

Photodestruction of poly(vinyl chloride)

II. Influence of monochromatic ultraviolet radiation on physical properties of polymer

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The photooxidative degradation of poly(vinyl chloride) by the action of monochromatic radiation of the wavelength of 405 ± 10 nm in air was studied at 25°C. The influence of exposure on physical properties of polymer film was examined. There were determined: limiting angle of wetting Θ , surface energy σ_s , temperature of glass transition T_g , optical properties (absorption in the u.v., visible, and i.r. region), content of gel fraction, and molecular weight of the soluble fraction of the exposed sample. It has been found that the hydrophilicity of the surface of sample, absorption in the u.v. and i.r. region, and content of gel fraction increase with exposure of poly(vinyl chloride) while the value of T_g and molecular weight of soluble fraction decrease.

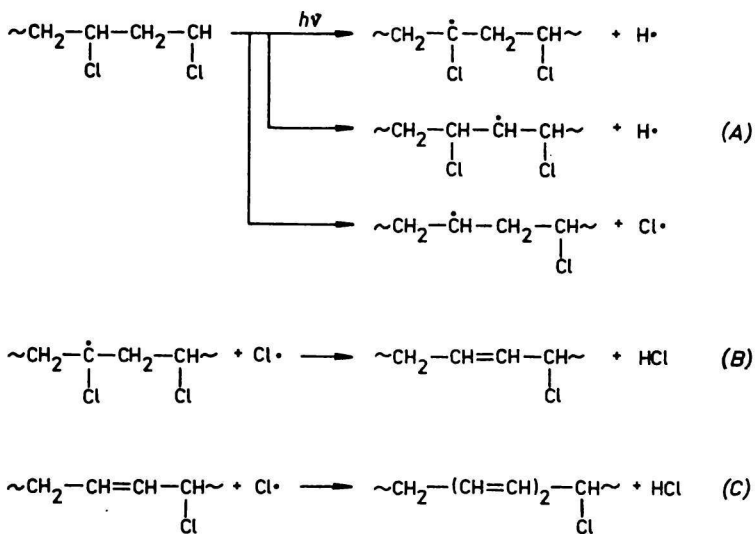
Была изучена фотоокислительная деградация поливинилхлорида при воздействии монохроматического излучения с длиной волны 405 ± 10 нм на воздухе при температуре 25°C. Было изучено влияние экспозиции на физические свойства полимерного фильма: на предельный угол смачивания Θ , на поверхностную энергию σ_s , температуру стеклования T_g , оптические свойства (абсорбция в УФ, ИК и видимой областях), содержание гелевой составляющей и на молекулярный вес растворимой компоненты облученного образца. Было найдено, что с возрастающей выдержкой облучения поливинилхлорида повышаются гидрофильность поверхности образца, абсорбция в УФ и ИК областях и содержание геля, в то время, как T_g и молекулярный вес растворимой компоненты понижаются.

Like many polyolefins, poly(vinyl chloride) (PVC) does not distinctly absorb in visible and near region of ultraviolet spectrum. Therefore it could be expected that the visible light should not produce any change in physical and chemical properties of PVC either in air or vacuum. Nevertheless, the opposite is true. This fact is due

to the presence of impurities accompanying commercial samples. In spite of the fact that the problem of light stability has been given great attention, we do not yet know the mechanism of photooxidative PVC degradation with satisfactory precision. The selection of the wavelength (405 nm) was governed by the absorption spectrum of PVC (absorbance is negligible in this region), emission spectrum of high-pressure mercury discharge lamp (the portion of photons of $\lambda = 405$ nm is larger enough), and our experimental possibilities.

According to literature, the light degradation of PVC is ascribed to defects in main chain of the type: carbonyl groups, hydroperoxides, and unsaturated bonds as well as to the initiating effects produced by the rests of catalysts and metal impurities [1]. The absolute value of concentration of these defects and impurities may be under the threshold of sensitivity of the spectral and chemical methods of determination, but their effect on mechanism of light and thermal destruction manifests itself owing to multiplication action in the system of consecutive and parallel reactions.

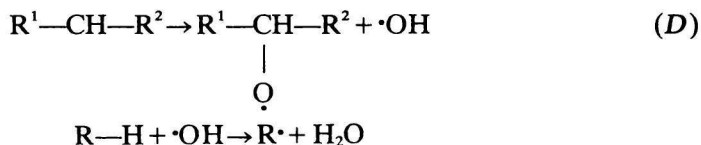
The basic process in photochemical oxidation of PVC is dehydrochlorination which gives rise to conjugated double bonds. That shows itself by successive colouring of the investigated sample. Most authors of the published papers dealing with photooxidative degradation of PVC [1—10] are inclined to believe that the process of dehydrochlorination obeys a radical mechanism which may be described by the Scheme 1



Scheme 1

The arising polyenes are ready to react with present oxygen in the excited singlet $^1\text{O}_2$ ($^1\Sigma_g^+$, $^1\Delta_g$) and triplet $^3\text{O}_2$ state and especially with ozone O_3 . These reactions give mainly hydroperoxides, cyclic peroxides, and carbonyl compounds of different types. Some of these compounds are often present in the starting PVC.

The presence of hydroperoxides results in acceleration of dehydrochlorination because the products of their decomposition are prone to abstract hydrogen atoms from the chain of PVC



etc.

In contradiction to these views, it has been ascertained by many authors [11—17] concerned with investigations of the photodegradation of PVC in inert atmosphere (N_2) that the presence of radical inhibitors of the type of hydroquinone does not affect the rate of dehydrochlorination. This fact led to formulation of the theory of polar mechanism of the HCl splitting from PVC in the process of photodegradation. This theory is supported by the experimentally ascertained accelerating effect of the metal chlorides (FeCl_3 , ZnCl_2) [13—15]. It is also remarkable that no dehydrochlorination takes place in PVC at temperatures under 0°C .

From the point of view of significance of individual defect structures in PVC for photodegradation, the influence of the carbonyl groups functioning as photo-initiators is most frequently emphasized [18—20]. As a matter of fact, the photodecomposition of alkyl chlorides proceeds only in the presence of carbonyl compounds [18] and benzophenone sensitizes the photodehydrochlorination of PVC [19]. The number of crosslinks arising in the photooxidative degradation of PVC linearly increases with the rate of formation of the carbonyl groups [21]. The same relation is also valid for the rate of colouring of PVC [22]. The rests of solvents, especially tetrahydrofuran, dichloroethane, *etc.* [23], hydroperoxides [16, 22, 24, 25], and olefinic terminal groups [11, 26, 27] have an unfavourable effect on the photodegradation stability of PVC. The presence of peroxidic radicals in exposed PVC was ascertained by the e.p.r. method [25].

The aim of this study is to examine the photooxidative degradation of PVC exposed to monochromatic radiation of the wavelength of 405 nm in air at laboratory temperature especially as regards change in the surface properties of a thin film, optical properties, and content of gel fraction. Since the investigations were performed with a polymer carefully deprived of ionic impurities, the results may contribute to elucidation of the primary significant mechanism.

Experimental

Polymer

A polymer of Czechoslovak provenance (W. Pieck Chemical Works, Nováky) was used for the study. It was deprived of residual emulsifiers and initiators by tenfold extraction with distilled and redistilled water and twofold extraction with ethanol of spectral purity. Afterwards, it was dried for three months in dark *in vacuo* at 45°C. The samples in the form of films were prepared by casting from a 2% solution of polymer in tetrahydrofuran which was deprived of peroxides by the standard procedure consisting in refluxing with solid KOH in dark in nitrogen atmosphere [28]. The mean molecular weight (viscosity average) of the investigated PVC was $M_w = 110\,000$. The average width of films varied in the range 12–13 μm .

Exposure equipment

The PVC films were stretched in a cell and exposed in the equipment consisting of a high-pressure mercury discharge lamp HBO-500 (Narva BGW, Berlin, GDR), optical modulating quartz system, temperature-controlled holder cell, and actinometric system (ferric oxalate actinometer or photoelectric actinometer for long-lasting exposures). The discharge lamp was supplied from a stabilized source. The intensity of impinging monochromatic radiation was $I_0 = 2.03 \text{ J m}^{-2} \text{ s}^{-1}$.

Limiting angle of wetting

The limiting angle of wetting was measured with a reflex goniometer (Kernco Instruments Co., USA) temperature-controlled by means of a double thermostating equipment accurate to $\pm 0.1^\circ\text{C}$. The precision of determining the limiting angle of wetting varied according to the measuring liquid (ethylene glycol, anal. grade, glycerol, anal. grade, redistilled water, triethylene glycol, ethylene glycol monoethyl ether) in the range between $\pm 0.3^\circ$ and $\pm 2^\circ$. The volume of an applied measuring drop was constant and equal to 3 μl . Photographic records were used to reading in the region of low angles Θ and higher temperatures. The measurement of Θ was always performed at least six times in the medium of saturated vapour of the measuring liquid.

Spectral measurements

The ultraviolet and visible spectra were taken with a spectrograph Specord UV VIS (Zeiss, Jena) while the infrared spectra were recorded with a spectrophotometer Perkin—Elmer, Model 599.

Determination of gel fraction

The weighed films of exposed samples (about 500 mg) were dissolved in 50 ml of cyclohexanone for 24 h at 50°C and subsequently for 2 h at 80°C. The soluble fraction was separated from insoluble gel particles by filtration through a porous crucible S 4. The gel fraction was successively several times washed with cyclohexanone thermostatted at 80°C, acetone (three times) at laboratory temperature and dried in vacuum to constant weight.

Determination of glass transition point

As evident from Fig. 10, a procedure based on the temperature dependence of limiting angle of wetting [36] was used for this determination. The points of inflection of the curve $\Theta = \Theta(T^{-1})$ were determined by numerical procedure.

Results and discussion

For photochemical experiment, the solid PVC must be deprived of the rests of solvents, especially tetrahydrofuran (THF). As pointed out by some authors [29], the residual THF manifests itself in the infrared spectrum by characteristic absorption at about 1700 cm^{-1} . The exposure of a film containing THF gives rise to hydroxytetrahydrofuran showing a characteristic absorption at 1730 cm^{-1} and

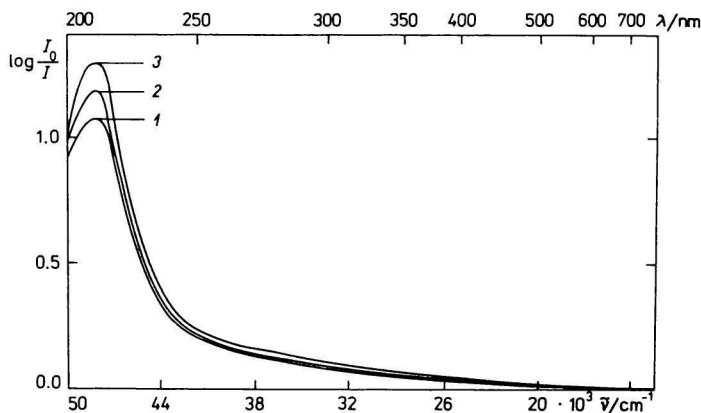


Fig. 1. Ultraviolet spectrum of the exposed samples of PVC.
1. 0 h; 2. 15 h; 3. 40 h.

butyrolactone which absorbs at 1780 cm^{-1} [29]. The presence of solvents also manifests itself by a characteristic absorption in the ultraviolet region. The presence of residual THF and water shows itself by a characteristic absorption band with the maximum at 280 nm and a more distinct band at 220 nm. The results of measurements represented in Fig. 1 reveal only the presence of one absorption band the height of which almost linearly increases with progressing photooxidative degradation (Fig. 2). This band may be assigned to a complex of chromophores

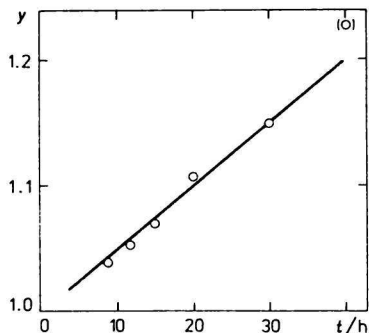


Fig. 2. Dependence of the $n \rightarrow \pi^*$ transitions on exposure.

with the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions ($-\bar{\text{C}}\bar{\text{I}}$, $-\bar{\text{O}}-$, $-\text{C}=\text{O}$, ...).

The infrared spectrum of the investigated sample of PVC is represented in Fig. 3. Its analysis may be based on the paper by *Krimm and Liang* [30] and a review in the book written by *Dechant et al.* [31]. The distinct band at 2970 cm^{-1} corresponds to stretching vibrations of the C—H bonds, the band at 2962 cm^{-1} to vibrations of the C—H bonds in the crystalline region of polymer, and the band at 2855 cm^{-1} to vibrations of the C—H bonds in the amorphous region of polymer. The bands at $1700\text{--}1800\text{ cm}^{-1}$ are to be attributed to hydroxytetrahydrofuran and butyrolactone arisen from residual THF. The absorption band at 1426 cm^{-1} can be assigned to vibrations of the apliphatic methylene groups. The region $1203\text{--}1338\text{ cm}^{-1}$ may be attributed to vibrations of the C—H bonds in the $-\text{CHCl}-$ groups and the region at 1100 cm^{-1} to vibrations of the $-\text{C}=\text{C}-$ bonds. As obvious from Fig. 3, the PVC used may be regarded as amorphous because it does not exhibit the characteristic maximum at 690 cm^{-1} . Because of the presence of the maximum at 655 cm^{-1} , a larger amount of syndiotactic structures may be assumed [31]. The presence of residual solvent is without doubt indicated by the characteristic doublet in the region $1720\text{--}1770\text{ cm}^{-1}$ [32, 33].

A decrease in number of the C—H bonds is observable during the photooxidative degradation of PVC (Figs. 4 and 6), which is evidently due to dehydrochlorination. The content of the C—H bonds linearly decreases with increasing exposure.

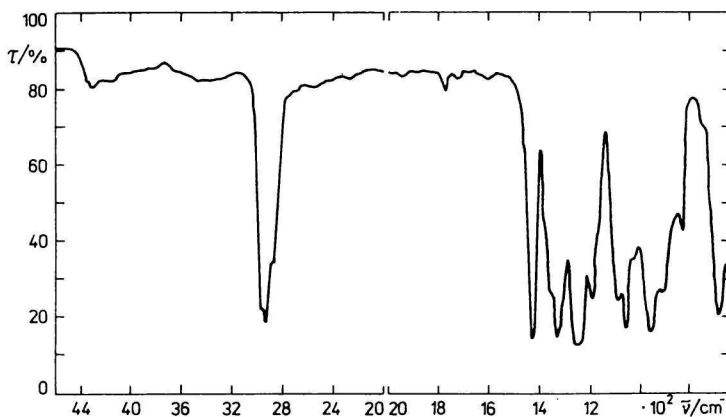


Fig. 3. Infrared spectrum of the nonirradiated PVC (irradiated for 0 h).
Spectrum taken with Specord 71 IR.

The change in infrared spectrum of the destroyed PVC is remarkable in the region $1700\text{--}1800\text{ cm}^{-1}$ (Fig. 5). Two absorption bands are observable in this region. One of them corresponds to the carboxyl group while the second one can be attributed to the carbonyl group of an arising aldehyde. The concentration of the carbonyl groups exponentially increases in the first moments of photooxidation, reaches the limiting value and subsequently remains constant during further exposure. The sigmoid character of this temporal dependence (Fig. 7) suggests an autocatalytic influence of the formed carbonyl groups on the process of dehydrochlorination. As alleged by some authors [34, 35], the probability of breaking of the C—H and C—Cl bonds is equal. Owing to dehydrochlorination, the number of the C—Cl bonds decreases with progressing photooxidative destruction and the double bonds formed are the cause of generation of cyclic peroxides and hydroperoxides and lastly after breaking of the main chain the cause of the formation of terminal aldehyde groups.

Besides the breaking of the main chain, a crosslinking sets in and results in the formation of insoluble gel residues (Figs. 8 and 9). The linear dependence of the content of gel fraction on exposure is, to a certain degree, surprising. However, it may be explained as follows: The carbonyl groups arising in the volume of polymer sample participate in consecutive reactions for a limited period of time. The reaction source of free oxygen in the internal volume of polymer gets exhausted in the course of time. If a lasting supply of oxygen into the internal volume of polymer were ensured, the dependence of gel fraction on exposure should exponentially rise because of photosensitizing effect of the formed carbonyl groups which should take away oxygen and be operative as an additional driving force. The linear dependen-

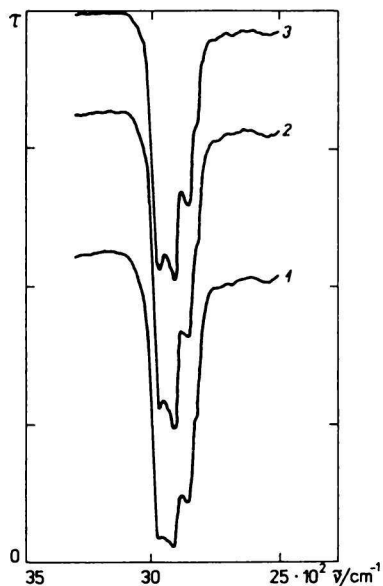


Fig. 4. Detail of the infrared spectrum of PVC films.
1. 0 h; 2. 9 h; 3. 40 h.

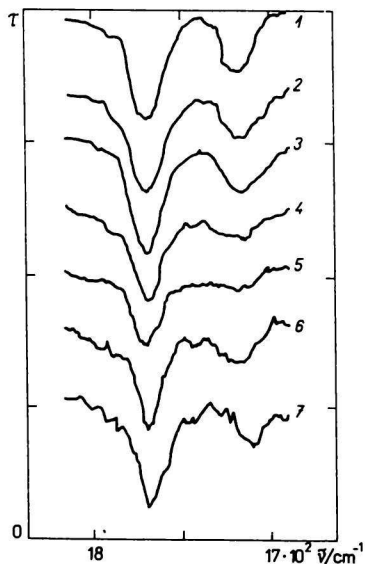


Fig. 5. Detail of the infrared spectrum of PVC samples.
Enlarged four times.
1. 0 h; 2. 9 h; 3. 12 h; 4. 15 h; 5. 20 h;
6. 30 h; 7. 40 h.

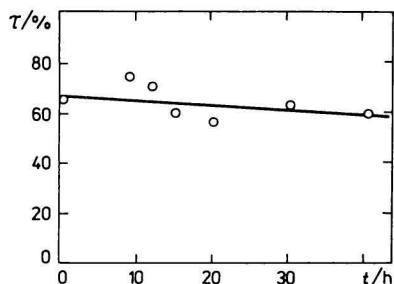


Fig. 6. Decrease in the CH bonds (absorption band at 1338 cm^{-1}) as a function of exposure time.

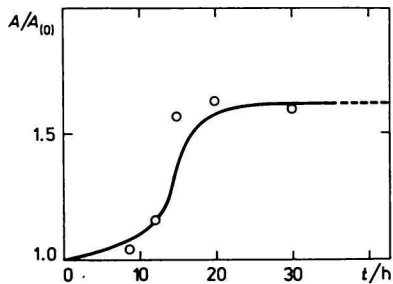


Fig. 7. Variation of relative increase in carbonyl groups with exposure.

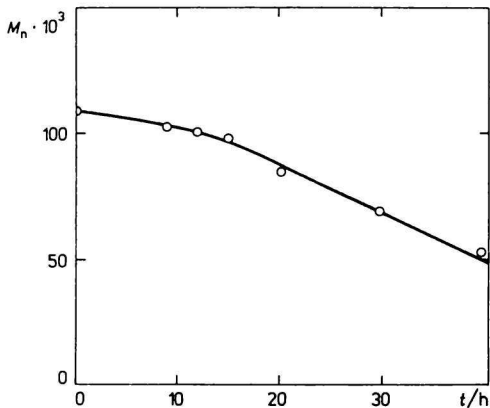


Fig. 8. Variation of relative molecular weight of the soluble fraction with photooxidation time.

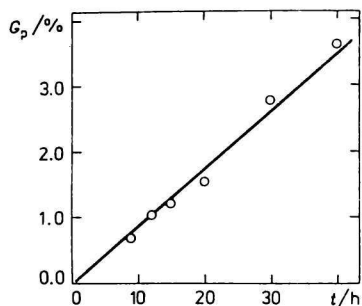


Fig. 9. Dependence of the gel fraction on photooxidation time.

ce indicates the course of a few competing reactions among which there are some which support the formation of new carbonyl groups (photosensitization, photodisproportionation, etc.) while the others reduce the concentration of these groups

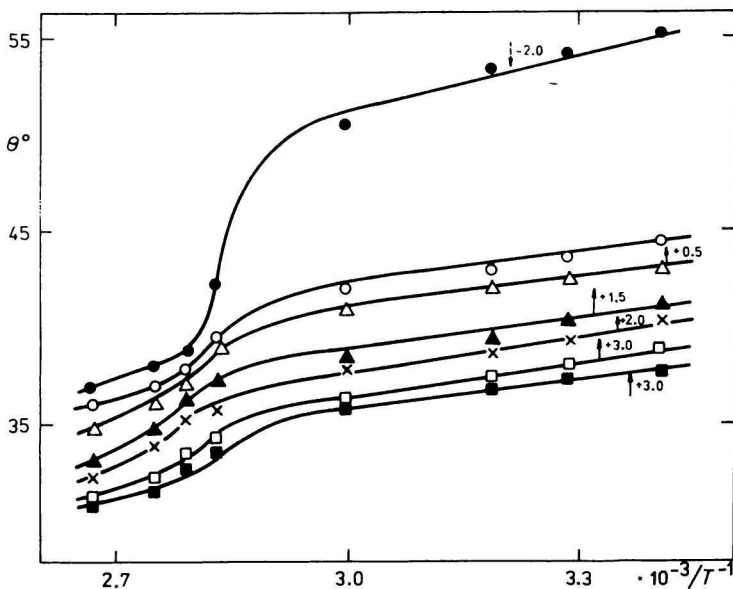


Fig. 10. Limiting angle of wetting of the exposed films of PVC.

● Irradiation; ○ irradiated for 9 h; △ 12 h; ▲ 15 h; × 20 h; □ 30 h; ■ 40 h.

(decarboxylation, photodecomposition, etc.). The decrease in surface as well as volume concentration of the C—H bonds appears most distinctly in the interface polymer—O₂. For this reason, the limiting angle of wetting of the destroyed samples was measured in the temperature range 20—100°C.

As obvious from Fig. 10, the temperature dependence of the limiting angle of wetting sensitively reacts to the point of inversion of the second order. In the region of phase transition (in the region of T_g) a rapid decrease in the angle of wetting appears which is due to a change in surface energy of the solid polymer phase.

As evident from the data given in Table 1, T_g changes with increasing exposure of PVC to ultraviolet radiation and simultaneously the transition interval of T_g is washed in a broader temperature interval. Owing to increased content of the polar hydrophilic groups in the surface layer of destroyed PVC, a more intensive sorption of different kinds of occlusion vapour (especially H₂O) takes place on the surface, which manifests itself by a slight relative extreme on the plot of T_g against the length of exposure (T_g determined from temperature dependence of Θ on T [36]). As a matter of fact, a photoactivated desorption of the sorbed vapour from the surface of the investigated samples of PVC takes place in the first stage of exposure.

The further decrease in the angle of wetting and glass transition temperature accompanying destruction may be explained by a formation of hydrophilic groups in the surface of polymer sample. The simultaneous formation of crosslinks between chains results in increasing kinetic elasticity which manifests itself by decrease in T_g and broadening of the transition region about T_g .

On the basis of available data concerning the evaluation of polar and dispersion interactions in liquid systems, we tried by the method according to *Fowkes* [37] to

Table 1
Temperatures of glass transition (T_g) of the exposed films of PVC

Exposure time h	Temperature of glass transition T_g /K	Limiting angle of wetting of the PVC surface with ethylene glycol 0°, 25°C
0	349.4	42.3
9	357.8	38.6
12	357.0	38.0
15	356.0	37.3
20	355.3	37.0
30	354.5	37.0
40	354.0	36.5

estimate the value of σ_s for PVC during exposure. Ethylene glycol, glycerol, triethylene glycol, ethylene glycol monoethyl ether, and water [38] were used as liquids possessing known σ_L^d and σ_L^p . The calculation is based on the following equation

$$\frac{[1 + \cos \Theta] \sigma_L}{2[\sigma_L^d]^{\frac{1}{2}}} = [\sigma_s^d]^{\frac{1}{2}} + [\sigma_s^p]^{\frac{1}{2}} \left(\frac{\sigma_L - \sigma_L^d}{\sigma_L^d} \right)^{\frac{1}{2}} \quad (1)$$

$$\sigma_s = \sigma_s^d + \sigma_s^p$$

where σ_s^d is the nonpolar and σ_s^p is the polar component of the surface energy σ_s . The obtained data are listed in Table 2 which shows clearly that $[\sigma_s]_{\text{PVC}}$ only slightly increases with exposure whereas the polar component σ_s^p changes considerably, *i.e.* increases. This fact may be explained by the formation of polar carbonyl, hydroxyl, and peroxidic groups in the surface of exposed samples, which is also confirmed by Fig. 7.

Table 2
Values of surface energy of the exposed films of PVC

Exposure time h	Temperature, K					
	293.2			313.2		
	σ_s^d *	σ_s^p	σ_s	σ_s^d	σ_s^p	σ_s
0	37.5	2.7	40.2	31.0	6.1	37.1
9	26.5	12.2	38.7	23.5	9.5	33.0
12	26.6	12.7	39.3	24.3	14.0	38.3
15	26.1	13.6	39.7	25.1	13.7	38.8
20	25.6	14.3	39.9	24.1	15.1	39.2
30	25.7	14.6	40.3	24.1	15.5	39.6
40	25.8	15.1	40.9	24.4	15.5	39.9

* Dimension of the quantities denoted by σ is mN m^{-1} .

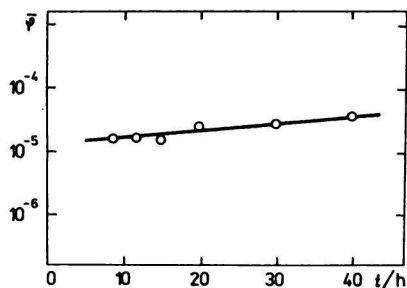


Fig. 11. Variation of the mean quantum yield with photooxidation time.

The mean integral quantum yield of the photooxidative destruction of PVC was calculated from the temporal change in ultraviolet spectra and data obtained by means of a ferric oxalate actinometer. As evident from Fig. 11, the value of this quantity increases with exposure, which also indicates a sensitizing effect of arising chromophores of the carbonyl and polyene type.

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