Photodestruction of poly(vinyl chloride). I. Changes in transport properties and critical angle of wetting due to the exposure to polychromatic ultraviolet radiation

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Dedicated to Academician V. Kellö, in honour of his 60th birthday

The influence of exposure of poly(vinyl chloride) to polychromatic ultraviolet radiation on transport properties and the critical angle of wetting was investigated. The kinetics of formation of the polymer swollen layer in the systems poly(vinyl chloride)—dimethyl ketone and poly(vinyl chloride)—ethyl methyl ketone were studied. The measured values of apparent average diffusion coefficients in the systems investigated varied within the range 5×10^{-11}—4×10^{-10} m^2 s^{-1} and increased with exposure in an equal manner as the activation energy of diffusion which varied in the interval 0.4—0.7 kJ mol^{-1}. It was found that the value of $[\eta]$ of the investigated samples increased at the first moments of the exposure to ultraviolet radiation while the critical angle of wetting of the poly(vinyl chloride) films by water decreased.

Исследовано изменение транспортных свойств и предельного угла смачивания поливинилхлорида после действия полихроматического УФ-облучения. Изучалась кинетика образования полимерного набухшего слоя в системе поливинилхлорид—диметилкетон или метилэтилкетон. Измеренные средние кажущиеся коэффициенты диффузии изучаемых систем находились в интервале от 5×10^{-11} до 4×10^{-10} м² с⁻¹ причем они повышались при увеличении облучения также как и энергия активации диффузии, имеющая значение в диапазоне 0,4—0,7 кдж моль⁻¹. Было обнаружено, что в первый момент облучения имеет место повышение $[\eta]$ изучаемых образцов, а предельный угол смачивания поверхности поливинилхлорида водой понижается.

The assumption of radical mechanism [1—5] is a general view of the photodegradation of poly(vinyl chloride) (PVC). There are different opinions about initiation of this reaction, but HCl is assumed to be the main product while the result of

dehydrochlorination is a sequence of unsaturated polyenes. It has been ascertained that the absorption of light linearly increases with the degree of dehydrochlorination of the PVC samples while the colour of these degraded samples changes from yellow to red, which is due to the sequence of the conjugated double bonds [1, 6, 7].

Dole states that degradation is initiated in the spots with labile chlorine which may be also generated by high-energy radiation [2].

It results from the study of the e.p.r. spectra that a polyene free radical initiates the reaction in irradiated PVC [1, 2, 8]. On irradiation, the concentration of free polyene radicals does not change, but the concentration of conjugated double bonds increases. The electron delocalization in polyene radicals gives a symmetric singlet e.p.r. signal.

It may be assumed that the energy transfer is a very important part of the u.v. degradation mechanism. *Gibb* [9] states that the wavelength of 254 nm is optimum for initiation of the PVC decomposition.

Other mechanical influences affect the PVC degradation, too. *Papko* [10] has revealed that the thermal degradation of PVC may follow the radical, molecular, and ionic mechanism while the contribution of each of them depends on reaction conditions. In general, it may be assumed that the influence of the ions present cannot be neglected. *Partchamazad* [11] has put forward a mechanism of ionic active radicals according to which the radical intermediates are sensitive to polarity of the reaction mixture.

The rate of the PVC decomposition considerably increases in the presence of molecular oxygen when compared with the rate of this process in inert atmosphere or *in vacuo*. In photooxidation of PVC we may also observe reactions involving breaking of main bonds, which results in a substantial decrease in molecular weight of the polymer. Simultaneously, some addition reactions take place, but their rate is usually much smaller than the rate of the photolytic reactions in the absence of oxygen [5].

The aim of this study was to investigate the influence of polychromatic ultraviolet radiation on transport resistivity of PVC against a low-molecular liquid penetrant. As a matter of fact, if the polymer chains are broken and polydiene structures arise in a photochemical destruction of PVC, the result of these transformations must consist in an increase in mobility of the fundamental kinetic units of chains (segments), which manifests itself in increasing value of the apparent average diffusion coefficient and overall width of the swollen polymer layer (PSL). Simultaneously, the thermodynamic conditions of mixing of the polymer with a polar solvent deteriorate owing to the splitting-off of HCl and formation of nonpolar diene structures. It may be supposed that the free radicals arising on the surface of exposed samples will easily react with oxygen present to give hydroperoxides owing to which their physical character changes. The hydrophility of the

surface of PVC showing itself in decreasing critical angle of wetting by water ought to increase with increasing exposure to ultraviolet radiation.

Experimental

Materials and preparation of samples

The emulsion polymer of vinyl chloride, commercial denotation Geon 121 (UK), was used.

The polymers were deprived of the rests of catalysts, emulsifiers and other impurities by multiple extraction with redistilled water and methyl alcohol at laboratory temperature. Tetrahydrofuran deprived of peroxides before use by reflux with KOH was used as a solvent.

The solvents used for measurements, *i.e.* dimethyl ketone, ethyl methyl ketone, and cyclohexanone were anal. grade chemicals. Before use they were redistilled and their purity was checked by measuring the index of refraction accurate to four decimal places.

The PVC films were prepared by casting from a 2% solution in tetrahydrofuran (THF) on a glass Petri dish in nitrogen without admission of light. These films were exposed to polychromatic ultraviolet radiation of a high-pressure mercury lamp (500 W) for 1, 3, 5, and 7 h at a distance of 0.64 m from the source of u.v. radiation. The irradiation was performed in an instrument "Schlieren — Aufnahmegerät 80" in air at laboratory temperature (22°C).

The kinetic measurements of the layer width δ were carried out with PVC samples of the size $7 \times 7 \times 0.11$—0.14×10^{-9} m³ at temperatures 20, 25, 30, 35, and 40°C by means of a simple optical device described earlier [12, 13]. Dimethyl ketone and ethyl methyl ketone were used as solvents. Assuming validity of the equation [12, 13]

$$\delta = (2Dt)^{\frac{1}{2}} \qquad (1)$$

we can immediately read the value of the apparent average diffusion coefficient D from the slope of straight line.

The viscosities were measured with a dilution high-speed viscometer according to Seide and Deckert. The diameter of capillary (K4) was so chosen that the corrections for kinetic energy and capillary curvature were negligible. The volume of solution for measurement was 1.5 ml and cyclohexanone was used as a solvent. The concentrations of PVC were measured in the interval $(0.27$—$0.52) \times 10^{-3}$ kg of sample per 0.1 kg of solvent at temperatures 20, 25, 30, 35, and 40°C. Before each measurement, the solution was allowed to stand for 30 min to balance and stabilize the temperature accurate to ± 0.1°C.

The limiting viscosity numbers $[\eta]_H$, $[\eta]_s$, and $[\eta]_k$ were used for characterization of nondegraded and degraded samples. The definitions and methods of determination of the limiting viscosity numbers are known and described in literature [14—16].

The angle of wetting was measured by means of a simple experimental device which consisted of the following parts:

1. Measuring instrument — an optical projection apparatus in the optical axis of which an axial cross was build. The image of a drop adhering to the surface of the sample was projected on this cross.

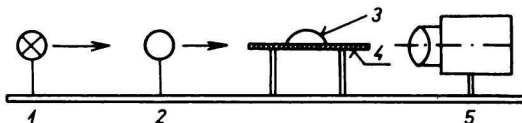2. Stand — on which the sample was placed.

3. Source of light.

Fig. 1. Diagram of the experimental device for measuring the critical angle of wetting.
1. Source of light; *2.* optical filter; *3.* drop of measuring liquid; *4.* the measured sample; *5.* circle goniometer.

The diagram of the experimental device is represented in Fig. 1. The accuracy of determining the angle of wetting was $\pm 2°$. The time dependence of the angle of wetting enables us to read the value of the angle of wetting Θ at the time moment $t = 0$.

Results and discussion

The instance of kinetic curve representing the dependence of the overall PSL width on time in case of varying value of the temperature parameter is given in Fig. 2. This characteristic course was found for all systems investigated. Thus we may state that eqn (*1*) conveniently describes the time dependence of the overall PSL width in rather wide time interval for both solvents used. The surface of the sample is saturated immediately after making contact of both phases. It may be assumed that the observed scattering of experimental points in the function $\delta^2 = f(t)$ is due to varying width of the measured foil as well as to inhomogeneous distribution of aggregate structures in the whole volume of the sample [12].

According to accepted general morphological conception, a solid amorphous polymer consists of disordered chain molecules wound into incidental structureless considerably entangled coils with free nonoccupied space which forms the so-called "free volume". The increase in rubber-like behaviour with increasing molecular weight is a result of this entanglement of chains. The existence of excess free volume is a real basis for interpretation of many phenomena, besides others, of the high values of diffusion coefficients of gases and liquid penetrants in the solid amorphous polymer phase. The values of diffusion coefficients in the systems studied calculated from eqn (*1*) vary within the range 5×10^{-11}—4×10^{-10} m^2 s^{-1} whereas the corresponding values in crystalline phase are rather lower (Tables 1 and 2).

The values found experimentally show unambiguously that the value of slope of the line describing the time dependence of the overall width of PSL (*i.e.* the average apparent diffusion coefficient) increases with temperature (Figs. 2 and 3, Tables 1 and 2). This statement is in good agreement with the general theory of diffusion phenomena in polymers.
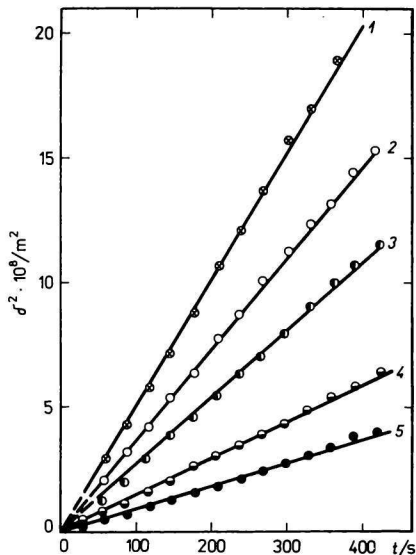
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Fig. 2. Dependence of the PSL width on time for the system PVC—dimethyl ketone, no irradiation.
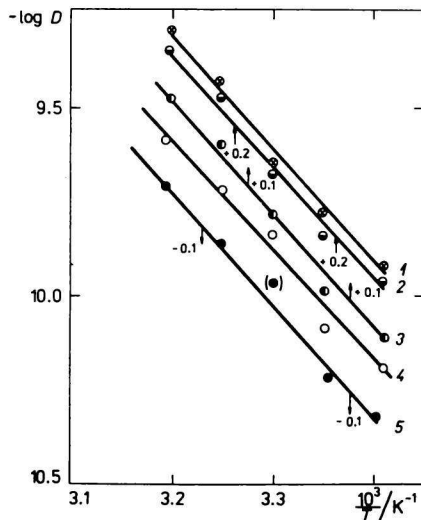1. 40°C; 2. 35°C; 3. 30°C; 4. 25°C; 5. 20°C.

Fig. 3. Variation of the average apparent diffusion coefficient with temperature for different times of irradiation of PVC in the system PVC—dimethyl ketone.
1. 7 h; 2. 5 h; 3. 3 h; 4. 1 h; 5. 0 h.

The value of diffusion coefficient (Fig. 4, Tables 1 and 2) also increases with the time of irradiation of polymer which is due to degradation by light, *i.e.* decomposition of the macromolecular substance into smaller molecular units. The decomposition of polymer is likely to obey radical mechanism. Simultaneously, its dehydrochlorination proceeds [1—5]. In conformity with *Papko* [10], we may assume that the degradation follows both molecular and ionic mechanism. The participation of ionic mechanism in the degradation of PVC by light was also confirmed by the experimental results obtained by *Partchamazad* and *Khosrovi* who proposed a mechanism of ionic active radicals [11]. The mobility of polymer chains must increase with irradiation time and simultaneously the height of potential barrier for molecules of the solvent at the interface liquid—solid phase decreases. That is the fundamental factor determining the movableness of macromolecular chains. Formally, all these influences are reflected in the values of diffusion coefficients. On the basis of the results presented in Tables 1 and 2, the different values of diffusion coefficient may be regarded as a result of different degree of interaction polymer—solvent, *i.e.* of the values of activity coefficients which directly determine the value of thermodynamic factor [17] of diffusion coefficient.

As obvious from Fig. 3 (where for clearness individual curves are shifted in the sense of arrow by a given value — log D), the logarithmic dependence of diffusion
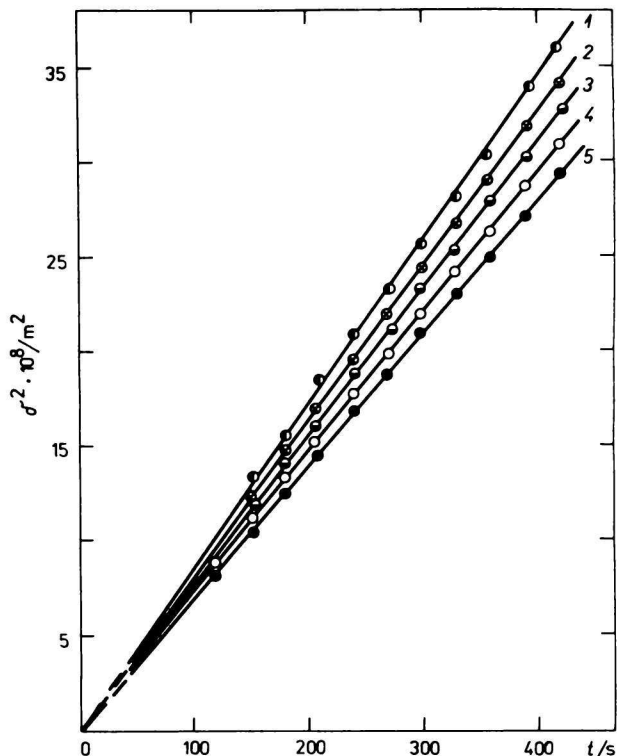
Fig. 4. Dependence of the PSL width on time for the system PVC—ethyl methyl ketone, temperature 40°C.
Time of irradiation: 1. 7 h; 2. 5 h; 3. 3 h; 4. 1 h; 5. 0 h.

Table 1

Values of the average apparent diffusion coefficients D
in the system PVC—dimethyl ketone

Temperature °C	$D \cdot 10^{11}$, m² s⁻¹				
	Time of irradiation, h				
	0	1	3	5	7
20	4.7	5.1	6.3	7.1	8.2
25	7.0	8.0	8.6	9.3	10.1
30	12.0	13.2	13.6	14.3	15.4
35	18.0	19.4	20.2	21.3	23.0
40	25.2	25.9	27.9	29.6	32.8

Table 2

Values of the average apparent diffusion coefficients D
in the system PVC—ethyl methyl ketone

Temperature °C	$D \cdot 10^{11}$, m^2 s^{-1}				
	Time of irradiation, h				
	0	1	3	5	7
20	10.2	12.0	12.8	13.3	14.2
25	16.0	18.0	18.5	19.0	20.4
30	23.5	25.9	26.0	28.4	31.4
40	34.9	36.5	38.4	40.5	43.4

coefficient on temperature of the solvent molecules in solid PVC may be described
by a widely-used equation of the Arrhenius type

$$D_i = D_i^0 \exp\left(-\frac{E_D}{RT}\right) \tag{2}$$

The values of preexponential factors D^0 and activation energies E_D are given in
Table 3.

At the first moments of exposure, substantial changes appear in the organized
structure of the solid PVC phase. These changes are accompanied by increase in
absorptivity of the u.v. radiation owing to formation of the polyene chromophores
which accelerate the process of chain breaking. This fact is the most conspicuous
during the first hour of irradiation and manifests itself in a characteristic course of

Table 3

Values of the activation energy of diffusion E_D and preexponential factors D^0

System	Time of irradiation h	$E_D \cdot 10^2$ J mol^{-1}	D^0 m^2 s^{-1}
PVC—dimethyl ketone	0	654	41.5
	1	564	21.6
	3	568	27.0
	5	575	28.1
	7	581	37.4
PVC—ethyl methyl ketone	0	476	13.5
	1	390	5.5
	3	401	7.0
	5	410	7.0
	7	422	11.6

the relationship between the activation energy of diffusion and time. The values of activation energy obtained with irradiated samples are smaller than those obtained with nonirradiated samples. The accuracy of determining diffusion coefficients exhibits the relative error ± 3—6% and the error in determining activation energies is ± 5—11%.

The measurements of the infrared spectra of irradiated and nonirradiated samples show that the most conspicuous changes appear in the region 18×10^4—17×10^4 m^{-1} $\nu(C=O)$. The presence of two peaks is to be observed: the first one at 17.38×10^4 m^{-1} and the second one at 17.8×10^4 m^{-1} (Fig. 5). That may be explained by a progressive oxidation of instable chain sections accompanied in the first stage with formation of hydroperoxides which decompose and yield carbonyl compounds (Scheme 1)
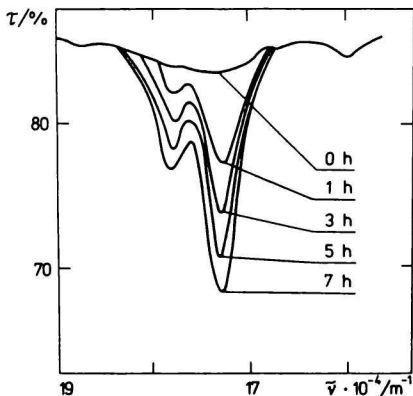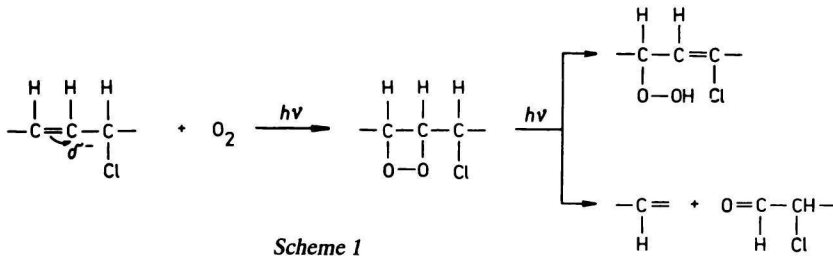
Scheme 1

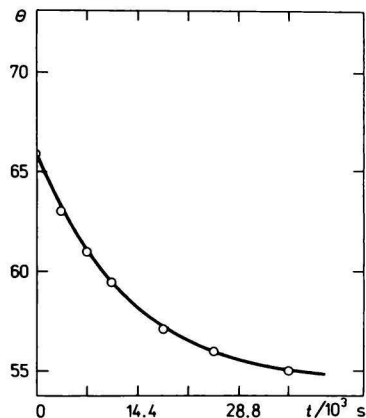*Fig. 5.* Part of the infrared spectrum corresponding to original and irradiated PVC.

Fig. 6. Variation of the critical angle of wetting with irradiation time.

The measurements of viscosity of the PVC samples in cyclohexanone carried out at different concentrations and temperatures provided characteristic curves and confirmed the validity of current extrapolation methods [14—16] for the systems investigated in the used concentration and temperature region (within the range of experimental errors). The calculated values of constants k_H, k_s, and k_K as well as the values of limiting viscosity numbers $[\eta]_H$, $[\eta]_s$, and $[\eta]_K$ are listed in Table 4. The numerical value of these constants is a function of the molecular weight of polymer, temperature, and probably of the degree of branching, as well [18]. The values of k_H most frequently reported in literature for solutions of polymers in good solvents vary in the range 0.2—0.6.

Table 4

Values of $[\eta]_H$, $[\eta]_s$, $[\eta]_K$, k_H, k_s, and k_K for the solutions
of PVC in cyclohexanone

Time of irradiation h	Temperature °C	$[\eta]_H$	$[\eta]_s$ 0.1 m³ kg⁻¹	$[\eta]_K$	k_H	k_s	k_K
0	20	0.45	0.47	0.45	1.99	1.92	1.05
	25	0.44	0.48	0.46	1.87	1.78	1.10
	30	0.47	0.47	0.44	1.87	1.78	1.17
	35	0.46	0.47	0.45	1.81	1.78	1.23
	40	0.47	0.49	0.46	1.79	1.75	1.25
1	20	1.32	1.25	1.21	0.26	0.16	0.10
	25	1.31	1.26	1.25	0.25	0.17	0.18
	30	1.32	1.27	1.29	0.20	0.14	0.15
	35	1.33	1.28	1.30	0.15	0.11	0.20
	40	1.33	1.28	1.30	0.14	0.95	0.23
3	20	1.15	1.06	0.94	0.49	0.29	0.26
	25	1.18	1.15	1.12	0.46	0.28	0.20
	30	1.18	1.19	1.14	0.43	0.27	0.26
	35	1.24	1.21	1.15	0.41	0.22	0.28
	40	1.26	1.20	1.15	0.37	0.21	0.32
5	20	1.05	1.00	0.95	0.55	0.54	0.29
	25	1.05	1.05	1.05	0.56	0.52	0.35
	30	1.10	1.10	0.99	0.54	0.53	0.34
	35	1.05	1.05	1.05	0.51	0.49	0.42
	40	1.10	1.12	1.15	0.52	0.52	0.44
7	20	0.50	0.48	0.50	1.72	1.68	0.92
	25	0.51	0.49	0.50	1.71	1.65	1.06
	30	0.53	0.53	0.51	1.73	1.68	1.04
	35	0.53	0.52	0.50	1.69	1.69	1.06
	40	0.52	0.53	0.52	1.70	1.65	1.11

The increase in the values of $[\eta]$ of irradiated PVC in comparison with the values of $[\eta]$ of nonirradiated PVC at short time of irradiation may be due to dehydrochlorination of PVC and incidental formation of the unsaturated polyenes which transform the structure and cause crosslinking of the irradiated PVC, which manifests itself by an increase in the value of $[\eta]$. A certain decrease in $[\eta]$ accompanying a longer irradiation may be explained by the fact that polyolefins and carbonyls arisen by degradation of PVC and proved by infrared spectra in the product of photooxidation (Fig. 5) absorb the light energy better (especially in the presence of molecular oxygen) and decompose into smaller molecular units at longer irradiation, which causes a decrease in probability of crosslinking.

Furthermore, the angles of wetting were measured in the system water——PVC—air. The dependence of the angle of wetting Θ on irradiation time exhibits a falling character (Fig. 6) and approximates to a definite limiting value. During irradiation, PVC is degraded, which is accompanied with the formation of different radical structures which easily react with the present molecules of singlet to give hydroperoxides and peroxides [1—5, 11]. For this reason, the hydrophility of the exposed samples increases, which results in decreasing value of the critical angle of wetting of PVC by water. The increase in water adhesion on the surface of PVC may be related to the formation of free radicals, ions, and unsaturated polyenes which are products of the light degradation of PVC.

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