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Luminescent Thermo- and Photocurable Silicones Doped with a Europium Complex

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Abstract—Two europium β-diketonates containing tris(trimethylsiloxysilylpropylamide) group in the ligand molecule were obtained by the reaction of the corresponding triethoxysilyl derivatives with trimethylsilanol. The siloxane groups provide solubility of the complexes in liquid silicone compositions, which is sufficient for obtaining luminescent flexible polysiloxane films doped with the europium complex.

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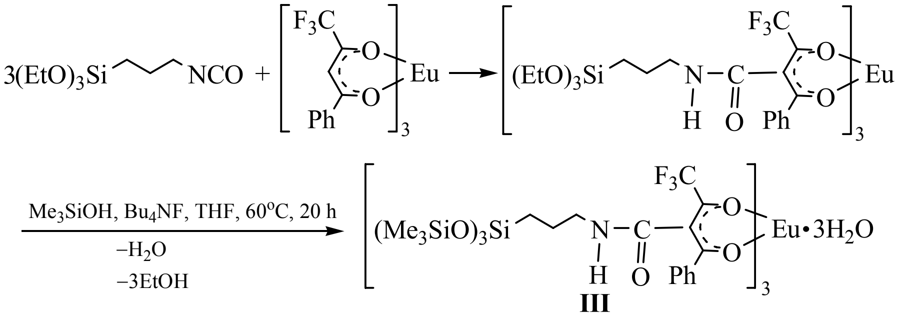
Luminescent organic films are of interest for photonics [1], integral optics [2], and solar energetics [3]. Europium coordination compounds convert efficiently UV radiation into red light, and therefore they can be used [4] for manufacturing thin film materials for agriculture. The film and glass containing lanthanides are obtained by polymerization of organic monomers and oligomers containing the corresponding complexes dissolved in them. A fairly high solubility of the lanthanides β-diketonates in acrylic monomers is provided by the presence of polar COOR groups related to the β-diketonate ligands by their chemical nature. Polyorganosiloxanes are low-polar compounds [5]. The compatibility problem for them can be solved by using oligosiloxane ligands. This paper presents a method for producing luminescent polysiloxane films doped with a europium complex containing silicon. The thermally curable silicone composition is a two-component mixture of polymethylphenylvinylsiloxane and polymethylphenylhydridosiloxane. SIEL 159–470 compound produced by the Russian Scientific Center "GNIIKHTEOS" was used as the photocurable composition.

We have demonstrated [6, 7] the possibility to synthesize europium, terbium, and erbium β-diketonates and ketoiminates with the silicon-containing functional ligands. The synthesized compounds were used to produce films and glasses by the sol-gel technique. The best luminescent properties exhibited the benzoyltrifluoroacetone derivatives. For the synthesis, anhydrous europium tris(benzoyltrifluoroacetonate) was brought into the reaction with 3-isocyanatopropyltriethoxysilane $(EtO)_3Si(CH_2)_3N{=}C{=}O$. To enhance the luminescent properties the phenanthroline was introduced as a neutral ligand into the molecule of the complex. Two compounds were obtained: europium tris[3-(3'-triethoxysilylpropylaminocarbonyl)-1,1,1-trifluoro-4-phenylbutane-2,4-dionate] $[(EtO)_3Si(CH_2)_3NHC(O)C\{{=}C(Ph)O\}\cdot\{C(O)CF_3\}]_3Eu$ (**I**) and europium tris[3-(3'-triethoxysilylpropylaminocarbonyl)-1,1,1-trifluoro-4-phenylbutane-2,4-dionate]-(1,10-phenantroline) $Eu[(EtO)_3Si(CH_2)_3NHC(O)C\cdot\{{=}C(Ph)O\}\cdot\{C(O)CF_3\}]_3Eu\cdot Phen$ (**II**) The performed tests showed that they possessed virtually no compatability with liquid silicone compositions. To increase the solubility of the complexes Me_3SiO groups were introduced into their molecules. Heating of compounds **I**, **II** with excess trimethylsilanol in THF solution in the presence of catalytic amounts of tetrabutylammonium fluoride led to the formation of trimethylsilylated derivatives, europium tris[3-{3'-tris-(trimethylsiloxy)silylpropylaminocarbonyl)-1,1,1-trifluoro-4-phenylbutan-2,4-dionate] trihydrate, $[(Me_3SiO)_3SiCH_2\cdot CH_2CH_2NHC(O)C\{{=}C(Ph)O\}\cdot\{C(O)CF_3\}]_3Eu\cdot 3H_2O$

(**III**) and europium tris[3-(3'-(trimethylsiloxy)silylpropylaminocarbonyl)-1,1,1-trifluoro-4-phenylbutan-2,4-dionate](1,10-phenantroline) $[(Me_3SiO)_3Si(CH_2)_3NHC\cdot(O)C\{=C(Ph)O\}\cdot\{C(O)CF_3\}]_3Eu\cdot Phen$ (**IV**).

The route of preparation of compound **III** is shown in the scheme below. The molecules of water released at the condensation with trimethylsilanol are included in the europium coordination sphere.



III

Figure 1 presents a region of the IR spectra of compounds **I** and **III** from 2000 to 450 cm^{-1}, which shows that the treatment with trimethylsilanol caused only the transformation of triethoxysisilyl group into tris(trimethylsiloxy)silyl one, while the β-diketonate fragment remained unchanged. In the IR spectrum a strong absorption band appeared at 843 cm^{-1} characteristic of Me_3Si group [8], while the absorption band at 952 cm^{-1} characteristic of $(EtO)_3Si$ group disappeared [9]. Significant changes occurred also in the region of vibrations of the Si–O–Si fragment (1050–1100 cm^{-1}). The preservation of europium tris(β-diketonate) fragment is manifested also by a strong cation photoluminescence of solutions of complexes **III** and **IV** in THF.

Silylated complex **III** is moderately compatibile with the silicon compositions, complex **IV** is poorly soluble. The phenanthroline complex **IV** completely prevents thermal polymerization due apparently to inactivation or inhibition of the platinum catalyst used to crosslink the polysiloxane chain by hydrosilylation reaction. The solubility of complex **III** in the phenyl-containing thermally curable compositions is higher than in the photocurable ones. We obtained liquid compositions containing 0.2–0.9 wt % of **III** in the photocurable composition and 0.5–1.5 wt % in the thermocurable, which provides a bright red-orange fluorescence of cured films at the irradiation with a mercury lamp DRT-240 without filters. The photoluminescence excitation is provided by the emission bands of the lamp at a wavelength of 312.6 and 365.0 nm. In thick layers (200–600 μm) the appearance of opalescence was observed.

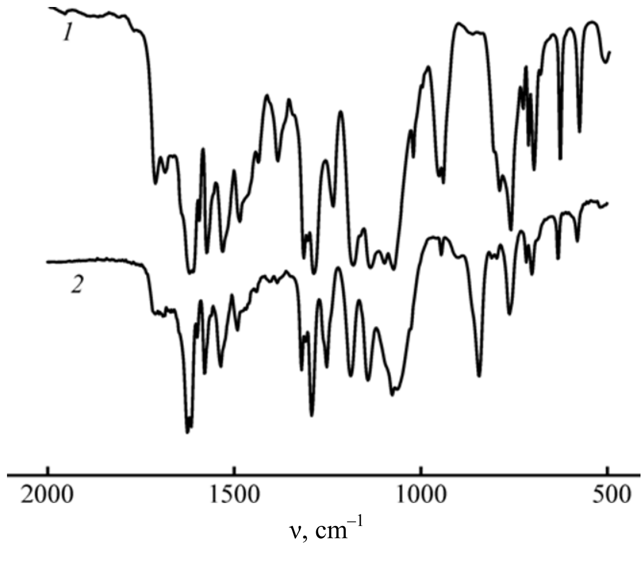


Fig. 1. IR spectra of complexes (*1*) **I** and (*2*) **III**.

Figure 2 shows the photoluminescence spectra of thermo- and photo-cured films containing 0.5 wt % of europium complex. The spectra contain emission bands at 537 nm ($^5D_1 \rightarrow {}^7F_1$), 583 nm ($^5D_0 \rightarrow {}^7F_5$), 595 nm ($^5D_0 \rightarrow {}^7F_1$), and 615 nm ($^5D_0 \rightarrow {}^7F_2$) characteristic of the Eu^{3+} cation. The most intense of these bands is the band of $^5D_0 \rightarrow {}^7F_2$ transition (615 nm). The fluorescence of the matrix of thermally cured film appears as a weak band at 395 nm.

Figure 3 shows the UV absorption spectra of the photocured films. The spectrum of the undoped film (Fig. 3, curve *1*) contains two absorption bands, at 240 and 280 nm, due to the presence of residual photoinitiator IRGACURE-184 $[C_6H_5C(O)\mathit{cyclo}\text{-}C_6H_{10}(1\text{-}OH)]$. The addition of lanthanide complex causes additional absorption band at 329 nm due to the electronic transitions in europium tris(β-diketonate) moiety.

The thermally curable composition is practically nonshrinking at the transition from liquid to solid state.

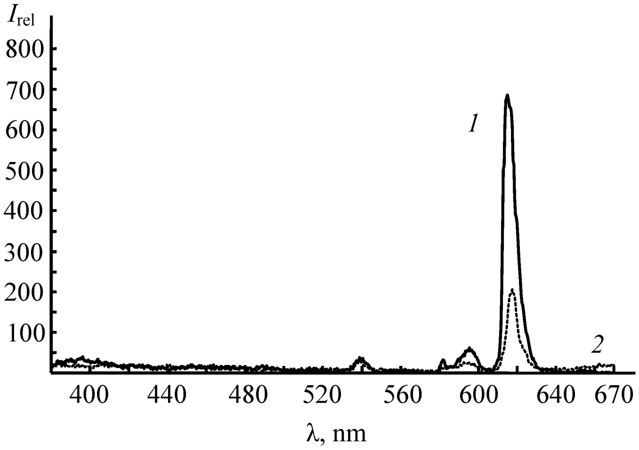


Fig. 2. The photoluminescence spectra of thermo- (*1*) and photo-cured (*2*) films doped with europium complex **III** at the excitation with light of wavelength 340 nm: (*1*) c = 0.52 wt %, film thickness 420 μm, (*2*) c = 0.50 wt %, film thickness 19 μm.

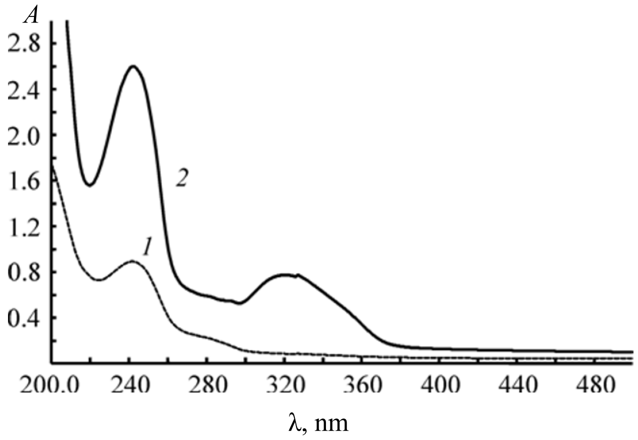


Fig. 3. Electron absorption spectra of photocured polysiloxane films: (*1*) without a complex, the film thickness 115 μm, (*2*) with the complex content 0.79 wt %, the film thickness 95 μm.

Its high viscosity leads to the formation of thick (up to 600 μm on Teflon substrates and 400 μm on the substrates of fused quartz) flexible films. Their thickness can be controlled by diluting the composition with an organic solvent (e.g., ether, hexane). The films can be easily removed from the surface of the Teflon substrate. The curing of a 5 mm thick layer in a small (8 mm in diameter) weighing bottle leads to the formation of a monolithic luminescent block. Lower viscosity of the photocurable composition provides the formation of a thinner layer on the surface of silica or quartz glass. At the irradiation with UV light the deposited layer should be covered by a transparent lavsan film to protect the process of polymerization against inhibition by atmospheric oxygen. The thickness of the films thus obtained was 20 to 100 μm.

EXPERIMENTAL

IR spectra of the compounds were taken from the liquid films between KBr plates on a FSM 1201 IR-Fourier spectrometer. The electron absorption spectra of the films on the substrates of fused quartz were measured on a Perkin-Elmer Lambda 25 spectrophotometer, fluorescence spectra, on a Perkin-Elmer LS-55 spectrofluorimeter. Photo-curing of siloxane films was performed using a quartz irradiating unit UCN-11 with a mercury lamp DRT-240. The spectrum of the lamp includes the following emission bands (wavelength, nm, in parentheses the average energy, %): 577.0 (70.4) 546.1 (71.75) 435.8 (62.4) 404.7 (35.9) 365.0 (100), 312.6 (68.0) 302.2 (31.2) 296.7 (14.3) 280.4 (10.3) 265.2 (23.4) 253.7 (26.1) 248.3 (10.5).

The thermally curable silicone composition consisting of vinyl (silicone A) and hydride (silicone B) components was obtained by the method of [10], silicone A is a mixture of poly(dimethyl)(methylphenyl)siloxane with terminal trivinylsiloxy groups and oligovinylsiloxane with the mass ratio of 100:5, silicone B is oligomethylhydrosiloxane, the catalyst is 1% solution of complex compounds of platinum in oligovinylsiloxane. Viscosity of the thermocurable silicone composition after mixing components A and B was 6000–8000 cSt. The photocurable matrix was a compound SIEL 159–470 produced by Russian Federation Research Center GNIIKHTEOS. Trimethylsilanol was synthesized by acid hydrolysis of hexamethyldisilazane [11]. The substrates of fused silica (3×12×40) and silicate glass (2×25×40) for the formation of films were treated for 10 h with a saturated solution of NaOH in isopropyl alcohol, then for 10 h with chromic acid solution, washed with water, and dried at 120–150°C.

Europium tris[3-{3'-tris(trimethylsiloxy)silylpropylaminocarbonyl}-1,1,1-trifluoro-4-phenylbutan-2,4-dionate] trihydrate (III). To a solution of 0.31 g of compound **I** in 3 ml of THF was added 1 ml of trimethylsilanol and 0.001 g of tetrabutylammonium fluoride. The reaction mixture was heated for 20 h at boiling, filtered, the volatile products were distilled off, and the residue was heated in a vacuum for 1 h at 100°C to obtain 0.33 g of compound **III** as a viscous yellow liquid. Found, %: C 41.03, H 6.38. $C_{69}H_{123}Eu\cdot F_9N_3O_{21}Si_{12}$. Calculated,%: C 41.62, H 6.23.

Preparation of films by thermal curing. To 0.345 g of silicone A was added 0.019 g of 10% solution of compound **III** in THF, the mixture was stirred, and 0.047 g of silicone B was added. The mixture was thoroughly stirred, kept for 2 h to remove air bubbles and applied to substrates of fused silica, silicate glass, and Teflon. After 12 h the substrates coated with a liquid layer were heated in an oven for 2 h at 130–135°C. Thick (400–600 μm) elastic opalescent films were obtained, with concentration of europium complex 0.52 wt %, glowing red under a mercury lamp. A viscous composition was diluted with ether and applied to the substrate, and thus a transparent layer was obtained of 10 to 50 μm thickness.

Preparation of films by the photo-curing. To 0.23 g of the silicone compound SIEL 159–470 was added 0.02 g of 10% solution of compound **III** in THF, the mixture was stirred, held for 2 h to remove air bubbles, and applied to substrates of fused silica, silicate glass, and Teflon. After 2 h, the substrate coated with a liquid layer was covered with a thin (20 μm) lavsan film and irradiated for 20 min with the full light of a mercury lamp DRT-240 at a distance of 30 cm. The films with thickness of 20–100 μm were obtained with a concentration of the europium complex 0.87 wt %, glowing red under a mercury lamp. The film is easily removed from the surface of Teflon and remains on the lavsan cover.

The samples were explored in the Analytical center of the Institute of Organometallic Chemistry, Russian Academy of Sciences.

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