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Reaction of Perylene-3,4,9,10-tetracarboxylic Acid Dianhydride with 3-Aminopropyltriethoxysilane and Hexamethyldisilazane

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Abstract—The reaction of perylene-3,4,9,10-tetracarboxylic acid dianhydride with 3-aminopropyltriethoxysilane and hexamethyldisilazane was investigated. A possibility of obtaining a new dye resistant to UV light and heating (up to 300ºC), consisting of structural fragments of perylene-3,4,9,10-tetracarboxydiimede, diethoxysiloxane, and 3-aminopropylethoxysiloxane was demonstrated. A compound obtained in 43% yield by heating (7 h, 180–200ºC) perylene-3,4,9,10-tetracarboxylic acid dianhydride with excess 3-aminopropyltriethoxysilane in the presence of catalytic amounts of zinc acetate is an oligomer appropriate for the sol–gel process, displays strong luminescence in the red spectral region (540–620 nm), and has good film-forming properties. The participation of hexamethyldisilazane consists in binding water molecules formed in the reaction of perylene-3,4,9,10-tetracarboxylic acid dianhydride with 3-aminopropyltriethoxysilane and in the formation of trimethylsilanol which replaces a part of the EtO groups at the silicon atoms by a more bulky Me_3SiO groups, causing significant increase in the solubility of the dye in organic solvents and silicon sol–gel monomers. The hydrolysis of silicon-containing dye and subsequent dehydration of the resulting gel lead to the formation of insoluble xerogel.

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A perylene-3,4,9,10-tetracarboxylic acid dianhydride [1, 2] is a crystalline compound of bright red color, insoluble in water and organic media, displaying strong luminescent properties, stable against heating and light. The manufacturing of colored and luminescent materials of organic and hybrid organic–inorganic structure [3] requires the use of soluble dyes. This problem is commonly solved by the introduction into the molecule of the dianhydride of organic substituents in the aromatic framework or into the anhydride fragments. Good results were obtained with long-chain aliphatic amines with branched organic radicals [4–6]. The reaction proceeds at the two anhydride groups by the replacement of oxygen atoms by nitrogen. An attempt to obtain an organosilicon derivative [7] was performed along the following procedure: (1) the synthesis of carboximide anhydride with a long branched aliphatic substituent at the nitrogen atom, (2) the reaction of this intermediate with allylamine, (3) the hydrosilylation with trimethoxysilane of the unsaturated compound formed. Now we present the results of a study of the reaction of perylene-3,4,9,10-tetracarboxylic acid dianhydride with 3-aminopropyltriethoxysilane and hexamethyldisilazane, which leads to the formation of soluble ethoxysiloxane derivatives of perylenetetracarboxylic acid diimide. Compounds of this type should be compatible with the sol–gel organosilicon monomers [8] and the varnishes [9] hardened by the condensation mechanism. In the process of structurization of the coating the functionalized dye is attached chemically to the polysiloxane chain and embedded in it. The organo-silicon coatings [9–12] are superior to the purely organic compounds by several characteristics. They have high thermal, frost and light resistance, high hydrophobicity, and excellent electrical insulating characteristics. In this regard, the use of new heat- and light-resistant pigments in conjunction with organo-silicon monomers, polymers and varnishes seems most appropriate.

The perylene-3,4,9,10-tetracarboxylic acid dianhydride is known to poorly react with primary amines.

Dye **I** solubility in alkoxysilanes and sol–gel film formation tests

Organoalkoxysilanes[a]	Ratio, v/v	Concentration, wt %	Characteristics of the liquid composition	Characteristic of a solid film	
				3–5 μm	35–55 μm
3-Aminopropyltriethoxysilane	–	14.0	Dark red	Red, semi-transparent	Dark red, not transparent
3-Aminopropyltriethoxysilane–tetraethoxysilane	1:10	1.40	Red, muddy	Pink, muddy	Red, muddy
3-Aminopropyltriethoxysilane–tetraethoxysilane	1:20	0.70	**I** does not dissolve	–	–
3-Aminopropyltriethoxysilane–$PhSi(OMe)_3$	1:10	1.40	Dark red	Rose, transparent	Red, opalescent
3-Aminopropyltriethoxysilane–$PhSi(OMe)_3$	1:20	0.70	Dark red	Rose, transparent	Red, opalescent
3-Aminopropyltriethoxysilane–$PhSi(OMe)_3$	1:100	0.14	Red	Pale pink, transparent	Red, transparent

[a] The curing duration of the films obtained by centrifuging is 5–7 h, by pouring 3 days, the film thickness is 3–5 μm and 35–55 μm, respectively.

The first attempt to obtain a silicon-containing perylene pigment [13] by the reaction of the perylene-3,4,9,10-tetracarboxylic acid dianhydride with 3-aminopropyltriethoxysilane in water phase at high temperature was performed in a pressure reactor. It resulted in obtaining a cross-linked insoluble polyorganosilsesquioxane containing perylene fragments. The perylene dyes soluble in organic media were obtained by the reaction of perylene-3,4,9,10-tetracarboxylic acid dianhydride with an excess of primary organic amine in the medium of quinoline at 180–230°C with zinc acetate additive in amount up to 2 mol per 2.5 mol of the dianhydride [14]. The reaction in molten imidazole decreased the temperature to 140–150°C and reduced the zinc acetate amount to the catalytic quantity [7]. Our aim to obtain a soluble dye based on the perylene-3,4,9,10-tetracarboxylic acid dianhydride and 3-aminopropyltriethoxysilane does not allow these two well-known and practically used methods, since further processing of reaction mixtures and purification of the target product includes the use of aqueous acids and alkalis. In such conditions only insoluble perylene–silsesquioxane pigments can be obtained. Therefore, we chose the method of synthesis with an excess of 3-aminopropyltriethoxysilane or its mixture with hexamethyldisilazane with a minimum of the zinc acetate additive.

Stirring the perylene-3,4,9,10-tetracarboxylic acid dianhydride with an excess of 3-aminopropyltriethoxysilane at room temperature in the absence of a catalyst leads to a weak coloring that indicates a slight dissolution of the solid fused aromatic compound in the liquid colorless organosilicon amine. Heating in the presence of catalytic amounts of zinc acetate causes a deepening of color, but the reaction proceeds slowly. After 7 h of vigorous stirring at 180–200°C the reaction mixture still contained undissolved dianhydride. Yield of the perylenetetracarboxylic acid diimide organosilicon derivative (**I**) was 43%, red-black shiny particles, moderately soluble in toluene, chloroform, methylene chloride, DMF, and phenyltrimethoxysilane, readily soluble in 3-aminopropyltriethoxysilane and insoluble in hexane, ethanol, acetonitrile, tetraethoxysilane, and methyltrimethoxysilane. The solubility decreases in the sequence of the solvents: 3-aminopropyltriethoxysilane > THF > $CHCl_3 > CH_2Cl_2 > PhSi(OMe)_3 >$ DMF > toluene.

Applying a thin layer of concentrated solution of compound **I** in 3-aminopropyltriethoxysilane to silicate glass using a centrifuge gave a bright red semi-transparent solid coating 3–5 μm thick that solidified in air in 3–5 h and had good adhesion to the surface. Pouring a mixture of compound **I** with 3-aminopropyltriethoxysilane and $PhSi(OMe)_3$ on quartz substrate gave transparent red films satisfying the conditions of measuring absorption and emission spectra (see the table).

The films were subjected to heat treatment in air for 3 h at 100, 150, 200, 250, 300, 350, 400ºC. The appearance of some cracks was observed after heating to 300ºC. Strong cracking and peeling from the substrate

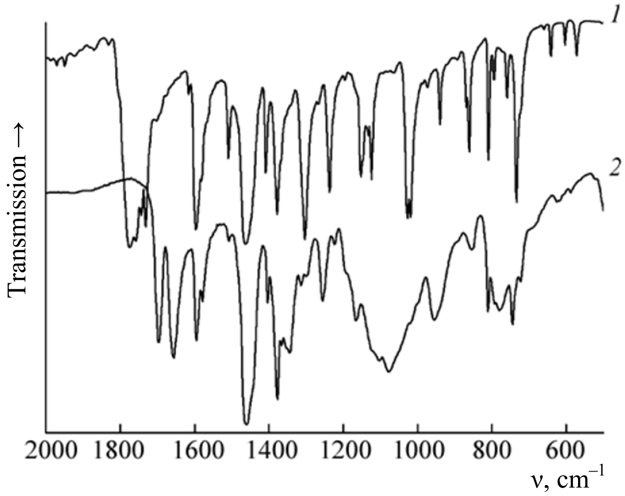


Fig. 1. IR spectra of (*1*) perylene-3,4,9,10-tetracarboxylic acid dianhydride and (*2*) compound **I** (suspensions in mineral oil).

occurred at 400ºC. Throughout the temperature range studied, the film remained transparent, no fading or change in color was observed, indicating a high thermooxidative stability of both polysiloxane matrix and perylene dye.

The reaction product of perylenetetracarboxylic acid dianhydride with 3-aminopropyltriethoxysilane was identified using the IR and electronic spectroscopy, spectrofluorimetery, XRD, and elemental analysis. The films were used to measure the absorption and emission spectra. The introduction of silicon-containing groups leads to fundamental changes in the IR spectrum of the reaction product compared to the original perylene-3,4,9,10-tetracarboxylic acid dianhydride (Fig. 1). An intense structured band centered at 1768 cm^{-1} belonging to the anhydride fragment disappears and two bands appear of amide groups, 1696 cm^{-1} (amide I) and 1656 cm^{-1} (amide II). A series of bands at 1164, 1076, 952, 780 cm^{-1} belongs to the groups $Si(OEt)_3$, $Si(OEt)_2$, and SiOSi. The presence of the latter is proved by a significant broadening of the most intense absorption band at 1100 cm^{-1}. In the spectrum of the resulting compound remained a series of narrow bands at 1593, 1578, 1402, 1315, 856, 810, 744 cm^{-1}, belonging to the vibrations of the aromatic fragment.

Figure 2 shows the EAS of the film and its transformation upon heating. In the red region of the spectrum there is an absorption band with clearly

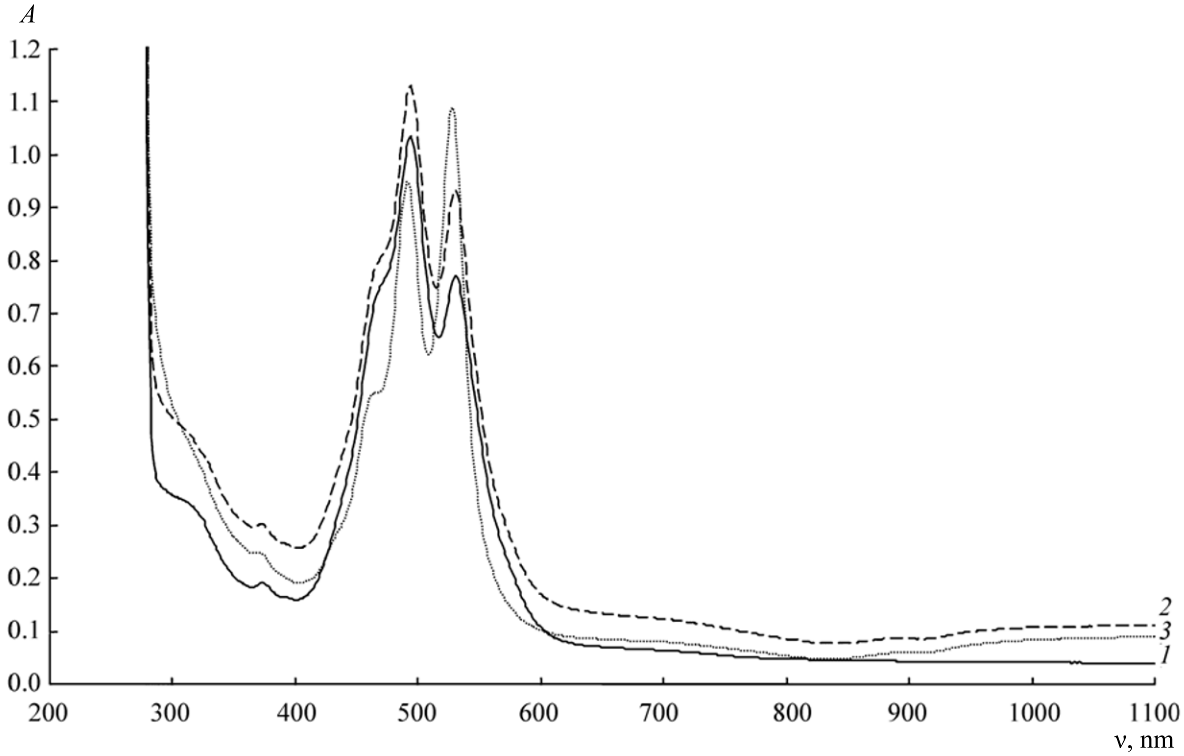


Fig. 2. Changes in the electronic spectrum of the film of compound **I** in 3-aminopropyltriethoxysilane–$PhSi(OMe)_3$ upon heating: (*1*) initial, (*2*) 100ºC, (*3*) 100–150–200ºC.

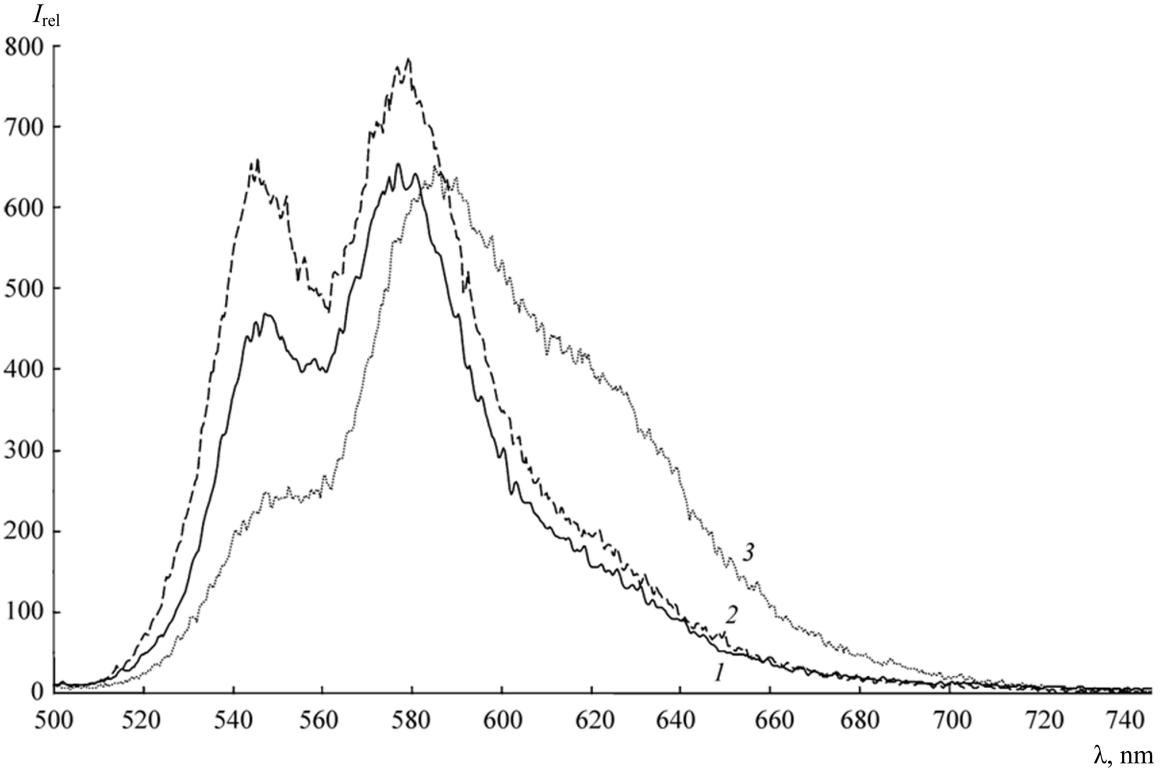


Fig. 3. Transformation of the photoluminescence spectrum of the film upon heating: (*1*) 100–150ºC, (*2*) 100–150–200–250ºC, and (*3*) 100–150–200–250–300–350ºC, $\lambda_{exc} = 490$ nm.

manifested vibronic structure. The heating reduces the short-wavelength (495 nm) and increases the long-wavelength (531 nm) modes. The overall intensity of the absorption band remains practically unchanged. Variations of the vibronic components suggest that at heating to 200°C the film cured in air at room temperature continuesbe subjected to structuring processes that restricts the oscillations fluctuations of individual fragments. Therewith, the overall increase in the optical density is practically not observed, that is, the applied layer retains its original transparency.

In the spectrum of the photoluminescence excitation there is a series of bands in the range 300–50 nm. The most intense are the bands at 459, 492, and 526 nm, the most corresponding to the absorption spectrum. In the emission spectrum two peaks at 539, 583 nm and a shoulder at 623 nm are observed.

Figure 3 shows the transformation of the photoluminescence spectrum upon successive heating the film at 150, 250, and 350ºC. The figure shows that the spectrum as a whole does not considerably vary. There is some increase in the intensity of the long-wavelength shoulder at 623 nm as a consequence of structuring of the coating.

The stability against light of the dye incorporated in the sol–gel matrix was investigated under the action of unfiltered UV light generated by a medium-pressure mercury lamp (240–320 nm). Fig. 4 shows the transformation of the EAS during prolonged (40 h) exposure of the film to the light in air. The intensity of the absorption band decreases slightly after the first 3 h of irradiation. After 15 h, there is an increase in the absorption in the short-wavelength range (300–450 nm) due to the accumulation of defects in the film leading to the light scattering. In the long-wavelength region the similar effect was not observed, but after 40 h of exposure to UV the absorption increases markedly throughout the measured wavelength in the range from 300 to 700 nm. The absorption band shape suffers the changes similar to those observed at the heating of the film (Fig. 2), but less pronounced. Prolonged (40 h) exposure of thick (120 μm) layer leads to the formation of wrinkles on the surface and appearance of a weak opalescence. Photobleaching and delamination from the substrate does not occur.

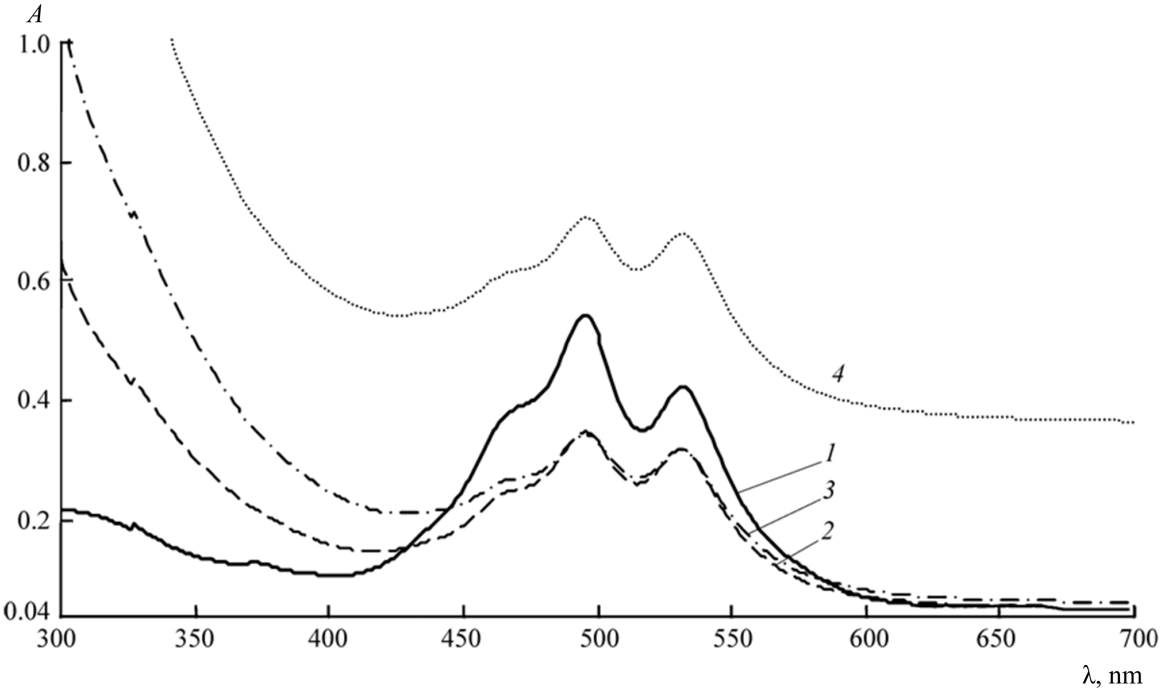


Fig. 4. Transformation of the electronic spectrum of the film at exposing to UV light, h: (*1*) 0.2, (*2*) 5, (*3*) 15, and (*4*) 40.

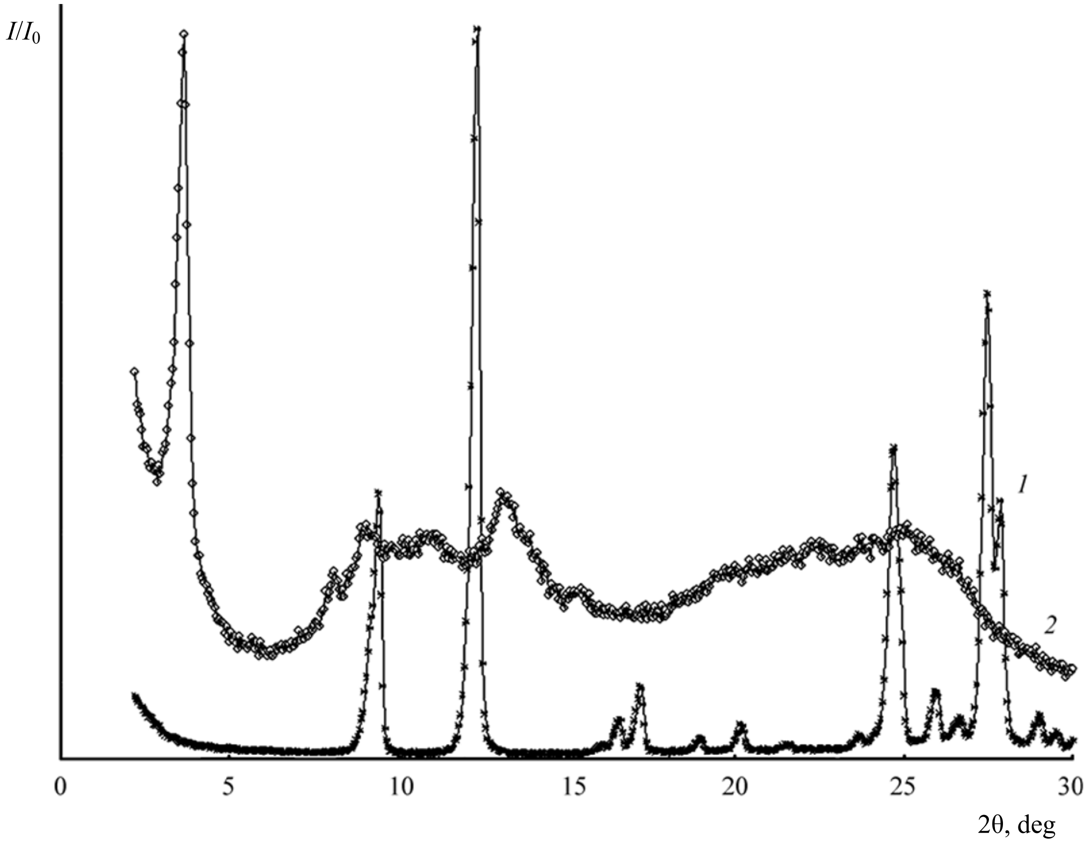
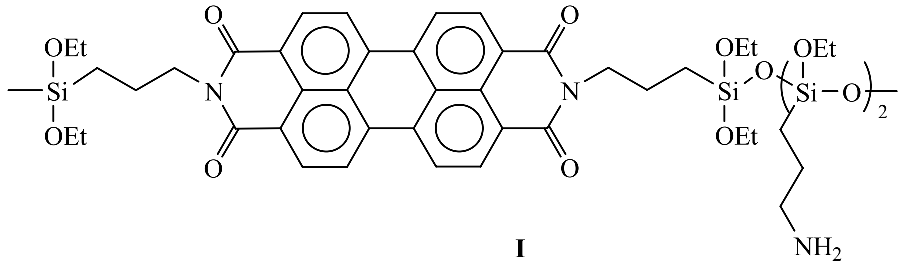


Fig. 5. Diffractograms of (*1*) perylene-3,4,9,10-tetracarboxylic acid dianhydride and (*2*) compound **I**.

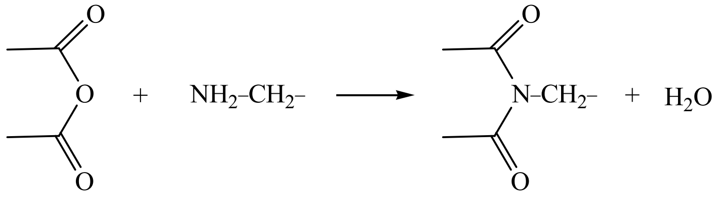
The comparison of X-ray diffraction patterns of the perylene-3,4,9,10-tetracarboxylic acid dianhydride and the compound **I** (Fig. 5) shows the following. The original dianhydride is a highly crystalline compound. The interaction with 3-aminopropyltriethoxysilane destroys its structure and transforms the system in two-phase state: an amorphous, with a halo in the range 2θ from 7° to 15° and from 18° to 30°, and a fine-crystalline, with a strong reflection in the small-angle reflection range (interplanar distance about 23 Å), and a number of weak peaks.

The elemental analysis allowed us to suggest a formula of the resulting compound as a siloxane oligomer containing in its main chain one fragment of perylenetetracarboxylic diimide per two diethoxysiloxane and one 3-aminopropylethoxysiloxane fragments.



I

An idealized structure of the perylenetetracarbocylic acid bis(3-triethoxysilylpropylimide) cannot be obtained under the applied conditions due to the presence of water released in the reaction course. The presence of water results in the hydrolysis of triethoxysilyl groups. The intermediately formed silanols condense to form disiloxanes.



$$—\mathrm{Si(OEt)_3} + \mathrm{H_2O} \longrightarrow —\mathrm{Si(OEt)_2OH} + \mathrm{EtOH}$$

$$—\mathrm{Si(OEt)_2OH} + —\mathrm{Si(OEt)_3} \longrightarrow —\mathrm{Si(OEt)_2}—\mathrm{O}-\mathrm{Si(OEt)_2}— + \mathrm{EtOH}$$

$$—\mathrm{Si(OEt)_2OH} + —\mathrm{Si(OEt)_2OH} \longrightarrow —\mathrm{Si(OEt)_2}—\mathrm{O}-\mathrm{Si(OEt)_2}— + \mathrm{H_2O}$$

Thus, the reaction of perylenetetracarboxylic acid dianhydride with an excess of 3-aminopropyltriethoxysilane leads to a silicon-containing perylene dye limitedly compatible with the organosilicon sol–gel monomers and polar organic solvents. The reason for limited solubility may be the insufficient length of the organosilicon fragments in the molecules of the dye, and the presence of high molecular polymers, including cross-linked ones. The polymerization and cross-linking of ethoxy derivatives proceeds on account of the water release in the reaction course. In order to partially prevent this process, hexamethyldisilazane was added to the reaction mixture, which can bind the released water under the conditions of high-temperature reaction giving trimethylsilanol and ammonia. It is known [15] that trimethylsilanol can readily enter in the transetherification of triethoxysilyl group forming the $\mathrm{(Me_3SiO)}_n\mathrm{(EtO)}_{3-n}\mathrm{Si}$ fragments. It is also known [16] that hexamethyldisilazane reacts at elevated temperature with 3-aminopropyltriethoxysilane to form a cyclic product, 2,2-diethoxy-1,2-azasilolidine. The addition of hexamethyldisilazane should increase the yield and solubility of the compounds obtained, partially preventing the hydrolysis reactions and increasing in the volume of silicon substituents.

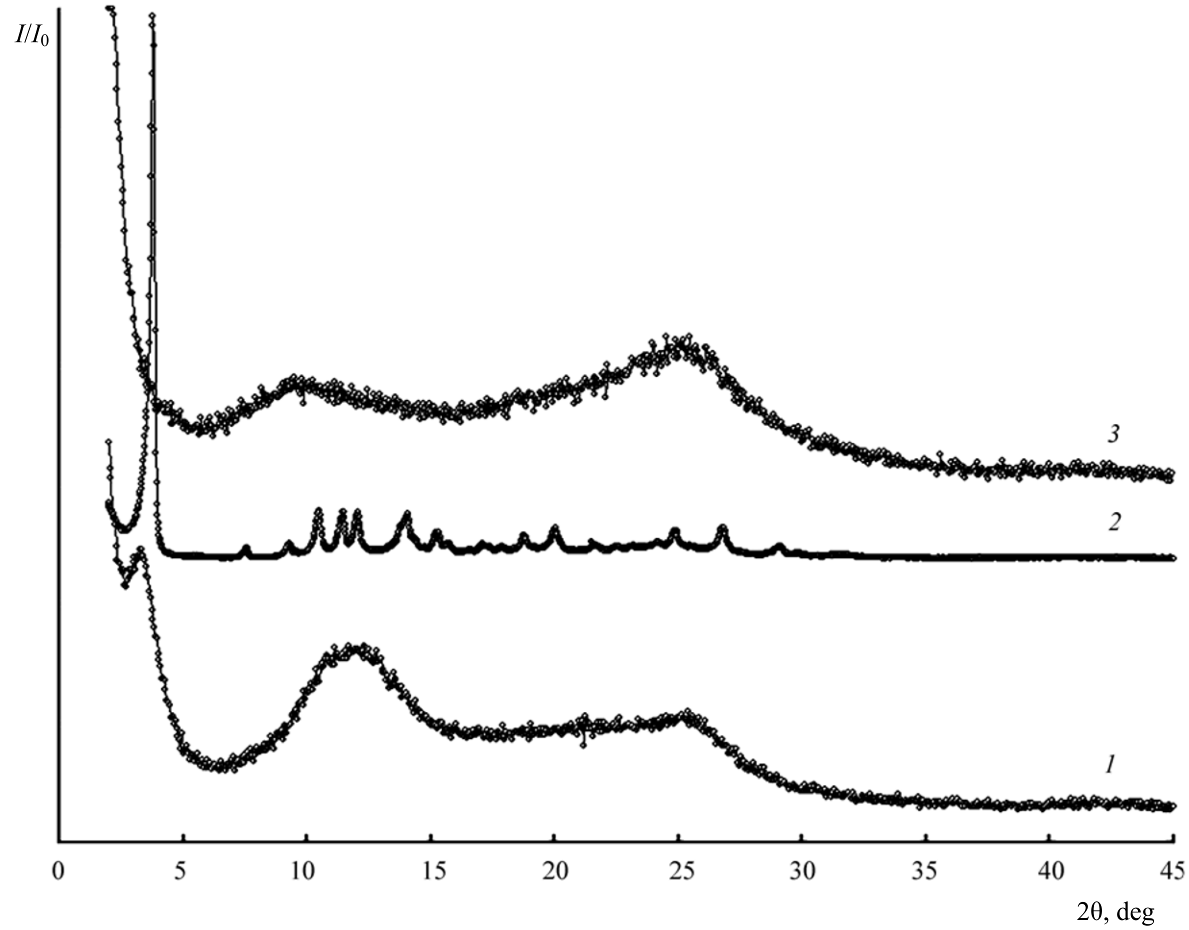


Fig. 6. Diffractograms of compounds: (*1*) **II**, (*2*) **III**, (*3*) and xerogel **IVa**.

Heating perylene-3,4,9,10-tetracarboxylic acid dianhydride with 3-aminopropyltriethoxysilane in the presence of hexamethyldisilazane indeed led to a strong increase in the solubility of the silicon-containing perylene dye (**II**). The product obtained is actually easily soluble in all the above mentioned solvents (except acetonitrile) and sol–gel monomers, as well as in hexane. In the IR spectrum of the compound a strong absorption band appeared at 845 cm^{-1} belonging to the $SiMe_3$ group. In the ^1H NMR spectrum the integral intensities of the signals belonging to the protons of methyl groups in the fragments $(CH_3)_3SiO$ and CH_3CH_2O are comparable. This fact indicates a sufficiently high degree of replacement of the ethoxy substituents by trimethylsiloxy group. The comparison of X-ray diffraction patterns of two soluble dyes, **I** and **II,** shows (Fig. 5, curve *2* and Fig. 6, curve *1*) that the latter is more amorphous, apparently due to the influence of bulky trimethylsilyl groups hindering the ordered orientation of the aromatic perylene fragments (π-staking). The HPLC method gives a graphic representation of the complex chemical composition of the soluble fraction of the dye. The chromatogram of the mixture formed in the reaction of dianhydride with 3-aminopropyltriethoxysilane and hexamethyldisilazane shows the presence of about 15 compounds, the oligomers with varied chain lengths and with different relative position of groups OEt and $OSiMe_3$. The best separation is achieved on a column filled with the solid carrier Silasorb SPH 600, having silanol groups on its surface. The retention volume of the components of the mixture is reduced significantly at the use of Separon SGX CN modified with nitrile groups as a carrier, but the separation selectivity falls.

The elemental analysis allows us to suggest an idealized formula of the oligomeric product **II** as two fragments of compound **I**, one with two EtO groups replaced by $EtOMe_3SiO$ and another with one replaced EtO group:

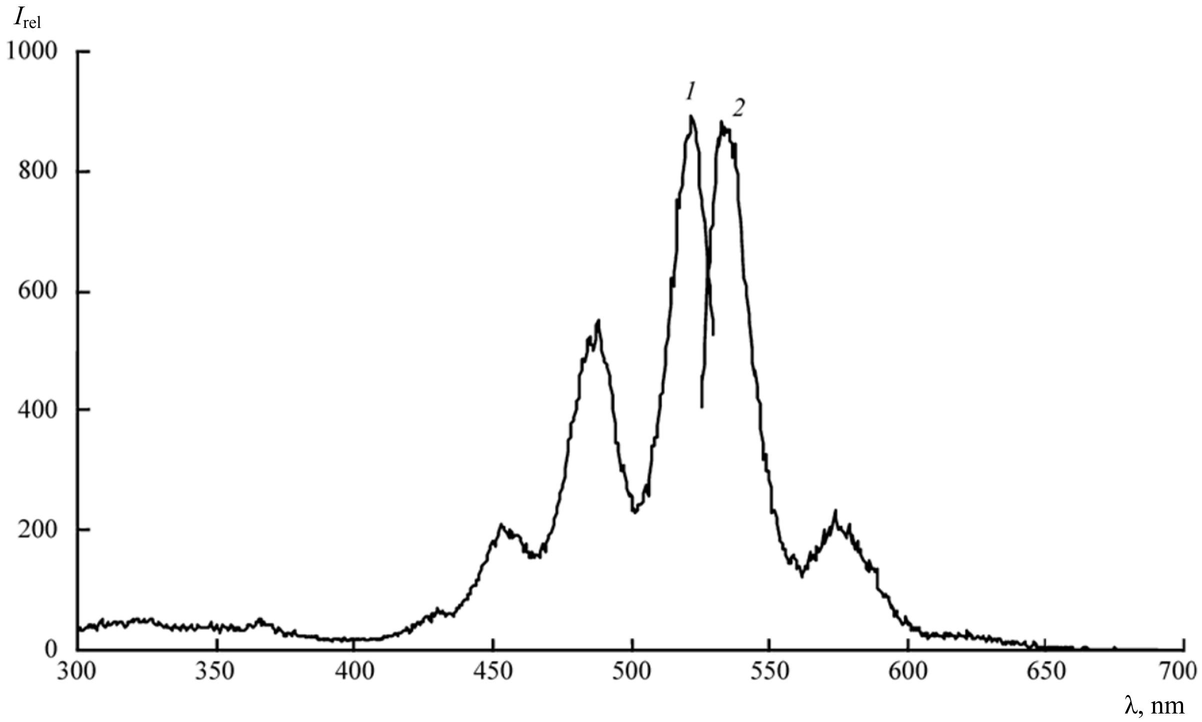


Fig. 7. Luminescence excitation spectrum (*1*, λ_{reg} = 542 nm, *c* = 9.72×10^{-4}%) and emission spectrum (*2*, λ_{exc} = 514 nm, *c* = 1.39×10^{-5}%) of dye **II** in CH_2Cl_2.

$\mathrm{Si(OEt)(OSiMe_3)(CH_2)_3N}$▬$\mathrm{N(CH_2)_3Si(OEt)(OSiMe_3)OSi(OEt)(CH_2CH_2CH_2NH_2)}$–O–
$\mathrm{Si(OEt)_2(CH_2)_3N}$▬$\mathrm{N(CH_2)_3Si(OEt)(OSiMe_3)OSi(OEt)(CH_2CH_2CH_2NH_2)}$–O–

where N▬N means a perylenediimide fragment, $\mathrm{N(CO)_2(C_6H_2)_4(CO)_2N}$.

The electron absorption spectrum, as well as the excitation and the emission spectra were measured from a dilute solution of dye **II** in methylene chloride (Fig. 7) with rhodamine 6G as reference compound. From these data the relative quantum yield of photoluminescence was calculated at φ = 52%. It is known [4, 5, 7] that the quantum yield of photoluminescence of individual perylenediimides obtained from the perylene-3,4,9,10-tetracarboxylic acid dianhydride and primary amines depends on the degree of purification and is close to 100% for high-purity samples. The small value of φ is explained by the large set of oligomers and isomers that are present in the resulting dye **II**. The Stokes shift is 13 nm. The absorption and emission spectra of dyes **I** and **II** differ slightly. The vibronic structure of the spectrum is retained both in solution and in film.

The participation of disilazane in the reaction consists only in the binding water molecules released in the reaction of dianhydride with 3-aminopropyltriethoxysilane. Additional experiments showed that hexamethyldisilazane does not react with the perylene-3,4,9,10-tetracarboxylic acid dianhydride in the presence of catalytic amounts of zinc acetate even at prolonged heating (110ºC, 15 h).

The presence of Me_3SiO groups does not prevent the reaction of hydrolytic polycondensation of compounds obtained in the reaction of perylene-3,4,9,10-tetracarboxylic acid dianhydride with 3-aminopropyltriethoxysilane and hexamethyldisilazane. The processes of acid and alkaline hydrolysis were studied using a mixture of solvents toluene–ethyl alcohol. The precipitated products are the X-ray amorphous large-disperse (HCl) or fine-disperse (NH_4OH) particles of dark red color, insoluble in water and organic solvents. Figure 6 shows the X-ray diffractogram of compound **II** and one of the xerogels, which implies that the degree of amorphization increases markedly relative to the original product. In the IR spectrum the series of absorption bands of ethoxysilyl fragments at 1167, 1079, 955, 780 cm^{-1} is converted into a broad intense band of the SiOSi asymmetric vibrations centered at 1076 cm^{-1}. Absorption in the region of 3350–3370 cm^{-1} associated with the presence of residual (not condensed) silanol groups is of low intensity and is changed only slightly depending on the conditions of the hydrolysis reaction.

In the reaction of perylene-3,4,9,10-tetracarboxylic acid dianhydride with 3-aminopropyltriethoxysilane and hexamethyldisilazane a significant amount (57–43%) of insoluble product **III** is formed, which cannot be identified as the unreacted dianhydride. According to X-ray phase analysis, it is a crystalline compound, in the diffractogram of which (Fig. 6, curve *2*) there are no reflections related to the original dianhydride. IR spectrum is largely identical to the spectrum of the soluble product. The main difference is the markedly smaller intensity of the absorption bands of SiOEt and SiOSi fragments in the region of 1160–950 cm^{-1} and a greater absorption intensity in the region of imide and anhydride fragments (1690–1590 cm^{-1}). According to the elemental analysis, the carbon content in the insoluble compound is higher, while that of nitrogen and silicon is much lower than in the soluble form. It can be assumed that it is a reaction product of dianhydride at a single anhydride group. For example, the analysis of the derivative obtained in the presence of the hexamethyldisilazane is satisfactory consistent with the calculated for the compound with the organosilicon moiety at the nitrogen atom of the composition $CH_2CH_2CH_2Si(OEt)_2OSiMe_3$.

Thus, the studies of the reaction showed a possibility of obtaining a new dye resistant to UV light and elevated temperature, consisting of the structural fragments of peryilene-3,4,9,10-tetracarboxylic acid diimide, diethoxysiloxane, and 3-aminopropylethoxysiloxane units. With hexamethyldisilazane as an additional agent the solubility of the resulting dye in organic solvents and sol–gel monomers increases due to the partial replacement of ethoxy groups at the silicon atom by the bulky trimethylsiloxy groups, as well as because of the prevention of the hydrolysis reactions and cross-linking of the oligosiloxane chains. The synthesized compounds are the oligomers for the sol–gel process showing an intense luminescence in the red spectral region and having good film-forming properties.

EXPERIMENTAL

IR spectra of compounds were taken from liquid films between the KBr, CaF_2 plates or from suspensions in mineral oil on a FTIR spectrometer FSM 1201. Electron absorption spectra were measured on a Perkin-Elmer Lambda 25 spectrophotometer, fluorescence and fluorescence excitation spectra were obtained on a Perkin-Elmer LS-55 spectrofluorimeter. The spectral width of the slits of excitation and recording monochromators was 2.5 nm, and at the registration of absorption spectra, 1 nm. The film was mounted at an angle of 45° to the excitation light, and the fluorescence emission was recorded from the surface. In addition, in front of the registration monochromator was introduced the adjustment built-in filter blocking the scatterred and reflected excitation light. The spectra obtained were automatically corrected for the spectral sensitivity of the photomultiplier and the spectral curve of the filter. The ^1H NMR spectra were taken from solution in $CDCl_3$ on a Bruker Avance DPX-200 instrument (200 MHz) at 25ºC, internal reference Me_4Si. X-ray diffraction analysis was performed on a DRON-3M diffractometer with Cu-K_α radiation and a graphite monochromator on the diffracted beam.

The purity of initial compounds (3-aminopropyltriethoxysilane and hexamethyldisilazane) was monitored by GLC on a Tsvet-800 chromatograph with 0.3×300 cm column, 5% silicone SE-30 on the solid carrier Inerton-AW, detection by thermal conductivity. The composition of the dye was determined by HPLC on a liquid chromatograph Knauer equipped with a spectrophotometric detector. The separation was carried out on 6×100 mm columns, sorbent Silasorb SPH 600 5 μm, and 3.3×150 mm with Separon SGX CN 5 μm, eluent hexane–THF 5:1.

3-Aminopropyltriethoxysilane (from Altaikhimprom, Slavgorod) and hexamethyldisilazane (from Kremnii-polymer, Zaporozh'e) were subjected to rectification before use. Perylene-3,4,9,10-tetracarboxylic acid dianhydride (from Acros Organics) was used without further purification.

Quartz substrate (3×12×40) for forming the films was treated for 10 hours with a saturated solution of NaOH in isopropanol, followed by 10 h with chromate mixture, washed with water and dried at 150–170ºC.

Reaction of perylene-3,4,9,10-tetracarboxylic acid dianhydride with 3-aminopropyltriethoxy-

silane. A mixture of 30 ml (28.6 g, 1.3×10^{-1} mol) of 3-aminopropyltriethoxysilane, 2.0 g (5.1×10^{-3} mol) of perylene-3,4,9,10-tetracarboxylic acid dianhydride, and 0.05 g of $Zn(OAc)_2$ was heated for 7 h at 180–200°C at vigorous stirring. After cooling, to the reaction mixture 30 ml of toluene was added, the liquid was decanted, the residue was centrifuged, toluene and excess 3-aminopropyltriethoxysilane were removed in a vacuum at heating the flask to 200ºC. A solid caked mass was obtained, which was difficult to remove from the walls of the flask. It was dissolved in 20 ml of toluene, and 80 ml of hexane was added. The precipitate formed was heated in vacuum to 150ºC. 1.93 g (43%) of compound **IV** was isolated as red-black shiny fine particles, leaving a bright red color on paper and fabric. Dilute solutions in toluene and DMF are yellow, in THF and $CHCl_3$ red, in ethanol, hexane and acetonitrile the compound obtained does not dissolve. IR spectrum (ν, cm^{-1}): 1696 s (amide I), 1656 s (amide II), 1593 s, 1578 m 1402 m 1348 s, 1315 w, 1254 s ($SiCH_2$), 1164 sh (SiOEt), 1103 sh (SiOEt), 1076 v.s (SiOEt), 952 s (SiOEt), 856 w, 810 m, 780 s (SiOEt), 744 s. Found, %: C 55.83, H 6.51, N 5.17, Si 11.32. $C_{48}H_{66}N_4O_{13}Si_4$. Calculated, %: C 56.56, H 6.53, N 5.50, Si 10.99.

The reaction of perylene-3,4,9,10-tetracarboxylic acid dianhydride with 3-aminopropyltriethoxysilane and hexamethyldisilazane. A mixture of 2.0 g (5.1×10^{-3} mol) of perylene-3,4,9,10-tetracarboxylic acid dianhydride, 14.3 g (6.46×10^{-2} mol) of 3-aminopropyltriethoxysilane, 11.6 g (7.21×10^{-2} mol) of hexamethyldisilazane, and 0.05 g of $Zn(OAc)_2$ was heated for 15 h in argon to 160–175°C at vigorous stirring. The reaction mixture was centrifuged, and from the liquid part was distilled off in a vacuum 10.5 g of a clear colorless liquid raising the temperature of the flask to 200ºC. In the cooled trap was additionally collected 4.3 g of liquid. The residue in the flask (2.8 g) at 120–130°C is a sticky black tar, at 25°C it is a black frozen melt that cannot be removed from the walls of the flask. It was dissolved in 20 ml of toluene, the solvent was removed in a vacuum under intensive shaking, the flask was heated to 150ºC. Compound **II** (2.8 g) was isolated as large black and red particles, easily ground. IR spectrum (ν, cm^{-1}): 2968 s, 2952 s, 2892 s (CH), 1699 v.s, 1659 v.s [C(O)N], 1596 s, 1439 s, 1339 s (CH) , 1254 s (CH_2Si), 1167 m, 1103 sh, 1079 v.s, 955 m (SiOEt), 955 m, 847 v.s ($SiMe_3$), 807 m, 780 m (SiOEt), 756. The ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.18 m (CH_3Si), 0.982 t (CH_2Si), 1.22 m ($C\underline{H}_3CH_2O$), 1.96 m ($CH_3C\underline{H}_2O$), 4.23 m ($CH_2C\underline{H}_2CH_2$), 4.43 m (CH_2N), 8.61 m (CH-aryl). Found, %: C 56.72, H 6.97, N 3.96, Si 13.35. $C_{89}H_{118}N_6O_{22}Si_9$. Calculated, %: C 56.97, H 6.34, N 4.48, Si 13.43. The precipitate after centrifugation was washed with toluene, dried in a vacuum and then heated to 100ºC. 1.33 g of compound **III** was obtained as a bright red powder. IR spectrum, cm^{-1}: 1689 v.s (C=O, amide I), 1653 v.s (N–H, amide II), 1593 s (CH), 1405 m (CH), 1336 s (CH), 1298 w (CH), 1251 s ($SiCH_3$), 1167 m (SiOEt), 1079 w.s (SiOEt), 955 s (SiOEt), 847 s ($SiMe_3$), 807 s (CH), 780 s (SiOEt), 744 s ($SiMe_3$). Found, %: C 63.29, H 5.36; N 2.75; Si 8.86. $C_{34}H_{33}NO_8Si_2$. Calculated, %: C 63.83, H 5.20; N 2.19; Si 8.75.

Hydrolysis of compound II. *a.* To 0.74 g of compound **II** in 5 ml of toluene was added 10 ml of 95% EtOH, 2 ml of H_2O, and 2 drops of concn. HCl. The reaction mixture was stirred with a magnetic stirrer. After 5 h at the bottom and on the walls of the flask began to appear a solid, after 12 h the amount of precipitate increased. After 5 days, the mixture was filtered, the precipitate was washed with tetrahydrofuran and ethanol, dried in a vacuum and then heated to 170ºC. Xerogel **IVa** (0.13 g) was isolated as large black and red particles. IR spectrum (ν, cm^{-1}): 3370 w (SiOH), 1694 v.s 1650 v.s [C(O)N], 1595 v.s, 1377 s, 1254 m (CH), 1075 v.s (SiOSi), 845 m ($SiMe_3$), 811 m, 722 w. Found, %: C 54.61, H 5.05, N 5.65, Si 13.90.

b. To 0.72 g of compound **II** in 5 ml of toluene was added 10 ml of 95% EtOH, 2 ml of H_2O and 0.2 ml of concn. ammonia A precipitate soon appeared, which after 12 h increased markedly in amount. After 5 days, the mixture was filtered, the precipitate was washed with THF and ethanol, dried in a vacuum, and then heated to 170ºC. 0.10 g of xerogel **IVb** was isolated as a fine (dusty) red-black powder. IR spectrum (ν, cm^{-1}): 3350 w (SiOH), 1698 s, 1660 v.s [C(O)N], 1595 v.s, 1377 m, 1253 m (CH), 1076 v.s (SiOSi), 845 m ($SiMe_3$), 811 w, 750 w. Found, %: C 53.30, H 5.30, N 5.63, Si 14.54.

Testing the thermal and light stability of the films. The films on quartz substrates of thickness 100–130 μm formed by pouring were cured in air at 25°C for 3 days and subjected to heating in air for 3 h at each of the following temperatures: 100, 150, 200, 250, 300, 350, and 400ºC. Tests for the light resistance was performed by exposing to the light of a medium pressure mercury lamp DRT-240. Distance from the lamp to the sample was 15 cm. During the irradiation, the film was heated to 50°C due to the absorption of thermal radiation from the lamp.

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