OLIGOSILOXANES END-FUNCTIONALIZED WITH N-HETEROCYCLES. A COMPARATIVE STUDY OF THE Si-R-X BOND REACTIVITIES

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A simple method is reported for the synthesis of di- and oligosiloxanes containing nitrogen heterocycles groups at the end of the chains such as: α,ω–bis-(3-(1-pyridinio)-propyl)-oligodimethylsiloxane iodide (**P₂Py**), α,ω–bis-(3-(1-(3-methylpyridinio))-propyl)-oligodimethylsiloxane iodide (**P₂Pyc**), 1,3-bis-(3-(1-pyridinio)-propyl)-tetramethyldisiloxane iodide (**P₃Py**) and 1,3-bis-(3-(1-(3-methylpyridinio))-methyl)-tetramethyldisiloxane iodide (**P₄Pyc**). A comparative study was made of the Si-R-X group reactivity in the reaction with two various pyridines. The obtained oligomers were analyzed by IR and ^{1}H-NMR spectrometries. Solubility tests were also made, emphasizing their modification depending on the siloxane chain length and end-groups nature.

INTRODUCTION

Considerable efforts have been made recently to modify oligodimethylsiloxane by the introduction of some functions to the organic groups from either side or in the end of the chain to make the polymer chemically reactive or to give it some special physical features. The high flexibility of the siloxane chain makes these functions accessible to external reagents. Thus they can be readily used as catalysts support, as polymer catalysts[1-3] or ion exchangers.

The organic groups attached to the Si atom have a definite influence on the siloxane properties modifying the low-temperature elasticity, the thermo-oxidative stability, the solubility and chemical reactivity features.[4] For example, the modification of the hydrofobicity of the siloxanes can be made by introduction of polar groups such as quaternary ammonium or pyridinium salts at the chain end.[5]

The pyridine ring provides a site that can be converted to a positively charged one by protonation with acids or by quaternization with alkylating agents. The pyridine ring also provides a site for complexation with various metal cations.[6]

It was also demonstrated that the polysiloxanes bearing quaternary ammonium salts showed bactericidal activity against bacteria such as *Escherichia coli* and *Aeromonas hydrophila* when incorporated into a polysiloxanes network. The quaternary ammonium salts containing polysiloxanes are also active in aqueous solution.[7]

This paper presents the synthesis of a new type of quaternary ammonium salts-terminated siloxanes, namely siloxanes containing pyridinium or 3-methyl-pyridinuim halides at both chain ends. Methylene or propylene groups are located between the silicon atom and the pyridinium groups.

RESULTS AND DISCUSSION

For the synthesis of the pyridinio- or 3-methyl-pyridinio- end-functionalized disiloxanes, the chemical transformation of the proper chloro-alkyl functionalized siloxane precursors was made. In these reactions, the chloro-propyl terminated siloxane precursor in the oligomer form was also used. The chloro-propyl end-functionalized oligosiloxane with a certain molecular weight (Mn = 650) was prepared by equilibration of

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octamethylcyclotetrasiloxane (**D₄**) with 1,3-bis-(chloropropyl)-1,1,3,3- tetramethyldisiloxane (**P₃Cl**) in a certain molar ratio (1:1) at 100ºC, for 17 hours. The anionic polymerization of the cyclosiloxanes has not been used for synthesis of 3-chloropropylsiloxanes so far because the γ–chloride was believed not to tolerate the anionic centers which could be consumed at least in a series of side reactions.[8] Therefore, in this paper, for the synthesis of the desired oligomer, the cationic catalyzed equilibration of **D₄** was performed (Scheme 1). A synthetic cation-exchanger was used as catalyst (2.5% wt. reported to reaction mixture weight).

The reaction time was established on the basis of previous studies.[9] During this reaction, disiloxane was used as chain transfer agent (or chain blocker) and it played two major roles. Firstly, it determined the terminal functional groups, and secondly, it regulated the molecular weight of the obtained linear oligomer.
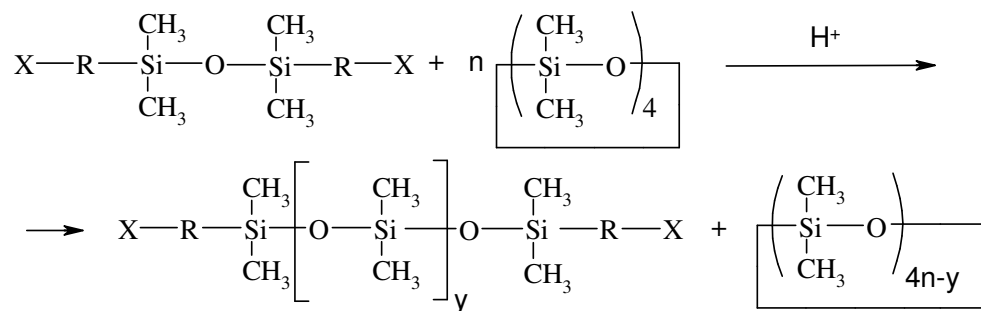

With R, X, y having the following significance:

Sample Code	R	X	y
P_2Cl	$-CH_2-CH_2-CH_2-$	Cl	5
P_3Cl	$-CH_2-CH_2-CH_2-$	Cl	0
P_4Cl	$-CH_2-$	Cl	0

Scheme 1

The chlorine atom in α or γ–position to silicon may be substituted by other atoms (iodine, bromine, amine, quaternary ammonium salts, etc.). So, oligo- or polysiloxanes bearing 3-chloropropyl groups can give access to the modifications of the polymers.

Participation of a p orbital of the halogen atom and a bonding orbital of the sp^3 carbon forms the C-X bonds.
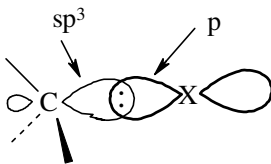
Sp^3 orbitals of the carbon atom have a small volume and the overlapping of electronic orbital decreases as the p orbital volume of the halogen atom increases, which influences:

– the C-X bond length and energy;
– the C-X bond polarity and polarizability.

In the case of alkyl halides an increase of the bond length is observed, simultaneously with a decrease of the bond energy as the volume of the halogen atom increases in the order:

$$X = F < Cl < Br < I$$

R-X bond reactivity increases

Therefore, the chloroalkyl group at the chain end of the siloxane was converted to iodoalkyl group by halogen substitution with potassium iodide (SN2 reaction) (Scheme 2) because the iodoalkyl group reacts with the tertiary amine much easier than the chloroalkyl group.[10] The reactions occurred with good yields (80-88%).
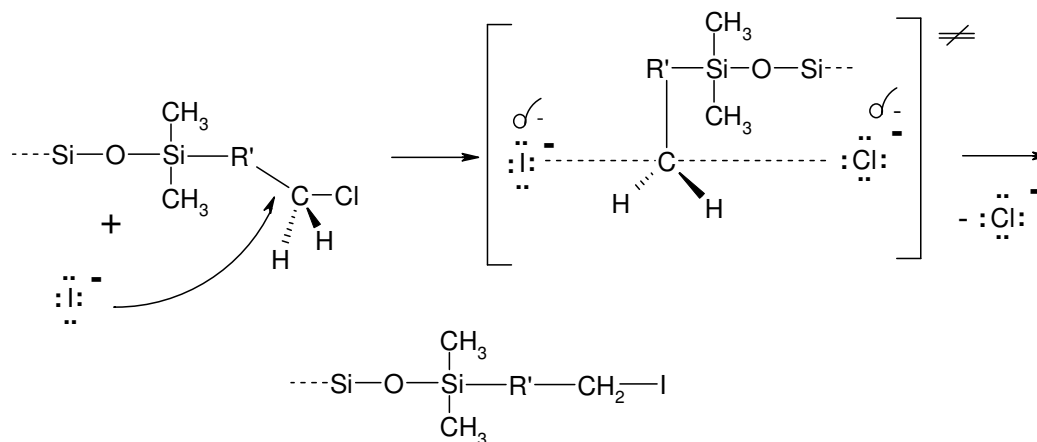
Scheme 2

The reaction of the obtained bis-iodoalkyl-siloxane derivatives with pyridine and 3-methyl-pyridine (β-pycoline) proceeded in bulk to afford pyridinio or 3-methyl-pyridinio iodide end-functionalized alkyl siloxanes, according to Scheme 3.
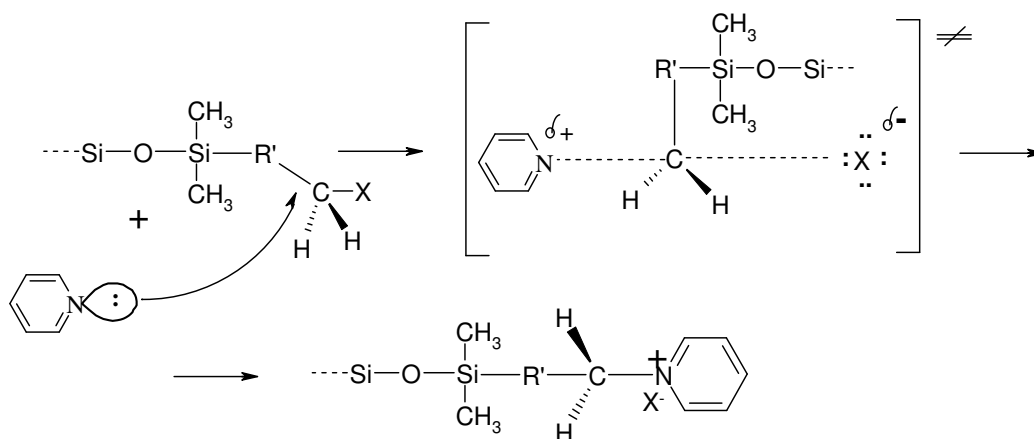
X=I, Cl   Scheme 3

In these reactions the number of siloxane units in the siloxane chain remained unchanged. This was verified by ^{1}H-NMR (Fig. 1), from the ratio of the integrated signals for the methyl protons of dimethylsiloxane units (Ha; δ = 0,1 ppm) *versus* the protons of one methylene group (for example: Hb; δ = 0,7 ppm); so, in P_2I, P_2Py and P_2Pyc the number of siloxane units, y = 4. Because a purification of the iodide derivative was not made, two triplets appear in the ^{1}H-NMR spectrum of P_2I in the range δ = 3-4 ppm corresponding to the protons from the $\equiv$ Si-CH$_2$-CH$_2$-C$\underline{H}_2$- groups of the two coexisting halide derivatives.

In the ^{1}H-NMR spectra of the final compounds (P_2Py and P_2Pyc), due to the pyridine ring's influence, the shift in the signal at 5 ppm for the $\equiv$ Si-CH$_2$-CH$_2$-C$\underline{H}_2$- and at 2.1-2.5 ppm for the $\equiv$ Si-CH$_2$-C$\underline{H}_2$-CH$_2$- methylene protons in P_2Pyc relative to the corresponding protons (3.1-3.8 and 1.8-2.2, respectively) in P_2I is noticed.

The products were also analyzed by IR spectrometry, which showed all the characteristic peaks for the proposed structures (1050-1100 cm^{-1}: Si-O-Si, 800, 1260 cm^{-1}: Si-CH$_3$, 1400-1440 cm^{-1}: -CH$_2$-N$^+\equiv$, 1600 cm^{-1}: -HC=N-, 2950 cm^{-1}: C-H aliphatic, 3010-3040 cm^{-1}: C-H aromatic, 3000-3300 cm^{-1}: -CH$_2$-N$^+\equiv$) (Fig. 2).

Depending on the nature of reactant, differences from the point of view of the reaction conditions (time and temperature) are noticed, according to the data in Table 1.
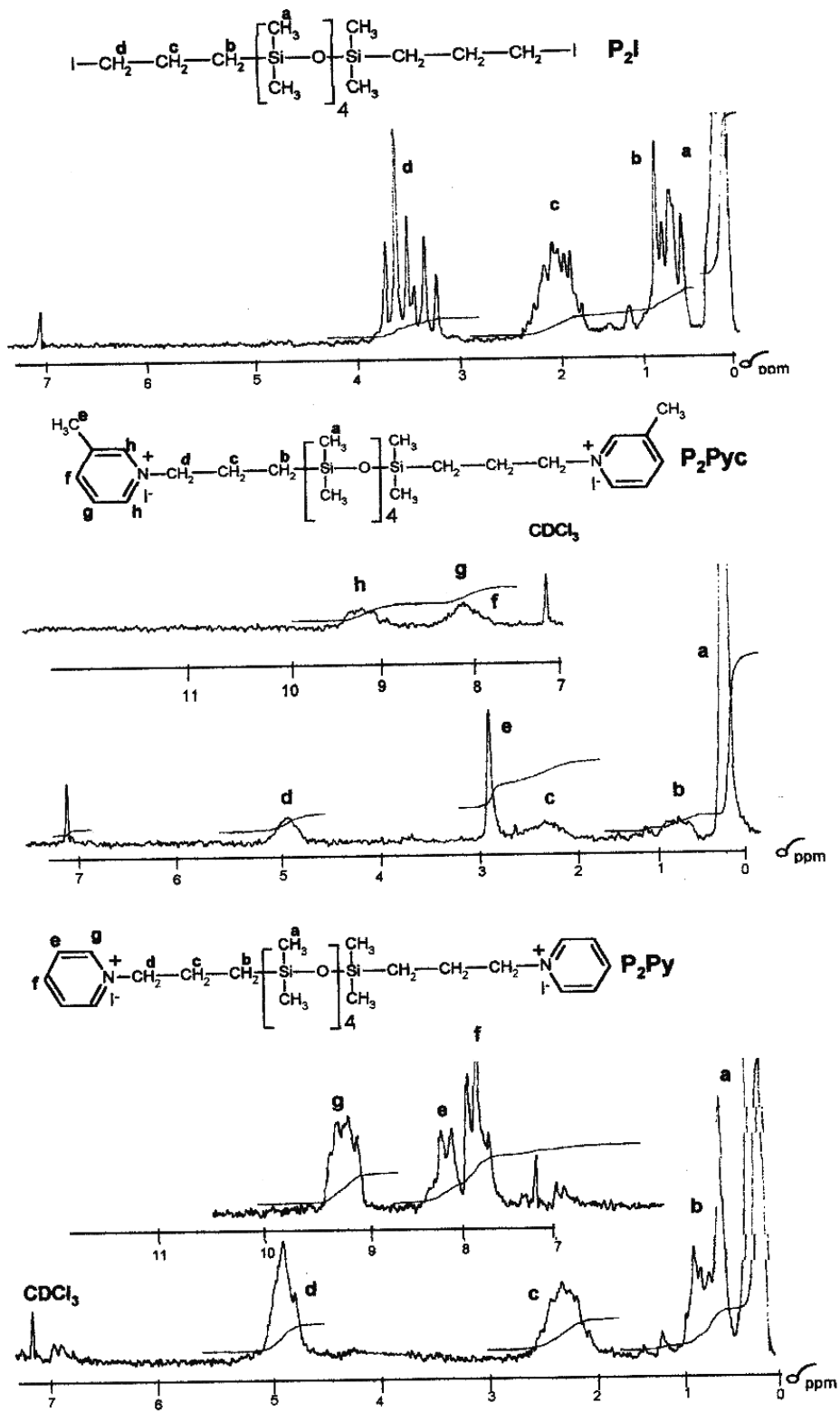
Fig. 1 – Illustrative ¹H-NMR spectra for: P₂I: α,ω–bis-(3-iodo-propyl)-oligodimethylsiloxane; P₂Pyc: α,ω–bis-(3-(1-(3-methylpyridinio))-propyl)-oligodimethylsiloxane iodide; P₂Py: α,ω–bis-(3-(1-pyridinio)-propyl)-oligodimethylsiloxane iodide.
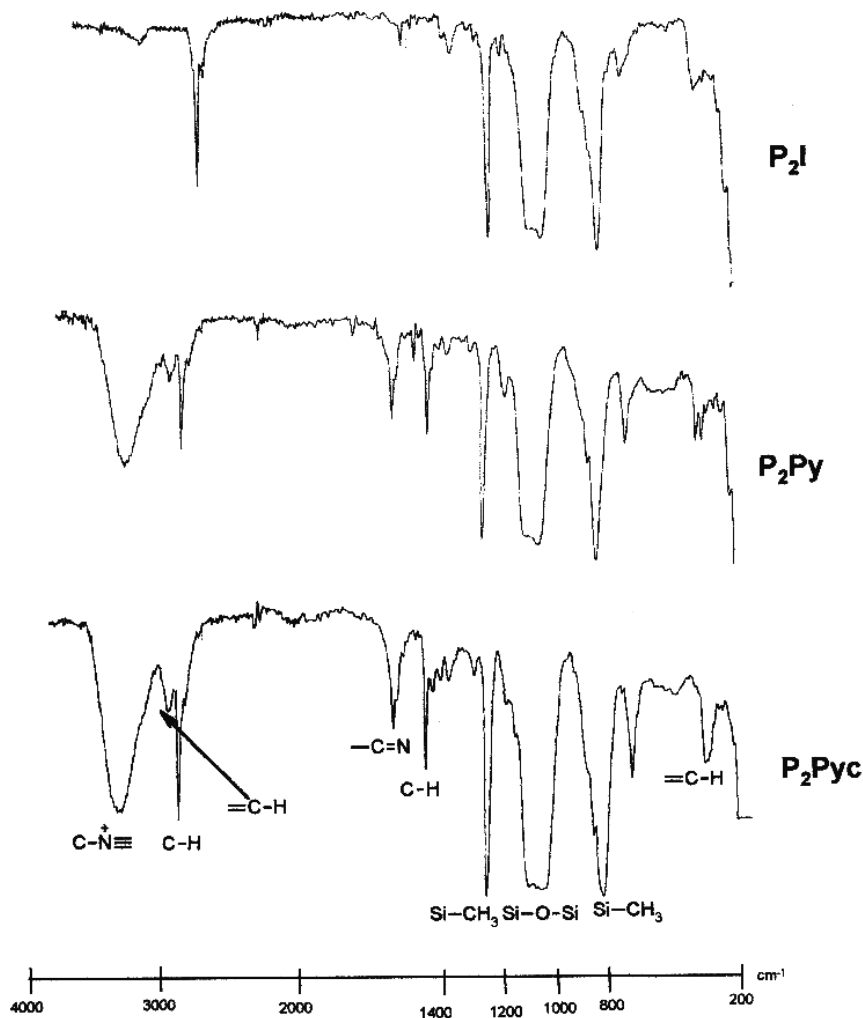
Fig. 2 – IR spectra for: P_2I: α,ω–bis-(3-iodo-propyl)-oligodimethylsiloxane; P_2Pyc: α,ω–bis-(3-(1-(3-methylpyridinio))-propyl)-oligodimethylsiloxane iodide; P_2Py: α,ω–bis-(3-(1-pyridinio)-propyl)-oligodimethylsiloxane iodide.

From Table 1 it can be observed that P_3Py_2 product can be obtained easier and with a better yield than P_3Py_1. Consequently, the iodide derivative (P_3I) is more reactive than the chloride derivative (P_3Cl). Reactivity differences were also observed in the case of P_4Pyc_1 (from P_4Cl and Pyc) and P_4Pyc_2 (from P_4I and Pyc). Due to the presence of the CH_3 group with electron-donating ability, 3-pycoline should be more reactive than pyridine; this can not be sustained by Table 1 data since the reaction occurred at different temperatures *i.e.* reflux temperatures of the respective compounds.

The reaction times were established on the basis of preliminary tests and ^{1}H-NMR spectra analysis. Samples were taken at various reaction times, until the disappearance of the ^{1}H-NMR signal specific for the -C$\underline{H}_2$-I protons (*i.e.* 3.3-3.8 ppm in P_2I) was observed and only the signal for C$\underline{H}_2$-N$^+\equiv$ (*i.e.* 4.8-5.0 ppm in P_2Py) remained.

The purification of the samples was made on the basis of the solubility differences.

In Table 2 qualitative solubility tests results in various solvents, arranged by their solubility parameter values, are shown. The presence of the nitrogen heterocycles in siloxanes structure modifies their solubility. Thus, different from starting siloxanes, the reaction products are soluble in almost all polar solvents.

Table 1

The reaction conditions and the obtained products

Sample (code)	Reactants	Time (h)	Temperature	Products aspect	Yield (%)
P_3Py_1	P_3Cl + Py	18	115°C	Yellow waxy solid	40
P_3Py_2	P_3I + Py	12	115°C	Yellow waxy solid	45
P_2Py	P_2I + Py	17	115°C	Brown oil	40
P_2Pyc	P_2I + Pyc	15	145°C	Brown viscous oil	45
P_4Pyc_1	P_4Cl + Pyc	11	145°C	Brown oil	35
P_4Pyc_2	P_4I + Pyc	10	145°C	Dark-brown oil	40

Table 2

The comparative solubilities of the reactants and products

Solvent/ Code	Siloxane	Py	Pyc	P_3Py_2	P_2Py	P_2Pyc	P_4Pyc_2
Diethyl-ether	+	+	+	-	+-	-	+-
CCl_4	+			-	-	+-	-
Toluene	+			-	-	+-	-
$CHCl_3$	+	+	+	+-	+	+	+-
THF	-			-	+-	+-	+
Acetone	+			+-	+	+	+
NMP	-			+	+	+	+
DMF	-			+	+	+	+
EtOH	-	+	+	+	+	+	+
DMSO	-			+	+	+	+
MeOH	-			+	+	+	+
H_2O	-	+	+	+	+	+	+

+ soluble; **+-** partially soluble; **-** insoluble

EXPERIMENTAL

Materials

1,3-bis-(chloromethyl)-1,1,3,3-tetramethyldisiloxane (P_4Cl) and 1,3-bis-(chloropropyl)-1,1,3,3- tetramethyldisiloxane (P_3Cl) supplied by ABCR GmbH & Co.

Octamethylcyclotetrasiloxane (D_4), 3-methyl-pyridine (3-pycoline, Pyc), pyridine (Py) supplied by Fluka AG.

Potassium iodide supplied by Fluka AG was used.

Solvents: diethyl-ether, carbon tetrachloride (CCl_4), toluene, chloroform ($CHCl_3$), tetrahydrofuran (THF), acetone, 1-methyl-2-pyrrolidinone (NMP), N,N-dimethylformamide (DMF), ethanol (EtOH), dimethyl sulfoxide (DMSO), methanol (MeOH), water (H_2O).

All these reactants and solvents were used as received.

Catalyst: Purolite CT–175, a styrene-divinylbenzene ion exchanger with -SO_3H groups (4.1 mequiv./g) was dehydrated by azeotropic distillation with toluene followed by vacuum drying at 110 C.

Measurements

The infrared spectra were run on a Specord M80 Carl Zeiss Jena Spectrometer using KBr pellet technique. ^{1}H-NMR spectra were recorded on a JEOL C-60 HL Spectrometer using $CDCl_3$ as the solvent.

Procedure

a) Synthesis of αω-bis-(chloropropyl)-oligodimethylsiloxane (P_2Cl)

αω-bis-(chloropropyl)-oligodimethylsiloxane was prepared by equilibration of D_4 with 1,3-bischloropropyltetramethyldisiloxane (P_3Cl) according to the procedure: 1,3-bis-(chloropropyl)-1,1,3,3-tetramethyldisiloxane (6mL, 0.01mol) was added to D_4 (3.1 mL, 0.01 mol) and 0.24 g cation exchanger Purolite CT-175 (2.5%) and the mixture was stirred for 17 h at 100°C. Then, the reaction mixture was filtered to remove the cation exchanger, and low-molecular-weight compounds were removed by heating at 150°C in vacuum (10 mm Hg) to afford 9.1 g P_2Cl as a transparent liquid (yield: 83%).

b) General method for the synthesis of the bis-(iodoalkyl)-siloxane derivatives (P_2I, P_3I, P_4I)

A solution containing 8 mmol bis-(chloroalkyl)-siloxane derivative and a large excess of KI (85 mmol) in 50 mL 2-butanone was refluxed for 30 h in a one-necked, flat-bottom flask, equipped with a reflux condenser, a drying tube and a magnetic stirrer.

Then, the reaction mixture was concentrated and 25 mL diethyl ether were added to the residue. The mixture was filtered to remove excess potassium iodide and potassium chloride by-product, and then it was washed with water and 2% sodium bisulfite aqueous solution. The organic layer was separated, dried over sodium sulfate and diethylether was evaporated. Bis-(iodoalkyl)-siloxane derivatives were obtained as yellow viscous liquids (80-88 % yields).

c) Preparation of the pyridinio or 3-methyl-pyridinio iodide end-functionalized alkyl siloxanes

The reaction was carried out in a two-necked, flat-bottom flask, equipped with reflux condenser, drying tube, nitrogen inlet and magnetic stirrer and heated in a thermostatted silicone oil bath. For a typical procedure, $3.8654 \cdot 10^{-3}$ mol iodo derivative and 10mL pyridine were charged in the reaction vessel and the reaction mixture was refluxed according to the data from Table 1. Samples were withdrawn at various reaction times for ^{1}H-NMR analysis. In the end, the excess pyridine was removed by vacuum distillation and the residue was purified on the basis of the solubility differences (Table 2) to afford pyridinio iodide end-functionalized alkyl siloxanes as yellow waxy solids or brown viscous oils (35-45% yields).

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