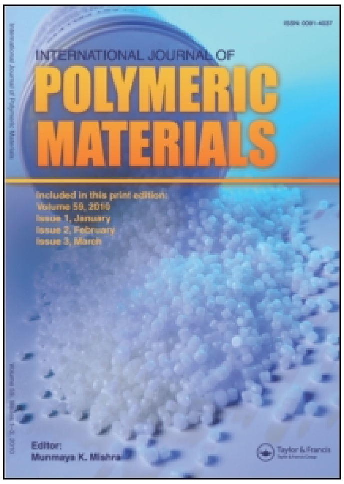

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The Mechanisms of Polystyrene Destruction Under Influence of Powerful UV-Radiation: Initial Stages

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Physical processes stipulating photoinitiation of polystyrene destruction under influence of powerful UV-radiation treatment are considered. The experimental results on its photolysis at UV-irradiation in different spectral ranges are given confirming the decisive role of triplet-triplet transfer of excitation energy from benzene rings to simple bonds, and triplet-triplet annihilation on the initial stages of photodestruction.

KEY WORDS Polystyrene, degradation, UV-radiation.

THEORY AND DISCUSSION

Photodestruction and photooxidation have been studied in many articles,[1–4], but the published data do not permit to develop a consistent theory of these processes and are often contradictory.[1]

Till now the mechanisms of polystyrene photolysis (PS) under influence of long-wave UV-radiation ($\lambda_1 > 280$ nm)[5] have been studied in detail, this radiation being badly absorbed by PS (absorption factor is $\alpha_1(\lambda_1) < 10\ \text{cm}^{-1}$,[6] of middle-wave UV-radiation ($240 < \lambda_2 < 280$ nm) for which $10 < \alpha_2(\lambda_2) < 10^3\ \text{cm}^{-1}$,[6,7] and a mechanism of PS destruction under effect of short-wave and vacuum UV-radiation ($210 < \lambda_3 < 240$ nm, $10^3 < \alpha_3(\lambda_3) < 10^5\ \text{cm}^{-1}$; $160 < \lambda_4 < 210$ nm, $\alpha_4(\lambda_4) > 10^5\ \text{cm}^{-1}$ and $100 < \lambda_5 < 160$ nm, $\alpha_5(\lambda_5) > 10^5\ \text{cm}^{-1}$.[7]

The initial stage of PS destruction process is explained by absorption of the radiation within λ_1 hydroperoxides arising in PS at radical polymerization in presence of oxygen[5]; radiation with λ_2-benzene rings[1] having B-stripe with maximum $\lambda(B) \simeq 260$ nm and $\alpha(B) \simeq 2.2 \times 10^3\ \text{cm}^{-1}$; radiation with λ_3 and λ_4-benzene rings having E_2 stripe ($\lambda(E_2) \simeq 220$ nm, $\alpha(E_2) \simeq 7.10^4\ \text{cm}^{-1}$) and E_1-stripe ($\lambda(E_1) \simeq 195$ nm, $\alpha(E_1) \simeq 4.8 \times 10^5\ \text{cm}^{-1}$), accordingly, and radiation with λ_5-simple bonds.[7]

It is considered that absorption of UV-radiation with $\lambda < 280$ nm stipulates excitation of benzene rings from a lower S_0 to a first S_1 excitated singlet state which later, as a result of intercombination conversion, transfers to a triplet state T_1.[1]

The second stage of photodestruction is explained (initial radical formation) by reactions of the benzene rings in a triplet state: dissociation of C_6H_5—C—bond, or break of C—C and C—H bonds excited by way of intramolecular energy transfer from benzene rings to T_1-state. It is considered that the most important process in PS photolysis is the break of C—H—bond.[1]

However, in the framework of ideas developed in the literature about initial stages of PS photolysis mechanisms it is yet unclear, first, what exactly an absorption stripe of the benzene ring (E_1, E_2 or B) is responsible for photoinitiation of macromolecule destruction and creation of the initial radicals. Usually the initiation reaction is explained by B-stripe,[1] although photochemical researches are carried out, as a rule, under effect of complete UV-radiation from mercury lamps in the spectrum of which there are stripes with wave lengths correspondent to E_1 and E_2-stripes of the benzene ring.[8]

It can be assumed that photochemical activity of radiation with wave lengths λ_2, λ_3, and λ_4 absorbed by B, E_2 and E_1-stripes accordingly, is very different.

Second, the micromechanisms of intramolecular energy transfer from benzene rings in $T_1(B)$-state to C—C and C—H—bonds and their dissociations are still unclear taking account of the fact that the triplet state $T_1(B)$ is the lowest excited electronic state the energy of which is less than the energy of C—C and C—H—bonds break.[2]

It is natural to suppose that break of these bonds proceeds from triplet states arising as a result of the triplet-triplet transfer of benzene ring electronic excitation energy in $T_1(E_1)$ state (formed due to absorption of one photon with λ_4), or in $T_n(E_2)$ and $T_n(B)$ states formed due to absorption of one more photon with λ_2, λ_3 and λ_4 by benzene rings in $T_1(B)$ and $T_1(E_2)$ states.

The possibility of such two-quantum micromechanism of dissociation of C—C and C—H—bonds in PS under influence of UV-radiation with wave lengths λ_2 and λ_3 seems to be quite real if one takes into account that "in case of lighting with the near UV light aromatic compound solutions in rigid media the two-quantum reactions are realized more often than one-quantum ones."[9]

The goal of this work was experimental testing of the said views on PS destruction mechanisms under UV-radiation. The experiments were carried out on PSM-115 PS specimens in the form of ϕ 40 mm discs with 1 mm thickness obtained by pressure cast under standard modes of processing.

UV-radiation treatment was carried out in open air at 300K with DRT-230 medium pressure mercury lamp in different spectral ranges ($\lambda > 280$ nm, filter BS-4; $\lambda > 210$ nm, filter BS-12; $\lambda > 180$ nm); with a source of continuous UV-radiation LOS-2 having an interference filter and giving off a radiation stripe with maximum $\lambda_m = 253$ nm and width $\Delta\lambda \simeq 18$ nm; with an excimer laser, model 2220, produced by QUESTEK and radiating light pulses with duration $\tau \simeq 15$ ns, wave length $\lambda = 193$ and 248 nm and frequency $f = 10$–40 Hz. The intensity of radiation was measured with the use of a calibrated vacuumized thermal column having a quartz window, with sensitivity 4 W/V.

The diagnostics of PS macromolecules destruction under effect of UV-radiation was realized according to the change of critical surface wetting tension, $\Delta\sigma_c = \sigma_c - \sigma_c^0$, where σ_c and σ_c^0 are critical wetting tensions, on the radiated and non-radiated surfaces accordingly. σ_c^0 and σ_c were determined according to Zisman[10] with the use of propyl alcohol solutions in distilled water with alcohol concentration from 0 to 25 volumetric %, and with surface tension from 72 to 30 erg/cm². As for the studied specimens $\sigma_c^0 \simeq 32$ erg/cm² than an interval of the measured values $\Delta\sigma_c$ was 40 erg/cm². A random error in measurement of σ_c^0 and σ_c did not exceed 0.5 erg/cm².

The choice of such method to study PS photolysis was stipulated by the fact that at UV-radiation with light $\lambda = 193$ nm destruction processes with participation of air oxygen developed in the undersurface layer with thickness $\sim 10^{-2}$ μm, and the studying of photolysis products in such a thin layer is very difficult.[7] It is natural to assume that $\Delta\sigma_c$ is proportional to concentration of oxidation photodestruction products in the undersurface layer, as they are oxygen-containing groups which influence specific free energy of the surface.[11]

Excimer lasers give excellent opportunities to study PS photodestruction as they permit to affect in resonance on a polymer in the set absorption stripe and vary the intensity of radiation in a wide range which is important at studying two-quantum processes.

Figure 1 shows dependencies $\Delta\sigma_c$ on radiation doses $\mathcal{D} = N\tau I$ (N is the amount of laser pulses) at different fixed intensity (I) of light pulses in the wide range of 3 to 380 kW/cm², with a wave length $\lambda = 193$ nm. It is clear that with the growth

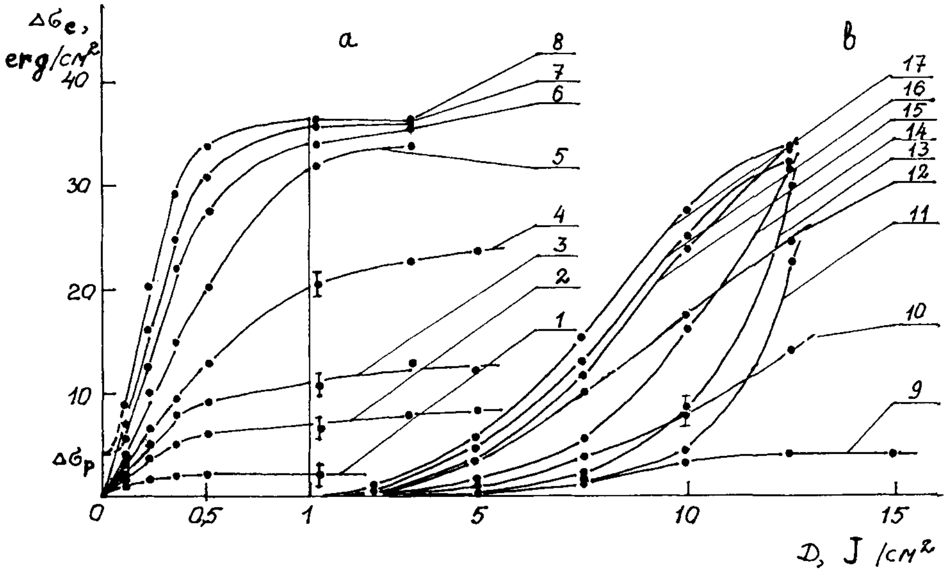

FIGURE 1 Dependence of the change in critical surface wetting tension ($\Delta\sigma_c$) on a dose of radiation treatment ($\mathcal{D}$) with a wave length $\lambda = 193$ nm (1–8), $\lambda = 253$ nm (9), $\lambda = 248$ nm (10–17) at different irradiation intensities (kW/cm²): 1, 380; 2, 160; 3, 110; 4, 80; 5, 46; 6, 3; 7, 10; 8, 5.6; 9, 1.5×10^{-6}; 10, 120; 11, 15; 12, 105; 13, 39; 14, 53; 15, 73; 16, 91; 17, 83. $\Delta\sigma_p$ is a change in critical surface wetting tension linked to additives' photolysis.

of a summary dose $\Delta\sigma_c$ value grows, and at small doses there is a linear dependence $\Delta\sigma_c$ from $\mathcal{D}$ at greater intensities $I \geqslant 10$ kW/cm^2,

$$\Delta\sigma_c = K_1 D \tag{1}$$

and square-law dependence at small intensities $I \leqslant 5.6$ kW/cm^2

$$\Delta\sigma_c = \Delta\sigma_p + K_2\mathcal{D}^2 \tag{2}$$

where: K_1 and K_2 are parameters depending on I, $\Delta\sigma_p$ is a value of $\Delta\sigma_c$ received by extrapolation of the dependencies $\Delta\sigma_c$ from D_2 at $D \rightarrow 0$.

As the experiments have shown, $\Delta\sigma_p$ value is random and fluctuates from specimen to specimen in the range of 1 to 4 erg/cm^2 being linked, probably, to photolysis of additives (the type of carbonile groups and a monomer[1]) appearing in PS in the process of technological treatment. Here, their complete photodestruction at small ($I \leqslant 5.6$ kW/cm^2) intensities is seen at radiation doses $D_v \gtrsim 0.1$ J/cm^2, whereas at greater ($I > 10$ kW/cm^2) intensities their "burning-out" takes place at more smaller D_v values.

At great radiation doses, $D \geqslant 1.2$ J/cm^2, dependencies $\Delta\sigma_c$ on D have a saturated character.

To clear up the character of dependencies of K_1 and K_2 parameters on I the results obtained were processed and dependencies $\Delta\sigma_c$ on I built at fixed radiation doses (see Figure 2). It can be seen that in the built dependencies the maximum is viewed at $I'_M \simeq 5.6$ kW/cm^2.

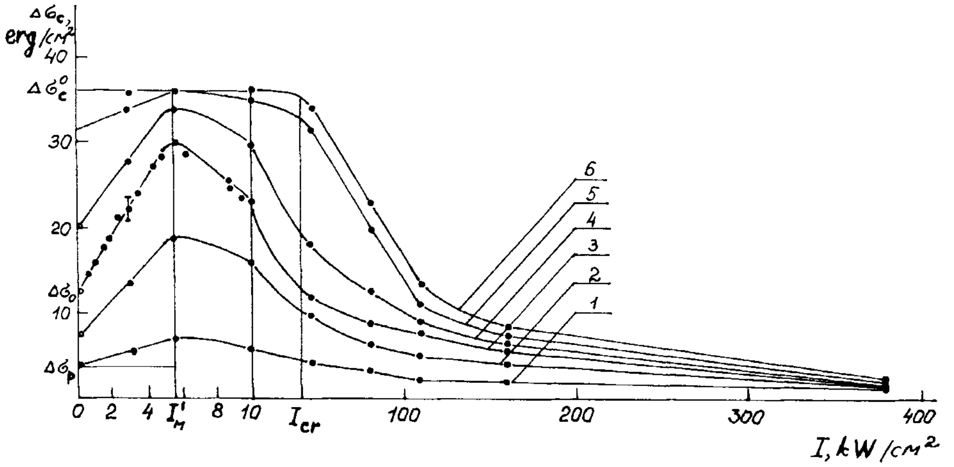

FIGURE 2 Dependence of the change of critical surface wetting tension ($\Delta\sigma_c$) on the intensity of radiation treatment (I) with a wave length $\lambda = 193$ nm at different irradiation doses (J/cm^2): 1, 0.1; 2, 0.23; 3, 0.35; 4, 0.5; 5, 1.2; 6, 3.5. Denominations $\Delta\sigma_p$, $\Delta\sigma_o$, $\Delta\sigma_c^0$, I'_M, I_{cr} see in the text. The light dots are the results of $\Delta\sigma_c$ measurements at radiation treatment with light of a mercury lamp with intensity $I = 3.5 \times 10^{-3}$ W/cm^2.

Accurate measurements of $\Delta\sigma_c$ dependence on I at D = 0.35 J/cm^2 and the change of I from 0.3 to 10 kW/cm^2 have shown that at $I < I'_M$

$$\Delta\sigma_c = \Delta\sigma_0 + K_3 I \tag{3}$$

and at $I > I'_M$

$$\Delta\sigma_c = K_4 I^{-0.5} \tag{4}$$

where: K_3 and K_4 are parameters depending on D; $\Delta\sigma_0$ is a value of $\Delta\sigma_c$ received by extrapolation of $\Delta\sigma_c$ dependence on I at $I \to 0$ and corresponding to $\Delta\sigma_c$ value being measured at small intensities (see below). Considering (1) and (2) we can have at small irradiation doses $D \leq 0.35$ J/cm^2 and $I < I'_M$

$$\Delta\sigma_c = \Delta\sigma_p + (K_0 + K_5 I)\mathscr{D}^2 = \Delta\sigma_p + [(K_0 + K_5 I)N\tau I]\,[N\tau I] \tag{5}$$

and at $I > I'_M$

$$\Delta\sigma_c = K_6 \mathscr{D} I^{-0.5} = K_6 N\tau I^{0.5} \tag{6}$$

where: K_0, K_5 and K_6 are parameters.

At great doses $D \geq 1.2$ J/cm^2 $\Delta\sigma_c$ dependencies on I practically coincide, and at $I \leq I_{cr} \simeq 40$ kW/cm^2

$$\Delta\tau_c \simeq \Delta\sigma_c^0 = \text{const} \tag{7}$$

and at $I > I_{cr}$

$$\Delta\tau_c = K_7 I^{-1} \tag{8}$$

where: K_7 is a parameter.

An analysis of the given results have shown that under the UV-radiation influence on PS with a wave length λ_4 absorbed by E_1-stripe of benzene rings the initial stages ($D \leq 0.35$ J/cm^2) of oxidation photodestruction are connected with the two successive processes taking place in the matrix (see (5)): first, formation of primary radicals and intermediate products (of peroxide and hydroperoxide type[1]); second, formation of polar groups from intermediate products.

The first process at small intensities is one-quantum and at great intensities ($K_5 I > K_0$) generation of the primary radicals occurs simultaneously according to one- and two-quantum mechanisms in the following way. Absorption of UV-radiation with λ_4 leads to one-quantum excitation of benzene rings to state $S_1(E_1)$. Then the intercombination conversion to state $T_1(E_1)$ takes place, the triplet-triplet transfer of excitation energy of a part of β benzene rings to the triplet states of C—C— and C—H bonds and their break occurs with formation of the primary radicals (a one-quantum mechanism).

A part (I – β) of benzene rings in state $T_1(E_1)$ transfers to states $T_1(E_2)$ and $T_1(B)$ as a result of relaxation of the electronic excitation energy, and absorbing a quantum transfers to state $T_n(E_2)$ and $T_n(B)$ where the triplet-triplet transfer of excitation energy to C—C and C—H—bonds and their break occur (a two-quantum mechanism).

It seems that the second process is one-quantum which can be easily explained by strong absorption of UV-light with λ_4 by peroxides, hydroperoxides and other intermediate products.[1,7]

The presence of maximum in dependencies $\Delta\sigma_c$ on I at fixed doses can be explained by the fact that with increase of I to I'_M increases concentration of benzene rings, n_T, in triplet state $T_1(E_1)$ up to a certain critical concentration, n_{cr}, which corresponds to a critical distance R_{cr} = 10 – 15Å between the excited benzene rings when the conditions for triplet-triplet annihilation are realized.[9] This is confirmed by experimentally seen at $I > I'_M$ dependence (6) which can be easily obtained from the equality of excitation speed W_v of benzene rings in state $T_1(E_1)$ ($W_v \sim I$) and speed of triplet-triplet annihilation $W_a \sim n_T^2$ taking account of the fact that $\Delta\sigma_c \sim n_T$.

At great irradiation doses ($D \geqslant 1.2$ J/cm^2) and deep stages of photodestruction of PS the dependence (7) seen at $I < I_{cr}$ can be explained by the equality of the speed in formation of polar oxygen-containing groups in PS macromolecules in a thin ($\sim 10^{-2}$ μm) undersurface layer and by the speed of their photodestruction with formation of low molecular volatile oxygen-containing products (carbon oxide and dioxide, water, etc.)[1] diffusing from an undersurface layer of PS to environment.

At $I > I_{cr}$ the speed of photodestruction of oxygen-containing groups considerably increases ($\Delta\sigma_c$ decreases with the growth of I) which is stipulated by laser heating of the polymer undersurface layer and its transfer from a glass-like to high elastic state at $I > I_{cr}$ being accompanied by the great increase of photoprocess speeds.[1] About considerable increase of photodestruction speed at $I > I_{cr}$ testifies also the fact that at PS radiation treatment with light pulses $I > 160$ kW/cm^2 visual changes are seen on the surface increased with the increase of a dose, i.e. there is an accumulation effect in UV-destruction of a polymer.[12]
Essentially another, S-like character, have dependencies $\Delta\sigma_c$ on D received under influence on PS with light pulses of fixed intensity in the range od 15 to 120 kW/cm^2 with $\lambda = 248$ nm shown in Figure 1b. At small irradiation doses $D \leqslant 10$ J/cm^2 there is a square-law dependence $\Delta\sigma_c \sim \mathcal{D}^2$; at greater doses $D \geqslant 12.5$ J/cm^2 deviations from such dependence different for different I are seen.

Processing of the received data (Figure 3) have shown that as in case of PS treatment with light pulses $\lambda = 193$ nm, irradiation of the polymer with pulses $\lambda = 248$ nm in dependencies $\Delta\sigma_c$ on I at fixed doses the maximum is seen at intensity $I''_M \simeq 80$ kW/cm^2 (see Figure 2 and Figure 3). At small doses ($D \leqslant 10$ J/cm^2) and intensities $I < I''_M$ there will be:

$$\Delta\sigma_c = \Delta\sigma_p + K_8\mathcal{D}^2I^2 = \Delta\sigma_p + K_8[N\tau I^2]\,[N\tau I^2] \qquad (9)$$

and at $I > I''_M$

$$\Delta\sigma_c = K_9\mathcal{D}^2 I^{-1} = K_9 N^2 \tau^2 I \qquad (10)$$

where: K_8 and K_9 are parameters.

At greater doses ($D > 10$ J/cm^2) a sharp increase of $\Delta\sigma_c$ is discovered up to the boundary value of $\Delta\sigma_k^0$ at $I < I''_M$ (compare curves 3 and 4 in Figure 3) as well as inverse relationship $\Delta\sigma_c \sim I^{-1}$ at $I > I''_M$.

Attention is also drawn by the fact that radiation treatment of PS with small intensive UV-light with $\lambda = 253$ nm and $I = 1.5 \times 10^{-3}$ W/cm^2 stipulates only a small growth of $\Delta\sigma_c$ up to $\simeq 4$ erg/cm^2 at doses $D \leq 10$ J/cm^2, and at greater doses (from 10 to 200 J/cm^2) $\Delta\sigma_c$ remains the same: $\Delta\sigma_c \simeq 4$ erg/cm^2.

An analysis of the received results shows that at PS radiation treatment with UV-light λ_2 absorbed by B-stripe of benzene rings the initial stages of PS photodestruction ($\mathcal{D} \leq 10$ J/cm^2) and formation of oxygen-containing groups are linked to the two successive two-quantum processes proceeding in the matrix (see (9)): 1) formation of radicals and intermediate products (of peroxide and hydroperoxide type),[1] and 2) formation of polar groups from the intermediate products.

The fact that there is a two-quantum mechanism of primary radicals' generation is confirmed first of all by relationship (10) as in the considered cases triplet-triplet annihilation occurs at the speed of benzene rings excitation to states $T_n(B)$ $W_v \sim I^2$, and thus $\Delta\sigma_c \sim n_T \sim I \sim \mathcal{D}^2 I^{-1}$. Secondly, this conclusion proceeds from the comparison of UV-radiation intensities I'_M and I''_M which correspond to the same critical concentration n_{cr} of benzene rings in highly excited triplet states. Because

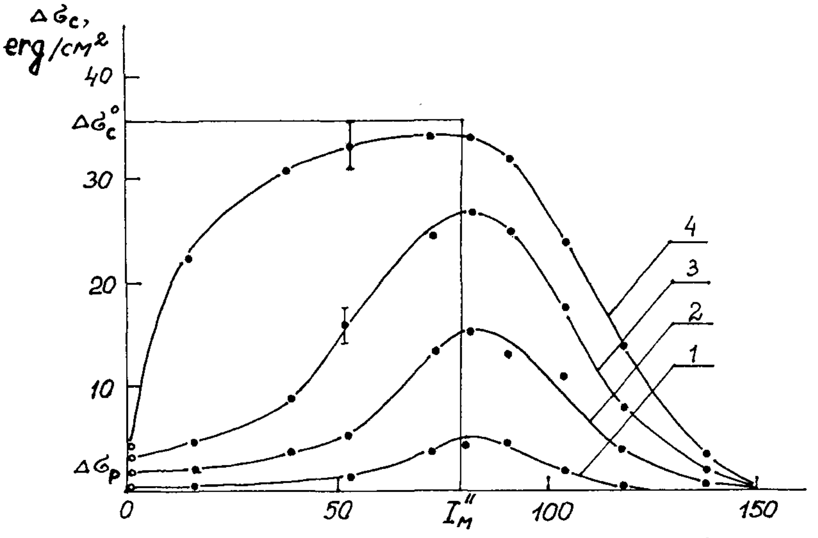

FIGURE 3 Dependence of the change in critical surface wetting tension ($\Delta\sigma_c$) on the intensity of radiation treatment (I) with a wave length $\lambda = 248$ nm at different irradiation doses (J/cm^2): 1, 5; 2, 7.5; 3, 10; 4, 12.5. Denominations $\Delta\sigma_p$, $\Delta\sigma_c^0$, I''_M see in the text. The light dots are the results of $\Delta\sigma_c$ measurements at UV-light treatment with a wave length $\lambda = 253$ nm and intensity $I = 1.5 \times 10^{-3}$ W/cm^2.

of the square-law relationship W_v and I at radiation treatment of PS with light $\lambda = 248$ nm the same critical concentration will be achieved at I''_M which is by $[\alpha(\lambda_4)/\alpha(\lambda_2)]^{0.5}$ times greater than I'_M. As $\alpha(\lambda_4) = (220 - 300) \times \alpha(\lambda_2)$, then $I''_M = (15 - 17)I'_M$ which is well agreed with the test values.

One can pay attention also to the fact that the marked effect of the two-quantum processes of initial radicals' generation is seen at $I'_2 \gtrsim 1$ kW/cm^2 for UV-radiation with $\lambda = 193$ nm and at $I''_2 \gtrsim 15$ kW/cm^2 for UV-light with $\lambda = 248$ nm. This relationship of intensities I'_2 and I''_2 is also well agreed with our ideas.

The formation of polar groups from the intermediate products (peroxide type) under influence of UV-radiation with λ_2 can be confirmed by the sharp increase of $\Delta\sigma_c$ at the growth of radiation doses from 10 to 12.5 J/cm^2 (at $I < I''_M$) stipulated as it seems by expressed chain diversified radical reactions of PS matrix photooxidation. Further increase of a radiation dose ($\mathcal{D} > 12.5$ J/cm^2) there will proceed processes in the matrix which are analogous to the above mentioned under the influence of UV-light with λ_4.

It should be underlined that photodestruction of PS macromolecules under the influence of UV-radiation with λ_2 is connected with the proceedings of two-quantum processes and practical realization of which requires rather great ($I > 10$ kW/cm^2) UV-light intensity. Small $\Delta\sigma_c$ seen under effect of UV-radiation with λ_2 and small intensity ($I \sim 10^{-3}$ W/cm^2) probably are conditioned by additives' photoreactions.

From this proceeds that PS destruction under the influence of weak UV-radiation described in the literature is linked either to additive photoinitiation by radiation

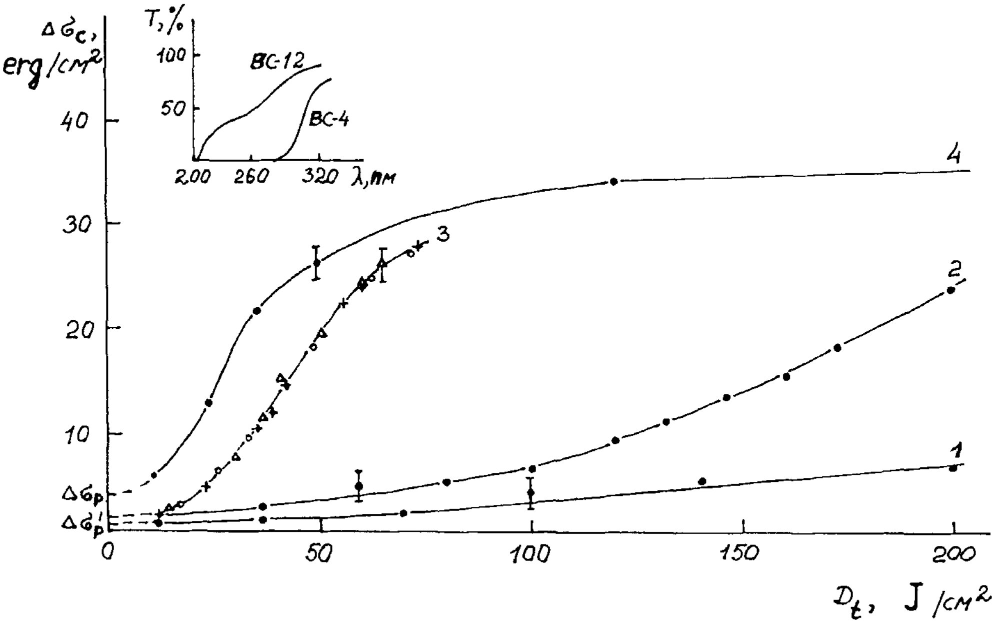

FIGURE 4 Dependence of the change in critical surface wetting tension ($\Delta\sigma_c$) on a total irradiation dose ($\mathcal{D}_t$) with different wave lengths (λ) and radiation treatment intensity (I): 1, $\lambda > 210$ nm, $I = 6.9 \times 10^{-3}$ W/cm^2; 2, $\lambda > 210$ nm, $I = 1.22 \times 10^{-2}$ W/cm^2; 3, $\lambda > 180$ nm; the light dots $- I = 3.5 \times 10^{-3}$ W/cm^2; crosses: $I = 6.9 \times 10^{-3}$ W/cm^2; triangles $- I = 1.22 \times 10^{-2}$ W/cm^2; 4, $\lambda = 193$ nm, $I = 3$ kW/cm^2.

with wave lengths λ_1 and λ_2 or to photoinitiation of PS macromolecules by UV-radiation with λ_3 and λ_4 which is always present in the radiation of mercury lamps. The latter assumption is confirmed by the fact that UV-light with λ_3 and λ_4 is absorbed by PS with absorption coefficients α_3, $\alpha_4 \gtrsim 10^5$ cm^{-1} which are more than by two orders higher than α_1 and α_2, i.e., the absorbed radiation dose $\mathcal{D}_a = \alpha\mathcal{D}$ for λ_3 and λ_4 will be by more than 100 times greater $\mathcal{D}_a$ for λ_1 and λ_2.

To check up the expressed ideas about PS photolysis mechanism we staged experiments on UV-radiation treatment of specimens at low light intensities in different spectral ranges. When PS was treated with $\lambda < 280$ nm radiation there were no changes of $\Delta\sigma_c$ at a total dose $\mathcal{D}_t$ = It (t is radiation treatment time) up to 200 J/cm^2. This result means that additives located in the undersurface layer are not photoinitiated by the light $\lambda > 280$ nm.

At UV-radiation treatment of PS with λ = 253 nm only photodestruction of additives occurs leading to random values of $\Delta\sigma_p$ not exceeding 4 erg/cm^2 (see above).

In the treatment of PS with mercury-lamp radiation of high (complete) intensity $I_1 = 1.22 \times 10^{-2}$ W/cm^2 gone through BS-12 light filter which passes radiation with $\lambda > 210$ nm (see the insert in Figure 4) essential dependence of $\Delta\sigma_c$ on $\mathcal{D}_t$ is seen (see curve 2 in Figure 4) which testifies about photochemical activity of radiation with λ_3 being absorbed by E_2-stripe of benzene rings. Reduction of the radiation intensity to $I_2 = 6.9 \times 10^{-3}$ W/cm^2 leads to a considerable decrease of $\Delta\sigma_c$ values at the same doses (compare curves 1 and 2 in Figure 4).

The processing of the obtained results showed that

$$\Delta\sigma_c = \Delta\sigma_p + K_{10}\mathcal{D}_t^2 I^2 = \Delta\sigma_p + K_{10}[I^2t]\,[I^2t] \qquad (11)$$

where: K_{10} is a parameter. It means that at PS radiation treatment with this radiation being absorbed by E_2-stripe of benzene rings the initial stages of photodestruction are linked to the two successive two-quantum processes proceeded in the matrix as was described above for radiation with λ_2. It should be underlined that greater photochemical activity of radiation with λ_3 in comparison with that with λ_2 is stipulated by the fact that $\alpha_3(\lambda_3)$ approximately by 100 times greater than $\alpha_2(\lambda_2)$.

Quite another character has dependence $\Delta\sigma_c$ on $\mathcal{D}_t$ received at PS radiation treatment from a full light of a mercury lamp with $\lambda > 180$ nm being absorbed by E_1, E_2 and B-stripe (see curve 3 in Figure 4.). Simultaneously it was established that the change in radiation intensity from $I_1 = 1.22 \times 10^{-2}$ to $I_3 = 3.5 \times 10^{-3}$ does not influence dependence of $\Delta\sigma_c$ on $\mathcal{D}_t$ (see curve 3 in Figure 4), which at small doses will be:

$$\Delta\sigma_c = \Delta\sigma_p + K_{11}\mathcal{D}_t^2 = \Delta\sigma_p + K_{11}[It]\,[It] \qquad (12)$$

(K_{11} is a parameter) which is analogous to relationship (5) (at low radiation intensity, $K_5 I << K_0$) received at PS UV-radiation treatment with λ = 193 nm.

This means that PS photodestruction under the effect of radiation with λ_4, λ_3, λ_2 and λ_1 is mainly linked to the radiation with λ_4 being absorbed by E_1-stripe of benzene rings which carries out PS macromolecule photoinitiation and formation of intermediate products due to one-quantum absorption and transformation of the said products into polar oxygen-containing groups also at one-quantum absorption. That's why the photochemical activity of radiation treatment with λ_4 is considerably higher than the activity of radiations with λ_3, λ_2 and λ_1 although a part of mercury lamp irradiation contained in the interval 180–210 nm amounts only to 1–2%.[8]

Using values of $\Delta\sigma_o = 12$ erg/cm^2 and $\Delta\sigma_p = 4$ erg/cm^2 obtained at PS radiation treatment with $\lambda = 193$ nm and $\mathcal{D} = 0.35$ J/cm^2 (see Figure 2), and comparing the difference $\Delta\sigma_o - \Delta\sigma_p = 8$ erg/cm^2 with differences $\Delta\sigma_c - \Delta\sigma_p'$ received at PS radiation treatment with the full mercury lamp light (curve 3 in Figure 4) one can see that dose $\mathcal{D} = 0.35$ J/cm^2 corresponds to a summary dose $\mathcal{D}_t \simeq 35$ J/cm^2. This result means that a part of radiation in the interval 180–210 nm really amounts to 1%.

Taking account of the latter event we have transfered dependence $\Delta\sigma_c$ on $\mathcal{D}$ from Figure 2 to Figure 4 (curve 4), this dependence being received at $I = 3$ kW/cm^2.

The comparison of curves 3 and 4 in Figure 4 helps imagine a contribution of the two-quantum processes to PS photooxidation destruction. At the same time curve 3 in Figure 4 being transfered to Figure 2 is well agreed with the results of the curves' extrapolation, Figure 2, at $I \rightarrow 0$.

Thus, all the totality of experimental data on UV-radiation treatment of PS points to the fact that the initial stages of PS photolysis are connected with proceeding in the matrix of the two successive processes: photoinitiation with formation of primary radicals and intermediate products and transformation of the latter into polar oxygen-containing groups. Both processes can be one- and two-quantum depending on the radiation wave length and its intensity. Of paramount importance in the process of photoinitiation is triplet-triplet transfer of excitation energy from benzene rings to C—C and C—H—bonds and triplet-triplet annihilation.

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