LASER-INDUCED DEGRADATION OF POLYVINYL CHLORIDE
I: QUANTUM YIELD OF DEHYDROCHLORINATION

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Summary

The stability of polyvinyl chloride (PVC) films to UV and visible light was examined. From the linear relationship between the amount of hydrogen chloride evolved and the number of photons absorbed, the dehydrochlorination quantum yield of UV-irradiated PVC was estimated to be 0.011 in a nitrogen atmosphere and 0.015 in pure oxygen. The quantum efficiency is reduced by half by inducing the degradation with the 488 or 514.5 nm radiation of an argon ion laser. The initiation of the PVC photodegradation is assumed to involve an intramolecular energy transfer from excited singlet states of polyenes to the allylic C—Cl bond. From the lack of any oxygen inhibition effect it is inferred that β-chloropolyenyl radicals have a short lifetime (less than 1 μs) and disappear before being scavenged by oxygen by splitting off chain carrier chlorine radicals.

1. Introduction

Polyvinyl chloride (PVC) is known to be very sensitive to the action of both light and oxygen, thus restricting its use for outdoor applications. Under UV irradiation PVC undergoes a very fast dehydrochlorination process with the formation of polyene sequences which are responsible for the discoloration of the irradiated polymer. Whilst the mechanism of this degradation has been extensively studied [1 - 4] in order to improve the photochemical stability of PVC, little information is available on the quantum efficiency of the dehydrochlorination process. In a previous study [5] we determined the quantum yield of hydrogen chloride (HCl) formation in the photolysis of PVC in solution. This work has now been extended to the degradation of PVC films irradiated in the presence of nitrogen or pure oxygen.

Most of the investigations on the photodegradation of PVC have been performed using UV light of wavelengths below 300 nm since pure PVC does not absorb the terrestrial solar radiations. Chromophoric impurities which

arise during the polymerization or the processing (carbonyls, hydroperoxides, unsaturations etc.) have been considered to be mainly responsible for the initiation of the observed natural weathering of this material. It thus appears to be of practical importance to evaluate the ability of the photons emitted in the visible range to induce the degradation of PVC.

In order to determine the quantum yield of dehydrochlorination in the visible light photolysis of PVC, the polymer was first degraded by UV irradiation in nitrogen to allow the build-up of long conjugated polyene sequences which absorb in the visible range; the degraded PVC film was then exposed to the blue-green monochromatic radiations of an argon ion laser. The efficiency of these photons could thus be determined and compared with the results obtained using the more energetic UV photons.

2. Experimental

2.1. Materials

The polymer used in this study was an unstabilized commercial material (FB 8021 from Rhône-Poulenc), synthesized by bulk polymerization at 60 °C, with number-average and weight-average molecular weights of 30 000 and 63 000 respectively, as determined by osmometry and light scattering. The PVC was photolysed as thin films of thickness 30 μm and area 15 cm^2; they were cast from 1,2-dichloroethane solutions (1.5 g (100 ml)$^{-1}$). Remaining traces of solvent were carefully removed by a final drying at 80 °C *in vacuo* (10^{-5} Torr) for 6 h.

2.2. Irradiation

UV irradiations were performed at room temperature in a quartz reactor under a pressure of 900 Torr of pure nitrogen with a Philips (HPK 125 W) middle pressure mercury lamp. The light intensity (1.5 $\times$ 10^{-7} einsteins s^{-1} cm^{-2}) and the fraction of incident light absorbed by the PVC film were determined using the potassium ferrioxalate system developed by Hatchard and Parker [6] and slightly modified recently by Bowman and Demas [7]. Initially the PVC film absorbs approximately 3% of the incident light; its UV–visible absorbance increases steadily with exposure time and reaches 45% after 1 h of irradiation.

The HCl evolved during the photolysis of PVC was pumped off from the reactor and was measured by volumetric titration using 0.01 N aqueous sodium hydroxide. Polyene formation or consumption was followed by UV and visible spectroscopy of the polymer film in the quartz reactor using a Cary 15 spectrophotometer.

After 75 min of UV photolysis in nitrogen the conversion degree of the degraded polymer was estimated to be 3.5% (number of HCl molecules evolved per monomer unit). Fresh nitrogen or oxygen was then introduced into the reactor under a pressure of 900 Torr and the PVC film was exposed to the 488 or 514.5 nm radiation of an argon ion laser (Spectra Physics

model 170). These photons have energies of 58.5 kcal mol^{-1} and 55.5 kcal mol^{-1} respectively and are absorbed by polyenes with sequence lengths of 12 and 14 respectively [8]. The optical density of the UV-degraded PVC film was 0.5 at 488 nm and 0.36 at 514.5 nm. By using a divergent optical device the laser light pencil was converted into a parallel beam with a square section of approximately 20 cm^2. The power of the laser was adjusted in order to obtain the same photon flux density as that for the UV irradiation: 35 mW cm^{-2} for the 514.5 nm emission and 37 mW cm^{-2} for the 488 nm emission. Under these conditions the temperature of the irradiated sample was always below 40 °C, thus avoiding any thermal degradation of the polymer.

3. Quantum yield of dehydrochlorination in PVC photolysis

During the UV irradiation of PVC, HCl is evolved with an increasing rate in both nitrogen and oxygen atmospheres (Fig. 1). The irradiated film becomes coloured and absorbs the UV-visible light increasingly, owing to the formation of conjugated polyene sequences of various lengths up to about 20:

$$-(CH_2-CHCl)_n- \quad \xrightarrow{h\nu} \quad -(CH=CH)_n- + nHCl \qquad (1)$$
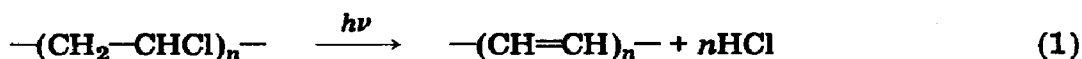
When the PVC film, degraded for 75 min by UV irradiation in nitrogen, was further exposed to the 514.5 nm radiation of the argon ion laser, dehydrochlorination still proceeded but with a slower rate than that in the UV irradiation (Fig. 1). This indicates that green photons which have an energy of approximately 55 kcal mol^{-1} are energetic enough to induce the dehydrochlorination process in PVC. We have checked that the dehydrochlorination observed did not result from any thermal effect; a PVC film that was not UV degraded prior to laser irradiation showed no change in the UV spectrum or any HCl formation after 2 h of exposure to the 514.5 nm radiation.

During the laser photolysis of PVC in a nitrogen atmosphere the UV absorbance increased, both above and below 514.5 nm (Fig. 2), indicating the production of polyenes with sequence lengths both longer and shorter than 14. At the same time HCl was evolved with an increasing rate, in a similar manner to that in the UV photolysis. This accelerated kinetics was generally assumed to result from some catalytic effect of the HCl evolved on the degradation of the polymer [9] or from the photolysis of the oxidation products [10]. In a previous study on the photodegradation of PVC in solution [5] we have shown that the accelerated kinetics observed results in fact from the increased absorption of light by the irradiated polymer since the quantum yield of dehydrochlorination remains constant and independent of the extent of reaction. This applies also for the photolysis of PVC films, as shown in Fig. 3 where the amount of HCl evolved
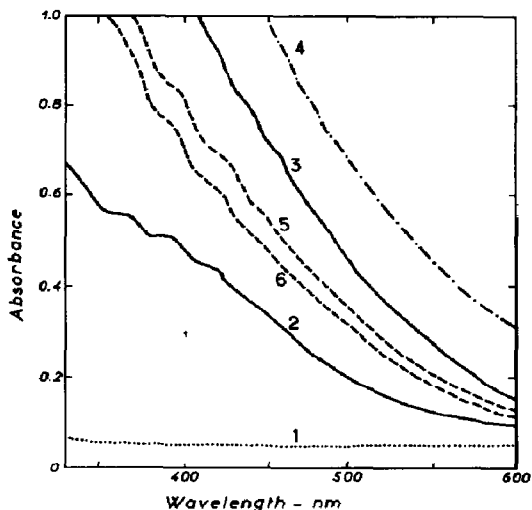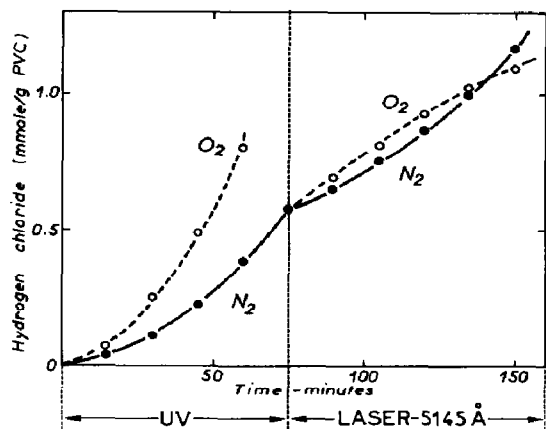
Fig. 1. Kinetics of the dehydrochlorination of PVC film in the UV and 514.5 nm photolysis in the presence of nitrogen (●) or oxygen (○): light intensity, 1.5×10^{-7} einsteins s^{-1} cm^{-2}.

Fig. 2. UV–visible spectra of PVC film: 1, ···, unirradiated; 2, 3, ———, UV irradiated in nitrogen for 30 and 75 min; 4, – · – · –, UV irradiation in nitrogen for 75 min and 514.5 nm irradiation in nitrogen for 60 min; 5, 6, – – –, UV irradiation in nitrogen for 75 min and 514.5 nm irradiation in oxygen for 30 and 60 min.
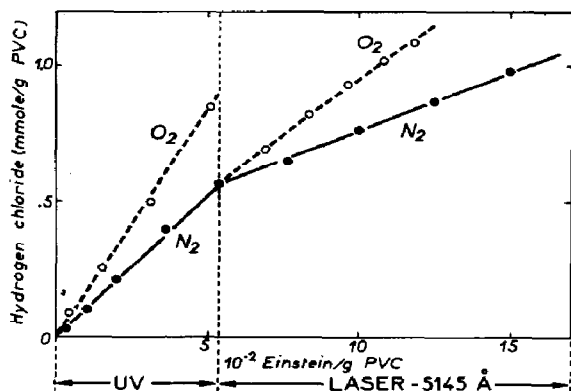

Fig. 3. Amount of HCl evolved from the polymer as a function of the number of photons absorbed by the polymer in the UV and 514.5 nm photolysis of PVC film in the presence of nitrogen (●) or oxygen (○).

was plotted as a function of the number of photons absorbed by the polymer. The slope of the straight line obtained corresponds to the quantum yield of dehydrochlorination:
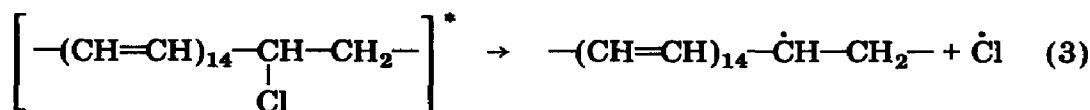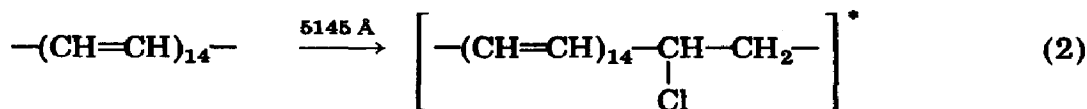
$$\Phi_{HCl} = \frac{\text{number of HCl molecules evolved per gram of PVC}}{\text{number of quanta absorbed per gram of PVC}}$$

For the UV photolysis of PVC films in the presence of nitrogen or pure oxygen, Φ_{HCl} was estimated to be 0.011 and 0.015 respectively (and not 0.11 and 0.15 as indicated erroneously in a preliminary note [11]). For the 514.5 nm laser photolysis of UV-degraded PVC, the dehydrochlorination quantum yield dropped to 0.005 in a nitrogen atmosphere and to 0.009 in pure oxygen. Similar results were obtained using the 488 nm laser emission, Φ_{HCl} being approximately 10% higher than that with the 514.5 nm emission.

It should be mentioned that during the laser-induced photooxidation of degraded PVC the dehydrochlorination process is still developing but with a decreasing rate (Fig. 1) whereas the UV absorbance drops concomitantly (Fig. 2) because of a bleaching reaction of the conjugated polyenes by oxygen [12]. Here again a plot of the amount of HCl evolved against the absorbed dose yields a straight line (Fig. 3), thus indicating that the decrease in the rate of HCl formation results only from a reduced absorption of light by the oxygen-irradiated polymer. The estimated value of 0.009 for the dehydrochlorination quantum yield Φ_{HCl} compared with that of 0.005 in nitrogen shows that the photodegradation of PVC is significantly enhanced in the presence of oxygen in spite of the bleaching reaction.

4. Mechanism of the visible-light-induced degradation of PVC

The decrease in the quantum efficiency observed when argon ion laser radiations were used instead of UV radiations was expected because of the lower energy of these laser photons. However, our results indicate that the blue–green light which is absorbed by polyenes with sequence lengths of 12 - 14 is still about half as efficient as UV light (250 - 400 nm) in promoting the degradation of PVC. Since the dissociation energy of C—Cl bonds in PVC is much higher (74 kcal mol^{-1} [13, 14]) than the energy of the laser photons used, we have to assume that the bond which is primarily cleaved in the photodegradation of PVC is the labile allylic C—Cl bond, the dissociation energy of which would be increasingly lowered as the sequence length of the polyenes increases [14] (reactions (2) - (4)).

$$-(CH{=}CH)_{14}- \xrightarrow{5145\,\text{Å}} \left[-(CH{=}CH)_{14}-\underset{\underset{Cl}{|}}{CH}-CH_2- \right]^{\bullet} \qquad (2)$$

$$\left[-(CH{=}CH)_{14}-\underset{\underset{Cl}{|}}{CH}-CH_2- \right]^{\bullet} \rightarrow -(CH{=}CH)_{14}-\dot{C}H-CH_2- + \dot{C}l \qquad (3)$$
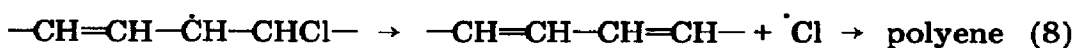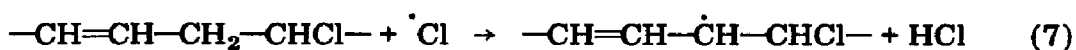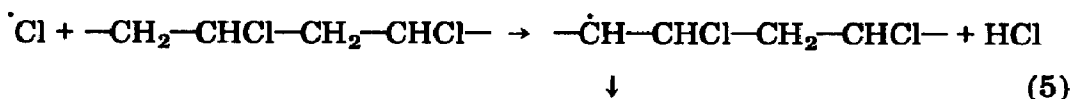
According to our results the dissociation energy of the C—Cl bond next to the end of a polyene with 14 conjugated double bonds would be as low as 55 kcal mol^{-1} or even less.

The chlorine radical evolved in reaction (3) is expected to react with the polymer by abstracting a hydrogen atom, preferentially from a methylene group [15], either from the adjacent CH_2 of the polyenyl radical, thus increasing the polyene sequence length (cage reaction (4)),

$$-(CH=CH)_{14}-\dot{C}H-CH_2- + \dot{C}l \rightarrow -(CH=CH)_{14}-CH=CH- + HCl \quad (4)$$
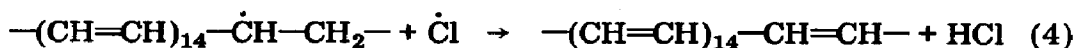
or from a methylene group of another chain, thus inducing the "zip" dehydrochlorination process with the formation of new polyenes (reactions (5) - (8)):

$$\dot{C}l + -CH_2-CHCl-CH_2-CHCl- \rightarrow -\dot{C}H-CHCl-CH_2-CHCl- + HCl$$
$$\downarrow \quad (5)$$

$$-\dot{C}H-CHCl-CH_2-CHCl- \rightarrow -CH=CH-CH_2-CHCl- + \dot{C}l \quad (6)$$

$$-CH=CH-CH_2-CHCl- + \dot{C}l \rightarrow -CH=CH-\dot{C}H-CHCl- + HCl \quad (7)$$

$$-CH=CH-\dot{C}H-CHCl- \rightarrow -CH=CH-CH=CH- + \dot{C}l \rightarrow polyene \quad (8)$$

This reaction scheme would account for the formation of polyenes with sequence lengths shorter than 14 observed during the 514.5 nm laser irradiation of PVC in nitrogen (Fig. 2).

The fact that we observed no inhibition by oxygen and no significant effect of the light intensity on the dehydrochlorination quantum yield suggests that the photodegradation of PVC is initiated by intramolecular energy transfer from polyene excited singlet states to the allylic C—Cl bond. Triplet states are less likely to be involved because of a very inefficient intersystem crossing process in polyenes [16]. As well as disappearing by cleavage of allylic C—Cl bonds (reaction (3)), S_1 states of conjugated polyenes tend to undergo *cis-trans* isomerizations or intramolecular reactions leading to cyclic structures [16]. These photoprocesses, which will result in a photobleaching of the polyenes [17], may provide an efficient deactivation pathway, thus reducing the extent of the dehydrochlorination in highly degraded PVC.

The lack of any oxygen inhibition effect also indicates that the polyenyl radical $-(CH=CH)_n-\dot{C}H-CHCl-$ which is responsible for the "zip" dehydrochlorination has a very short lifetime and will disappear by splitting off a chlorine atom before being scavenged by oxygen. By taking a rate constant for the scavenging of polyenyl radicals by oxygen of at least 5×10^8 M^{-1} s^{-1} [18] and a concentration of oxygen in the PVC film of 1.5×10^{-3} M [19], the lifetime of this polyenyl radical was calculated to be less than 1 μs. This might explain why it is so difficult to stabilize PVC against light and to prevent the chain dehydrochlorination from developing extensively, even in the presence of oxygen.

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