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Novel organosilicon monomer for preparing transparent matrices doped with lanthanide complexes

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Perfluoroadipic bis(trialkoxysilylpropyl)amide was synthesized as a mixture of five compounds with the general formula $(EtO)_n(MeO)_{3-n}$ $Si(CH_2)_3NHC(O)(CF_2)_4C(O)NH(CH_2)_3$-$Si(OMe)_n(OEt)_{3-n}$ (**1**, $n = 1, 2$). Hydrolysis of this product by a specified amount of water (1 : 4) gave oligomers $EtO[(HO)(EtO)Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OEt)_2O]_nH$ ($n = 7$—9). From oligomer solutions, transparent glassy thermally stable films were obtained. The film material was studied by IR spectroscopy, atomic force microscopy, transmission electron microscopy, and powder X-ray diffraction. Compound **1** and oligomers can efficiently solvate lanthanide diketonate complexes. They displace water from the metal coordination sphere, and this water is then spent for hydrolysis of trialkoxysilyl groups. The luminescence intensity of matrix films based on the oligomers depends on the concentration of lanthanide complexes and is very low at $\lambda_{exc} = 330$ nm, whereas the luminescence intensity of the Eu^{3+} cation is very high.

Key words: organosilicon compounds, lanthanide complexes, thin films.

The upgrading of basic elements of optical communication facilities, fiber-optic waveguides, lasers, and optical integrated circuits[1,2] requires the search for new transparent organic and inorganic materials. Their production is impossible without the use of thin film technology. The sol-gel chemistry method, unlike expensive and difficult-to-use physical methods[2] such as plasma spraying and reactive evaporation, or epitaxial growth, does not require complex equipment. The films were produced by casting, substrate dipping, centrifugation, and solution spraying. Curing usually takes place under mild conditions; therefore, organic substrates introduced in the initial colloid solutions can remain invariable. This method provides opportunities for the production of hybrid organic-inorganic materials.[3,4] Exceptionally promising[1,2,5] is the use of fluoroplastics and polyorganosiloxanes in the photonics and laser optics, because they exhibit high resistance to light, moisture, and heat and are transparent in the visible and UV spectral regions. In addition, they contain a reduced (as compared with purely organic polymers) number of C—H bonds whose high-energy vibrations induce the vibrational relaxation of the electronic excitation energy in near-IR devices, which is exceptionally important for the design of generating devices based on organic polymers and rare earth metal (lanthanide) complexes. However, usual fluoroplastics and silicones are practically unable to dissolve lanthanide complexes. The limited compatibility of the complex with the matrix material results in opalescence or opacification during structuring due to reduction of the solubility of the coordination compound on going from a solution in the monomer (or in an oligomer mixture) to the solid polymer. Previously, we found[6] that this problem can be easily solved by using organofluorosilicon sol-gel compositions containing compounds with imine, ester, or amide groups. However, sol-gel polymerization involves air moisture, which is absorbed by the thin layer of a composition applied on a substrate. The anhydrous lanthanide complexes can be hydrated by adding three to six water molecules, which is fairly undesirable. Therefore, in the development of compositions meant for the application of transparent luminescent films, it is necessary to resolve the compatibility problems between the complex and the matrix and luminescence quenching by vibrations of the O—H, N—H, and C—H bonds. Hence, the search for new sol-gel monomers or oligomers with clearly defined solvating and water-proof properties is a topical task.

The purpose of this work is the synthesis of a bifunctional organofluorosilicon compound by the reaction of perfluoroadipic ester and 3-aminopropyltriethoxysilane (APTES) and the preparation on this basis of optically transparent films doped with lanthanide complexes.

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Results and Discussion

Perfluoroadipic bis(trialkoxysilylpropyl)amide **1** was prepared from dimethyl perfluoroadipate and APTES (Scheme 1).

The reaction is accompanied by transalkoxylation at the silicon atom. According to GC/MS analysis, the product isolated by sublimation is a mixture of five alkoxysilanes corresponding to the general formula $(EtO)_3Si(CH_2)_3NHC(O)(CF_2)_4C(O)NH(CH_2)_3Si(OMe)(OEt)_2$ (**1**), since the integral intensity ratio for the methyl signals of the MeO and EtO groups in this mixture is 1 : 5. The reaction of APTES with diethyl ester in the preparation of the diamide would have ruled out transesterification. We used the dimethyl ester due to the ease of removal of methanol used for its synthesis. Previously,[6] for preparing films doped with lanthanide complexes we have already used trifluoroacetamide, which is also a mixture of compounds with methoxy and ethoxy groups in the trialkoxysilyl fragment. It was found that this difference in the alkoxy groups does not affect significantly the film-forming properties. Since only amide groups participate in the solvation of lanthanide complexes (methylpolysiloxanes do not dissolve them), the use of monomer **1** for preparing films doped with lanthanide complexes appears quite admissible.

According to powder X-ray diffraction, the crude reaction product differs from the mixture of sublimed alkoxysilanes **1** only by the absence of the amorphous component (Fig. 1). Therefore, the isolated product **1** can be regarded as a single-phase polycrystalline material.

It was found by IR spectroscopy that product **1** is fairly stable against hydrolysis under the action of air moisture. Only after powdered alkoxysilane **1** has been kept in air for 10 days, scarcely noticeable changes took place in its spectrum. The relative intensity of the absorption bands at 956 and 794 cm^{-1} corresponding to the Si—OEt and Si—OMe fragments slightly decreases and shoulders at 3460 and 1030 cm^{-1} appear, indicating that hydrolysis at the trialkoxysilyl groups takes place, giving rise to silanol and siloxane groups. Keeping in air for 2 months does not induce further changes in the IR spectrum. The so high hydrolytic stability of the compound that contains two trialkoxysilyl groups appears somewhat unexpected. Usually derivatives of this type are readily hydrolyzed in thin films under the action of air moisture and form cross-linked polyorganosiloxanes.[6] The inertness of compound **1** can be attributed to the presence of the water-repelling perfluorinated organic $(CF_2)_n$ fragment and also to close crystal packing preventing the fast reaction of alkoxysilyl groups with water molecules.

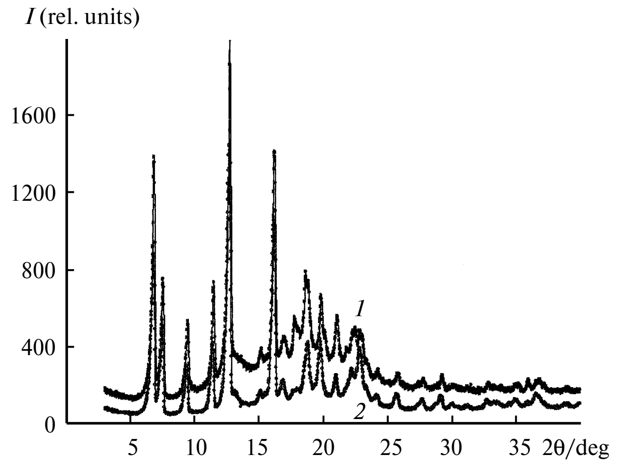
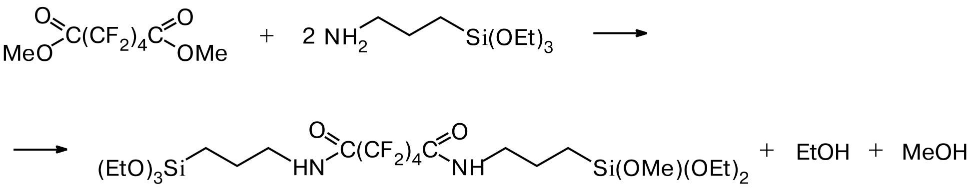


Fig. 1. X-ray diffraction patterns of compound **1** before (*1*) and after (*2*) sublimation.

Storage of solutions of compound **1** in acetone, THF, or $CHCl_3$ gives white, opaque, and rough films, and this is not accompanied by polycondensation. High tendency for crystallization is attributable to the well-known ability of organic amides[7] to form strong intermolecular hydrogen bonds. These give rise to ordered supramolecular structures.[8] The slight differences in the composition of the alkoxysilyl fragments of particular molecules of compound **1** do not considerably interfere with crystal ordering.

To bring compound **1** to the disordered amorphous state, one can use its hydrolysis to give soluble polysiloxanes suitable for the formation of transparent films with high optical characteristics. As shown by elemental analysis and IR spectroscopy data, hydrolysis of a solution of **1** in acetone with excess water yields the polysiloxane $[HO(O_{0.5})(EtO)Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OH)O]_n[O(HO)Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OH)O]_m$ (**2**, $m : n = 1 : 1$). Meanwhile, the reaction of powdered compound **1** with water catalyzed by ~0.1% Bu_4NF (the use of acids or alkalis could promote

Scheme 1



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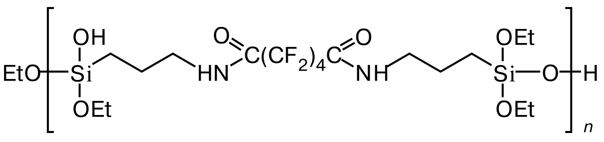
the reaction of the amide groups with water) gave rise to the polysiloxane $[O_{0.5}(HO)(EtO)Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OEt)(OH)O_{0.5}]_n$ (**3**). The amount of unreacted starting compound was 7% in the former case and 19% in the latter case. Both polymers were insoluble in organic solvents. Product **2** was fully amorphous, while **3** contained both amorphous and crystalline phases. The number and positions of reflections and their intensity ratios observed for the crystalline phases were the same as those for the starting compound **1** (Fig. 2). Thus, by hydrolytic polycondensation proceeding to a high degree, it is possible to convert crystalline compound **1** to amorphous polysiloxanes **2** and **3** insoluble in organic solvents.

Soluble oligomers needed for the formation of transparent films were prepared by partial hydrolysis of compound **1** in a THF solution. The addition of 3—4 moles of water per mole of $(EtO)_3Si(CH_2)_3NHC(O)(CF_2)_4C(O)NH(CH_2)_3Si(OMe)(OEt)_2$ and keeping the reaction mixture at ~20 °C for 4—7 days affords oligosiloxane **4** whose structure was determined by elemental analysis, gel permeation chromatography, and IR spectroscopy. The increase in the amount of water used for hydrolysis to 5—6 moles results in the formation of an insoluble polysiloxane precipitate apart from the oligomer occurring in solution.



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The oligomer has a unimodal narrow molecular-mass distribution (M_w/M_n = 1.1); according to HPLC, this was a mixture of compounds with ~50% content of the desired product. Oligosiloxane consists of seven to nine structural fragments of silicon-containing perfluoroadipic diamide connected to one another through disiloxane bridges, silanol groups being present at the chain ends and in the middle. The IR spectrum shows a very weak shoulder at 3453 cm^{-1} characterizing the SiOH fragments.

Seven-day storage of solutions of partly hydrolyzed diamide in which the starting **1** : H_2O molar ratio was 1 : 3 and more yields transparent colorless 5—10 μm-thick films with a smooth surface. If the solutions were applied 1—2 h after mixing the reactants, the surface of the resulting films was rough. Therefore, long-term keeping of the reaction mixtures appears necessary for the formation of high-optical quality coatings. Curing of the liquid layer on the silicate glass surface from a THF solution occurs after 1.0—1.5 h. According to IR spectroscopy, structural changes in the films formed continue to take place for additional 20 h. The shoulder at 3453 cm^{-1} somewhat decreases but the intensity of the siloxane absorption at 1040—1020 cm^{-1} increases. These changes attest to condensation of the silanol terminal groups.

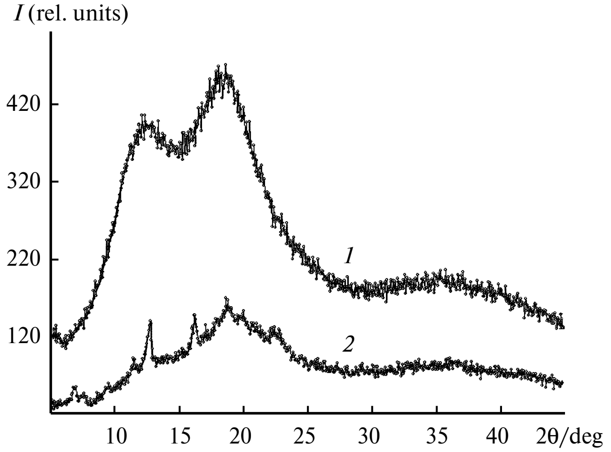

Fig. 2. X-ray diffraction patterns of hydrolysis products of compounds **2** (*1*) and **3** (*2*).

Powder X-ray diffraction investigation of the transparent coatings formed from solutions of oligomer **4** in THF on the silicate glass surface showed that they had a polycrystalline structure. However, the X-ray diffraction patterns of the films attest to the presence of considerable amounts of the amorphous components together with the crystalline phase identical to compound **1** (Fig. 3, curves *1* and *3*). This fact indicates that the crystallization pattern of both compound **1** and the oligomers is affected only by the formation of associates through hydrogen bonding between the amide groups. The optical transparency of the layer can be due to the presence of an amorphous phase in the material and to the decrease in the size of crystalline structures compared to those formed from monomer **1** under similar conditions.

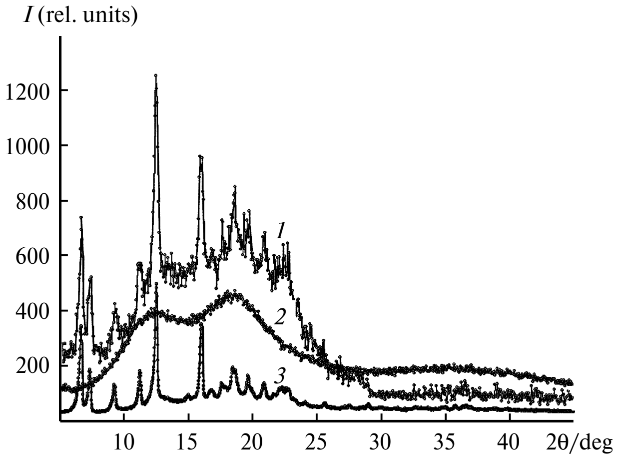

Fig. 3. X-ray diffraction patterns of the films of oligomer **4** (*1*), composition based on compound **1** containing 44.5% of complex **5** (*2*), and initial compound **1** (*3*).

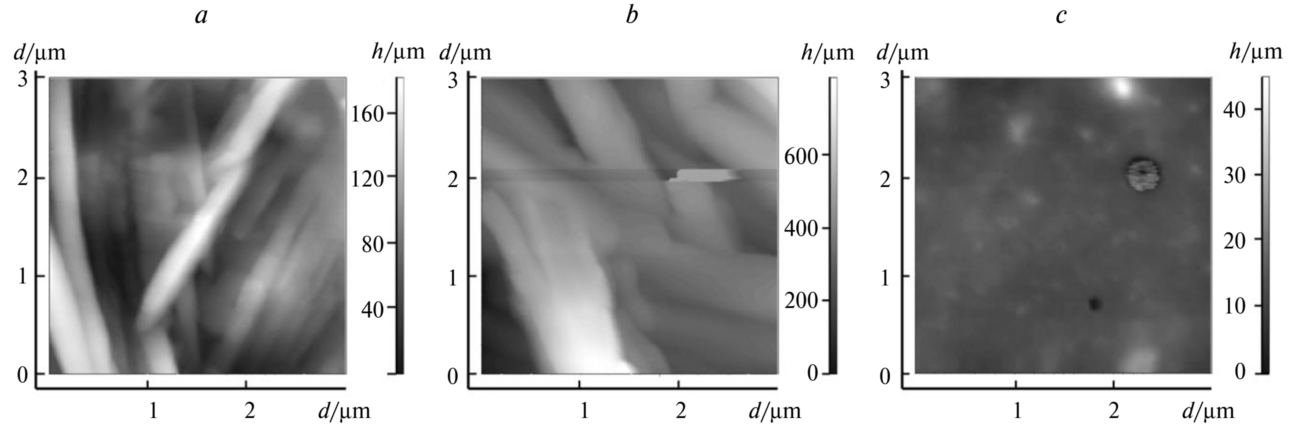

Fig. 4. AFM images of the film surfaces formed by oligomer **4** on silicate glass before heating (*a*), after heating at 100 (*b*) and 200 °C (*c*).

On the film surface image recorded by atomic force microscopy (AFM), one can clearly see the orderly arranged cylindrical fibers with approximately equal thickness (0.25—0.30 μm) (Fig. 4, *a*). After heating for 30 min at 100 °C, the weight of the films decreases by 30%, they become white and opaque, the fiber thickness increasing twofold (to 0.50—0.60 μm). The height (*h*) of the surface relief also increases: before heating, it was not more than 0.18 μm, while after heating, it reached 1.00 μm (Fig. 4, *b*). The polymer becomes insoluble in THF, and, hence, it becomes impossible to measure its molecular-mass characteristics. Heating of the films at 200 °C for 30 min results in a weight decrease by more than 20% and the disappearance of the fibers (Fig. 4, *c*). The surface of the film formed by the starting oligomer is hydrophobic (the water wetting contact angle is 97°). Therefore, on heating, the hydrolysis of the residual alkoxy groups under the action of air moisture does not take place. Hence, changes in the polymer surface and solubility are associated with the formation of cross-linked 3D structures upon condensation of molecules **4** by two reactions. One is the reaction of the neighboring silanol and alkoxysilyl groups with alcohol evolution and the other is the reaction of neighboring ethoxy groups with evolution of diethyl ether (both products were detected in the gas phase by GC/MS). However, the above-described fibers are observed only in the films formed on a continuous smooth surface. The application of oligomer solution on a metallic fine-meshed grid affords a porous film. Transmission electron microscopy study of the film showed that the pore size was 200—500 nm, which corresponds to the thickness of the fibers we observed in the coatings on glass substrates. This suggests that the fibers are formed upon the reaction of compound **4** with the surface onto which the solution is applied and that they are hollow.

Lanthanide β-diketonates are most convenient objects for the creation of transparent materials with luminescent properties.[1,9] They are stable in air and are readily soluble in polar organic media. Derivatives with fluorinated ligands are better compatible with fluorinated monomers and polymers. Solubility testing of lanthanide complexes in monomer **1** and in oligosiloxane **4** was carried out using praseodymium tris(hexafluoroacetylacetonate) trihydrate $Pr(HFA)_3 \cdot 3H_2O$ (**5**), europium tris(benzoyltrifluoroacetonate) hexahydrate $Eu(BTFA)_3 \cdot 6H_2O$ (**6**), anhydrous erbium tris(hexafluoroacetylacetonate) $Er(HFA)_3$ (**7**), and ytterbium tris(dipyvaloylmethanate) $Yb(DPM)_3$ (**8**). The highest attainable solubility was defined as the concentration of the complex at which drying of a solution of the composition in $CHCl_3$ or THF yielded a transparent solid film that retained its properties on storage in air for a long period of time (the observation lasted for three months). The data presented in Table 1 on the solubility of the complexes and on the quality of films formed from the **1**/$LnL_3 \cdot nH_2O$ compositions attest to good solvation properties of compound **1** with respect to the lanthanide β-diketonates with fluorinated ligands. Complex **8** containing the nonfluorinated ligand is almost incompatible

Table 1. Results of film formation study of perfluoroadipic diamide (**1**)

Lanthanide complex	*m* (wt. %)	Complex : **1** (mol.)	H_2O : **1** (mol.)	*t**	Film quality
—	—	—	—	5 min	Rough, white
5	25.2	1 : 3.5	0.9 : 1	10 min	Rough, opaque
	30.5	1 : 2.7	1.1 : 1	1.5 h	Rough, transparent
	44.5	1 : 1.5	2.0 : 1	10 days	Smooth, transparent
6	21.7	1 : 4.8	1.3 : 1	5 min	Rough, transparent
7	23.0	1 : 3.9	—	10 min	Rough, transparent

* Film curing time.

with compound **1**. The presence of a water molecule in the metal coordination sphere does not reduce the solubility but leads to an increase in the structuring time upon an increase in the concentration of the complex.

The reaction of the organofluorosilicon matrix with praseodymium and europium β-diketonates was studied by ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectrum of a solution of compound **1** in $CDCl_3$ containing $Pr(HFA)_3 \cdot 3H_2O$ (0.04 mol per mole of **1**) shows broadening of the proton signals of the $NCH_2CH_2CH_2Si$ fragment and their upfield shifts by 0.10, 0.07, and 0.04 ppm, respectively, compared to the spectrum of pure **1**. The observed effect is due to coordination of the amide group to the praseodymium cation. Complex **5** functions in this case as a lanthanide shift reagent.[10]

The IR spectra of the films obtained from compositions based on compound **1** and complexes **5** and **6** show clear-cut changes of the absorption bands of diketonate ligands, whereas the part of the spectrum corresponding to the matrix (*i.e.*, compound **1**) remains almost invariable. The initial coordination compounds are hydrated, which is confirmed by broad and rather intense O—H absorption bands at 3600—3300 cm^{-1}. However, the spectra of films show no absorption in this range, despite the fact that O—H stretching bands are expected to be broadened and rather intense due to the possibility of intermolecular interaction with the amide.[11] This implies that water has been displaced from the praseodymium and europium coordination sphere. The number and positions of absorption bands corresponding to the β-diketonate ligands also change. Thus the spectrum of the complex $Pr(HFA)_3 \cdot 3H_2O$ contains five absorption bands including more intense 1660 (shoulder), 1649, and 1628 cm^{-1} (shoulder) bands corresponding to ν(C=C) and ν(C=O) vibrations and less intense 1567 and 1543 cm^{-1} bands corresponding to ν(C=O) and δ(C—H) vibrations.[12] The spectrum of the same complex but incorporated in the matrix exhibits only three bands in this region: an intense band at 1654 cm^{-1} and less intense bands at 1554 and 1528 cm^{-1}. In the IR spectrum of the complex $Eu(BTFA)_3 \cdot 6H_2O$, the most intense absorption bands for the benzoyltrifluoroacetonate ligand occur at 1614, 1576, and 1533 cm^{-1}. In the transparent matrix doped with this complex, two high-frequency shoulders (1638 and 1625 cm^{-1}) appear at the 1614 cm^{-1} band, while the other bands shift insignificantly being located at 1578 and 1536 cm^{-1}. Thus, the solvation of complexes **5** and **6** with molecules **1** is accompanied by substantial changes in the metal coordination sphere.

As noted above, pure compound **1** is precipitated from solution as a finely crystalline opaque layer, which is not hydrolyzed for a considerable period of time. Therefore, the formation of transparent coatings, although with a rough surface, from this layer even at concentrations of complexes of up to 30% may imply a substantial change in the structure of the supported layer up to transition to the amorphous state. However, powder X-ray diffraction data indicate that the coatings remain crystalline, the X-ray diffraction patterns of the films and pure compound **1** are identical, no amorphous halo is observed. Apparently, the structure of **1** is substantially affected by the additive; the crystallite size decreases and becomes smaller than the visible light wavelength. Therefore, the film becomes transparent but its surface remains rough. Fast curing (5—10 min) means that the layer deposited from the solution is only dried ($CHCl_3$ is removed) but is not structured through Si—O—Si bond formation and consists of molecules **1**, which have been hydrolyzed to a minor extent. Therefore, at concentrations of up to 30% the supported layer is the crystalline phase.

Only when the $Pr(HFA)_3 \cdot 3H_2O$ concentration is 44.5% (see Table 1), a smooth film is formed from the composition based on alkoxysilane **1** over a period of 10 days. This pronounced increase in the content of complex **5** gives rise to a large amount of water of crystallization, which is liberated upon its dehydration and is spent for hydrolytic condensation of the trialkoxysilyl groups. The IR spectra of adhesive films have a broad weak absorption band at 3700—3470 cm^{-1} for O—H stretching vibrations of water, alcohols, and silanols. The spectra of solid films do not exhibit this band, but have a shoulder at 1020—1040 cm^{-1}, indicating removal of water from the complexes, evaporation of alcohols, and condensation of silanols to give Si—O—Si fragments in the film material. As can be seen from Table 1, for the maximum possible content of the $Pr(HFA)_3 \cdot 3H_2O$ complex, the composition contains two water molecules per molecule **1**. This water suffices to hydrolyze only two alkoxy groups to silanols. But their condensation gives one more water mole which is able to hydrolyze one more alkoxy group. The dehydration, hydrolysis, and condensation proceed slowly. Therefore, curing of a film with this high concentration of the lanthanide complex requires a long time. Thus, an absolutely smooth transparent matrix doped with a praseodymium complex is composed of polysiloxanes based on compound **1** in which only three alkoxy groups have been hydrolyzed. This takes place only at very high (44.5%) content of the complex in the matrix. However, high optical characteristics of the cured layer are attributable to its amorphous properties (see Fig. 3, curve *2*).

Oligomer **4** has even higher dissolving capacity with respect to lanthanide complexes. Transparent glassy coatings are formed from compositions containing up to 40—50% of praseodymium and europium β-diketonates. These complexes are crystalline; however, films with high contents of the complexes are amorphous (Fig. 5). The film structuring process takes 18—24 h and is also accompanied by displacement of coordinated water. Figure 6 shows the IR spectra of complex **6** in mineral oil and the composition consisting of compounds **4** and **6** (50%).

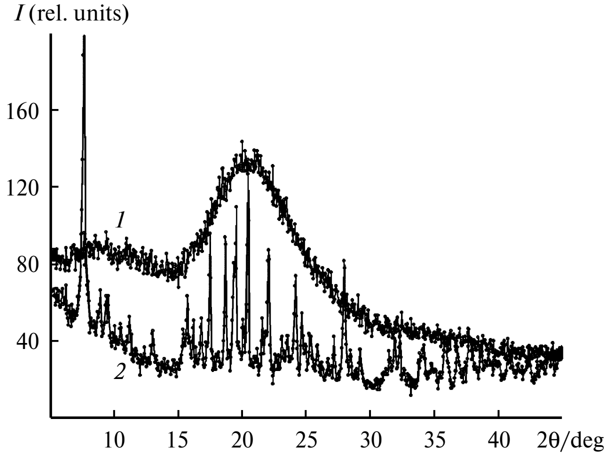

Fig. 5. X-ray diffraction patterns of films composed of the oligomer **4**—complex $Eu(BTFA)_3 \cdot 6H_2O$ composition (C_{Eu} = 8.4%) containing 50% of the complex (*1*) and the pure complex (*2*).

In the spectrum of the cured film, the absorption band at 3450 cm^{-1} corresponding to O—H vibrations is virtually missing, whereas in the spectrum of the complex, absorption in this region is clearly pronounced. However, oligomer **4**, unlike compound **1**, can form transparent smooth matrices containing the complex with the nonfluorinated ligand (ytterbium dipivaloylmethanate) in 28.6% amount.

The luminescence properties were studied in relation to the films cast on the surface of quartz substrates from saturated solutions of compound **4** and the europium complex in $CHCl_3$. The coating thickness was 10—20 μm, the curing time was 20 h, and the $Eu(BTFA)_3 \cdot 6H_2O$ concentrations were 0, 5, and 37 wt.%. The photoluminescence spectra excited at 245 nm are presented in Fig. 7, *a*. The spectra of all three films exhibit a broad emission band of the matrix (*i.e.*, oligomer **4**) with a maximum at 395 nm. The intensity of this band rapidly decreases with increase in the concentration of the coordination compound. The luminescence of the europium cation shows itself upon excitation at 330 nm as a series of narrow bands corresponding to transitions from the excited $^5D_0$ level to the ground multiplet ^7F_n level (Fig. 7, *b*). The $^5D_0 \rightarrow {}^7F_2$ transition is most intense (1000 rel. units). When the complex concentration is 37%, the matrix luminescence is very low. At the same excitation wavelength, the luminescence intensity of the matrix in the film made of oligomer **4** + 5% $Eu(BTFA)_3 \cdot 6H_2O$ composition is only 1% of the luminescence intensity of europium, *i.e.*, lower than the error of measurements. The organic-inorganic glasses and films obtained by the sol-gel method from organoalkoxysilanes are usually responsible for a broad photoluminescence band at 400—450 nm. The nature of this band and its relationship with the supramolecular structure of amorphous sol-gel coatings were studied previously.[13,14] Organosilsesquioxane structures with a size of 15—20 Å are considered to be luminescence centers. The results we obtained show that a similar emission band occurs also in the fluorescence spectra of organofluorosilicon films. However, its intensity depends on the excitation wave-

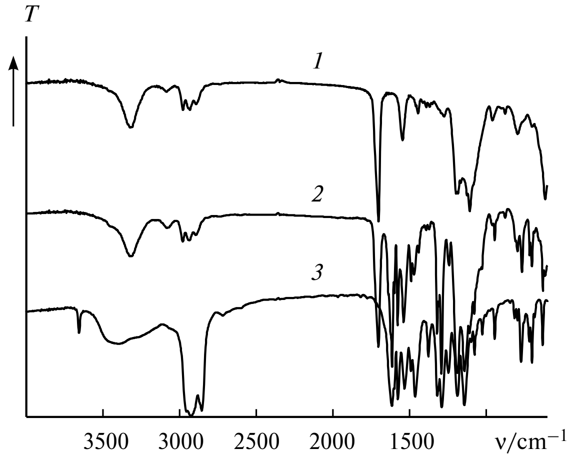

Fig. 6. IR spectra of the film composed of oligomer **4** (*1*), film based on oligomer **4** containing 50% of complex **6** (*2*) and pure complex **6** in mineral oil (*3*); *T* is transmission.

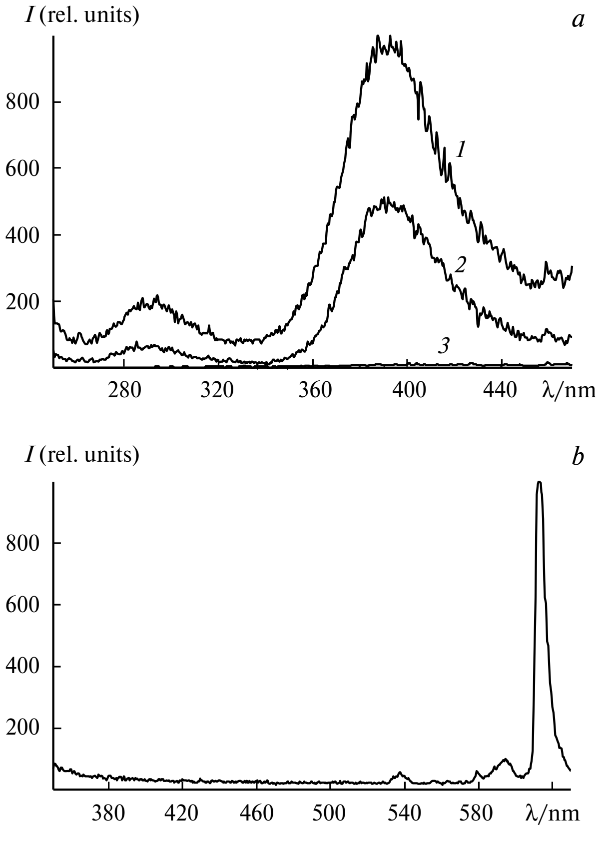

Fig. 7. Photoluminescence spectra of transparent films composed of oligomer **4** at λ_{exc} = 245 (*a*) and 330 nm (*b*); *a*: without addition of lanthanide complexes (*1*) and containing complex $Eu(BTFA)_3 \cdot 6H_2O$ in amounts of 5 (*2*) and 37% (*3*); *b*: 5% $Eu(BTFA)_3 \cdot 6H_2O$.

lengths, being maximum for λ_{exc} = 245 and minimum for λ_{exc} = 330 nm. The addition of europium β-diketonate even in a quantity of 5% also induces degradation of this band, which may result either from change in the film structure or from violet luminescence quenching by the coordination compound.

Thus, we synthesized perfluoroadipic bis(trialkoxysilylpropyl)amide **1** and soluble oligosiloxane **4**, which have a polycrystalline structure. As shown by analysis of X-ray diffraction patterns, their crystallization pattern is mainly affected by formation of associates through hydrogen bonding between the amide groups. Compounds **1** and especially **4** have high solvation capacities with respect to lanthanide β-diketonates and, what is especially important, they are able to displace water molecules from the lanthanide coordination sphere, these water molecules being spent for hydrolysis of trialkoxysilyl groups of these compounds. In the luminescence spectrum of the film based on oligomer **4** with a europium complex content of 5% at λ_{exc} = 330 nm, the intensity of the $^5D_0 \rightarrow {}^7F_2$ transition is high (1000 rel. units). The luminescence intensity of the matrix is very low under the same conditions.

Experimental

The IR spectra of compounds as liquid films between the KBr plates were recorded on FSM 1201 and Bruker Vertex 70 FT IR spectrometers, ^1H NMR spectra were run on a Bruker Avance DPX-200 instrument (200 MHz) at 25 °C using Me_4Si as an internal standard and $CDCl_3$ as the solvent. GC/MS analysis was carried out on a PolarisQ/TraceGCUltra GC/MS spectrometer under the following conditions: a 60-m long TR 35 MS column 0.25 mm in diameter was heated from 60 to 300 °C, the injector temperature was 300 °C, and the carrier gas (helium) flow rate was 1 mL min^{-1}. Positive ion electron ionization mass spectra were measured at 70 eV in the mass number range of 29—600. The luminescence properties of the films were studied on a Perkin—Elmer LS-55 spectrofluorimeter with a front-face attachment for film luminescence. The measurements were carried out at a spectral slit width of exciting and measuring monochromators of 2.5 nm, which accounts for rather high noise level (see Fig. 7). The film surfaces were studied by atomic force microscopy (AFM) on a Solver-P47 AFM microscope, Powder X-ray diffraction study was carried out on a DRON-3M diffractometer (computerized, Cu-Kα radiation, graphite monochromator on a diffracted beam), scanning step 0.02 deg, acquisition 10 s. The molecular-mass distribution was determined on a Knauer Smartline chromatograph with Phenogel Phenomenex 5u columns (300×7.8 mm) using a refractometer as the detector. THF was used as the mobile phase at a flow rate of 2 mL min^{-1}. The calibration was performed by polystyrene standards with molecular masses of 3420—2570000. HPLC analysis of oligomer **4** was carried out on a Knauer liquid chromatograph with Silasorb 600 SPH columns (100×6 mm) and a UV spectrophotometer as the detector (λ = 230 nm). A hexane—THF mixture (5 : 1) at a flow rate of 1.5 mL min^{-1} was used as the mobile phase. The oligomer films were studied on a Jeol 1200EX2 transmission electron microscope. Perfluoroadipic acid difluoride (P&M Invest company, Moscow, 97%) was used as received; APTES (Altayhimprom company, Yarovoe, Altay Region) was distilled at reduced pressure where the fraction containing only the γ-isomer was isolated. Chloroform, THF, methanol, and acetone were purified by known methods.[15]

Dimethyl perfluoroadipate. A solution of methyl alcohol (9.93 g, 0.309 mol) in diethyl ether (10 mL) was added dropwise over a period of 1 h under argon to a cooled (0—5 °C) and stirred solution of perfluoroadipic acid difluoride (9.90 g, 0.034 mol) in diethyl ether (10 mL). The reaction mixture was stirred for 10 h under argon. Then diethyl ether and excess methanol were distilled off from the reaction mixture under atmospheric pressure. The residue was distilled *in vacuo* collecting the fraction with b.p. = = 35—50 °C (1 Torr) to give 8.76 g (82%) of dimethyl perfluoroadipate. Found (%): C, 29.80; H, 2.05. $C_8H_6F_8O_4$. Calculated (%): C, 30.20; H, 1.90. IR, ν/cm^{-1}: 2969, 1444 (C—H), 1787, 1199 (C(O)O), 1325, 1146, 1097, 1076 (C—F), 955, 800 (O—Me).

Reaction of dimethyl perfluoroadipate with APTES. Dimethyl perfluoroadipate (3.36 g, 10.5 mmol) was added in small portions with stirring to APTES (4.67 g, 0.021 mol). After hardening of the reaction mixture, it was heated for 1 h at 36—40 °C *in vacuo* to remove methanol. This gave 6.99 g (97%) of the product as the mixture of alkoxysilanes $(EtO)_3Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OMe)(OEt)_2$ (**1**) and dimer $[(EtO)_3Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OMe)(OEt)]_2$. IR, ν/$cm^{-1}$: 3299, 3078 (N—H), 1699 (>C=O, amide I), 1549 (N—H, amide II), 1305, 1277, 1182, 1082 (C—N, N—H, C—F), 958, 794 (Si—O—C). ^1H NMR, δ: 0.66 (m, 4 H, $—CH_2Si—$); 1.22 (m, 15 H, $O—CH_2—C\underline{H}_3$); 1.72 (m, 4 H, $—CH_2C\underline{H}_2CH_2$); 3.39 (m, 4 H, $—NHC\underline{H}_2—$); 3.48, 3.56, 3.57 (all s, 3 H, OMe); 3.83, 3.72 (both m, 10 H, $O—C\underline{H}_2Me$); 7.03 (br.s, 2 H, NH).

Vacuum sublimation at 135—170 °C gave 6.0 g (87%) of a white powder, which was a mixture of five alkoxysilanes with the general formula $(EtO)_3Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OMe)(OEt)_2$. The contents of individual compounds in the mixture was as follows: $(EtO)_3Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OEt)_3$, 47%; $(EtO)_3Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OMe)(OEt)_2$), 40%; $(EtO)_2(MeO)Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OMe)(OEt)_2$, 9%; $(EtO)_3Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OMe)_2(OEt)$, 3%; $(EtO)_2(MeO)Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OMe)_2(OEt)$, 1%. M.p. = 90 °C. Found (%): C, 40.22; H, 6.34. $C_{23}H_{42}F_8N_2O_8Si_2$. Calculated (%): C, 40.46; H, 6.20. IR, ν/cm^{-1}: 3464, 3297, 3074 (N—H), 1700 (>C=O, amide I), 1548 (N—H, amide II), 1305, 1277, 1182, 1082 (C—N, N—H, C—F), 958, 794 (Si—O—C). ^1H NMR, δ: 0.66 (m, 4 H, $—CH_2—Si—$); 1.23 (m, 15 H, $O—CH_2—C\underline{H}_3$); 1.72 (m, 4 H, $—CH_2—C\underline{H}_2—CH_2—$); 3.39 (m, 4 H, $—NH—C\underline{H}_2—$); 3.56, 3.57 (both s, 3 H, OMe); 3.83 (m, 9 H, $O—C\underline{H}_2—Me$); 7.01 (br.s, 2 H, NH).

EI MS (70 eV), *m/z* (I_{rel} (%)): **$(EtO)_3Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OEt)_3$:** 651 $[M - OEt]^+$ (7), 605 $[M - HOEt - OEt]^+$ (17), 248 $[(EtO)_3Si(CH_2)_3NHCO]^+$ (32), 220 $[(EtO)_3Si(CH_2)_3NH]^+$ (61), 174 $[(EtO)_2Si(CH_2)_3NH]^+$ (47), 79 (100); **$(EtO)_3Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OMe)(OEt)_2$:** 637 $[M - OEt]^+$ (10), 591 $[M - HOEt - OEt]^+$ (28), 248 $[(EtO)_3Si(CH_2)_3NHCO]^+$ (26), 234 $[MeO(EtO)_2Si(CH_2)_3NHCO]^+$ (24), 220 $[(EtO)_3Si(CH_2)_3NH]^+$ (68), 206 $[MeO(EtO)_2Si(CH_2)_3NH]^+$ (40), 174 $[(EtO)_2Si(CH_2)_3NH]^+$ (47), 160 $[MeO(EtO)Si(CH_2)_3NH]^+$ (42), 111 $[EtOSiF_2]^+$ (86), 79 (100); **$(EtO)_2(MeO)Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OMe)(OEt)_2$:** 623 $[M - OEt]^+$ (6), 577 $[M - HOEt - OEt]^+$ (13), 234 $[MeO(EtO)_2Si(CH_2)_3NHCO]^+$ (20), 206 $[MeO(EtO)_2Si(CH_2)_3NH]^+$ (40), 174 $[(EtO)_2Si(CH_2)_3NH]^+$

(20), 160 $[\mathrm{MeO(EtO)Si(CH_2)_3NH}]^+$ (28), 111 $[\mathrm{EtOSiF_2}]^+$ (100); **$\mathbf{(EtO)_3Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OMe)_2(OEt)}$:** 623 $[\mathrm{M - OEt}]^+$ (7), 577 $[\mathrm{M - HOEt - OEt}]^+$ (14), 248 $[\mathrm{(EtO)_3Si(CH_2)_3NHCO}]^+$ (23), 220 $[\mathrm{(EtO)_3Si(CH_2)_3NH}]^+$ (63), 192 $[\mathrm{(MeO)_2EtOSi(CH_2)_3NH}]^+$ (30), 174 $[\mathrm{(EtO)_2Si(CH_2)_3NH}]^+$ (36), 160 $[\mathrm{MeO(EtO)Si(CH_2)_3NH}]^+$ (30), 125 (100), 79 (71); **$\mathbf{(EtO)_2(MeO)Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OMe)_2(OEt)}$:** 609 $[\mathrm{M - OEt}]^+$ (7), 563 $[\mathrm{M - HOEt - OEt}]^+$ (9), 234 $[\mathrm{MeO(EtO)_2Si(CH_2)_3NHCO}]^+$ (24), 206 $[\mathrm{MeO(EtO)_2Si(CH_2)_3NH}]^+$ (60), 192 $[\mathrm{(MeO)_2EtOSi(CH_2)_3NH}]^+$ (30), 174 $[\mathrm{(EtO)_2Si(CH_2)_3NH}]^+$ (34), 160 $[\mathrm{MeO(EtO)Si(CH_2)_3NH}]^+$ (27), 125 (78), 111 (59), 92 (100).

Hydrolysis of compound 1. *A*. A 7% solution of compound **1** in acetone (the amount of diamide was 0.86 g) was added dropwise over a period of ~10 min to distilled water (20 mL). The reaction mixture was stirred for 24 h. The resulting white powder was filtered off, washed with water, and dried in air; its weight was 0.45 g. Washing with $\mathrm{CHCl_3}$ and drying *in vacuo* gave 0.39 g of the product $[\mathrm{HO(O_{0.5})(EtO)Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OH)O}]_n[\mathrm{O(HO)Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OH)O}]_m$ ($m : n = 1 : 1$). Found (%): C, 30.27; H, 4.03. $\mathrm{C_{26}H_{37}F_{16}N_4O_{12.5}Si_4}$. Calculated (%): C, 30.56; H, 3.65. IR, ν/cm^{-1}: 3670—3520 (O—H), 3458, 3322, 3080 (N—H), 1704 (>C=O, amide I), 1547 (N—H, amide II), 1309, 1274, 1202, 1181, 1143, 1108 (C—N, N—H, C—F), 1040 (Si—O—Si), 970, 910, 804 (Si—O—C).

B. Water (7.5 mL) containing the catalyst $\mathrm{Bu_4NF}$ (~0.1 wt % of the amount of substance to be hydrolyzed) was added to powdered dry compound **1** (0.46 g). The reaction mixture was stirred for 24 h. The powder was filtered off, washed with water, and dried in air; its weight was 0.31 g. Washing with $\mathrm{CHCl_3}$ and drying *in vacuo* gave 0.22 g of the polysiloxane $[\mathrm{O_{0.5}(HO)(EtO)Si(CH_2)_3NH(O)C(CF_2)_4C(O)NH(CH_2)_3Si(OEt)(OH)O_{0,5}}]_n$. Found (%): C, 33.94; H, 5.26. $\mathrm{C_{16}H_{26}F_8N_2O_7Si_2}$. Calculated (%): C, 33.92; H, 4.63. IR, ν/cm^{-1}: 3730—3536 (O—H), 3455, 3303, 3080 (N—H), 1699 (>C=O, amide I), 1548 (N—H, amide II), 1305, 1274, 1183, 1082 (C—N, N—H, C—F), 1040—1015 (Si—O—Si), 956, 799 (Si—O—C).

C. Wet THF containing a specified amount of water was added to a solution of compound **1** in THF and the mixture was stirred. The **1** : $\mathrm{H_2O}$ molar ratios were varied from 1 : 2 to 1 : 6. The film-forming properties of solutions of hydrolyzates were studied every day for a week and then after one more week. From solutions with **1** : $\mathrm{H_2O}$ molar ratio of 1 : 4 to 1 : 6, the oligomers $(\mathrm{O(EtO)Si(CH_2)_3NHC(O)(CF_2)_4C(O)NH(CH_2)_3Si(OEt)_2O_{0.5}})_n$ (**4**) were isolated. Found (%): C, 36.94; H, 5.26. $\mathrm{C_{18}H_{29}F_8N_2O_{6.5}Si_2}$. Calculated (%): C, 36.91; H, 4.99. $M_\mathrm{n} = 4711$, $M_\mathrm{w} = 5187$, $M_\mathrm{w}/M_\mathrm{n} = 1.1$. IR spectrum of oligomer **4** film, ν/cm^{-1}: 3459 (O—H), 3318, 3085 (N—H), 1703 (>C=O, amide I), 1546 (N—H, amide II), 1309, 1291, 1274, 1182, 1108 (C—N, N—H, C—F), 957, 795 (Si—O—C).

Determination of the solubility of lanthanide complexes. A solution of compound **1** in chloroform or a solution of oligomers **4** in THF was added in small portions (each 0.0009—0.006 g) to a weighed portion of the lanthanide complex (0.01—0.05 g) until the complex completely dissolved.

Film formation. Solutions of pure compound **1** in chloroform, oligomers **4** or those containing a lanthanide complex were cast as thin films onto a glass substrate and left in air to complete hardening. The film thickness was 10—20 μm. The time of solvent removal from the films was determined by weighing; this was ~5 min.

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