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PHOTOSENSITIZING PROPERTIES OF POLYCONJUGATED ORGANIC POLYMERS

For polymers with a system of conjugated bonds the presence of semiconducting properties is characteristic (^{1}). The photosensitizing action of crystalline organic dyes is also, apparently, connected with their semiconducting properties. A. A. Krasnovskii and G. P. Brin showed that crystalline phthalocyanines—organic semiconductors—possess a photosensitizing action in the reaction of oxidation of ascorbic acid by oxygen (^{2}). Therefore it could be expected that polyconjugated systems would also possess photosensitizing properties.

The present communication is devoted to the study of the influence of the photosensitizing action of polymers with a system of conjugated bonds in the reaction of oxidation of ascorbic acid. To observe the oxidation kinetics, the micromanometric Warburg—Barkroft method was used. Experiments were carried out with an aqueous solution of ascorbic acid under illumination* with red (longer than 600 mμ), white light from an incandescent lamp, and ultraviolet (mercury line 365 mμ) light. Before the experiments the polymers were ground and sieved through a sieve with hole size 0.1-0.05 mm.

To a weighed portion of polymer (100 mg), placed in the reaction vessel of the apparatus equipped with a manometric tube, distilled water (10 ml) was added. The vessel was thermostatted in the dark with shaking for 15 min, and then the oxygen absorption with time was measured in the dark and under illumination. Analogous measurements were also carried out in the presence of ascorbic acid. The rate of oxidation

Fig. 1. Kinetic curves of oxygen absorption by ascorbic acid in the presence of polymers possessing photosensitizing properties, under ultraviolet (*I, II, III*) and white (*I′, II′, III′*) light. *I, I′*—heat-treated polyacrylonitrile; *II, II′*—poly-Schiff base; *III, III′*—polypropiolic acid.

* Light intensity: red $I_{\mathrm{k}} = 2.5\cdot10^4$, white $I_{\mathrm{b}} = 3.7\cdot10^4$, ultraviolet $I_{\mathrm{u.f.}} = 2.6\cdot10^5$ erg/cm$^2\cdot$sec.

Table 1

Figure 1: Kinetic curves of oxygen absorption by ascorbic acid in the presence of polymers possessing photosensitizing properties, under ultraviolet (I, II, III) and white (I′, II′, III′) light. I, I′—heat-treated polyacrylonitrile; II, II′—poly-Schiff base; III, III′—polypropiolic acid.

Figure 1: Figure 1: Kinetic curves of oxygen absorption by ascorbic acid in the presence of polymers possessing photosensitizing properties, under ultraviolet (I, II, III) and white (I′, II′, III′) light. I, I′—heat-treated polyacrylonitrile; II, II′—poly-Schiff base; III, III′—polypropiolic acid.

Photosensitizing properties of products of the thermal transformation of polyacrylonitrile (PAN)

No. of samples	Sample name	Heat-treatment conditions: temp., °C	Heat-treatment conditions: time, h	Electrophysical data: electrical conductivity, σ_{20}, $\Omega^{-1} \cdot \mathrm{cm}^{-1}$	Electrophysical data: activation energy of conductivity, E, eV	Oxidation rate, $\mathrm{mm}^3/\mathrm{min} \cdot 10$: white light	Oxidation rate, $\mathrm{mm}^3/\mathrm{min} \cdot 10$: u.-v.
1	Initial PAN	–	$< 10^{-20}$	–	–	0	0
2	PAN, heat-treated	200	10^{-19}	2,0	–	1,1	2,5
3	PAN, heat-treated	200	10^{-19}	1,8	–	2,1	5,0
4	PAN, heat-treated	350	3	10^{-14}	1,0	0	6,0
5	PAN, heat-treated	450	3	10^{-7}	0,25	3,5	26,0
6	PAN, heat-treated	720	3	$0{,}5 \cdot 10^{-1}$	0,17	0	1,3
7	PAN, heat-treated in solution	220	18 min	–	–	7,5	13,7

No. of samples	Sample name	Heat-treatment conditions: temp., °C	Heat-treatment conditions: time, h	Electrophysical data: electrical conductivity, σ_{20}, $\Omega^{-1} \cdot$ cm^{-1}	Electrophysical data: activation energy of conductivity, E, eV	Oxidation rate, mm^3/min· 10: white light	Oxidation rate, mm^3/min· 10: u.-v.
8	PAN, heat-treated in an ammonia atmosphere	330	6	10^{-9}	0,87	4,2	16,5

was calculated from the slope of the kinetic curve of photosensitization of oxygen absorption, which follows zero order.

Table 2

Photosensitizing properties of polyquinoline obtained by polymerization of quinoline with opening of the heterocycle

Sample name	Polymerization conditions: temperature, °C	Polymerization conditions: duration, h	Oxidation rate in u.-v., mm^3/min · 10
Polyquinoline	370	2	7,5
Polyquinoline	370	5	25,4
Polyquinoline	370	10	31,7
Polyquinoline	370	15	29,3

The polymers used as photosensitizers belonged to the following classes: poly-Schiff bases, polyazines, polypropyolic acid; polyquinoline obtained by polymerization of quinoline with opening of the heterocycle; products of the thermal transformation of polyacrylonitrile. The methods of preparation and properties of these polymers are described in papers (3–6). The indicated polymers are insoluble colored substances with an absorption maximum in the ultraviolet region. The long-wavelength tail of the absorption spectrum for some of them covers the entire visible region. In air, the indicated polymers are p-type semiconductors (1).

It was specially shown that ascorbic acid, neither in the dark nor under illumination under the experimental conditions, absorbs oxygen (the long-wavelength absorption edge of aqueous ascorbic acid solutions lies at 300 mμ). The polymers under consideration should be divided into two groups: some of them exert a sensitizing action only—

Table 3

Sample name	Electrical conductivity, σ_{20}, $\Omega^{-1} \cdot cm^{-1}$	Activation energy of conductivity, eV	Oxidation rate, $mm^3/min \cdot 10$: white light	Oxidation rate, $mm^3/min \cdot 10$: u.-v.
Polypropyolic acid	$6{,}0 \cdot 10^{-15}$	2,0	0	7,5
Poly-Schiff base based on: para-phenylene-diamine with glyoxal	$7{,}1 \cdot 10^{-19}$	2,0	2,5	8,9
Poly-Schiff base based on: para-phenylene-diamine with diacetyl (initial)	$1{,}2 \cdot 10^{-17}$	2,0	3,4	15,6
Poly-Schiff base based on: para-phenylene-diamine with diacetyl (heat-treated at $t = 450°$)	$1{,}1 \cdot 10^{-8}$	0,64	2,4	5,6

Sample name	Electrical conductivity, σ_{20}, $\Omega^{-1} \cdot \text{cm}^{-1}$	Activation energy of conductivity, eV	Oxidation rate, $\text{mm}^3/\text{min} \cdot 10$: white light	Oxidation rate, $\text{mm}^3/\text{min} \cdot 10$: u.-v.
Poly-Schiff base based on: para-phenylenediamine with benzil (initial)	$1{,}3 \cdot 10^{-15}$	2,6	0,8	5,3
Poly-Schiff base based on: para-phenylenediamine with benzil (heat-treated at $t = 500^{\circ}$)	–	–	0	0

upon illumination, i.e., they are typical photosensitizers; in others, illumination is accompanied by a weakening of the sensitizing properties.

Figure 1 gives the kinetic curves for oxygen absorption by ascorbic acid in the presence of substances that are photosensitizers.

As can be seen from these data, products of the thermal transformation of polyacrylonitrile, polypropiolic acid, and certain poly-Schiff bases have a photosensitizing action in the oxidation of ascorbic acid. In all cases the activity of these polymers as photosensitizers in the near ultraviolet (λ 365 mμ) is greater than in the visible region. Table 1 compares the rates of the photochemical oxidation of ascorbic acid in the presence of products of the thermal transformation of polyacrylonitrile with certain semiconducting properties of these substances.

Table 4

Effect of illumination on the sensitizing properties of polynitriles and paracyanogen

Fig. 2. Kinetic curves of oxygen absorption by ascorbic acid in the presence of polypropionitrile, I —in the dark, II —in red light, III —in white light, IV —in u.-v. light

Figure 2: Fig. 2. Kinetic curves of oxygen absorption by ascorbic acid in the presence of polypropionitrile, I —in the dark, II —in red light, III —in white light, IV —in u.-v. light

Name of sample	Rate of oxidation of ascorbic acid, $mm^3/min \cdot 10$	Rate of oxidation of ascorbic acid, $mm^3/min \cdot 10$	Rate of oxidation of ascorbic acid, $mm^3/min \cdot 10$	Rate of oxidation of ascorbic acid, $mm^3/min \cdot 10$
	in the dark	in red light	in white light	in u.-v.
Polypropionitrile	5.0	4.0	3.2	2.7
Paracyanogen	17.0	7.0	0	2.2
Polyacetonitrile	5.1	3.7	5.0	2.3

Fig. 2. Kinetic curves of oxygen absorption by ascorbic acid in the presence of polypropionitrile: *I* —in the dark, *II* —in red light, *III* —in white light, *IV* —in u.-v. light.

As the thermal transformation of polyacrylonitrile is intensified, its activity as a photosensitizer passes through a maximum, and the maximum value of the rate is characteristic of a polymer having a dark conductivity of 10^{-7} $ohm^{-1} \cdot cm^{-1}$ at an activation energy of electrical conductivity of 0.25 eV. The fact that sample No. 6 did not exhibit photosensitizing activity indicates that the observed phenomenon is not connected with the formation of carbon, since the occurrence of carbon-like structures is most characteristic during the high-temperature destruction of polyacrylonitrile.

As was shown earlier (^{1}), thermal transformations in the first stages are accompanied by the formation of a polyconjugated system through C=N bonds. Further heat treatment leads to dehydration, the occurrence of intermolecular bonds, followed by the formation of fused structures. The thermal transformation of polyacrylonitrile in an ammonia atmosphere is accompanied by an increase in electrical conductivity while retaining a considerable activation energy (0.87 eV). It is characteristic that in the presence of polyacrylonitrile obtained by thermal transformation in solution, i.e., under conditions excluding the formation of fused structures, oxidation of ascorbic acid proceeds at a rather high rate.

As can be seen from the data in Table 2, as the duration of thermal polymerization of quinoline increases, a sharp rise in the rate of photooxidation of ascorbic acid takes place only in the early stages.

Polypropiolic acid, and poly-Schiff bases based on para-phenylenediamine with glyoxal, benzil, and diacetyl, also possess appreciable activity as photosensitizers.

As is evident from Table 3, during the thermal transformation of the poly-Schiff bases, accompanied by an increase in electrical conductivity and a decrease in activation energy, the rate of photosensitization decreases.

Unlike the polymers considered, polyacetonitrile, polypropionitrile, poly-1,2-dibromopropionitrile, and paracyanogen, being dark catalysts for the oxidation of ascorbic acid, reduce their catalytic activity in the light. This is manifested in the fact that the rate of oxidation of ascorbic acid in the presence of these substances is considerably higher in the dark than in the light (Table 4).

It is characteristic that in all cases, on going from red light to white light and further to ultraviolet, this effect increases. Fig. 2 presents kinetic curves for oxygen absorption by ascorbic acid in the presence of polypropionitrile.

Thus, heat-treated polyacrylonitrile, polyquinoid, polypropiolic acid, and poly-Schiff bases, in contrast to polynitriles, which catalyze the dark oxidation of ascorbic acid by atmospheric oxygen, are capable of photosensitizing this reaction. Illumination in the case of polynitriles leads to inhibition of the oxidation reaction of ascorbic acid. Further studies will be devoted to investigating the mechanism of the phenomena described.

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