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Photochlorination of Poly(vinyl Chloride).

I. Kinetics and Quantum Yield

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ABSTRACT

Casted PVC films have been chlorinated by UV irradiation in the presence of chlorine gas at room temperature. For each chlorine atom fixed to the polymer chain, one molecule of hydrogen chloride was found to be evolved. The observed slowing down of the chlorination rate was attributed to the decrease of the number of methylene groups available as chlorination proceeds. Calculated values of the chlorination quantum yield (Φ_{Cl}) are in the range 0.6 to 2 and remain constant for conversion degrees up to 40%. The observed influence of the light intensity on the quantum efficiency, $\Phi_{Cl} \approx I^{-0.5}$, confirms that chlorination of PVC proceeds by a chain reaction mechanism. The photochlorination process was shown to develop as far as 30 μm deep into a PVC film plasticized with 4% of casting solvent.

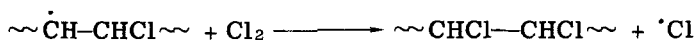
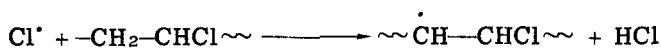
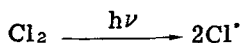
INTRODUCTION

One of the possible ways to improve the thermal stability of poly(vinyl chloride) (PVC) consists of introducing some additional chlorine atoms into the polymer backbone. Such a treatment increases

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both the glass transition temperature and the softening point, while it imparts superior mechanical and fire-resistance properties to the chlorinated material. The chlorination process can be easily induced by ultraviolet irradiation of the solid polymer in the presence of chlorine gas, a method which is now commonly used to obtain commercial chlorinated PVC.

The mechanism of PVC photochlorination has been thoroughly investigated [1-4] and is generally assumed to proceed by a chain reaction where chlorine radicals react preferentially with the hydrogens of the methylene groups:



In spite of the numerous studies devoted to this photochemical process, little information is available on the quantum efficiency of this chain reaction. The initial goal underlying the present work was thus to determine precisely the quantum yield of the photochlorination of PVC films and to evaluate the kinetic chain length. The penetration of the chlorination process into the polymer film has also been examined.

EXPERIMENTAL

Material

The polymer used was an unstabilized commercial material (RB 8021 from Rhône-Poulenc) synthesized by bulk polymerization at 60°C, with $M_n = 30,000$ and $M_w = 63,000$. PVC films, 5-100 μm thick, were obtained by casting from 1,2-dichloroethane (DCE) solutions at room temperature. After evaporation of the solvent, the film contained ~4% of retained DCE.

Irradiation

Samples were irradiated at 30°C in a glass reactor containing pure chlorine (1.2 bar) by using a middle pressure mercury lamp (Philips HPK 125 W) which emits mostly at 366 nm. The incident

light intensity ($1.9-18.3 \times 10^{-9}$ einstein/ $s \cdot cm^2$ *) and the fraction of incident light absorbed by the chlorine gas (~20%) were measured by using the potassium ferrioxalate actinometer [5]. During the irradiation, the polymer film remained completely transparent to the radiations of wavelength above 250 nm.

Analysis

The chlorine content of the PVC film before and after the chlorination was determined by gravimetric titration after treatment of the sample with sodium peroxide at 500°C, according to the Stoeckert method [6]. The amounts of hydrogen chloride evolved by the reaction were measured by volumetric titration with 0.01 N aqueous NaOH solution.

KINETICS OF THE PHOTOCHELORINATION

When the PVC film was photolyzed in the presence of pure chlorine, the chlorine content τ , initially at 56.8% for PVC, increased steadily with exposure time but at a decreasing rate. Figure 1 shows the chlorination kinetics obtained for three different light intensities with PVC films of 30 μm thickness. After 5 h of irradiation the chlorination rate is reduced by half and after 10 h to one-quarter of its initial value. This saturation phenomenon was interpreted in terms of a decrease of the number of sites susceptible to be chlorinated.

Since the $\cdot Cl$ radical is known to abstract hydrogen preferentially from the methylene group [7-9], the maximum value of the chlorine content that can be reached is 73.2% which corresponds to the formula $-(CHCl-CHCl)_n-$. The observed decrease of the rate of chlorination is thus assumed to result primarily from the decreasing amount of CH_2 groups which remain available for attack by chlorine radicals.

During the chlorination process, hydrogen chloride is evolved at a decreasing rate which is very similar to the rate of chlorine addition to the polymer (Fig. 2). It thus appears that, for each chlorine atom which has been chemically bonded to the PVC chain, one molecule of HCl is evolved, in agreement with the proposed mechanism.

For irradiation times above 10 h, the amount of HCl evolved is in increasing excess over the amount of Cl fixed. This might result from a photodegradation process which develops in the polymer exposed to UV radiation. Indeed, when the PVC film was placed parallel

* 1 einstein = 1 mol of photons; energy = $Lh\nu = 6.02 \times 10^{23} \times 6.63 \times 10^{-34} \times \nu$ (in J); here $\nu = 8.2 \times 10^{14} s^{-1}$ and $I = 1.95 \times 10^{-3} J/s \cdot cm^{-2}$.

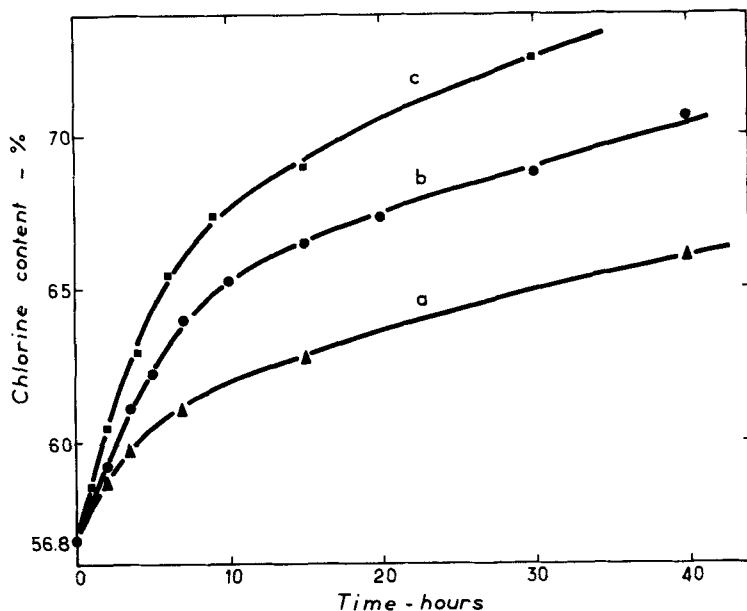


FIG. 1. Kinetics of the photochlorination of PVC films for various light intensities: a, 1.9×10^{-9} ; b, 6.1×10^{-9} ; c, 18.3×10^{-9} einstein/ $\text{s}\cdot\text{cm}^2$.

to the incident light (skimming beam) in order to avoid a direct exposure of the polymer, the chlorination proceeded as efficiently as previously but the amount of HCl evolved remained very close to the amount of chlorine added to the polymer, even for extended irradiation time (dotted line of Fig. 2). GPC analysis of the two chlorinated films clearly shows that the degradation process occurred only in the sample exposed to direct UV radiation (Fig. 3).

The fact that the chlorination efficiency is similar in both experiments also indicates that the direct irradiation of the polymer film is not necessary to induce the chlorination process which is thus initiated mainly by the chlorine radicals generated at the surface or in the close vicinity of the polymer film.

QUANTUM YIELD OF CHLORINATION

In order to evaluate the quantum efficiency of this photochemical reaction, a mathematical treatment of the observed exponential kinetics is required. If chlorine radicals react only with methylene groups, the rate of chlorination R_{Cl} at time t will be proportional to

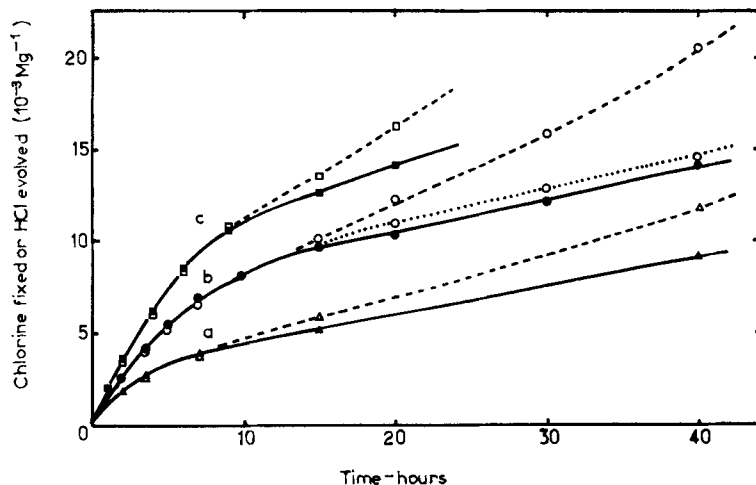


FIG. 2. Amount of Cl fixed (—) and of HCl evolved (---) in the photochlorination of PVC films for various light intensities; (•••) HCl evolved from a PVC film parallel to the UV beam: a, 1.9×10^{-9} ; b, 6.1×10^{-9} ; c, 18.3×10^{-9} einstein/s·cm².

the concentration of unreacted CH₂ groups and to the absorbed light intensity (I_a):

$$R_{Cl} = \frac{dx}{dt} = \Phi_{Cl} I_a \left(\frac{n - x}{n} \right) \tag{1}$$

where n is the initial number of CH₂ groups in PVC, i.e., the number of monomer units, and x is the number of CH₂ groups which have been chlorinated at time t. The proportionality factor Φ_{Cl} is precisely the quantum yield of chlorination, namely, the number of units which have been chlorinated per photon absorbed.

Integration of Eq. (1) between time 0 (where x = 0) and t leads to the following kinetic equations:

$$n \log \left(\frac{n}{n - x} \right) = \Phi_{Cl} I_a t \tag{2}$$

$$x = n \left[1 - \exp \left(- \frac{\Phi_{Cl} I_a t}{n} \right) \right] \tag{3}$$

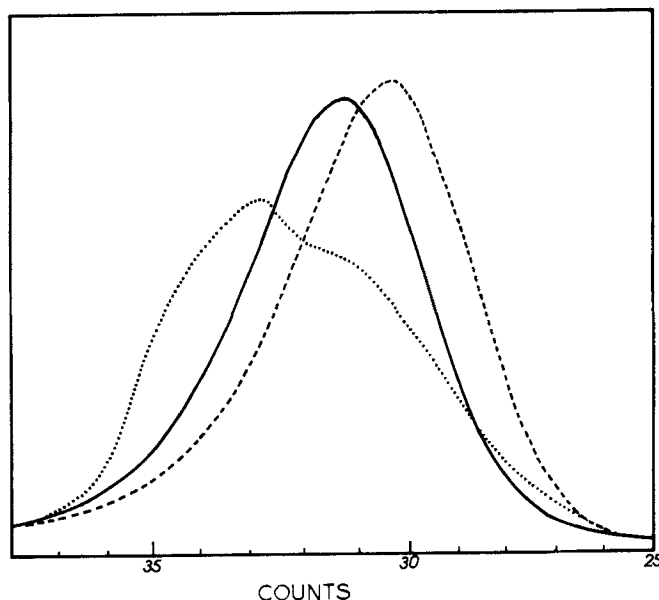


FIG. 3. GPC molecular weight distribution of PVC samples: (—) before chlorination, (· · ·) after 20 h of chlorination by direct UV exposure of the film, (- -) after 20 h of chlorination with the film parallel to the UV beam.

Equation (3) accounts for the observed increase of the chlorine content of the irradiated PVC (Fig. 1), at least as long as no CCl_2 structures are formed. By introducing in these equations the chlorine content of the polymer initially (56.8%) at time t (τ) and at infinite dose (73.2%), the ratio $n/(n-x)$ of the CH_2 groups in PVC and in the chlorinated polymer can be expressed in the following form:

$$\frac{n}{n-x} = \frac{73.2 - 56.8}{(73.2 - 56.8) - (\tau - 56.8)}$$

and Eq. (2) becomes

$$n \log \left(\frac{16.2}{73.2 - \tau} \right) = \Phi_{\text{Cl}} I_a t \quad (4)$$

The quantum yield of the photochlorination of PVC can then be

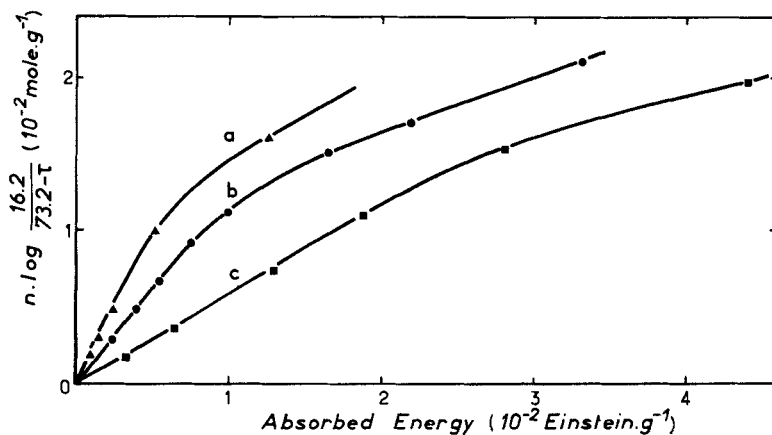


FIG. 4. Determination of the chlorination quantum yield in the light-induced chlorination of PVC films for various light intensities: a, 1.9×10^{-9} ; b, 6.1×10^{-9} ; c, 18.3×10^{-9} einstein/ $s \cdot cm^2$.

evaluated from the slope of the straight line that should be obtained by plotting the left-hand term of Eq. (4) against the product $I_a \times t$

which corresponds to the number of photons absorbed. Figure 4 shows that the value of this logarithmic expression indeed increases linearly with the absorbed dose, at least during the first 10 h of irradiation. The quantum efficiency of the photochlorination of PVC thus remains constant with estimated values of 0.6, 1.1, and 2.0, depending on the intensity of light. It should be mentioned that, since a substantial fraction of the chlorine radicals formed by UV irradiation is expected to disappear by recombination before being scavenged by the reactive sites of the PVC film, these calculated values of Φ_{Cl} are certainly

underestimates. A more accurate determination is now being carried out by increasing the number of PVC films placed into the reactor in order to enhance the probability of scavenging of the chlorine radicals by the polymer chain.

The observed decrease of Φ_{Cl} to about half its original value after 10 h of irradiation is difficult to account for. Whatever the light intensity, it occurs when the chlorine content of the polymer exceeds 63%, i.e., when about 40% of the CH_2 sites have been chlorinated. A possible explanation would have been to consider that, as the number of available CH_2 groups is decreasing, $\cdot Cl$ radicals react increasingly with the less reactive $CHCl$ groups to yield CCl_2 structures. However, this would shift the limit value of the polymer chlorine content above 73.2% and thus increase the value of the logarithmic expression of Eq. (4), a trend which would be just the opposite of the one observed

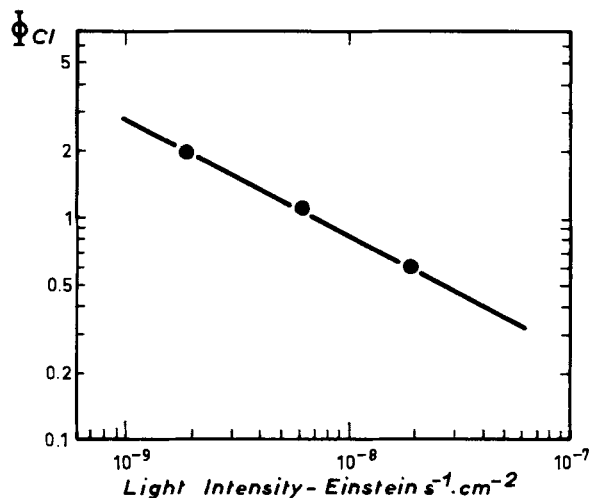


FIG. 5. Dependence of the chlorination quantum yield on the light intensity in the photochlorination of PVC films.

experimentally. This slowing up effect should rather be related to a change in the physical properties of the polymer (e.g., permeability to chlorine) and/or a reduced accessibility of the chlorine radicals to the reactive sites of the polymer chain as the chlorination proceeds.

INFLUENCE OF THE LIGHT INTENSITY ON Φ_{Cl}

If the photochlorination of PVC proceeds, as expected, by a chain reaction, the rate of chlorination should be less than first order in rate of initiation, i.e., in intensity of light. However, since the rate of chlorination decreases steadily with irradiation time, a direct comparison of the rates observed for different intensities is meaningless. A better estimate of the kinetic law can be reached by considering the values of the chlorination quantum yield which were shown to remain constant, at least during the first stages of chlorination.

It is well known that, when a photochemical process occurs by a chain reaction, the quantum yield will decrease with an increase of the intensity of light. Photochlorinations performed at three different light intensities in the range 1.9×10^{-9} to 1.83×10^{-8} einstein/s·cm² show indeed that Φ_{Cl} is roughly proportional to the reciprocal of the square root of the intensity: $\Phi_{Cl} \sim I^{-0.5}$ (Fig. 5). This result indicates that, in spite of the relatively low values of Φ_{Cl} , the photochlorination

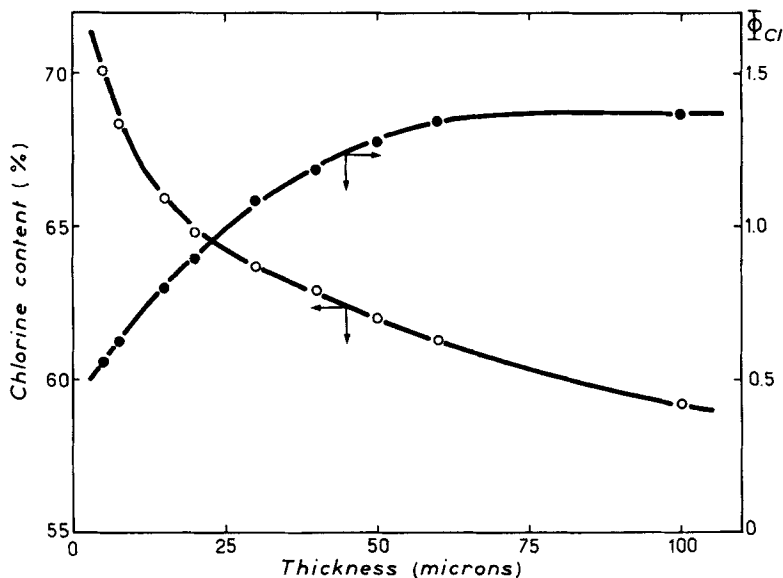


FIG. 6. Influence of the film thickness on the chlorination quantum yield of PVC films ($I = 6.1 \times 10^{-9}$ einstein/s \cdot cm 2).

process develops with long kinetic chain lengths in a PVC film plasticized with a few percent of solvent.

PENETRATION OF THE CHLORINATION INTO THE POLYMER FILM

In order to evaluate how deep the chlorination process can develop into the polymer film, quantum yields of chlorination were determined for PVC samples of various thicknesses in the range 5 to 100 μ m. Figure 6 shows that, as expected, the overall chlorine content of the irradiated polymer drops rapidly by increasing the film thickness, while the calculated chlorination quantum yield increases concomitantly to reach a maximum value of ~ 1.4 for films of about 60 μ m thickness. It thus appears that chlorine radicals can penetrate into a PVC film as deep as 30 μ m since both sides of the sample are in contact with chlorine. However, it should be remembered that these films contain about 4% of 1,2-dichloroethane which may act as a plasticizer and facilitate the diffusion of chlorine radicals. Similar investigations are now being carried out on PVC films from which the casting solvent has been carefully removed.

CONCLUSION

Our kinetic investigations on the photochlorination of PVC films clearly show that, while the rate of chlorination decreases as the reaction proceeds, the quantum efficiency Φ_{Cl} remains constant, at least during the first stages of the process. From the reciprocal square-root dependence of Φ_{Cl} on the light intensity, it is inferred that the chlorination reaction develops with relatively long kinetic chains.

Values of the chlorination quantum yield will also depend on the temperature, the chlorine pressure and, above all, on the amount of polymer in the reactor since under the selected experimental conditions a substantial fraction of the chlorine radicals formed by UV irradiation is not reacting with the polymer, thus wasting some of the energy absorbed. The influence of these various factors on the quantum efficiency is now being investigated and will be reported in a succeeding paper, together with a more accurate determination of the kinetic chain length.

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