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Dedicated to the 90th Anniversary of Academician M.G. Voronkov

Synthesis of Polymetallophenylsiloxanes with the Predicted Metal Content

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Abstract—The possibility of the synthesis of polymetallophenylsiloxanes with the predicted metal content in the synthesized polymers is demonstrated. Variation of the spectral luminescent properties of polyterbium- and polyeuropiumphenylsiloxanes as a function of the metal content is studied.

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Many practically important properties of polymetallophenylsiloxanes (for example, their stability to thermooxidation [1]) depend not only on the nature of heteroatom but also on its content in the polymer chain. For polymers with the same heteroatom, these properties are often difficult to compare because of the absence of methods of synthesis, which would allow the preparation of polymers with the predetermined metal content. The most simple and universal method of synthesis of these compounds is the reaction of metal chlorides with sodium phenylsiliconates. According to the literature data, the ratio Si/M is limited to stoichiometric ratios, which are determined by the composition of the starting compounds [2]. The reaction is performed in a boiling mixture of organic solvents by the scheme: $M^nCl_n + n\ NaOSi{\equiv} \rightarrow M(OSi{\equiv})_n + n\ NaCl$, where n is the valence of the metal. If DMSO is used as one of the solvents, the process is not complicated by side reactions and the polymers formed are uniform in composition, which corresponds to the stoichiometric ratio [3].

The synthesis of polymers with lower metal content is possible by an increase in the ratio Si/Na in the starting sodium phenylsiliconates. Taking into account that sodium polyphenylsiliconate (Si/Na = 1) is easily obtained by the reaction of polyphenylsiloxane with NaOH in toluene in the presence of DMSO [3], it is presumable that, varying the initial ratio Si/Na, it is possible to obtain the corresponding phenylsiliconates.

$$x\,(C_6H_5SiO_{1.5})_n + NaOH \rightarrow [(C_6H_5SiO_{1.5})_xO_{0.5}Na]_n + H_2O,$$
$$x = 2–5,\ 8.$$

From the synthesis of compounds **I** and **II** with the ratio Si/Na = 2, 3, we have isolated crystalline products by partial distillation of the solvent. When the ratio Si/Na was increased to 4 (**III**), we failed to isolate a crystalline product, and complete removal of DMSO from the formed siliconate is difficult because of its high boiling point. The data of elemental analysis of phenylsiliconates **I, II** are given in Table 1.

The obtained compounds are readily soluble in chloroform, toluene, carbon tetrachloride, and poorly soluble in petroleum ether. The IR spectra of compounds **I** and **II** are similar. The presence of DMSO in the salts is confirmed by the presence of absorption maxima at 2980 and 1050 cm^{-1}. The absence of absorption in the range 3100–3600 cm^{-1} should be mentioned, indicating the absence of hydroxy groups in the sodium phenylsiliconates. The absorption in the range 1000–1132 cm^{-1} has complex vibrational structure, which is indicative of the presence of various structural fragments in the products.

The treatment of phenylsiliconates with trimethylchlorosilane under optimal conditions [4] resulted in

Table 1. Data of elemental analysis of sodium phenylsiliconates **I** and **II**

Comp. no.	Si/M	Yield, %	Found, %		Formula	Calculated, %	
			Si	Na		Si	Na
I	2	87.5	15.4	6.5	$[C_6H_5SiO_{1.5}]_2O_{0.5}Na \cdot 0.8\,DMSO$	15.8	6.5
II	3	94.0	17.2	4.8	$[C_6H_5SiO_{1.5}]_3O_{0.5}Na \cdot 0.8\,DMSO$	17.5	4.8

products of polydisperse character, and their molecular masses vary within a wide range (Fig. 1).

The obtained results allow a conclusion only on the molecular weight distribution of sodium phenylsiliconates, but they do not reveal the uniformity in composition (that is, the uniformity of distribution of sodium in oligomers).

As was shown earlier, the reaction of metal chlorides with sodium phenylsiliconates in the presence of DMSO is not complicated by side processes. Therefore, examining the composition of the obtained polymers, it is possible to conclude on the distribution of sodium in the starting compounds.

The synthesis of the polymers was carried out using the directly prepared solutions of sodium phenylsiliconates without their preliminary isolation. The uniformity of the initial compounds was judged from the character of distribution of the metal atoms in the fractions of polymers. In Table 2 are presented yields and the data of elemental analysis of the polymers synthesized by the reaction of compound **I** (Si/Na = 2) with aluminum, cobalt, europium and terbium chlorides under the conditions, which are optimal for the synthesis of polymetallophenylsiloxanes in toluene with the preliminarily added 12-fold excess of DMSO to 1 mol of metal chloride.

The obtained compounds are solids, readily soluble in the main organic solvents and insoluble in saturated hydrocarbons, not melting up to the temperature of decomposition. Polycobaltophenylsiloxane is blue, poly-alumo-, polyeuropio- and polyterbiophenylsiloxanes are colorless. From the gel permeation chromatography data (GPC), their molecular mass exceeds 5000, and they contain low molecular compounds. The ratio of silicon to the metal in all compounds is equal to the initial one, and there is only a slight nonuniformity of distribution of the metal in fractions.

In our opinion, the obtained data are indicative of the fact that, in spite of polydispersity of the starting compound **I**, the distribution of sodium in it is uniform, since only in this case the polymers uniform in composition can be formed. Besides, a rather uniform structure is confirmed by the data of the IR spectroscopy (absorption in the range 1000–1100 cm^{-1} has simple vibrational structure).

Compound **II** was used for the synthesis of poly-alumo-, polyeuropio- and polyterbiophenylsiloxanes with the ratio Si/M = 9, as well as of polycobaltophenylsiloxane (Si/M = 6). The data of elemental analysis, fractionation (by fractional precipitation in the system chloroform–petroleum ether), and the yields of the obtained polymetallophenylsiloxanes are given in Table 3.

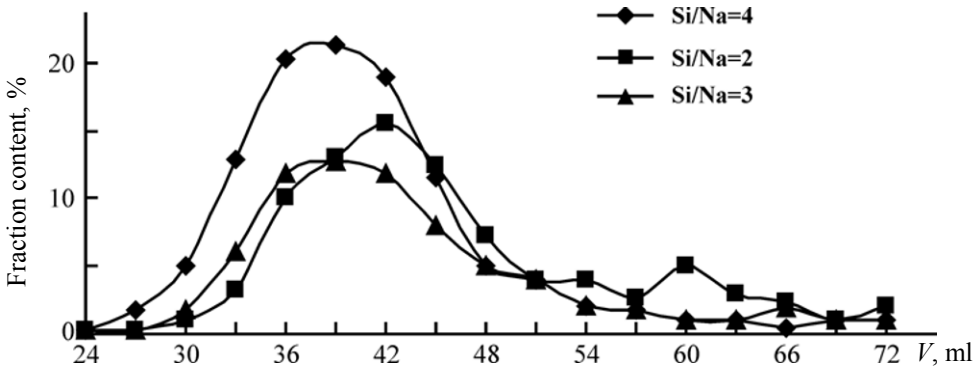

Fig. 1. Gel chromatograms of the products of treatment of compounds **I–III** with trimethylchlorosilane.

Table 2. Data of elemental analysis of polymetallophenylsiloxanes prepared from compound **I**

Comp. no.	Initial ratio Si/M (*m*)	Obtained ratio Si/M	Yield, %	Found, %			Calculated for $(PhSiO_{1.5})_mM^nO_{n/2}$, %		
				Si	M	C	Si	M	C
VII	6	6.0	93.1	20.5	3.3	49.8	20.2	3.3	52.4
Fraction 1		6.0	25.8	19.7	3.2		18.9	3.0	
Fraction 2		6.0	34.1	20.3	3.3		19.6	3.1	
Fraction 3		6.0	40.1	19.3	3.1		19.4	3.1	
IV	4	4.0	95.4	18.6	10.2	48.1	18.9	10.0	48.7
Fraction 1		3.2	51.2	17.8	12.2		18.4	12.1	
Fraction 2		4.5	44.1	18.5	8.9		19.2	9.0	
IX	6	5.9	90.0	17.4	16.7	45.2	17.5	16.6	45.1
Fraction 1		6.0	42.3	17.5	16.5		17.6	16.7	
Fraction 2		5.9	57.7	17.4	16.7		17.5	16.6	
XIII	6	6.0	92.6	17.8	16.1	45.4	17.7	16.0	45.5
Fraction 1		6.0	58.7	17.7	16.0		17.7	16.0	
Fraction 2		6.0	33.9	17.7	16.0		17.7	16.0	

The obtained compounds are solids; their color corresponds to that described above, the intensity of the color of polycobaltophenylsiloxane is weaker. The solubility and molecular masses are the same as those described above. The ratio of silicon to the metal in all compounds is equal to the initial one, but it is noteworthy that on going to heterosiloxanes with lower metal content the nonuniformity in composition increases.

The increase in the ratio of silicon to sodium in the starting compound **III** to 4 results in the formation of compound **VI** with Si/Co = 8. The polymer in its properties and visual appearance does not differ from the earlier obtained polycobaltophenylsiloxanes. The initial ratio Si/M is retained in the polymer, but the data of fractionation by fractional precipitation show that the ratio Si/M in the fractions of compound **VI** varies within rather wide limits. The nonuniformity of the structure of the obtained polymer **VI** as compared to that of polymer **V** is increased, as proved by the data of the IR spectroscopy: the absorption in the range 1000–1100 cm^{-1} has more complex vibrational structure. The obtained data are indicative of the fact that the nonuniformity of distribution of sodium in the starting sodium phenylsiliconate increases.

Further increase in the ratio Si/Na in the starting phenylsiliconates allowed to prepare polymers **XI, XV** (Si/M = 15) and **XII, XVI** (Si/M = 24) based on sodium phenylsiliconates with Si/Na = 5 and Si/Na = 8. The data of elemental analysis and the yields of the obtained polyheterosiloxanes are presented in Table 4.

It should be noted, that the ratio of silicon to the metal in all compounds is equal to the initial one, but their nonuniformity in composition increases. The IR spectra of absorption of the polymers are identical to the IR spectra of the polymers with a higher metal content.

Therefore, varying the ratio Si/Na in the synthesis of the starting sodium polyphenylsiliconates, it is possible to obtain polymetallosiloxanes with a lower metal content in the polymers, in which the ratio Si/M is equal to the initial ratio. However, with the increase of Si/M, the nonuniformity of the polymer composition increases, which, in turn, is indicative of the increase of nonuniformity of sodium distribution in the starting sodium polyphenylsiliconates with larger ratios Si/Na.

+3-Charged lanthanide ions, especially Eu^{3+} and Tb^{3+}, possess unique spectral luminescent properties:

Table 3. Data of elemental analysis of polymetallophenylsiloxanes prepared from compound **II**

Comp. no.	Initial ratio Si/M (*m*)	Obtained ratio Si/M	Yield, %	Found, %			Calculated for $(PhSiO_{1.5})_mM^nO_{n/2}$, %		
				Si	M	C	Si	M	C
V	6	6.0	95.4	18.6	10.2	48.1	18.9	10.0	48.7
Fraction 1		4.6	51.2	17.8	12.2		18.4	12.1	
Fraction 2		18.8	44.1	18.5	8.9		19.2	9.0	
VIII	9	9.0	92.9	20.7	2.3	53.6	20.8	2.2	53.5
Fraction 1		8.8	55.8	20.8	2.3		20.7	2.2	
Fraction 2		9.1	44.1	20.8	2.2		20.8	2.2	
X	9	9.0	89.0	18.6	11.7	48.5	18.4	11.6	45.1
Fraction 1		9.2	48.8	18.0	11.1		18.2	11.5	
Fraction 2		8.6	29.2	14.1	9.3		14.5	9.2	
Fraction 3		8.3	20.4	9.1	6.2		9.0	6.5	
XIV	9	8.9	96.0	18.5	11.3	48.2	18.8	11.4	48.5
Fraction 1		8.8	54.6	17.8	11.0		18.0	11.2	
Fraction 2		9.1	24.2	17.1	10.2		17.0	10.0	
Fraction 3		7.2	22.2	12.0	9.0		12.5	9.4	

Table 4. Data of elemental analysis of polymetallophenylsiloxanes prepared from compounds **III–V**

Comp. no.	Initial ratio Si/M (*m*)	Obtained ratio Si/M	Yield, %	Found, %			Calculated for $(PhSiO_{1.5})_mM^nO_{n/2}$, %		
				Si	M	C	Si	M	C
VI	8	8.0	99.8	19.7	5.2	51.8	20.2	5.3	52.0
Fraction 1		5.0	70.0	19.4	8.3		19.4	8.3	
Fraction 2		9.1	15.0	20.4	4.8		20.4	4.7	
XI	15	15.4	91.0	19.8	7.3	50.9	19.8	7.5	51.0
XV	15	14.8	89.0	20.0	7.4	51.2	19.9	7.3	51.1
XII	24	23.8	87.8	20.6	4.9	52.8	20.5	4.8	52.7
XVI	24	24.4	85.0	20.3	4.5	52.5	20.5	4.6	52.8

high quantum yield of luminescence, monochromaticity of radiation, simple Stark structure of the spectra [5]. It should be mentioned, that the data on the luminescent properties of polymetalloorganosiloxanes of rare earth metals are very limited, therefore we have investigated the spectral luminescent properties of polyterbio- and polyeuropiophenylsiloxanes with various metal content. To gain a more detailed picture,

we have synthesized polyterbio- and polyeuropiophenylsiloxanes with Si/M = 3 and Si/M = 1 using the earlier described procedures [6].

When irradiated with the UV light, polyterbio- and polyeuropiophenylsiloxanes show luminescence characteristic for the specific ion (pink for europium and green for terbium). Specific peculiarities of the studied polyphenyl siloxanes of rare earth metals are a larger half-width of the luminescence lines (diffusivity of the spectra) and lower intensity of luminescence as compared to a number of crystalline compounds of rare earth metals (organic acids, β-diketonates). The diffusivity of the luminescence lines in the investigated polymers suggests a larger nonuniformity of the proximate surrounding of the luminescence centers (Eu^{3+}, Tb^{3+}) relative to the crystalline compounds of europium and terbium with the island structure, as well as a larger effectiveness of degradation of the electron excitation energy to the lattice vibrations. The luminescence spectrum of polyeuropiophenylsiloxane consists of four broad intense lines corresponding to the transition $^5D_0$–$^7F_2$ with the maxima at 16345, 16310, 16160 and 16082 cm^{-1}; two lines of medium intensity of the $^5D_0$–$^7F_1$-transition with the maxima at 16940 and 16798 cm^{-1}, and a single line of the $^5D_0$–$^7F_0$-transition with the maximum at 17288 cm^{-1}. In the luminescence spectra of polyterbiophenylsiloxane the main part of irradiation is due to the $^5D_4$–$^7F_5$-transition, consisting of two most intense lines with the maxima at 18423 and 18255 cm^{-1}; a single line of the $^5D_4$–$^7F_6$-transition with the maximum at 17079 cm^{-1}, and a single line of the $^5D_4$–$^7F_4$-transition with the maximum at 20396 cm^{-1}.

The excitation spectra of polyeuropiophenylsiloxanes appear as a set of narrow discrete lines corresponding to the intraionic *f*–*f*-transitions of Eu^{3+}. The most intense bands belong to the $^7F_2$←$^5L_6$ (395 nm) and $^7F_0$←$^5D_1$ (465 nm) transitions. The analysis of the luminescence excitation spectra points to the absence of the intramolecular energy transfer from the levels of the polyphenylsiloxane ligand. Therefore, the observed photoluminescence of europium polyphenylsiloxanes is due to photophysical processes, occurring in europium ion itself, without energy transfer from the ligand. A similar picture is observed for polyterbiophenylsiloxanes. The analysis of the excitation spectrum points to the absence of intramolecular energy transfer from the levels of the ligand to the levels of Tb^{3+}. The most intense band corresponds to the $^5G_6$, $^5D_3$←$^7F_6$ transfer (380 nm).

The absence of intramolecular energy transfer from the levels of the polymer ligand to the levels of the lanthanide ion provides an understanding of the relatively low intensity of photoluminescence of the studied polymetallophenylsiloxanes as compared to some brightly luminescing crystalline complexes of europium and terbium of the island structure.

The intensity of luminescence of the lanthanide ions in compounds depends on concentration of the ions of the rare earth metals and is determined by the processes of the energy transfer from the levels of the ligand to the resonance level of the lanthanide ions, the processes of nonradiative deactivation of the resonance levels of the lanthanide levels, and the mechanism of interaction of the lanthanide ions with each other in the excited state [7, 8]. The concentration quenching, caused by the interaction of ions of the same type (for example, Eu^{3+}or Tb^{3+}) in the excited state, is enhanced with the increase in the concentration of the ions, and is different in various systems. The concentration quenching is caused by the nonradiative deactivation of the energy of excitation as a result of collisions of the luminescing ions with other ions.

Figure 2 represents the dependence of intensity of photoluminescence of $Eu^{3+}$and Tb^{3+} on their concentration in the compounds.

A characteristic feature of the studied europium and terbium compounds is the absence of concentration quenching at large concentrations of the activating ions, up to 50%. For example, in macromolecular complexes of europium and terbium with copolymers of acrylic acid, methacrylic acid, and their esters the concentration quenching is observed at concentrations as low as 6–8% [7]. Apparently, the lower effectiveness of nonradiative deactivation is explained by more rigid structure of the polymer backbone of polyheterosiloxanes as compared to the earlier described compounds.

Noteworthy is the independence (within the experimental error) of the lifetimes of $Eu^{3+}$and Tb^{3+} from the metal content in the polymers with different Si/M ratio (Fig. 3). That means approximate identity of the proximate surrounding of the lanthanide ions of that in the investigated polymers regardless of concentration of the metal.

EXPERIMENTAL

Sodium phenylsiliconate I (Si/Na = 2). A mixture of 8.7 g (0.068 mol) of polyphenylsiloxane in 87 ml of

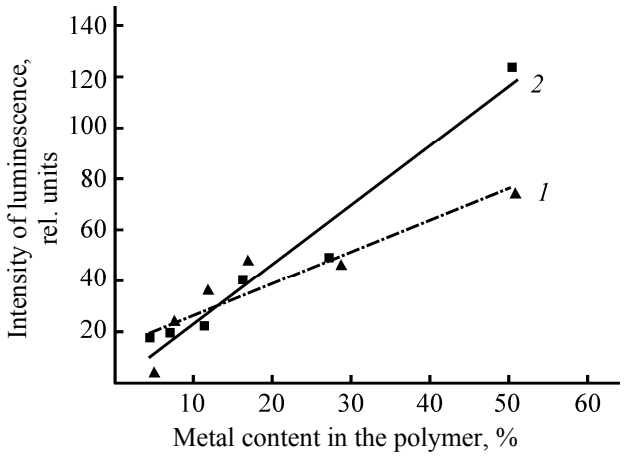

Fig. 2. Dependence of intensity of luminescence of (*1*) Tb^{3+} and (*2*) Eu^{3+} on the metal content in polymetallophenylsiloxanes.

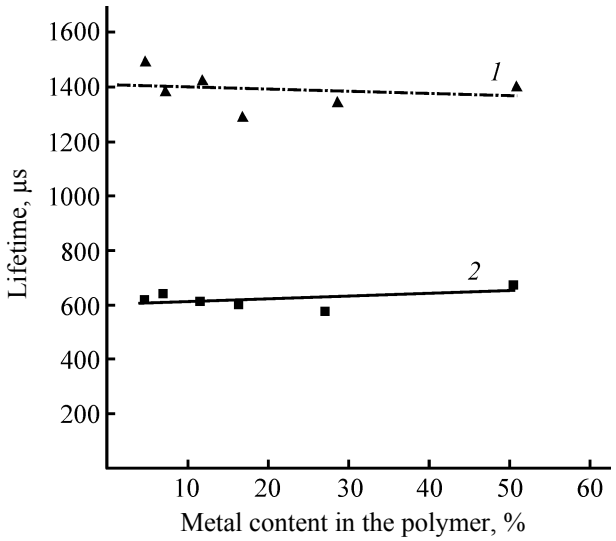

Fig. 3. Dependence of lifetime of (*1*) Tb^{3+} and (*2*) Eu^{3+} on the metal content in polymetallophenylsiloxanes.

toluene and 1.35 g (0.034 mol) of NaOH in 10 ml of dimethylsulfoxide was refluxed until the alkali was fully dissolved and separation of water in the Dean-Stark trap ceased. The obtained solution was used for the synthesis of the corresponding polymetallophenylsiloxanes.

Sodium phenylsiliconate II (Si/Na = 3) was prepared similarly from 9.1 g (0.071 mol) of polyphenylsiloxane in 91 ml of toluene and 0.95 g (0.024 mol) of NaOH in 9 ml of DMSO.

Sodium phenylsiliconate III (Si/Na = 4) was prepared similarly from 9.3 g (0.072 mol) of polyphenylsiloxane in 98 ml of toluene and 0.72 g (0.018 mol) of NaOH in 10 ml of DMSO.

Reaction of sodium phenylsiliconate I with trimethylchlorosilane. To the solution of 0.034 mol of **I** in 10 ml of DMSO and 87 ml of toluene 5.5 ml of trimethylchlorosilane [$(CH_3)_3SiCl$:NaOH = 1.5:1] was added dropwise with stirring and cooling. After 1 h, the precipitate of NaCl was separated by centrifugation (1.9 g, 96%), the filtrate was treated with six portions of water to remove DMSO, then dried over calcium chloride. After removal of toluene at 60°C (25 mm Hg), 9.7 g (84.7%) of the target product was obtained.

Reaction of sodium phenylsiliconate II with trimethylchlorosilane was performed similarly. Yield 10.2 g (91.2%).

Reaction of sodium phenylsiliconate III with trimethylchlorosilane was performed similarly. Yield 9.6 g (89.3%).

Synthesis of polycobaltophenylsiloxane IV (Si/Co = 4). Mixture of 4.02 g (0.017 mol) of $CoCl_2 \cdot 6H_2O$ in 50 ml of toluene and 16 ml of DMSO was refluxed until the water separation in the Dean-Stark trap ceased. The obtained solution was added to the freshly prepared solution of sodium phenylsiliconate (I) at stirring and cooling. The reaction mixture was stirred at room temperature for 6 h, then refluxed for 3.5 h until the water separation in the Dean-Stark trap ceased. The precipitate of NaCl was separated by centrifugation. Toluene was distilled off, the polymer was isolated from the DMSO solution by precipitation with 4-fold excess of water, dried at 100°C (20 mm Hg). Yield 9.2 g (95.4%).

Polymetallophenylsiloxanes **V–XVI** were prepared similarly.

Polycobaltophenylsiloxane V (Si/Co = 6) was prepared from 18.1 g (0.14 mol) of polyphenylsiloxane, 1.9 g (0.047 mol) of NaOH, and 5.61 g (0.023 mol) of $CoCl_2 \cdot 6 H_2O$. Yield 19.5 g (97.5%).

Polycobaltophenylsiloxane VI (Si/Co = 8) was prepared from 18.1 g (0.14 mol) of polyphenylsiloxane, 1.4 g (0.035 mol) of NaOH, and 4.28 g (0.018 mol) of $CoCl_2 \cdot 6 H_2O$. Yield 19.7 g (99.8%).

Polyalumophenylsiloxane VII (Si/Al = 6) was prepared from 11.61 g (0.09 mol) of polyphenylsiloxane, 1.8 g (0.045 mol) of NaOH, and 3.62 g (0.015 mol) of $AlCl_3 \cdot 6 H_2O$. Yield 11.52 g (93.1%).

Polyalumophenylsiloxane VIII (Si/Al = 9) was prepared from 17.4 g (0.135 mol) of polyphenylsiloxane, 1.8 g (0.045 mol) of NaOH, and 3.62 g (0.015 mol) of $AlCl_3 \cdot 6\,H_2O$. Yield 16.89 g (92.9%).

Polyterbiophenylsiloxane IX (Si/Tb = 6) was prepared from 3.7 g (0.01 mol) of $TbCl_3 \cdot 6\,H_2O$, 7.7 g (0.06 mol) of polyphenylsiloxane, and 1.2 g (0.03 mol) of NaOH. Yield 9 g (90%).

Polyterbiophenylsiloxane X (Si/Tb = 9) was prepared from 8.5 g (0.06 mol) of polyphenylsiloxane, 0.9 g (0.02 mol) of NaOH and 2.8 g (0.007 mol) of $TbCl_3 \cdot 6\,H_2O$. Yield 8.9 g (89%).

Polyterbiophenylsiloxane XI (Si/M = 15) was prepared from 9.2 g (0.075 mol) of polyphenylsiloxane, 0.6 g (0.015 mol) of NaOH, and 1.9 g (0.005 mol) of $TbCl_3 \cdot 6\,H_2O$. Yield 7.8 g (78%).

Polyterbiophenylsiloxane XII (Si/M = 24) was prepared from 9.3 g (0.072 mol) of polyphenylsiloxane, 0.36г (0.009 mol) NaOH, and 1.14 g (0.003 mol) $TbCl_3 \cdot 6\,H_2O$. Yield 8.77 g (87.8%).

Polyeuropiophenylsiloxane (XIII) (Si/Eu = 6) was prepared from 3.87 g (0.03 mol) of polyphenylsiloxane, 0.6 g (0.015 mol) of NaOH, and 2 g (0.005 mol) of $EuCl_3 \cdot 6\,H_2O$. Yield 4.4 g (92.6%).

Polyeuropiophenylsiloxane XIV (Si/Eu = 9) was prepared from 8.5 g (0.06 mol) of polyphenylsiloxane, 0.9 g (0.02 mol) of NaOH, and 2.8 g (0.007 mol) of $EuCl_3 \cdot 6\,H_2O$. Yield 9.6 g (96%).

Polyeuropiophenylsiloxane XV (Si/M = 15) was prepared from 5.8 g (0.045 mol) of polyphenylsiloxane, 0.36 g (0.009 mol) of NaOH, and 1.14 g (0.003 mol) of $EuCl_3 \cdot H_2O$. Yield 5.6 g (89%).

Polyeuropiophenylsiloxane XVI (Si/M = 24) was prepared from 1.14 g (0.003 mol) of $EuCl_3 \cdot H_2O$, 9.3 g (0.072 mol) of polyphenylsiloxane and 0.36 g (0.009 mol) of NaOH. Yield 8.5 g (85%).

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