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FLUORESCENCE AND ABSORPTION OF POLYSTYRENE EXPOSED TO UV LASER RADIATION

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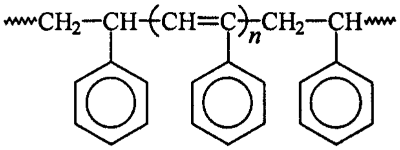
We show that when polystyrene is exposed (for 15–60 sec) to a UV laser light beam (λ = 248 nm), its absorption and luminescent properties change significantly. In the irradiated polymer, optical centers are formed with absorption bands in the 280–460 nm region and fluorescence bands in the 330–520 nm region. We have established the chemical structure of the optical centers for fluorescence of polystyrene.

Key words: *polystyrene, UV laser, fluorescence.*

Introduction. Polystyrene (PS) is a thermoplastic that has diverse practical applications. It has a combination of valuable properties: it is transparent, it is very translucent over a broad spectral range (λ > 290 nm), it is one of the lightest plastics (density 1.040–1.065 g/cm^3), it is hard and rigid, resistant to aggressive media, a good dielectric, etc. This polymer is used as a material for making optical glasses (n_D = 1.59) [1]. Optical lenses made from polystyrene glass have low spherical and chromatic aberrations. The polymer under consideration is highly radiation resistant compared with other synthetic polymers [2] and exhibits radioluminescence. It is specifically due to the indicated properties that polystyrene is widely used as the base for plastic scintillators [3, 4].

A disadvantage is the susceptibility of this polymer to photodegradation. Exposure of the polymer to UV light causes (under vacuum or in an inert atmosphere) evolution of molecular hydrogen, which is accompanied by a change in its luminescent spectral properties. When polystyrene films and solutions are exposed to light from a mercury lamp at a wavelength of 254 nm, the optical density increases in the 300–400 nm region and yellowing occurs [5–8]. The irradiated films and solutions have a broad fluorescence band in the 350–500 nm region with indistinct maxima at 353 nm, 370 nm, 390 nm, 430 nm, and 450 nm [7, 8]. The authors of the indicated papers have hypothesized that each of the maxima corresponds to an emission band belonging to a certain optical center. A structure of the following general type has been assigned to these optical centers:



The bands with the indicated maxima have been assigned to structures formed with n = 2–5, respectively. However, the authors of [6–8] acknowledged that they could not unambiguously determine the structure of the optical centers arising in photochemically modified polystyrene, or determine whether in this case structures with π systems were formed, including benzene rings and polyene moieties. At the same time, in [8] work was cited hypothesizing that one of the optical centers formed possibly has the structure of *trans*-stilbene.

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This work is devoted to study of the changes in the luminescent spectral properties of polystyrene initiated by UV laser radiation, and determination of the structures arising upon such exposure and responsible for the spectral changes.

The experiment. The objects of investigation were samples of polystyrene films and solutions of concentration $C = 10^{-3}$ M. We used spectral grade cyclohexane as the solvent. The samples were irradiated by a light beam (cross section 1 cm^2) from a Compex 200 excimer laser (Lambda Physik GmbH, Germany) with λ = 248 nm. Films of thickness 23 μm were irradiated by pulses at a frequency of 1 Hz, pulse duration 20 nsec, pulse energy 30 mJ. Irradiating the films with a pulse energy of more than 40 mJ causes a considerable change in the shape of the sample (warping of the film). One of the film samples (designated as F-30) was irradiated with 30 pulses. Another film sample was irradiated with 60 pulses (F-60). For the solutions, we used different irradiation conditions: pulse energy 100 mJ, pulse duration 20 nsec, frequency 10 Hz. The first solution was irradiated with 150 pulses (S-150), the second was irradiated with 300 pulses (S-300), the third solution was irradiated with 600 pulses (S-600).

The UV absorption spectra of the samples were recorded on a Shimadzu UV-365 spectrophotometer (Japan), and the fluorescence spectra were recorded on a Perkin-Elmer MPF-44 spectrofluorimeter (USA).

Discussion of results. The spectral studies of polystyrene films and solutions allowed us to establish that laser UV irradiation initiates formation of new fluorescence and absorption optical centers in the polymer. The spectral composition of the fluorescence depends on the wavelength of the exciting light, which suggests formation of different optical centers. Centers with emission in the 330–380 nm region arise for relatively brief irradiation, while centers emitting in the 380–490 nm region arise with longer irradiation of the samples. As the exposure time increases, the concentration of the first centers decreases while the concentration of the second centers increases.

With the goal of determining the spectral characteristics of the optical centers, we selected excitation wavelengths that resulted in the recorded spectrum corresponding in some cases to predominantly one of the optical centers. The data obtained are presented in Figs. 1–3. Fig. 1 shows the fluorescence spectra of the irradiated polymer films and solutions, obtained for excitation with light at λ = 310 nm. The fluorescence spectrum of F-30 represents a structured band (Fig. 1a, curve 1) with maxima at 335, $\underline{350}$, and 365 nm (the main maximum is underlined). The emission band for F-30 practically coincides with the emission band of *trans*-stilbene (curve 3), selected as the model compound. The fluorescence spectrum of *trans*-stilbene has maxima at 336 and $\underline{352}$ nm, and also an inflection at 369 nm. Based on this, we conclude that the spectrum of sample F-30 is determined predominantly by emission from a single optical center which we designate as I. The spectra for F-30 and stilbene are somewhat different in the region $\lambda > 365$ nm. This difference is associated with the fact that light at 310 nm excites not only center I in the film but also the other center (II), the emission band of which is shifted toward longer wavelengths. The contribution of emission from center II to the spectrum of sample F-60 is much greater, while the intensity of the 335 nm and 350 nm peaks is appreciably reduced (curve 2).

The polystyrene solutions proved to be more resistant to UV laser radiation, and stood up under irradiation by several hundred pulses. The fluorescence spectrum of S-150 (for excitation by 310 nm light) proved to be similar to the fluorescence spectrum of F-60 (see Fig. 1). Longer exposure of the solutions is accompanied by transformation of their fluorescence spectra. The intensity of the emission spectrum for S-300 and especially S-600 decreases in the 325–400 nm region, while on the other hand it increases in the 400–450 nm region (Fig. 1b, curves 2 and 3). At λ = 403 nm, the intensity of emission is virtually the same for all three solutions, i.e., we are dealing with an isosbestic point. The noted character of the changes in the spectra of the solutions suggests an increase in the concentration of optical centers with longer wavelength emission as the irradiation dose increases.

Emission of the indicated centers is more pronounced in spectra obtained by excitation with light at λ_{ex} = 340 nm and 365 nm. The fluorescence spectrum of S-150 (λ_{ex} = 340 nm) has the shape of a broad band with a maximum at 380 nm and inflections at 365 nm and 400 nm (Fig. 2a, curve 1), and is similar to the spectrum of diphenylbutadiene (DPBD) (curve 4). The emission band for DPBD is structured and has maxima at 360.3 nm, 379.5 nm, and 399.2 nm. Based on this similarity, we may hypothesize that this spectrum for a polystyrene solution is determined by the emission of predominantly a single optical center which we designate as III. We hypothesize that this center has a chemical structure close to that of the DPBD molecule. Evidence in favor of this hypothesis will be given below.

The optical center III also has a significant effect on formation of the fluorescence spectra of samples S-300 and S-600. The intensity of the band for center III is reduced in those spectra, but the long wavelength wing (400-490 nm) increases.

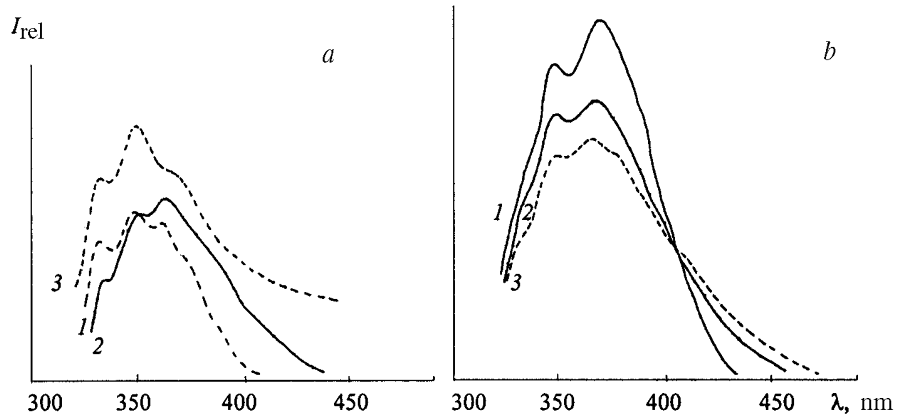


Fig. 1 Fluorescence spectra (λ_{ex} = 310 nm): a) F-30 (1), F-60 (2), *trans*-stilbene in cyclohexane (3); b) S-150 (1), S-300 (2), S-600 (3).

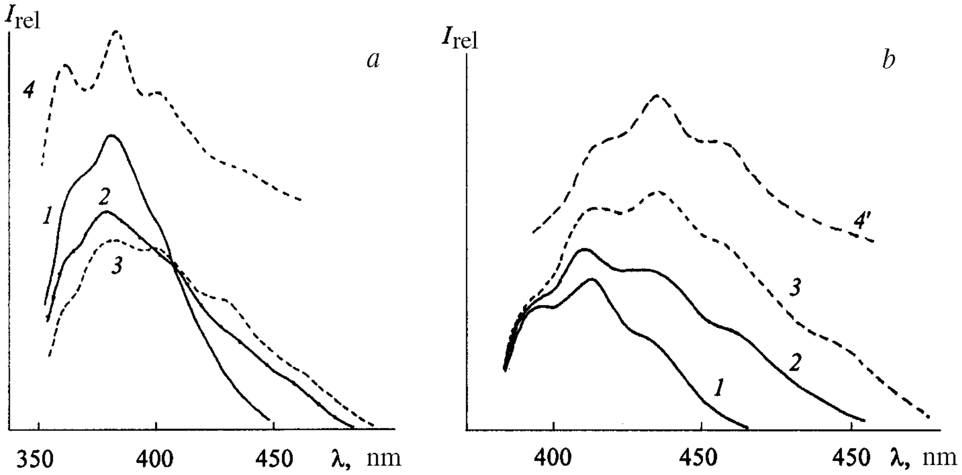


Fig. 2 Fluorescence spectra of S-150 (1), S-300 (2), S-600 (3), solution of diphenylbutadiene (DPBD) in cyclohexane (4), solution of DPBG in cyclohexane (4′); λ_{ex} = 340 nm (a) and 365 nm (b).

The fluorescence spectra of irradiated polystyrene solutions obtained by excitation with light at λ_{ex} = 365 nm are due to optical centers having longer wavelength emission. The main maximum of the emission spectra for samples S-150 and S-300 is located at λ = 410 nm (Fig. 2b, curves 1 and 2). We designate its corresponding emission center as IV. Sample S-600 fluoresces most intensely when excited by light with λ_{ex} = 365 nm. Its fluorescence spectrum is a structured band with maxima at 410 nm, 435 nm, and 458 nm (Fig. 2b, curve 3). We designate the optical center with main peak at 435 nm as V. The emission band for sample S-600 has a position and structure that is similar to that of the fluorescence band for diphenylhexatriene (DPHT), the maxima for which are located at wavelengths of 407 nm, 430 nm, and 452 nm (Fig 2b, curve 4′). Based on the noted similarity, we hypothesize that center V has about the same system of π-conjugated bonds as the DPHT molecule.

Analysis of the luminescent spectral data allowed us to conclude that exposure to radiation from a UV laser initiates formation of different optical emission centers in the polystyrene. Emission bands from centers I–V were most pronounced in the spectra. At the same time, obviously other, more weakly fluorescing centers are formed in the irradiated polymer, with spectral characteristics that could not be clearly determined. For three of the observed

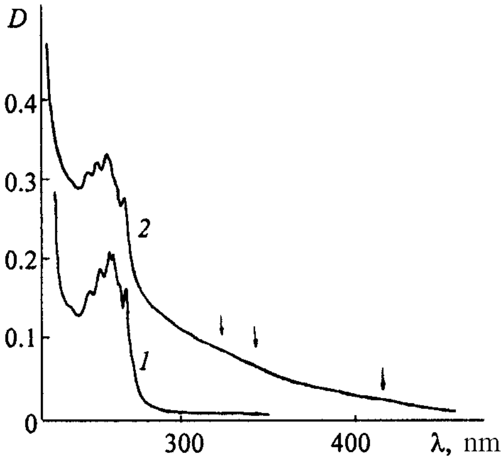
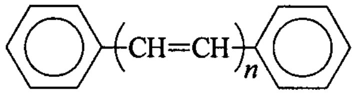


Fig. 3 Absorption spectra of polystyrene (PS) solutions in cyclohexane: original (1), S-600 (2).

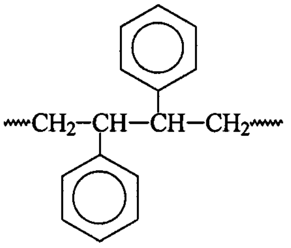
centers, we tentatively selected model compounds from the diphenylpolyene series, the molecules of which have the general structure:



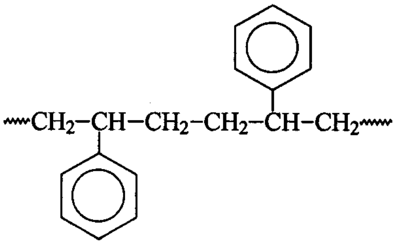
Stilbene (n = 1) corresponds to optical center I, DPBD (n = 2) corresponds to center III, and DPHT (n = 3) corresponds to center V.

We chose the indicated diphenylpolyenes as the model compounds based on the following considerations. As noted, in the literature it is strongly believed that fluorescent π-conjugated polyene moieties are formed as a result of photochemical conversions of polystyrene. When the relative arrangement of the benzene rings and polyene moieties is suitable, structures can arise with a π-system analogous to what we see in the diphenylpolyene molecules.

Let us discuss the conditions under which formation of optical centers I, III, and V is possible. It has been shown by NMR [9] that during polymerization, styrene molecules can be chemically bonded with each other not only "head to tail" but also "head to head" (D_1) and "tail to tail" (D_2), leading to formation of defective units in the polystyrene chain:

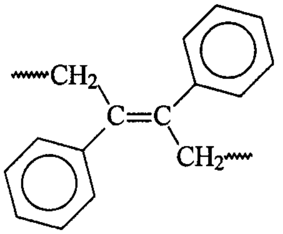


D_1

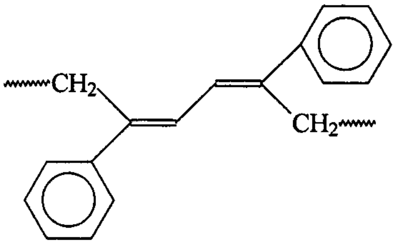


D_2

Based on data on the kinetics of polystyrene degradation, it has been hypothesized that photoconversion in this polymer especially occurs in defective units, since the chemical bonds in such units are weaker [6]. Therefore it seems reasonable that optical center I is formed as a result of dehydrogenation of the CH–CH bond of a D_1 unit, while center III is formed as a result of dehydrogenation of a chain fragment in the D_2 structure. Accordingly, centers I and III have the structures



and



We can assign the following structure to optical center V:

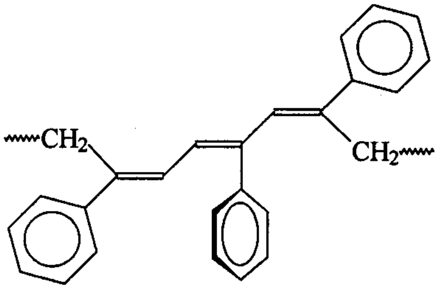


Fig. 3 shows the absorption spectra for a non- irradiated solution (curve 1) and a solution S-600 irradiated with UV laser light (curve 2). The spectrum of the non-irradiated solution consists of a structured band located in the 240–270 nm region, which belongs to the benzene chromophore. Furthermore, in the 275–295 nm region there is a weak absorption associated with the presence of traces of the original monomer (styrene) in the sample. The spectrum of sample S-600 extends toward the longer wavelength region compared with the spectrum of the original solution: all the way to 460 nm. The optical density curve in the 290–460 nm region does not contain distinct bands but rather has only indistinct peaks indicated by the arrows. Such an nondescript shape of the absorption spectrum associated with photochemically formed optical centers is due to the fact that the sample contains not only fluorescent structures but also nonfluorescent structures. In particular, the sample contains such diphenylpolyenes in the *trans* configuration (which are fluorescent) and in the *cis* configuration (for which no fluorescence is observed). Furthermore, obviously exposure of polystyrene to UV laser radiation initiates formation of other conjugated structures which were not identified in this work.

Conclusion. We have established that even brief exposure to a UV laser light beam (λ = 248 nm) induces significant changes in the luminescent and absorption properties of polystyrene films and solutions in cyclohexane. Optical centers are formed in the polymer with fluorescence bands in the 330–520 nm region and absorption bands in the 290–460 nm region. Some of the most intensely fluorescing centers have the structure of diphenylpolyene derivatives. It was shown previously that such optical centers are formed when polystyrene films are heat-treated [10].

The reaction of dehydrogenation of the molecular chain is the major step in chemical conversions of polystyrene leading to formation of π-conjugated systems when the polymer is exposed to UV light or ionizing radiation [2, 11] and when it is heat-treated. An analogous process also occurs in the case of poly-*p*-xylylene [12]. The indicated reaction is probably the initial step in carbonization of many polymers with a hydrocarbon molecular chain, leading to formation of polyconjugated polyene chains.

These processes probably play a definite role in deterioration of the scintillation efficiency of plastic scintillators based on polystyrene as they absorb higher doses of ionizing radiation [13]. The above-mentioned processes much be considered when using polystyrene as a matrix in optical studies. This is especially important in polarization studies of luminophores inserted into a polystyrene matrix [14].

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