

Crosslinking of polymers by the effect of ultraviolet radiation

Crosslinking of poly(vinyl alcohol) in the presence of terephthalic aldehyde

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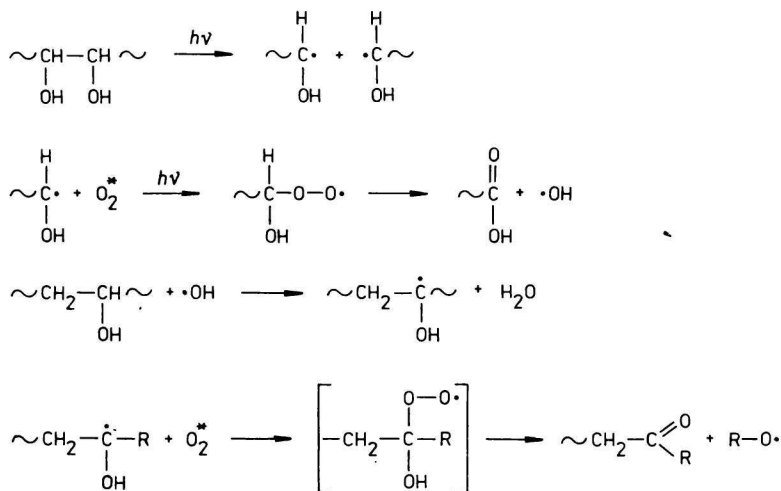
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The effect of the exposure of poly(vinyl alcohol) (PVA) to polychromatic ultraviolet radiation of a high-pressure mercury lamp in the absence or presence of terephthalic aldehyde (TPA) was studied. The crosslinking process was studied by following gel portion, viscosity of the dissolved portion, and kinetics of formation of the swollen surface layer (SSL) in the system PVA—water. It has been found that the crosslinking process in PVA is significantly influenced by the presence of TPA which takes part in the process both as a crosslinking agent and probable sensitizer. This view is confirmed by the results of viscometric and spectral measurements. The most marked changes are to be observed in the first stage of exposure. On the basis of kinetic study of the SSL formation in the investigated system, the values of the apparent mean diffusion coefficients have been determined. They vary within the range 1.7×10^{-11} — $3.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ and decrease with the content of TPA and exposure. The calculated values of activation energy of the diffusion of H_2O into PVA increase with the content of TPA and exposure from 76 to 105 kJ mol^{-1} for the investigated samples.

Было изучено влияние облучения поливинилового спирта (ПВС), без и в присутствии терефталальдегида (ТФА), полихроматическим УФ излучением ртутной разрядной лампы. Изучался процесс сшивания ПВС по определению доли геля, вязкости растворимой доли и кинетики образования набухшего поверхностного слоя (НПС) в системе ПВС—вода. Было обнаружено, что на процесс сшивания ПВС положительно отражается присутствие ТФА, который принимает участие в процессе как сшивательный агент, а также, вероятно, как сенсibilизатор. Последнее подтверждается измерениями вязкости и спектров. Самые сильные изменения наблюдались в первых фазах облучения. На основании изучения кинетики образования НПС изучаемой системы в воде были определены значения средних кажущихся коэффициентов диффузии, которые находились в диапазоне от $1,7 \times 10^{-11}$ до $3,1 \times 10^{-10} \text{ м}^2 \text{ с}^{-1}$, причем наблюдалось их уменьшение с содержанием ТФА и увеличением выдержки. Значения энергии активации диффузии H_2O в ПВС повышаются с содержанием ТФА и выдержкой от 76 до $105 \text{ кДж моль}^{-1}$.

The photochemical transformations of PVA have been given little attention in literature.

It has been ascertained [1, 2] that the light absorption in a solid PVA film increases with decreasing relative molecular weight, which can be explained by an increase in residual carbonyl groups originating from primary poly(vinyl acetate) [3—8] as well as oxidative cleavage of the C—C bonds of the vicinal CH—OH groups. On the basis of literature data [1, 2], it may be assumed that the C—C bond between the vicinal CH—OH groups of polymer chain splits according to Scheme 1. *Geuskens, Borsu, and David* [1] explain the sensitizing effect of the residual vinyl acetate member by the formation of a seven-membered cycle due to the activated oxygen atom of the carbonyl group, which results in destruction of the



Scheme 1

basic unit without splitting off of the side acetal group. These authors [1] also explain the formation of crosslinked structures by assuming recombination of the radicals which arise as a product of hydrogen abstraction on the tertiary carbon atom by the singlet oxygen produced by the sensitizing effect of the excited carbonyl group. *Milinchuk and Klishpont* [9] explain the formation of gel portions in an exposed film of PVA by the formation of ester bridges due to condensation of the aldehyde and hydroxyl groups of vicinal chains. As already mentioned, the basic chain splits into fragments with double bonds [1] simultaneously with that process, the quantum yield being 1.0×10^{-2} . The quantum yields of the crosslinking processes are somewhat smaller.

Aqueous solutions of the thermally activated PVA in acid medium are transformed into gels by means of bifunctional agents which undergo condensation with organic hydroxyl groups in aqueous solutions. For instance, gels can be formed from a 2–10% aqueous solution of PVA containing 0.03–0.14% TPA at pH 1 and 20°C [2].

The aim of this study is to clear up the kinetics of the process of phototransformation of PVA by the effect of polychromatic ultraviolet radiation in the absence and in the presence of TPA functioning as a crosslinking agent and sensitizer. The changes in solubility, relative molecular weight and transport resistivity of the exposed and nonexposed films are presented.

Experimental

The measurements were carried out with PVA of Czechoslovak production, Sloviol R 16 (W. Pieck Chemical Works, Nováky) which contained 0.5% of vinyl acetate according to the information of the producer.

TPA was prepared from *p*-xylene by radical bromination succeeded by hydrolysis with concentrated sulfuric acid. The white crystals of TPA were purified by repeated recrystallization in methanol.

The redistilled water was prepared by distillation of aqueous solution of KMnO_4 . Other solvents used, *i.e.* anal. grade methanol, ethanol, and acetone were products of Lachema, Brno.

The PVA films were prepared by evaporating water from a 4% solution of PVA in Petri dishes at 20°C in air and in dark. Before evaporating, the following amounts of TPA were added into the solution of PVA: 0.0; 0.5; 1.0; 2.0; 4.0% of TPA calculated in relation to the weight of polymer. The films of the width $10^{-5} \text{ m} \pm 5\%$ and $3 \times 10^{-5} \text{ m} \pm 4\%$ were prepared. The PVA films were kept in dark.

A high-pressure mercury lamp HBO 500 (Narva, Berlin) in optical system with a quartz condenser was used for exposure of the films. The intensity of entrance polychromatic radiation was $2.03 \text{ J m}^{-2} \text{ s}^{-1}$. The films consisting of PVA and PVA with TPA with the width of $3 \times 10^{-5} \text{ m}$ used for measuring viscosity and width of the swollen surface layer were irradiated for 0, 1, 2, 3, and 5 h.

The content of gel portion was determined by the standard filtration procedure. Simultaneously, the concentration of the noncrosslinked polymer in the filtrate was determined. The results obtained in both cases were agreeing. The viscosity of the filtrate was measured with a viscometer K5 according to Seide and Deckert (Schott, Jena) at constant temperature ($25 \pm 0.1^\circ\text{C}$). The limiting viscosity numbers were determined by the extrapolation procedure on the basis of the Huggins equation from the viscosities measured at four concentrations in the range 0.6×10^{-3} – $1.8 \times 10^{-3} \text{ kg}$ of the sample dissolved in 0.1 kg of the solvent. The kinetic measurements of the width of SSL were performed with a simple optical device described in [10] at 25, 30, 35, and 40°C. Water, methanol, and ethanol were used as solvents. The values of the apparent mean diffusion coefficients D were calculated from the relationship $\delta^2 = 2Dt$.

Results and discussion

The ultraviolet spectra of the investigated samples did not differ from the spectra described in literature [8]. On adding TPA into PVA (the width of the foil 10^{-5} m), the intensity of the bands corresponding to the carbonyl group in the ultraviolet spectrum (Fig. 1) was shifted to longer wavelengths and decreased with exposure.

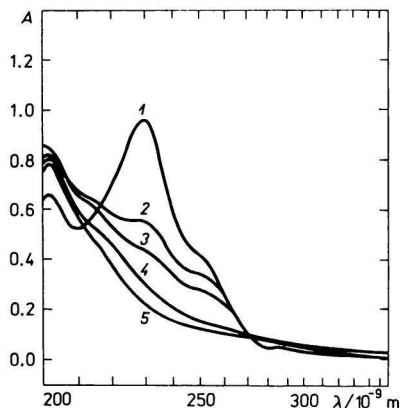
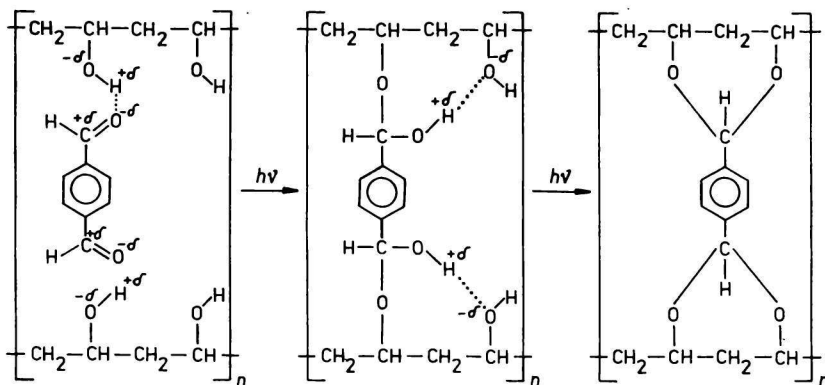


Fig. 1. Ultraviolet spectrum of PVA containing 2% of TPA for different irradiation times:
1. 0 s; 2. 300 s; 3. 1800 s; 4. 3600 s;
5. 10 800 s.

On the basis of analogy [11, 12] with *p*-isothiocyanatobenzaldehyde and *o*-nitrobenzaldehyde, the existence of the following crosslinking mechanism involving a photoactivated condensation reaction may be assumed (Scheme 2).

In the first moment, substantial changes in the structure of the solid PVA phase take place. The shift in the absorption band due to the transformation of the



Scheme 2

carbonyl groups into the carboxyl groups is the most marked in the initial five minutes and is accompanied by a colour change of the exposed foils into yellow. These changes also manifest themselves distinctly in mechanical properties of the films which, due to increasing exposure, become tougher.

After dissolving the irradiated films in water, it was possible, in accordance with the authors of [9], to observe a gel the amount of which depended on exposure of the irradiated sample (Table 1). The content of the gel portion increases exponentially with exposure, which confirms the existence of the crosslinking process. The amount of the crosslinks formed increases with percentage of TPA.

The viscometric measurements of the soluble portions of the PVA samples in water gave characteristic curves and confirmed applicability of the usual extrapolation procedures [13] for the investigated systems in the given concentration interval (in the range of experimental errors). The values of limiting viscosity numbers $[\eta]$ decreased with irradiation time and varied in the interval $0.041\text{--}0.071\text{ m}^3\text{ kg}^{-1}$ (Table 1). For equal irradiation time, the limiting viscosity numbers varied in a certain interval the extent of which contracted and approximated to higher values with increasing content of TPA.

Table 1

Values of limiting viscosity numbers $[\eta] \cdot 10^3 [\text{m}^3\text{ kg}^{-1}]$, for different times of irradiation of aqueous extracts containing noncrosslinked poly(vinyl alcohol) (numbers in parentheses give the gel portion of poly(vinyl alcohol) in wt %)

% TPA/PVA	Time of irradiation, h				
	0	1	2	3	5
0	71	72 (10)	58 (18)	47 (21)	41 (28)
0.5	70	64 (12)	62 (21)	54 (26)	41 (31)
1	68	65 (16)	56 (27)	52 (32)	43 (38)
2	69	74 (28)	64 (37)	57 (43)	54 (48)
4	74	78 (39)	70 (53)	66 (59)	64 (70)

The limiting viscosity number decrease of the soluble portion due to increasing exposure may be explained by two processes: Preferential crosslinking of portions with higher relative molecular weight or cleavage of the polymer chain in vicinity of an accidentally linked carbonyl group, as stated in literature [8].

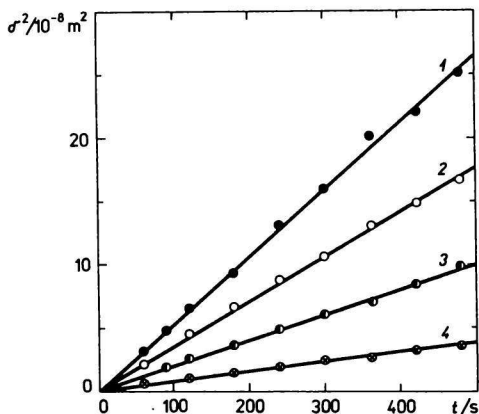
A confrontation of the content of the gel portion with limiting viscosity numbers of the soluble portion enables us to allege that the preponderance of the crosslinking process over photodestruction of the polymer chain manifests itself with increasing amount of TPA. Before the gel point, the limiting viscosity

number $[\eta]$ of the dissolved portion slightly increases and afterwards it decreases. The general and major reason for this decrease is a statistically conditioned building-in of longer chains into the gel.

A kinetic curve giving the dependence of the overall width of SSL on time with variable value of the temperature parameter (the PVA film contained 2 wt % of TPA and was irradiated for 2 h) is represented in Fig. 2. That characteristic course

Fig. 2. Variation of the width of the swollen surface layer with time for the system H_2O —PVA (containing 2 wt % of TPA), irradiation time 7200 s.

1. 313.15 K; 2. 308.15 K; 3. 303.15 K;
4. 298.15 K.



was found for all systems investigated. On this basis, we may state that the equation $\delta^2 = 2Dt$ satisfactorily describes the temporal dependence of the overall width of SSL in a relatively broad time interval for water. The saturation of the surface of sample takes place immediately after both phases have come into contact. It may be assumed that the observed spread of experimental points in the equation $\delta^2 = 2Dt$ is caused by variation of the width of foil as well as by nonuniform distribution of aggregate structures in the whole volume of the sample [10].

Table 2

Kinetic parameters of the swollen surface layer
System H_2O —PVA

Time of irradiation h	$D \cdot 10^{10} [\text{m}^2 \text{s}^{-1}]$				E_D kJ mol^{-1}	D^0 $\text{m}^2 \text{s}^{-1}$
	Temperature, K					
	298.15	303.15	308.15	313.15		
0	0.71	1.3	2.1	3.1	76.1	1.62×10^3
1	0.60	1.3	2.0	2.8	78.6	3.96×10^3
2	0.59	1.2	1.9	2.8	79.7	6.02×10^3
3	0.56	1.2	1.9	2.6	78.8	4.09×10^3
5	0.53	1.1	1.9	2.7	84.3	3.47×10^4

Table 3

Kinetic parameters of the swollen surface layer
System H₂O—PVA containing 1 wt % of TPA

Time of irradiation h	$D \cdot 10^{10} [\text{m}^2 \text{s}^{-1}]$				E_D kJ mol ⁻¹	D^0 m ² s ⁻¹
	Temperature, K					
	298.15	303.15	308.15	313.15		
0	0.70	1.3	2.1	3.0	74.9	1.01×10^3
1	0.60	1.2	2.0	2.8	79.8	6.25×10^3
2	0.53	1.2	1.9	2.7	83.1	2.21×10^4
3	0.48	1.1	1.8	2.7	88.2	1.54×10^5
5	0.45	1.1	1.8	2.6	89.5	2.54×10^5

The values of diffusion coefficients in the investigated systems calculated from the equation $\delta^2 = 2Dt$ vary in the range 1.7×10^{-11} — $31.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ (Tables 2—4). The relative error of the determination of diffusion coefficients is ± 4 —8%.

The experimental values show unambiguously that the value of the apparent mean diffusion coefficient increases with temperature (the percentage of TPA bound and time of irradiation are constant). This statement is in agreement with the general theory of diffusion processes in polymers. It is obvious from Tables 2—4 that the apparent mean diffusion coefficients decrease with percentage of TPA linked in PVA. They also decrease with time of irradiation, the most distinctly at initial exposures. A decrease in apparent mean diffusion coefficient accompanying crosslinking may be explained by a decrease in cooperative mobility of the segments of polymer owing to the formation of crosslinks. The mobility of the

Table 4

Kinetic parameters of the swollen surface layer
System H₂O—PVA containing 2 wt % of TPA

Time of irradiation h	$D \cdot 10^{10} [\text{m}^2 \text{s}^{-1}]$				E_D kJ mol ⁻¹	D^0 m ² s ⁻¹
	Temperature, K					
	298.15	303.15	308.15	313.15		
0	0.66	1.3	2.1	3.0	78.1	3.45×10^3
1	0.46	1.1	1.9	2.8	92.7	9.28×10^5
2	0.40	1.1	1.8	2.7	98.2	7.40×10^6
3	0.33	0.96	1.7	2.6	10.5	1.06×10^8

segments of polymer chains decreases with increasing exposure and gel portion content. Simultaneously, the height of the potential transfer barrier of the solvent molecules in the interface liquid phase—solid phase rises.

The experimental values of activation energy of diffusion E_D (Tables 2—4) calculated from the Arrhenius equation corroborate the above reasoning. The standard error of the average activation energies thus determined is 2—7%.

On the basis of the results given in Tables 2—4, the different values of the apparent mean diffusion coefficients D and activation energies of diffusion E_D may be regarded as a consequence of changed thermodynamic conditions which immediately determine the value of the thermodynamic factor of diffusion coefficient [14].

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