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Modifying Silica with Viologenic Groups

L. B. Dzaraeva, A. A. Arutyuniantz, A. S. Archegova, and A. N. Shpakov

Khetagurov North Osetian State University, ul. Vatuina 46, Vladikavkaz, 362025 Russia
e-mail: dzaraeva@mail.ru

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Abstract—Modification of silica with viologenic groups is described. *N,N*'-Diallyl-γ,γ'-dipyridinium dibromide obtained by the reaction of allyl bromide with γ,γ'-dipyridyl was hydrosilylated with triethoxysilane followed by copolycondensation of the synthesized bis(3-triethoxysilylpropyl)-γ,γ'-dipyridinium dibromide with tetraethoxysilane.

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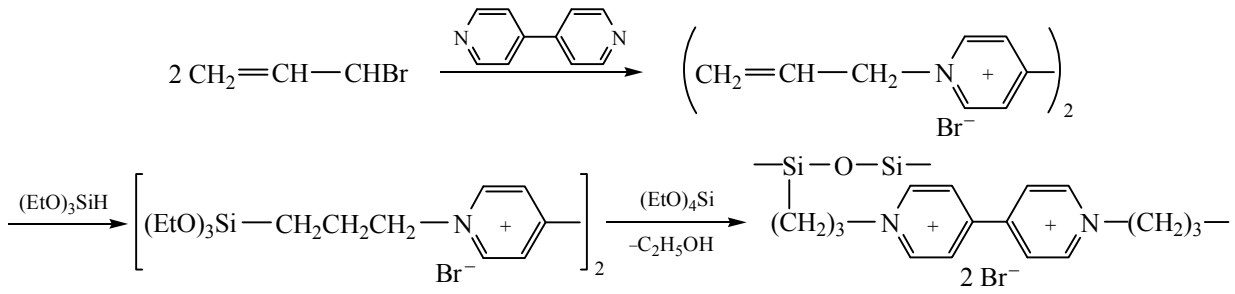
The polymers containing γ,γ'-dipyridinium "viologenic" groups attract interest as electron-ex-changing membranes [1], the redoxites. Their study is promising in connection with their possible semiconductor, fotoinitiator, and electrochromic properties, as well as their application in the systems converting solar energy into chemical or electrical one.

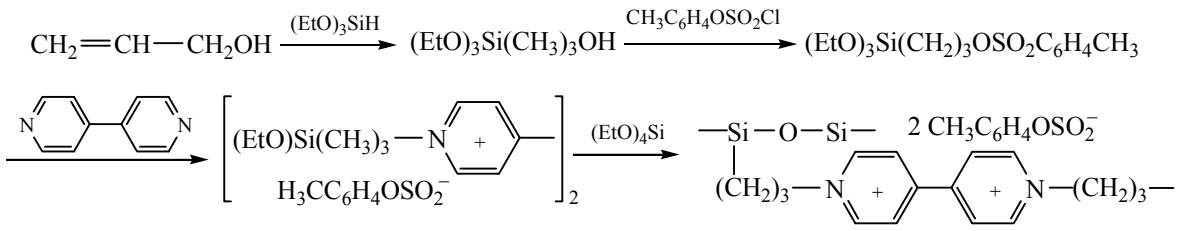
In continuation of the work [2] on the synthesis of the polymers with viologenic groups in the main chain, we modified silica with the viologenic groups using a sequence of reaction. Allyl bromide was reacted with γ,γ'-dipyridyl, the obtained *N,N*'-diallyl-γ,γ'-dipyridiny dibromide (**I**) was hydrosilylated with triethoxysilane, and the formed bis(3-triethoxysilylpropyl)-γ,γ'-dipyridinium dibromide was involved into copoly-condensation with tetraethoxysilane (**II**) to form polymer (**III**) (Scheme 1).

A similar polymer, but with the tosylate anion, was obtained by hydrosilylation of allyl alcohol with 3-hydroxypropyltriethoxysilane followed by the reaction of the formed 3-(triethoxysilyl)propanol with tosyl chloride and dipyridyl, and polycondensation of the obtained bis(3-triethoxysilylpropyl)-γ,γ'-dipyridinium ditosylate with tetraethoxysilane **IV**–**VII** (Scheme 2).

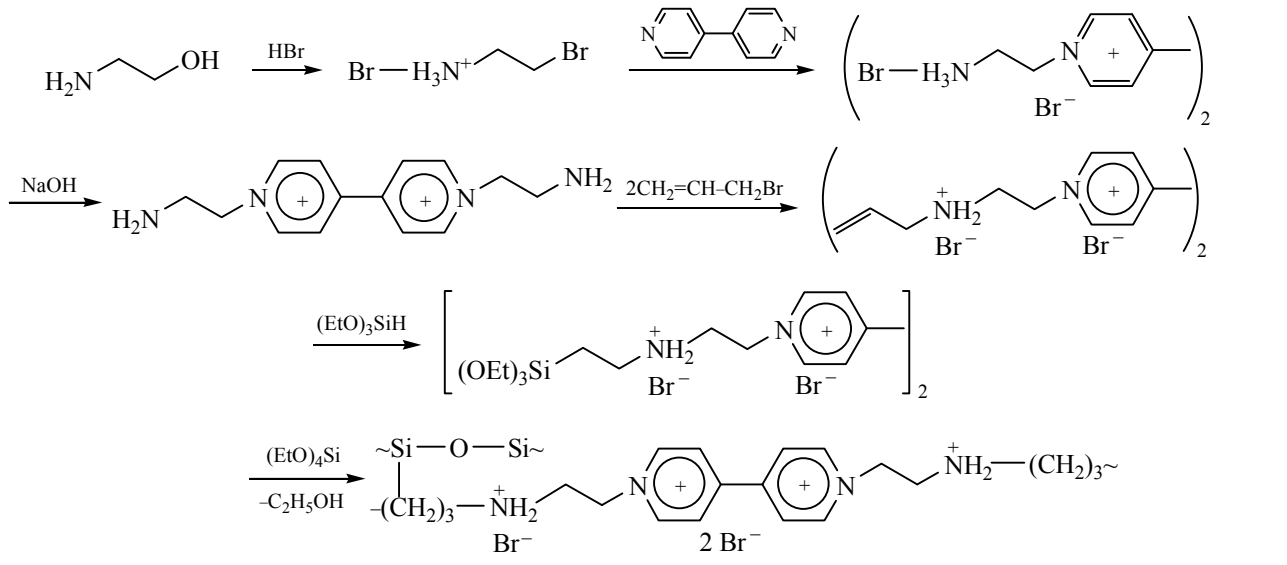
Scheme 1.



Scheme 2.



Scheme 3.

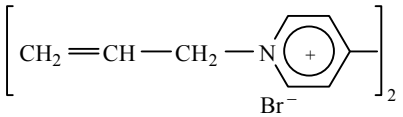
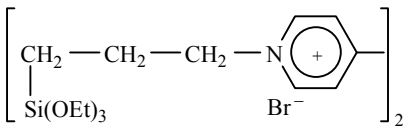
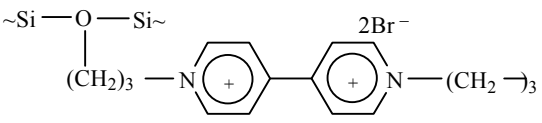


Another way to fix viologenic groups on the silica surface is as shown in Scheme 3.

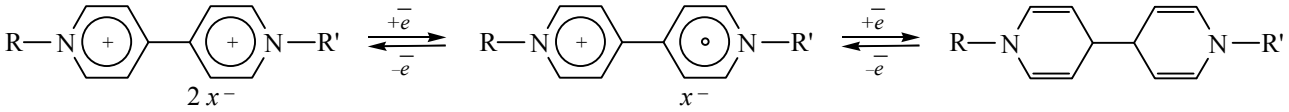
The β-bromethylamine hydrobromide was synthesized by the known procedure [3]. Bis(2-ammonioethyl)-γ,γ'-dipyridiny tetrabromide (**VIII**) was obtained by boiling β-bromoethylamine hydrobromide with dipyridyl in acetonitrile. Subsequent treatment of bis(2-ammonioethyl)-γ,γ'-dipyridinium tetrabromide **VIII** with alkali and further reaction of the formed bis(2-aminoethyl)-γ,γ'-dipyridinium dibromide (**IX**) with allyl bromide led to bis(2-allylammonioethyl)-γ,γ'-dipyridinium tetrabromide (**X**). Hydrosilylation of compound **X** and polycondensation of the formed bis[2-(3-triethylsilylpropyl)ammonioethyl]-γ,γ'-dipyridinium tetrabromide (**XI**) with tetraethoxysilane led to copolymer (**XII**).

In the IR spectra of the products of hydroxylation of allyl fragments of γ,γ'-dipyridinium groups there are absorption bands in the regions of 820 cm^{-1} and 1060 cm^{-1} indicating the presence of Si–C bonds. The spectra of copolymers (end products) include a band at 1010 cm^{-1}, which can be attributed to the Si–O–Si bonds.

Parameters of cyclic voltammograms of compounds **I–IV**

Comp. no.	Compound	Reduction				Oxidation	
		$-E_{nk}$, V	I_{nk}, μA	$-E_{na}$, V	I_{na}, μA	$-E_{na}$, V	I_{na}, μA
I		0.43 0.97	78 66	0.29 0.66	50 60	0.92 1.33	70 58
II		0.54 0.81 1.03	40 20 30	– – 0.96	– – 20	0.80 1.36 –	76 60 –
III		0.38 0.82	5 10			1.38	88
IV	$(EtO)_3SiH$	0.5 1.32	12 16			0.1	66

Scheme 4.



I: R = R' = CH_2=CH–CH_2–
x = Br

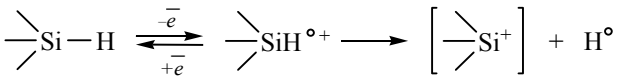
II: R = R' = CH_2–CH(Si(OEt)$_3$)–CH_2–
x = Br

III: R = ~Si(–O–Si~)(–$(CH_2)_3$~)
R' = –$(CH_2)_3$–
x = Br

The table lists the parameters of voltammograms of compounds **I–IV**. Based on the data in the table, we can conclude that the studied compounds can be both reduced and oxidized. Electrochemical characteristics of compounds **I–III** were measured from their solutions in DMF using cyclic voltammetry on a platinum electrode. DMF was selected as a solvent due to the low solubility of compounds in other aprotic solvents used commonly in organic electrochemistry. Reduction of compounds **I–III** proceeds according to Scheme 4.

The obtained values of the maximum currents (Fig. 1) which are close to those of a model compound (2,4,6-triphenilpyrylium perchlorate) permit an assumption that the dication is reduced with the transfer of one electron. In all cases anodic peaks are observed, indicating a relatively high stability of the species formed at the reduction. The second reduction stage is irreversible in all cases. Thus, for compounds **II** and **III** the secondary anodic peaks were not observed.

All the dications (see the table, Fig. 2) are capable of oxidation. The number of transferred electrons determined relatively to the reference compound ferrocene is close to unity. From the published sources it is known that triethoxysilan is reduced at a potential close to 0 V [4].



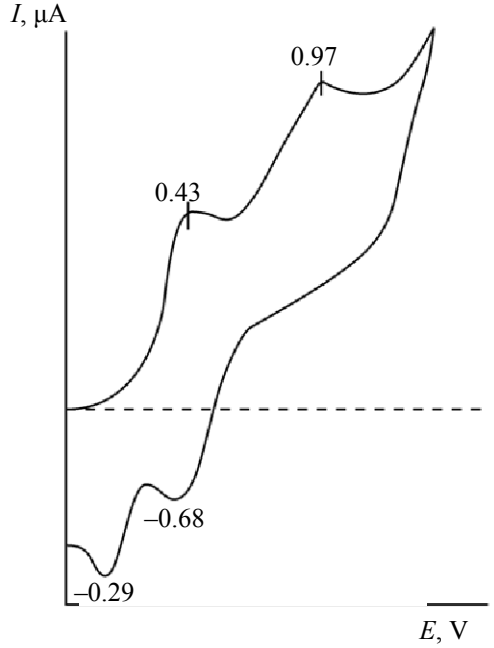


Fig. 1. Reduction of dicatione.

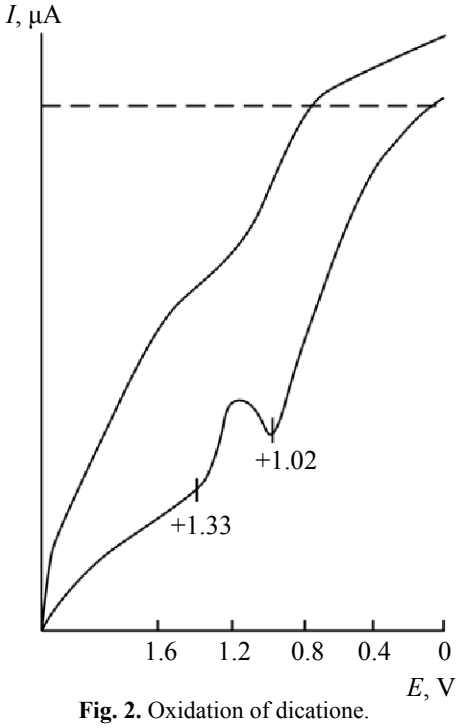


Fig. 2. Oxidation of dicatione.

It follows from the tabulated data that triethoxysilan (compound **IV**) is oxidized more readily than compounds **I** and **II**. Comparing the potentials of the first stage of oxidation of dications **I** and **II** with **IV**, it can be concluded that the ability to oxidation depends on the presence of viologenic fragment in the molecules of these substances.

The bipyridinium salts as well as respective polymeric derivatives are known to be capable of relatively easy forming stable cation radicals and (poly)-cation radicals [5, 6].

Investigation of these compounds using electron spin resonance (ESR) showed that reduction of compounds containing viologenic groups gives rise to radicals that are registered by ESR spectroscopy. The hyperfine structure is similar to that of well-known dibenzylviologen cation-radical: a_N = 0.42 mT, a_H = 0.14 mT (8H) and $a_H(CH_3)$ = 0.28 mT (4H). Delocalization of the unpaired electron is limited by bipyridinium fragment with the $(CH_2)_3$ group at the nitrogen atom, and does not affect the silicon-containing residues.

EXPERIMENTAL

***N,N*'-Diallyl-γ,γ'-dipyridinium dibromide (I)**. To 15.6 g (0.1 mol) of dipyridyl dissolved in a minimal amount of dimethylformamide was was added while stirring 15.6 g (0.13 mol) of allyl bromide, and the mixture was left untill precipitate separated. The precipitate was filtered off, washed with water and alcohol, and then with ether. A light yellow crystalline substance with mp 228°C (from ethanol) was obtained. Yield quantitative. Found, %: C 46.16, H 4.48; N 6.93; Br 3.97. $C_{16}H_{18}Br_2N_2$. Calculated, %: C 48.24, H 4.52; N 7.03; Br 4.02.

Bis(3-triethoxysilylpropyl)-γ,γ'-dipyridinium dibromide (II). To a mixture of 16.4 g (0.1 mol) of triethoxysilane, 38.8 g of *N,N*'-diallyl-γ,γ'-dipyridinium dibromide in isopropanol was added 5 ml of 0.06% solution of platinumhydrochloric acid in isopropanol (Speier catalyst) and the mixture was stirred at the boiling point of isopropanol at reflux. The reaction process was monitored by chromatography. After the reaction completion, isopropanol was distilled off and the residue was treated with ether for separation of catalyst. A crystalline substance of a light brown color was obtained, softening temperature 290–300°C (from ethanol). Yield 30 g (60%). Found, %: C 45.95; H 6.29; N 3.35; Si 7.12; Br 21.53. $C_{28}H_{50}Br_2N_2Si_2$. Calculated, %: C 46.28; H 6.88; N 3.85; Si 7.71; Br 22.03.

Copolymer by polycondensation of bis(3-triethoxysilylpropyl)-γ,γ'-dipyridiny dibromide with tetraethoxysilane (III). A mixture of 3 g (0.03 mol) of bis(3-triethoxysilylpropyl)-γ,γ'-dipyridinium dibromide, 1 ml of tetraetoxysilane, 4 g of concentrated hydrochloric acid and 50 ml of ethanol was refluxed until a precipitate separated completely, for ~24 h. The precipitate was filtered off, washed with water and alcohol, and dried. 2.3 g of not melting white substance was obtained. Yield 85%. Found, %: C 35.88; H 3.73; N 5.20; Si 5.25; Br 29.90. $C_{16}H_{20}BrN_2Si$. Calculated, %: C 44.85; H 4.67; N 6.54; Si 6.54; Br 37.38. Based on data from elemental analysis the degree of substitution in silica is ~80%.

3-Tosyloxypropyltriethoxysilane (IV, V). A mixture of 5.8 g (0.1 mol) of allyl alcohol, 16.4 g (0.1 mol) of triethoxysilane, 50 ml of isopropanol, 5 ml of 0.05% solution platinohydrochloric acid in isopropyl alcohol was refluxed under monitoring by chromatography. After the reaction completing, from the reaction mixture isopropanol was distilled off, the residue was cooled to –5°C, and to it was added 10.4 g of tosyl chloride and 50 ml of pyridine, and the mixture was shaken until complete dissolution of tosyl chloride and then without removing it from the ice bath, it was left for 3 h. Then at a temperature 5°C or below 100 ml of water was added, initially dropwise and then poured. The resulting tosylate was extracted with ether, the extract was washed with cold diluted solution of H_2SO_4, then with water and with a solution of $NaHSO_4$ and then it was dried over Na_2SO_4. After removing ether remained a colorless viscous liquid with a faint smell, decomposing when heated above 100°C. Found, %: C 50.83; H 7.07; Si 7.01; S 8.13. $C_{16}H_{28}O_6SSi$. Calculated, %: C 51.06; H 7.44; Si 7.44 ; S 8.51.

Bis(3-triethoxysilylpropyl)-γ,γ'-dipyridiny ditosylate (VI). To 3.12 g (0.02 mol) of dipyridyl dissolved in a minimum amount of DMF was added 15 g (0.04 mol) of 3-tosyloxypropyltriethoxysilane, the mixture was left to stand until complete formation of a precipitate which was filtered off, washed with water, alcohol, and ether, and dried. A colorless crystalline substance was obtained with softening temperature 250–260°C (from ethanol). Found, %: C 54.87; H 6.67; Si 5.89; N 2.97; S 5.58. $C_{12}H_{64}O_{12}N_2S_2Si_2$. Calculated, %: C 55.50; H 7.04; Si 6.16; N 3.08; S 7.04.

Copolymer by polycondensation of bis(3-triethoxysilylpropyl)-γ,γ'-dipyridinium ditosylate (VII) was obtained as the previous copolymer. A mixture of 9.3 g (0.01 mol) of bis(3-triethoxysilylpropyl)-γ,γ'-dipyridinium tosylate, 2 ml of tetraethoxysilane, 4 g of concentrated hydrochloric acid and 50 ml of ethanol was refluxed for 24 h. The precipitate was filtered off, washed with water and alcohol, and dried. Infusible white substance, 8 g, was obtained. Found, %: C 42.83; H 4.59; N 3.35; Si 3.56; S 8.5. $C_{28}H_{36}N_2O_6S_2Si$. Calculated, %: C 57.14; H 6.12; N 4.76; Si 10.88. The degree of substitution is ~75%.

Bis(ammonioethyl)-γ,γ'-dipyridinium tetrabromide (VIII). A mixture of 3 g (0.02 mol) of dipyridyl, 8 g (0.04 mol) of β-bromethylamine hydrobromide, and 30 ml of dry acetonitrile (distilled over P_2O_5) was refluxed with stirring. Within 20 minutes after the reaction started oil separated. The contents of the flask was cooled, the precipitate was filtered off, washed with acetonitrile, and dried. Yield 8.3 g (73%). A crystalline solid of dark orange color was obtained, mp 145°C. Found, %: C 29.36; H 3.72; N 9.36; Br 53.53; $C_{14}H_{22}Br_4N_4$. Calculated, %: C 29.68; H 3.88; N 9.42; Br 53.87.

Bis(ammonioethyl)-γ,γ'-dipyridinium dibromide (IX). Bis(ammonioethyl)-γ,γ'-dipyridinium tetrabromide was dissolved in 2 M aqueous NaOH and left for 12 h. Colorless needle-shaped crystals precipitated, which were filtered off, washed with water and alcohol, and dried, mp 120°C (from ethanol). Yield quantitative. Found, %: C 41.23; H 4.71; N 9.62; Br 56.47. $C_{14}H_{20}Br_2N_4$. Calculated, %: C 41.58; H 4.95; N 9.89; Br 56.59.

Bis(2-allyammonioethyl)-γ,γ'-dipyridinium tetrabromide (X). 8 g (0.02 mol) of bis(ammonioethyl)-γ,γ'-dipyridinium dibromide and 5 g (0.04 mol) of allyl bromide was dissolved in 30 ml of DMF and the mixture was refluxed for 3 h with stirring. The mixture was then cooled, the precipitate formed was filtered off, washed with water, alcohol, and ether, and dried. The obtained crystals are yellow-orange, mp 175°C (from ethanol). Found, %: C 36.81; H 4.31; N 8.13; Br 49.01; $C_{20}H_{30}Br_4N_4$. Calculated, %: C 37.15; H 4.64; N 8.66; Br 49.53.

Bis-2-(3-triethylsilylpropyl)ammonioethyl-γ,γ'-dipyridiny dibromide (XI). 6.74 g (0.01 mol) of bis-2-(3-triethylsilylpropyl)ammonioethyl-γ,γ'-dipyridinium dibromide was dissolved in 50 ml of isopropanol and to the solution was added 3.28 g (0.02 mol) of triethoxysilane, 0.001 g of H_2PtCl_3 in 5 ml of isopropanol (catalyst Speier). The mixture was boiled for 5 min, then cooled, the precipitate was filtered off, washed with ethanol and dried, mp 300°C (from acetonitrile). Found, %: C 39.02; H 5.97; N 6.03; Si 6.10; Br 32.57. $C_{32}H_{62}$ $Br_4N_4O_6Si_2$. Calculated, %: C 39.42; H 6.36; N 6.36; Br 32.85.

Copolymer by polycondensation of bis-2-(3-triethoxysilylpropyl)ammonioethyl-γ,γ'-dipyridinium tetrobromide with tetraethoxysilane (XII) was obtained similarly to previous copolymers. Solid non-melting white material. Found, %: C 26.25; H 3.54; Si 3.10; N 6.21; Br 35.49. $(C_{20}H_{32}Br_4$ $N_4Si)_n$. Calculated, %: C 35.50; H 4.73; Si 4.14; N 8.28; Br 47.33. From the data of elemental analysis follows the degree of substitution equal to ~75%.

REFERENCES

1. Vannikov, A.V. and Grishina, A.D., *Fotokhimiya polimernykh donorno-aktseptornykh kompleksov* (Photochemistry of Polymeric Donor–Acceptor Complexes), Moscow: Mir, 1984.
2. Dzaraeva, L.B., Klimov, E.S., Bumber, A.A., Begus, E.G., Berberova, N.T., and Okhlobystin, O.Yu., *Khim. Geterotsikl. Soedin*., 1985, no. 9, p. 1268.
3. Veigand-Hilgetag, A., *Metody eksperimenta v organicheskoi khimii* (Experimental Methods in Organic Chemistry), Moscow: Mir, 1969
4. Berberova, N.T., *Doctorate Sci. (Chem.) Dissertation*, Rostov-on-Don, 1991.
5. Krainov, I.P., Kramarenko, S.F., Dotsenko, E.I., Bumber, A.A., et al., *Khim. Geterotsikl. Soedin.*, 1986, no. 5, p. 626.
6. Dzaraeva, L.B., Bumber, A.A., Klimov, E.S., Kataev, V.A., et al., *Vysokomol. Soedin. B,* 1986, vol. 28, no. 5, p. 366.