reason for the lack of information concerning the nature of oxidation photoproducts. Many possible candidates have been postulated, among them α- and β-chlorocarboxylic acids,[7] α-[8] and β-chloro ketones, aliphatic aldehydes,[8] acid chlorides,[7] peracids,[9] and lactones.[10] Only a few of them can be considered as definitively identified, as we will emphasize later on.

Another reason for the lack of complete understanding arises from difficulties in controlling the oxygen saturation in PVC samples during irradiation. As a consequence of the low permeability of PVC to oxygen, PVC films of thickness greater than 100 μm are easily converted into complex systems in which photooxidation occurs in the first layers and photolysis proceeds in the core of the matrix.[11]

This paper presents data on the photoproducts obtained during photooxidation of rigid poly(vinyl chloride) studied in the form of thin films by means of IR absorption spectroscopy. A mechanism accounting for the photooxidation is proposed.

Experimental Section

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 dibutyltin maleate stabilizer (Irgastab T9) was mixed with the powder. The powder blend was finally pressed into thin films ($\approx$100 μm) at 20 bar and 190 °C for 45 s. The films so obtained were extracted with $CHCl_3$ in order to eliminate the stabilizer and then exposed to photodegradation. The absence of residual stabilizer was checked by UV and IR spectroscopy.

Irradiations were carried out in SEPAP 12.24 and SEPAP 12.24H units at a temperature of 60 °C. These units have been described in many papers (see, for example, ref 12–14). They allow irradiation at wavelengths above 300 nm in "dry" conditions (12.24) or in oxygenated water (12.24H).

UV–vis absorption spectra were recorded by using a Perkin-Elmer UV 554 equipped with an integrating sphere. Fourier transform IR (FTIR) spectra were recorded with either a Nicolet 20 SX or a Nicolet 5 SX spectrometer. Standard deconvolution programs were used (Bessel-type approximation).

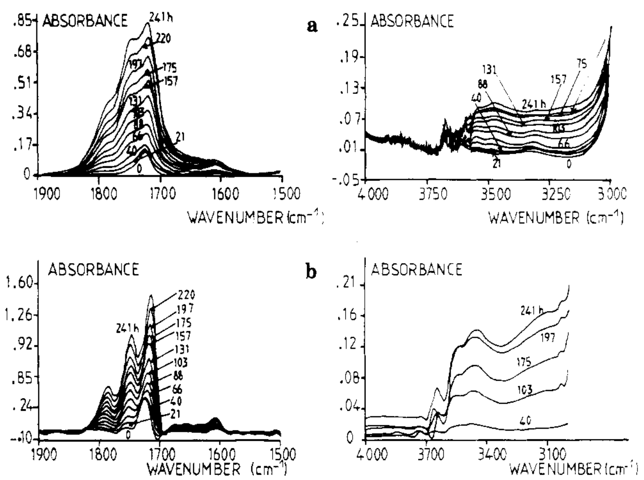


Figure 1. Development of IR spectra of poly(vinyl chloride) films in 4000–2800- and 1900–1500-cm^{-1} regions during SEPAP 12.24 irradiations: (a) direct spectra; (b) deconvoluted spectra.

Photoproducts can also be identified from in situ chemical treatments carried out in the matrix: for ammonia treatment, irradiated samples were suspended above a solution of pure ammonia. For treatments with diethylmethylamine, a solution of the amine in $CHCl_3$ (50%) was used. Solutions at 50% (volume) in $CHCl_3$ of NaOH (0.2 mol L^{-1} in MeOH) and H_2SO_4 (0.2 mol L^{-1} in MeOH) were used for other treatments. All these reactions were carried out at room temperature.

Hydroperoxide titrations were conducted by using SO_2 and ferrous ion methods described elsewhere.[15]

Treatment by water was conducted with photooxidized PVC films immersed for 17 h in hot water (55 °C).

Results and Discussion

Exposure of poly(vinyl chloride) films to UV light (>300 nm) led to development of IR bands in the hydroxyl and the carbonyl region: a very broad hydroxyl band developed between 3600 and 2800 cm^{-1} with a maximum at 3460 cm^{-1}, and a complex band developed around 1745 cm^{-1} (Figure 1a). Two maxima were observed at 1718 and 1745 cm^{-1} and a shoulder at 1780–1810 cm^{-1} (Figure 1b). Two maxima were observed in this shoulder. Their positions were determined by a deconvolution technique, and the corresponding wavenumbers were 1800 and 1785 cm^{-1} (Figure 1b). In fact, the product at 1800 cm^{-1} appeared first, but as the oxidation progressed, the photoproduct at 1785 cm^{-1} became predominant, and the product at 1800 cm^{-1} was no longer observed. The bands at 1718, 1745, and 1785 cm^{-1} increased simultaneously, and the rate of formation of the corresponding photoproducts presented an autoaccelerating shape (Figure 2). This behavior, already described,[7] has been explained by Decker.[16]

The deconvolution technique allowed us to characterize the low absorption that developed in the 1710–1500-cm^{-1} range. The products corresponding to this absorption were not easily detected in the nondeconvoluted spectrum. Four maxima were observed at 1695, 1650, 1605, and 1580 cm^{-1}. Recent observations carried out at our laboratory on photooxidation of poly(vinylidene chloride) led us to attribute the maxima at 1650 and 1580 cm^{-1} to the vibrations of isolated and conjugated double bonds, 1650 and 1580 cm^{-1}, respectively. The photoproducts at 1695 and 1605 cm^{-1} appeared at very low concentrations. They could correspond to α,β conjugated ketones, whose formation was also suspected in thermal oxidation of PVC, presently under investigation at the laboratory.

Several photooxidized samples were treated with NH_3, Et_2NMe, and NaOH. Figure 3 shows the behavior of a

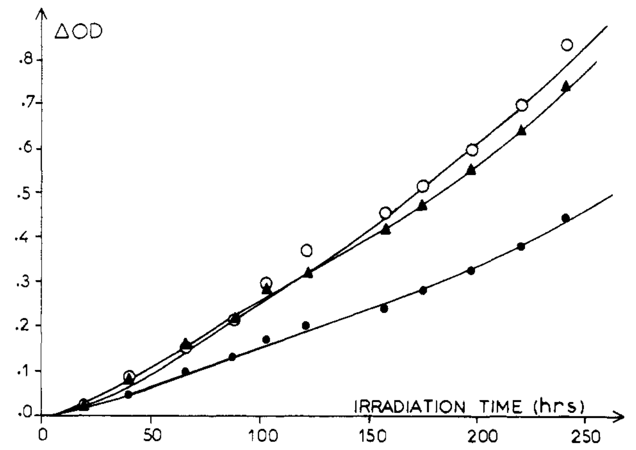


Figure 2. Development of carbonyl bands on exposure for PVC films on SEPAP 12.24 irradiation. Absorption measured at 1718 (○), 1745 (▲), and 1785 cm^{-1} (●).

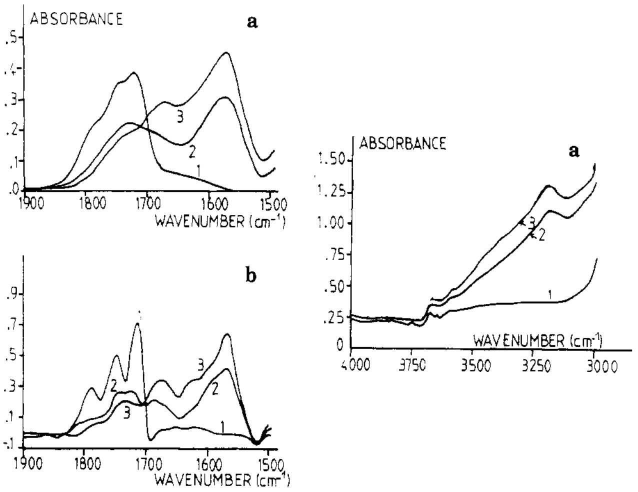
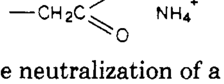


Figure 3. Influence of NH_3 treatment on infrared spectra (4000–2800 and 1900–1500 cm^{-1}) of films exposed for 70 h (curve 1) and then treated by NH_3 for 2 h (curve 2) and 17 h (curve 3): (a) direct spectrum; (b) deconvoluted spectrum.

sample photooxidized for 70 h and then treated with gaseous NH_3 for 17 h. The changes in the IR spectrum were recorded after several repetitions of this treatment until a stationary state was reached. The time of 17 h chosen to illustrate this experiment corresponded to this stationary state. A major decrease of the carbonyl band was observed which was concomitant with the development of a band around 1575 cm^{-1} (Figure 3a). Weak absorption bands appeared at 1685 and 1629 cm^{-1} (shoulder).

We had to use again the deconvolution technique formerly described for characterizing the decrease of the composite band around 1745 cm^{-1}. As shown in Figure 3b, the band at 1718 cm^{-1} was drastically reduced as well as the band at 1785 cm^{-1} (the photoproduct at 1800 cm^{-1} was no longer observed at this extent of the photooxidation reaction). In spite of the deconvolution, the bands at 1718 cm^{-1} and 1745 cm^{-1} were not totally separated, and the decrease of the band at 1718 cm^{-1} provoked a slight decrease of the band at 1745 cm^{-1}. In the hydroxyl region, the absorption increased, and a broad band peaking also at 3300 cm^{-1} was observed.

The absorption at 1575 cm^{-1} could be unambiguously attributed to a carboxylate ion of an ammonium salt:



$$-CH_2C\langle^{O^-}_{O}\quad NH_4^+$$

corresponding to the neutralization of a carboxyl group at 1718 cm^{-1}. The low absorptions 1685 and 1629 cm^{-1} were attributed to the formation of an amide (bands amide I and amide II, respectively) that would result from the reaction of an acid chloride and correspond to the decrease of the band at 1785 cm^{-1}. The absorption observed at 3300 cm^{-1} was attributed to the N–H stretching vibration of the secondary amide formed by the reaction with the acid chloride. The low decrease of the absorption at 1745 cm^{-1} attributed to an imperfect deconvolution could also indicate a reaction of the ketonic group with ammonia to form an imine group. However, no absorption band corresponding to this imine group was detected.

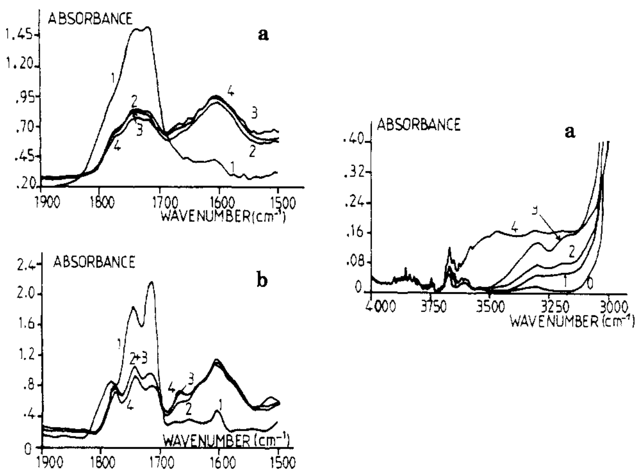


Figure 4. Influence of Et_2NMe treatment on infrared spectra (4000–2800 and 1900–1500 cm^{-1}) of films exposed for 251 h (curve 1) and then treated by Et_2NMe for 20 h (curve 2), 40 h (curve 3), and 80 h (curve 4): (a) direct spectrum; (b) deconvoluted spectrum.

Parts a and b of Figure 4 show the effect of treatment by Et_2NMe for 80 h. The development of a strong carboxylate band at 1580 cm^{-1} and a small amide band at 1668 cm^{-1} was concomitant with the decrease of the carbonyl band. (It may be noted that only one amide band was observed after treatment with the tertiary amine, opposite to the former treatment with ammonia, which led to the observation of two amide bands, I and II.)

Parts a and b of Figure 5 show the result of a treatment on preirradiated samples with a methanolic solution of sodium hydroxide for 4 h; the development of a carboxylate ion band was observed at 1590 cm^{-1}. After deconvolution of the carbonyl band, it was observed that the bands at 1718 and 1785 cm^{-1} had almost completely disappeared.

The effect of sulfuric acid on a sample treated by sodium hydroxide was studied: as shown on Figure 5a and 5b, the main effect of this treatment was to regenerate the carboxylic acid at 1718 cm^{-1}, while the carboxylate ion band at 1590 cm^{-1} disappeared completely. One could question the nonquantitative recovery of the carboxylic acid: in fact, under accelerated weathering conditions, carboxylated photoproducts are formed mainly at the surface of the exposed films[11,17] as a result of the low permeability of poly(vinyl chloride) to oxygen, and their formation is accompanied by much molecular fragmentation. Consequently, acids are formed in a very degraded layer at the surface of the sample. We postulate that the treatment by a base or an acid in liquid media had the undesirable effect of washing out the degraded surface and causing the disappearance of some of the acidic groups.

In order to confirm the attribution of the absorption band at 1785 cm^{-1} to acid chloride groups, the results of hydrolytic treatments on preexposed samples were investigated. Parts a and b of Figure 6 show the FTIR spectra obtained after hydrolysis for 17 h in distilled water

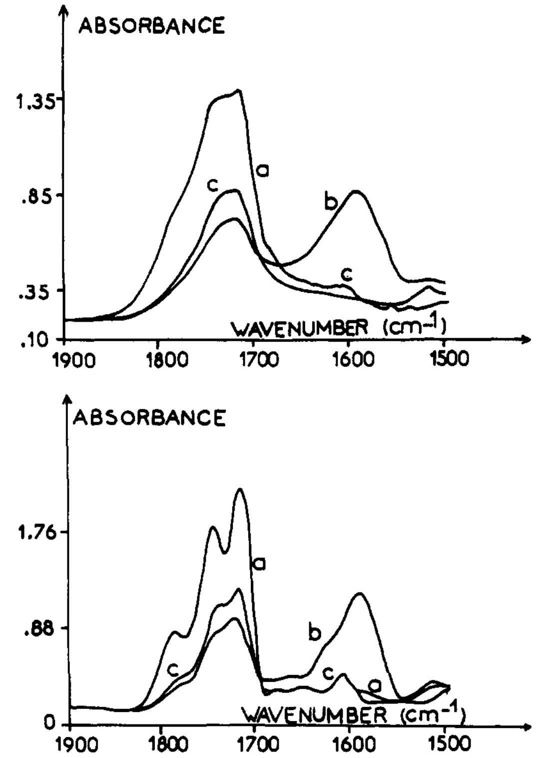


Figure 5. Influence of NaOH treatment followed by H_2SO_4 on infrared spectra (1900–1500 cm^{-1}) of films exposed for 251 h (curve a) and then treated by NaOH for 4 h (curve b) and by H_2SO_4 (curve c).

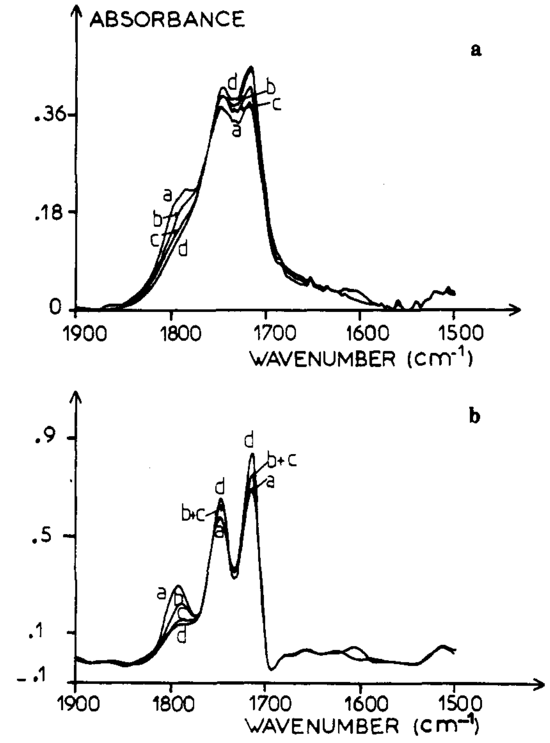


Figure 6. Effect of a hydrolytic treatment on IR spectra (1900–1500 cm^{-1}) of films exposed for 66 h (curve a) and then treated in H_2O (55 °C) for 80 min (curve b), 8 h (curve c), and 17 h (curve d): (a) direct spectrum; (b) deconvoluted spectrum.

at 55 °C. We observed a progressive disappearance of the band at 1785 cm^{-1} accompanied by an increase of carboxylic acid absorption at 1718 cm^{-1}. The incomplete conversion of acid chloride revealed the difficult accessibility of reactive groups in the deepest oxidative sites.

The influence of water on the photoproducts was also directly studied by means of irradiations of polymer samples in a SEPAP 12.24H apparatus. Parts a and b of Figure 7 show the results of irradiation for 678 h. The relative concentrations of the three photoproducts were found to be different from those obtained under "dry" conditions. It could be shown in the deconvoluted spectra that for a given amount of ketonic photoproducts (1745 cm^{-1}), the concentration of acid chloride was approximatively 35% less than that under dry conditions and the concentration of carboxylic acid 35% more.

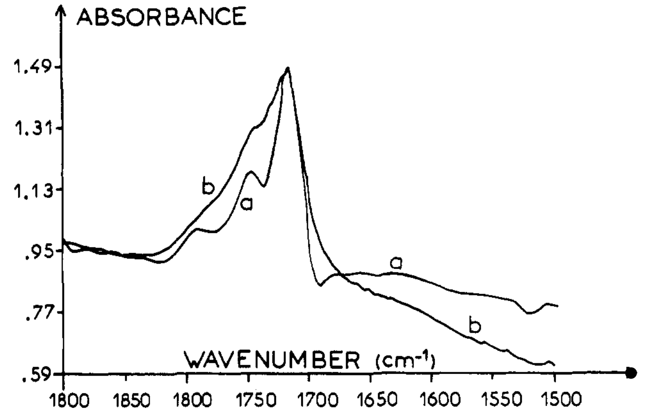
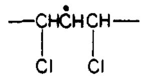


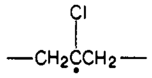
Figure 7. Evolution of IR spectra of PVC films during exposure in SEPAP 12.24H: (a) direct spectrum; (b) deconvoluted spectrum.

Mechanism of Photooxidation

Hydrogen abstraction from the polymer backbone can lead to the formation of two different types of alkyl radicals:

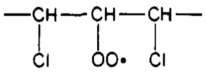

$-\underset{\text{Cl}}{\text{CH}}\dot{\text{C}}\text{H}\underset{\text{Cl}}{\text{CH}}-$

I

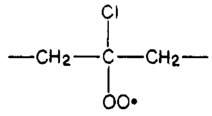

$-\text{CH}_2\overset{\text{Cl}}{\underset{\bullet}{\text{C}}}\text{CH}_2-$

II

Reaction of these radicals with molecular oxygen leads to peroxy radicals (III and IV) and preferentially to radical IV:[2,18,19]


$-\underset{\text{Cl}}{\text{CH}}-\underset{\text{OO}\bullet}{\text{CH}}-\underset{\text{Cl}}{\text{CH}}-$

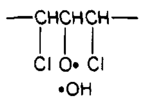
III


$-\text{CH}_2-\overset{\text{Cl}}{\underset{\text{OO}\bullet}{\text{C}}}-\text{CH}_2-$

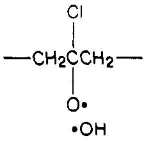
IV

Hydroperoxides are then formed and accumulate at a low stationary concentration ($c \approx 10$ mmol L^{-1}). They can be detected by their absorption in the region 3400–3300 cm^{-1}. However, their exact chemical structure cannot be determined by IR analysis (stretching of bonded O–H).

Homolysis of the O–O bond of these hydroperoxides has been found to occur under photolytic or thermolytic conditions. Macroradicals V and VI are obtained:


$-\underset{\text{Cl}}{\text{CH}}\underset{\underset{\bullet\text{OH}}{\text{O}\bullet}}{\text{CH}}\underset{\text{Cl}}{\text{CH}}-$

V


$-\text{CH}_2\overset{\text{Cl}}{\underset{\underset{\bullet\text{OH}}{\text{O}\bullet}}{\text{C}}}\text{CH}_2-$

VI

The evolution of these radicals constitutes the key to understanding the photooxidative mechanism of poly(vinyl chloride):

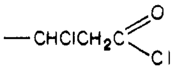
(1) Abstraction of hydrogen from the polymeric backbone leads to the formation of alcohols, observed by their absorption in the region 3400–3300 cm^{-1}.

Table I
IR Absorptions for Oxidation Photoproducts and Derivative Products

oxidation products			derivative products			
	absorbance, cm^{-1}					
structure	measd	calcd	reagent	IR max obsd, cm^{-1}	group	
$—CHClCH_2C(=O)OH$	1718	1717[a]	NH_3	1575	$—C(=O)O^-$	NH_4^+
			Et_2NMe	1580	$—C(=O)O^-$	$Et_2N^+(H)Me$
			NaOH	1590	$—C(=O)O^-$	Na^+
$—CH_2C(=O)Cl$	1785	1785[b]	H_2O	1718	$—CH_2C(=O)OH$	
			NH_3	1685	$—C(=O)NH_2$	(amide I)
				1629	$—C(=O)NH_2$	(amide II)
			Et_2NMe	1668	$—C(=O)NHR$	
$—CH_2CHClC(=O)CHClCH_2—$	1745	1745–1750[a]				
$—(CH=CH)_n—$	1650 (isolated), 1580 (conjugated)					
$—CH=CHC(=O)—$	1695 (isolated), 1605 (conjugated)					

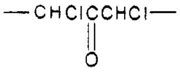
[a] Reference 22. [b] Reference 20.

(2) Acid chloride is observed, which shows a band at 1785 cm^{-1}. This acid chloride is formed by β-scission of the alkoxy radical VI with scission of the macromolecular chain. This product is then substituted in the β position by a chlorine atom and corresponds to the structure:



Hydrolysis of this photoproduct leads to a β-chlorocarboxylic acid observed by its absorption at 1718 cm^{-1}. It will be shown later that the water required for this reaction may be obtained in a parallel reaction involving the radical V. In polyethylene, carboxylic acids are observed at 1712 cm^{-1}.[21] Substitution by a chlorine atom on the β position is known to cause the C=O stretching frequency to increase by 5 cm^{-1},[22] while a shift of 15 cm^{-1} is observed for α-chlorinated carboxylic acids. The attribution of the absorption at 1718 cm^{-1} is then in good agreement with that of a β-chlorocarboxylic acid.

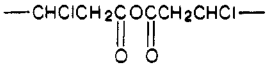
(3) Ketonic compound is formed and detected by an absorption band at 1745 cm^{-1}. This ketone is not a precursor of the carboxylic acid but is rather photostable in the matrix. We assume that this product is obtained by a cage reaction between the alkoxy radical V and hydroxyl radical, HO•. This reaction leads to the formation of water and of an α,α′-dichloro ketone:



$$—CHCl\underset{\overset{\|}{O}}{C}CHCl—$$

Empirical calculations permit one to check this attribution: it is well-known that ketones formed in the middle of the chain in polyethylene, for example, absorb at 1720 cm^{-1}.[23] Substitution of the β carbon atom by a chlorine atom causes an increase of 12–15 cm^{-1}.[22] Then two chlorine atoms in α and α′ positions are expected to cause an absorption of the C=O bond at 1744–1750 cm^{-1}.

(4) The absorption band at 1800 cm^{-1} has not been assigned. The product corresponding to this absorption is mainly observed at low levels of oxidation, and it reaches a very low stationary concentration. Hydrolytic treatment transformed this product to β-chlorocarboxylic acid. This product could be a β-chloro anhydride:

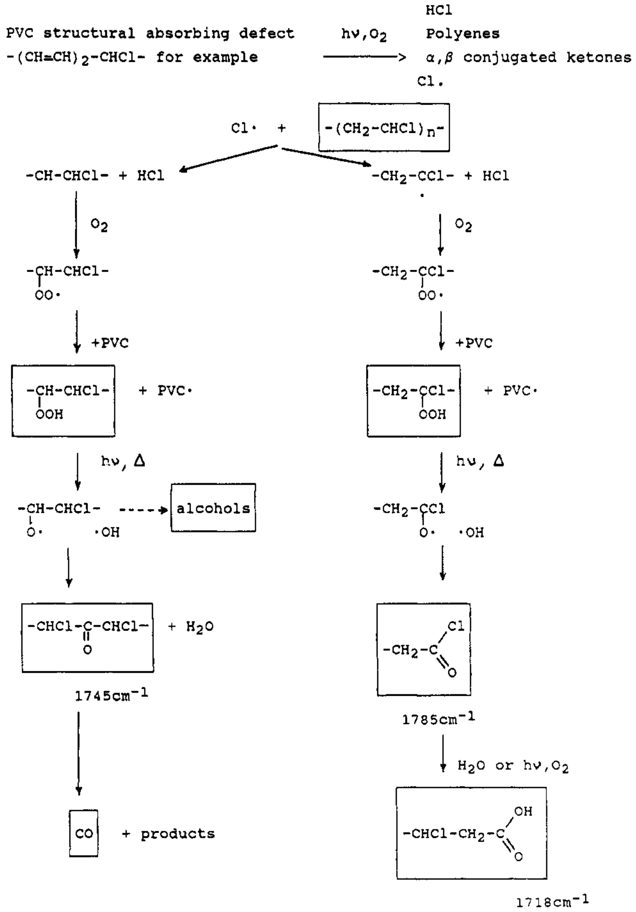


$$—CHClCH_2\underset{\overset{\|}{O}}{C}O\underset{\overset{\|}{O}}{C}CH_2CHCl—$$

(5) The products absorbing at 1650 and 1580 cm^{-1} are formed in very low concentrations. They have been attributed to double bonds and correspond to the polyenic sequences resulting from the well-known dehydrochlorination. It must be pointed out that the concentrations of polyenes obtained are very low in comparison with those of the carbonylated compounds previously described. The formation of polyenes is initiated by structural absorbing defects such as short polyenes. The oxidation of the polymer is propagated at random on the "normal" polymer chains.

(6) Some α,β-conjugated ketone groups are detected at 1695 and 1605 cm^{-1}. They are formed by oxidation of allylic radicals obtained after photoscission of a C–Cl bond of the structural defects formerly mentioned. Table I summarizes the IR bands of the photoproducts and their derivatives.

On the basis of this study, a mechanism accounting for photooxidation of poly(vinyl chloride) can be proposed:



Registry No. NH_3, 7664-41-7; NaOH, 1310-73-2; Lucovyl BB 9010, 9002-86-2.

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Surface-Induced Orientation of Symmetric, Diblock Copolymers: A Secondary Ion Mass Spectrometry Study

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Received September 23, 1988; Revised Manuscript Received December 14, 1988

ABSTRACT: Secondary ion mass spectrometry, SIMS, has been used to investigate a surface-induced orientation of symmetric, diblock polystyrene/poly(methyl methacrylate) copolymers, PS/PMMA, where either the PS or PMMA block was perdeuterated. SIMS yields a secondary ion intensity for carbon, hydrogen, and deuterium produced by sputtering of the copolymer film as a function of time (depth) from the surface with a measured depth resolution of 125 Å. Solution cast films of the copolymer from toluene, with thicknesses of 5×10^3 Å or less, were found to exhibit no preferential orientation of the microdomain morphology with respect to the surface. Annealing the copolymer films at 170 °C for 24 h produced dramatic orientation of the microdomains parallel to the surface of the film. This preferential alignment resulted in a periodic variation in the composition of either block that persisted through the entire thickness of the film. The periodicity, determined from model calculations, agreed with small-angle X-ray scattering results on the same but thicker films. PS exhibited an affinity for the free surface, while PMMA was preferentially located at the copolymer/substrate interface. At equilibrium and near-equilibrium conditions, the copolymer microdomains were aligned primarily parallel to the film surface with extensive lateral coherence. The thickness of the PS-rich layer at the air/copolymer surface was found to be one-half that of the microdomain in the bulk. Finally, interference microscopy results show that the thickness of an annealed film is quantized in that it is dictated by the alignment of the microdomains with respect to the surface and the periodicity of the microdomain morphology. Annealed films of the copolymer exhibit steps near the perimeter of the specimen, the height of which corresponds to precisely one period of the copolymer morphology.

Introduction

Most of the investigations involving molten block copolymers have focused on the bulk properties of these materials. Many of these studies have dealt with the microphase separation transition (MST) and the resulting equilibrium morphology. The type of ordered morphology that forms at the MST can be either spherical, cylindrical, or lamellar, depending on the relative molecular weights of the blocks in the copolymer. The size of the ordered domains is governed by the molecular weight of the blocks. Although block copolymers are finding increasing applications as thin-film adhesives and surfactants, only a few studies have focused on the behavior of block copolymers near surfaces.[1–9]

In this article we report on the investigation of the morphology from symmetric diblock copolymers of polystyrene/poly(methyl methacrylate) (PS/PMMA) near the copolymer/air and copolymer/substrate interfaces and in the bulk as measured by secondary ion mass spectrometry (SIMS). Up to now, most experiments on the surface behavior of block copolymers have focused on the use of X-ray photoelectron spectroscopy (XPS).[7–9] While XPS has good surface depth resolution, it is limited in penetration depth to ca. 70 Å. Transmission electron microscopy has also been used to study both the surface morphology and the effects of surface constraints on the block copolymer morphology.[3,4]

SIMS yields the relative secondary ion intensity profile of the atomic species under consideration as a function of time as an ion beam sputters through a specimen. Up to now, SIMS has been used mainly for the characterization of elemental distributions in inorganic materials; however, its application to organic materials is expanding.[10] SIMS

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0024-9297/89/2222-2581$01.50/0 © 1989 American Chemical Society