Based on the derived relations, it is possible to find the value of $\varepsilon_{NO}{}^* = 0.7$ $(\text{cm·torr})^{-1} = 5\cdot10^{-3}(\text{cm·Pa})^{-1}$ selectable. Then $K_9 = 0.9$ torr $= 120$ Pa, $K_7K_8 = 660$, $K_2K_3 = 165$, $K_6K_9 = K_1K_4 = 1.3\cdot10^{-8}$. When the equilibrium (8) shifts toward $(NO)_2{}^{**}$, $K_8 > K_7$. In the opposite case, $K_7 \geq K_8$. Such a case is possible if $\varepsilon_{(NO)_2}{}^* \approx \varepsilon_{NO}{}^*$. Then the right-hand side of expression (XI) is determined primarily by the magnitude of $\varepsilon_{(NO)_2}{}^{**} \approx 0.1$ $(\text{cm·torr})^{-1} = 0.75\cdot10^{-3}(\text{cm·Pa})^{-1}$. If one turns to the value $K_8 \approx 70$, then $K_7 \approx 10$ and $K_8{}^* \approx 3$. Available results do not allow for one to obtain definitive values of K_1 and K_4, because they do not bear direct information on the concentration of the NO·He compound. Typically, the stability of clathrates is lower than that of compounds which form by chemical bonds. For this reason one ought to expect that $K_4 > K_9$ and, correspondingly, $K_1 < K_6$. If one takes $K_4 \approx 10$ torr $= 1335$ Pa, then K_1 will equal $10^{-9}(\text{torr})^{-1} = 7.5\cdot10^{-12}$ Pa^{-1}.

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# INVESTIGATION OF ELECTRONIC SPECTRA
OF SOME POLY(ORGANOSILOXANES)

L. N. Pankratova, A. Yu. Poroikov,
and L. T. Bugaenko

The luminescence of siloxane polymers containing phenyl groups has been studied very inadequately [1], although such polymers are widely used as protective coatings under exposure to UV and ionizing radiation. The kinetic dependences of the luminescence of siloxanes during various stages of photophysical processes have not been studied previously. The effect of acceptor-type additives, the polycyclic aromatic hydrocarbons anthracene, phenanthrene, and fluorene, and their organosilicon analogs, on the photolysis and radiolysis of ring-chain poly(methylphenylsiloxanes) has been investigated [2, 3].

It was shown that the introduction of siloxodihydrophenanthrenyl (PA) structural repeating units and phenanthrene into poly(organosiloxanes) exerts a significant stabilizing effect because such additives have low-lying excitation levels and are therefore able to scatter a significant part of the absorbed energy without cleavage of chemical bonds in radiative and (or) radiationless transitions. Therefore, it seemed of interest to consider fluorescence and phosphorescence spectra of some poly(methylphenylsiloxanes) containing PA repeating units and to compare the phosphorescence spectra obtained by steady-state luminescence spectroscopy and luminescence of PA repeating units in block copolymers under pulsed photoexcitation by radiation with $\lambda = 308$ nm.

We investigated ring-chain methylphenylsiloxane oligomers (PMPS) synthesized by hydrolytic polycondensation in toluene containing 2.5 mole % PA repeating units with the general formula
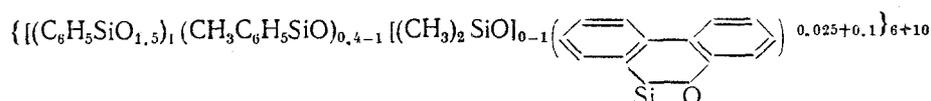
$$\{ [(C_6H_5SiO_{1.5})_1(CH_3C_6H_5SiO)_{0.4-1}[(CH_3)_2SiO]_{0-1}(\text{PA})_{0.025+0.1}\}_{6+10}$$
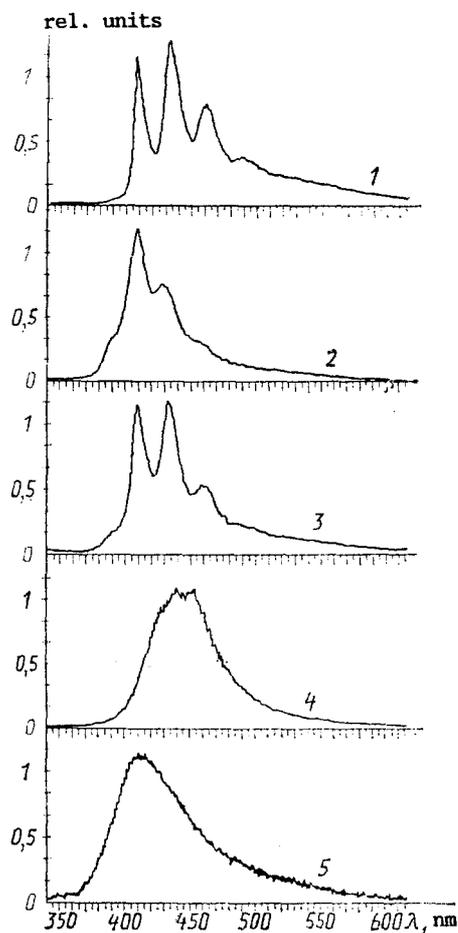
Fig. 1. Fluorescence spectra recorded with pulsed photoexcitation at 293 K. Fluorescence spectra of phenanthrene (1), phenanthrene introduced into PMPS (2) and block-copolymer (3) matrices, and PA repeating units in block-copolymer (4) and PMPS (5) matrices.

$(OC_2H_5)_{0-3}$, and siloxane block copolymers containing 2.5 mole % PA repeating units

$$\{[(CH_3)_2SiO]_1[C_6H_5SiO_{1.5}]_a[C_6H_5Si(OH)O]_{1-a} \left(\begin{array}{c} \end{array} \right)_{0.025}.$$
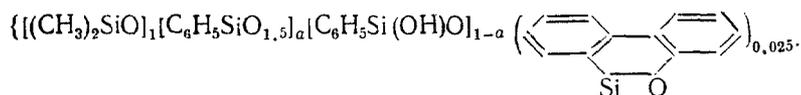
We compared the luminescence spectra of siloxanes containing PA repeating units with the spectra of poly(methylphenylsiloxanes) with the same structure containing additions of phenanthrene of the same concentrations as those of the PA repeating units. The investigations were carried out in a condensed phase on free films predeposited onto Ftoroplast (Teflon) plates by pouring from a 10% solution in toluene. Hardening of the PMPS was carried out at 400 K for 3 h. The block copolymers were hardened at 293 K by adding 2 mass % γ-aminopropyltriethoxysilane.

The phosphorescence spectra (using a phosphoroscope at 77 K) were recorded on a Hitachi MPF-4 spectrophotometer. Pulsed photoexcitation of the polymers was carried out with a Xe—Cl laser with wavelength 308 nm and energy density $2 \cdot 10^{-2}$—$8 \cdot 10^{-2}$ J/cm^2 (pulse duration ~30 nsec). The fluorescence spectra were recorded during the first ~40 msec after the excitation pulse, which was determined by the apparatus possibilities of the OSA multichannel optical analyzer that was used. Because the fluorescence intensity exceeded significantly the intensity of the slowly decreasing luminescence, it was assumed that the contribution of the luminescence to the integrated spectrum was small. We investigated the dynamics of the change of the spectral intensity of the slowly decaying luminescence beginning with delays of the moment of recording with respect to a laser pulse of 0.1—0.2 sec until disappearance of the luminescence (several seconds). The spectrum was not corrected for the spectral-sensitivity curve. The UV absorption spectra were recorded on an M-40 spectrophotometer in the range 200—600 nm, and the IR absorption spectra were recorded on an M-80 spectrophotometer in the range 400—4000 cm^{-1}.

The UV absorption spectra of the siloxanes containing PA repeating units contained three bands with maximums at 218, 270, and ~340 nm, the intensity of which decreased with increasing wavelength: they were close in nature to
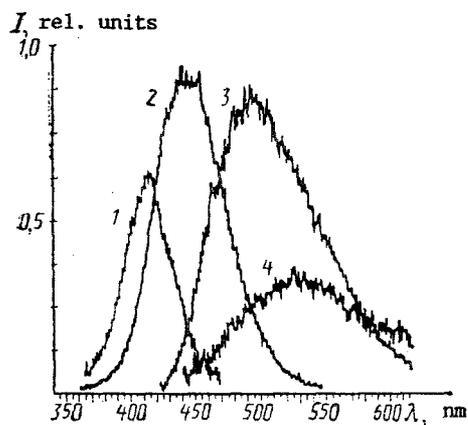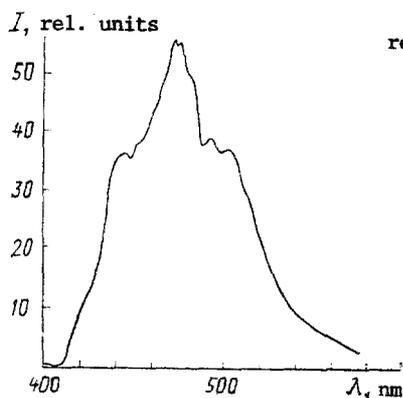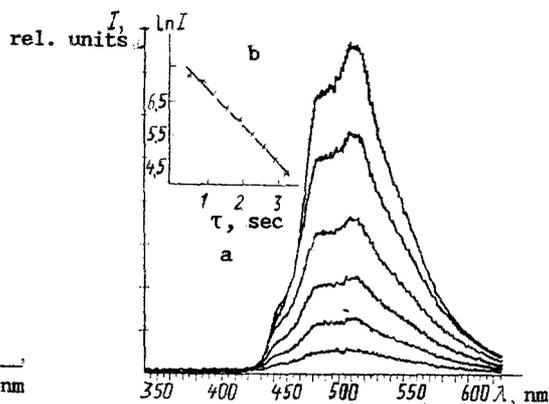
Fig. 2

Fig. 3

Fig. 4

Fig. 2. "Pure" spectral forms distinguished during analysis of dose dependence of fluorescence spectra of PA repeating units (pulsed photoexcitation): $\lambda_{max} = 410$ (1), 435 (2), 465 (3), and 500 nm (4).

Fig. 3. Phosphorescence spectrum of PA repeating units in PMPS and block copolymer under steady-state conditions at 77 K.

Fig. 4. Spectrum of slowly decreasing luminescence during pulsed photoexcitation (a) and time dependence of decrease of luminescence intensity at 293 K (b). The spectra in Fig. 4 were recorded with time interval $\tau = 0.3$ sec.

the corresponding absorption bands of phenanthrene with maxima at 242, 282, and ~340 nm, but the band fine structure that is characteristic of the spectrum of phenanthrene was not observed in the absorption spectrum of PA repeating units. In addition, the spectra of heterocyclic PA repeating units were shifted to the short-wave region in comparison with the spectra of phenanthrene [4, 5], which may indicate weakening of the degree of delocalization in the aromatic π system when a Si—O fragment was included in it. Thus, cleavage of the π-bonding system in the fragment at Si—C_{ar} bonds resulted in breakdown of the analogy with the spectrum of phenanthrene.

In the fluorescence spectra of crystalline phenanthrene deposited onto a quartz plate from a 2.5% solution in toluene, we observed well-resolved bands with maxima in the region of 410, 435, and 463 nm and a weak band at ~500 nm. The spectrum of phenanthrene introduced into PMPS contained two bands with $\lambda_{max} = 410$ and 430 nm, and also two discontinuities at ~390 and 465 nm; the spectrum of phenanthrene introduced into the block-copolymer matrix contained bands in the region of 410, 435, and 463 nm and also weak discontinuities at 395 and 490 nm. In Fig. 1 (curves 1—3), it is evident that the bands in the fluorescence spectra of phenanthrene were somewhat shifted to the short-wave region when it was introduced into PMPS and the block copolymers.

During pulsed photoexcitation by a Xe—Cl laser with $\lambda = 308$ nm, the fluorescence spectra of PA repeating units in the ring-chain and block copolymers consisted of single diffuse bands with a maximum at 415 nm in PMPS and 450 nm in the block copolymers (Fig. 1, curves 4 and 5), unlike in the spectra of phenanthrene that was introduced into the same polymers. The nature of the fluorescence spectra of the PA repeating units depended on the structure of the studied siloxanes. In this case, the shift of the bands in the fluorescence spectra of phenanthrene changed in the same direction in going from PMPS to the block copolymers. Thus, in the fluorescence spectra of both the PA repeating units and phenanthrene the effect of the polymer matrix was manifested in the same way.

We observed a strong dependence of the shape of the fluorescence spectra of the studied compounds on the dose of irradiation by the Xe—Cl laser (up to 300 J/cm^2). An analysis of the differences of the shapes of spectra of specimens with minimum, intermediate, and maximum doses (300 J/cm^2) made it possible to distinguish "pure" spectral forms of PA repeating units in PMPS and the block copolymers (Fig. 2). It is evident that the fluorescence spectrum of PA repeating units consisted of four bands with maxima at 410, 440, 465, and ~500 nm, and the band at 410 nm was present only in the spectrum of ring-chain PMPS. For PA repeating units of dimethylphenylsiloxane block copolymers, a band with a maximum at 410 nm was not observed (Fig. 1, curve 4). In addition (Fig. 2), bands at 440, 465, and ~500 nm were distinguished.

In the IR spectra of PMPS and the block copolymer irradiated by a dose of 300 J, we noted a decrease of the intensity of the absorption bands assigned to $\delta(Si-CH_3)$ and $\nu(Si-C_6H_5)$ and observed a diffuse absorption band assigned to $\gamma_{as}(Si-O-Si)$, but the general nature of the IR spectra of the irradiated siloxanes was preserved, which confirms the data on the stabilizing effect of PA repeating units [2, 6].

The phosphorescence spectra were recorded with a luminescence spectrophotometer at 77 K using a phosphoroscope. The phosphorescence spectrum of the PA repeating units had the shape of a wide band, in which we could distinguish maxima at 440, 470, and 500 nm for all the polymers containing PA repeating units (Fig. 3). In addition, we should note that, on the whole, the spectral regions of phosphorescence (during recording under steady-state conditions) and fluorescence (during pulsed photoexcitation) agreed. During pulsed photoexcitation at 293 K, we observed slowly decreasing luminescence (for more than 4 sec) only for PA repeating units in the dimethylphenylsiloxane block copolymer in the form of a rather narrow weakly resolved band with maxima near 475 and 515 nm and a discontinuity at 440 nm (Fig. 4a). Thus, during pulsed photoexcitation, the slowly decreasing luminescence was manifested in the same spectral range as the "pure" fluorescence form (Fig. 2, curve 3).

Such luminescence was not observed in the ring-chain PMPS nor in toluene solutions of the block copolymer containing PA repeating units. Such luminescence was not observed in the block copolymer heated to 400 K, and the luminescence was observed again during cooling of the preheated specimen to 293 K, but its intensity became somewhat lower. We measured the lifetime of luminescence of PA repeating units in the block copolymer, the intensity of which decreased according to a monoexponential kinetic curve and was characterized by lifetime $\tau = 0.9$ sec (Fig. 4b). We should note that at 293 K the phosphorescence of pure phenanthrene and also of phenanthrene introduced into the ring-chain PMPS and into the block copolymer was not observed during pulsed photoexcitation, and thus the luminescence of PA repeating units observed at 293 K could not be attributed by analogy to phenanthrene-type phosphorescence. The slowly decreasing luminescence of PA repeating units in the region of 440—510 nm was observed only in the rigid matrix of the bock copolymer at 293 K. Such luminescence was observed previously in phenanthrene solid solutions at helium temperatures and was identified as delayed fluorescence. The mechanism of its appearance was studied, e.g., in [7].

The experimental results that we obtained make it possible to attribute this luminescence to delayed fluorescence, as also indicated by the similarity of the distinguished fluorescence forms and the luminescence that we observed. We can assume that the main channel of excitation of delayed fluorescence (the $S_1 \rightarrow S_0$ transition) is the $(T_1 \rightarrow S_1)$ transition. In the case of a soft polymer matrix, rapid vibrational relaxation of the T_1 level occurs, which leads to low probability of this transition because the energy of the vibrationally unexcited level T_1 is less than the energy S_1 [8]. But in a rigid matrix the rate of such relaxation decreases, which leads to an increase of the probability of the $T_1 \rightarrow S_1$ transition because, in this case, transitions from T_1 vibrationally excited levels, in particular from S_1 levels in resonance with the system of S_1 levels, are possible.

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APPROXIMATION OF STRUCTURELESS BANDS IN THE ELECTRON
SPECTRA OF MOLECULES USING PEARSON CURVES

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The possibility of analytical description of the spectral contours of molecular bands in terms of parameters with a physically comprehensible meaning is attractive from the perspective of many problems of theoretical and applied molecular spectroscopy.

The use of the spectral moments

$$\mu_i = \int v^i\, B(v)\, dv; \qquad \bar{\mu}_i = \int (v - \bar{v})^i\, B(v)\, dv, \qquad \bar{v} = \mu_1/\mu_0, \tag{1}$$

as such parameters have definite advantages in comparison with other approaches; in Eq. (1), B(v) is the probability of optical electron transition, which depends on the radiation frequency v. These advantages are that:

low-order moments may be determined directly from experimental data [1];

the function B(v) is close to a Gaussian function in the vicinity of its maximum, permitting the hope that it may be reproduced on the basis of a small number of low-order spectral moments with an accuracy close to that attainable in modern experiments (the complete set of moments uniquely characterizes the function [2]);

the spectral moments may be calculated on the basis of information on the potential surfaces U_1 and U_2 of the initial and final electron states, respectively, and the electron moment of the transition M [3, 4].

In the semiclassical ($U_2 - U_1 = v$) Condon (M = const) approximation [3, 4], the expression for the spectral moments takes an extremely simple form

$$\mu_i \sim \int V^i\,(R)\, P\,(R); \qquad \bar{\mu}_i \sim \int (V\,(R) - \bar{v})^i\, P\,(R)\, dR, \tag{2}$$

where $V(R) = U_2(R) - U_1(R)$ is a difference potential depending on the internuclear coordinate R; P(R) is the distribution density of the molecules with respect to R in the initial state.

Detailed analysis of the semiclassical approximation of Eq. (2), together with a statement of the corresponding formulas, may be found in [4].

The problem of reproducing the distribution function on the basis of its moments is known as the moment problem [5]. Some well-known algorithms for its solution were described in [5—7]. However, for many purposes it is expedient to have an explicit analytical expression, even if approximate, for the function B(v) in terms of a small number of moments.