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A route to polysiloxanes with pendant imidazole groups

Hydrosilylation of *N*-allylimidazole hydrochloride with methyldichlorosilane

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Summary

Hydrosilylation of N-allylimidazole hydrochloride by methyldichlorosilane ($MeCl_2SiH$) under mild conditions leads to a high yield of N-[γ-(methyldichlorosilyl)propyl]imidazole hydrochloride - highly reactive monomer for synthesis of imidazole modified polysiloxanes. This compound was used as the substrate for the generation of new cyclooligosiloxanes with the imidazole group attached through the trimethylene bridge to a siloxane ring. The anionic ring-opening polymerization of these cyclics permits the controlled synthesis of polysiloxanes with imidazole groups pendant to the polymer chain.

Introduction

There has been considerable interest in the modification of polydiorganosiloxanes by the introduction of various organic functional groups pendant to the polymer chain to give the polymer specific physical properties or make it able to undergo particular chemical reactions(1-8). The attachment of a nitrogen heterocycle function, such as pyridine or imidazole, to the polysiloxane is of special interest as these groups are known to be efficient nucleophilic catalysts(9-14). Easily forming donor-acceptor complexes they may serve as catalyst supports(15-17) and may be used to fix other reactive groups to the polymer(18-19). The presence of nitrogen heterocycle base groups in the polysiloxane structure also modifies the solubility and surface properties of polysiloxane making it more hydrophilic(9). These groups could be exploited as well for the formation of charge on the polymer by quarternization, protonation or interaction with other Lewis acids. Charged polysiloxanes could be water soluble and could have interesting surface properties.

Hydrosilylation of an olefinic reagent bearing a functional group is the most commonly used reaction in the modification of polysiloxanes. The hydrosilane reactants are siloxane polymers containing SiH groups(20-23), cyclic siloxane oligomers bearing these groups(24,25) or monomeric silanes with an Si-H function and two hydrolyzable substituents at silicon(9,10). Substituted cyclic siloxanes or monomeric silanes are then polymerized to obtain the substituted polysiloxanes.

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Hydrosilylation of an olefinic species bearing a nitrogen base is often difficult. The reason is that the catalyst is poisoned by strong coordination of the base to the transition metal centre. In order to make this coordination weaker the reaction is carried out at temperatures as high as 130-150°C(9,26-28) but the reaction often proceeds slowly and leads to low yields of the hydrosilylation products(9,26). This may be particularly troublesome in the case of direct modification of polysiloxanes as prolonged heating of the SiH-containing polymer with a nitrogen base may result in cross-linking of the polymer(29,30). Since the substitution is only partial, considerable amount of the Si-H groups remains unreacted and polymer having both the base function and the Si-H function is unstable. In the modification of monomers also difficulties were encountered. Organodichlorosilanes, the cheapest and most commonly exploited Si-H reagents, cannot be directly used for the hydrosilylation in the presence of some heterocycle bases, such as imidazole, as they form strong crystalline complexes with the hydrosilanes(30). Thus, dialkoxysilanes are used in these reactions(9,10), requiring an additional step in synthesis, i.e. alkoxy group exchange for chlorine, leading to monomer of lower reactivity towards polysiloxane formation compared with corresponding dichlorosilanes.

We report here the efficient synthetic route which avoids these difficulties. The cheap monomer methyldichlorosilane hydrosilylates N-allylimidazole hydrochloride under mild condition, giving highly reactive difunctional silane monomer substituted with imidazole which is further transformed into imidazole modified polymer.

Experimental

Synthesis of N-[γ-(methyldichlorosilyl)propyl]imidazole hydrochloride 1

N-allylimidazole hydrochloride **2** was obtained with theoretical yield by passing gaseous HCl into a solution of N-allylimidazole in dried ether. White crystalline **2** precipitated from the solution. The solution of **2** (9.8 g) in 50 ml of methylene chloride and the Pt° Kerstedt catalyst (0.056 mmol) were kept at room temperature for 0.5 h in a 100 ml flask fitted with stirrer, condenser and dropping funnel. Then, 11.4 g of methyldichlorosilane was introduced. The reaction proceeded with exothermic effect and after 15 minutes the mixture became homogeneous. Stirring was continued for further 2 h. NMR analysis indicated that the reaction went to full conversion of the imidazole substrate into the hydrosilylation product. In another variant, the reaction was performed in toluene at 40°. The mixture changed its consistency as the reaction proceeded, but all the time it was heterogeneous. The hydrosilylation product was isolated with theoretical yield after its separation from the toluene layer. **1** appeared as a viscous liquid of consistency of honey. ^1H NMR ppm: 0.41 (3H, $C\underline{H}_3$), 0.74 (m, 2H, $SiC\underline{H}_2$), 1.84 (m, 2H, $SiCH_2C\underline{H}_2$), 4.15 (m, 2H, $C\underline{H}_2$-N), 7.12, 7.23, 9.28 (m, 3H, Imidazole), 15.0 (1H, $\underline{H}Cl$); ^{13}C NMR ppm: 4.3 (1C, $\underline{C}H_3$), 17.0 (1C, $Si\underline{C}H_2$), 23.0 (1C, $SiCH_2\underline{C}H_2$), 50.0 (1C, $\underline{C}H_2N$), 119.1, 120.6, 134.1 (3C, Im.); ^{29}Si NMR ppm: 32.1.

Synthesis of cyclic siloxanes: 1-[γ-(N-imidazolo)propyl]-1,3,3,5,5-pentamethylcyclotrisiloxane, 3 and 1-[γ-(N-imidazolo)propyl]-1,3,3,5,5,7,7-heptamethylcyclotetra-siloxane, 4

The solution of 12.5 g of **1** in 50 ml of dichloromethane was introduced slowly during 1.5 h to the vigorously stirred and cooled to 0-5°C solution of 1,1,3,3-tetramethyldisiloxane-1,3-diol (8.0 g) in 40 ml of triethylamine. The mixture was stirred for another 2 hrs and allowed to achieve the ambient temperature. The gas chromatography analysis with internal standard showed the formation of 92% of **3**. After filtration and extraction of the product remaining in precipitate with pentane distillation of combined filtrates gave 8.5 g of pure **3** (56%), b.p. 118/5 mmHg, ^{1}H NMR ppm: 0.07-0.1 (15H, $C\underline{H}_3$-Si), 0.45 (m, 2H, $SiC\underline{H}_2$), 1.73 (m, 2H, $SiCH_2C\underline{H}_2$), 3.85 (m, 2H, $C\underline{H}_2N$), 6.82, 6.96, 7.33 (m, 3H, Im.); ^{13}C NMR ppm: 0.5 (4C, $Si(\underline{C}H_3)_2$), -1.0 (1C, $CH_2Si\underline{C}H_3$), 13.5 (1C, $Si\underline{C}H_2$), 24.7 (1C, $SiCH_2\underline{C}H_2$), 49.2 (1C, $\underline{C}H_2N$), 118.5, 128.7, 136.7 (3C, Im.); ^{29}Si NMR ppm: -8.25 (2Si, $\underline{Si}(CH_3)_2$), -10.37 (1Si, $\underline{Si}CH_2$).

1,1,3,3,5,5-hexamethyltrisiloxane-1,5-diol (3,6 g) in 13 ml of TEA was added during 1h to vigorously mixed and cooled (0-5°C) **1** in 15 ml of dried methylene chloride. The mixture was stirred for another 2 h and allowed to achieve the room temperature. After the filtration and extraction procedure, the distillation gave 5.1 g of **4**, yield 87%, b.p. 125°C/1 mmHg, ^{1}H NMR ppm: 0.02-0.1 (21H, $SiC\underline{H}_3$), 0.42 (m, 2H, $SiC\underline{H}_2$), 1.76 (m, 2H, $SiCH_2C\underline{H}_2$), 3.84 (m, 2H, $C\underline{H}_2N$), 6.83, 6.97, 7.39 (m, 3H, Im.); ^{13}C NMR ppm: 0.5 (6C, $(\underline{C}H_3)_2Si$), -0.7 (1C, $\underline{C}H_3SiCH_2$), 13.6 (1C, $Si\underline{C}H_2$), 24.8 (1C, $SiCH_2\underline{C}H_2$), 49.3 (1C, $\underline{C}H_2N$), 118.5, 129.2, 136.9 (3C, Im.); ^{29}Si NMR ppm: -18.8 (3Si, $(CH_3)_2\underline{Si}$), -21.1 (1Si, $\underline{Si}CH_2$).

Anionic polymerization of 3

In a reactor fitted with magnetic stirrer purged with nitrogen 2.47 g of **3** in 2.3 ml of purified and freshly distilled THF was placed. By means of precision syringe 0.15 g of 2,6-di-t-butylpyridine, 150 μl of tridecane (G.C. standard) and finally 10^{-2} mol dm^{-3} of $BuMe_2SiOLi$ in THF was introduced to initiate the polymerization. Reaction was controlled by gas chromatography and was quenched by Me_3SiCl when the concentration of monomer dropped below 5% of its initial value. Solvent was evaporated and the polymer was heated in temperature 80°C/10^{-2} mmHg for 8 h. Poly-[(γ-N-imidazolopropyl)methylsiloxane-co-dimethylsiloxane], 2.2 g, $\overline{M}_n$ $2\cdot10^{4}$ was obtained. It was characterized by ^{1}H, ^{13}C and ^{29}Si NMR (Fig. 1). ^{1}H NMR ppm 0.04 (15H, $SiC\underline{H}_3$), 0.4 (b.m., 2H, $SiC\underline{H}_2$), 1.7 (b.m., 2H, $SiCH_2C\underline{H}_2$), 3.82 (b.m., 2H, $C\underline{H}_2N$), 6.83, 6.99, 7.39 (b.m., 3H, im.), ^{13}C NMR ppm 136.9, 129.3, 118.5 (3C, Im), 49.4 (1C, $\underline{C}H_2N$), 24.9 (1C, $SiCH_2\underline{C}H_2$), 14.1 (1C, $Si\underline{C}H_2$), 1.0 (2C, $(\underline{C}H_3)_2Si$), -0.1 (1C, $\underline{C}H_3SiCH_2$). ^{29}Si NMR ppm -21.5 (b.m. 2Si, $(CH_3)_2\underline{Si}$), -23.1 (b.m. 1Si, $CH_3\underline{Si}C\underline{H}_2$).

Hydrolytic polycondensation of 1

The solution of 6.3 g of **1** in 20 ml of methylene chloride was introduced during 1.5 h to the vigorously stirred 50 ml of 25% ammonia solution. The organic layer was separated.

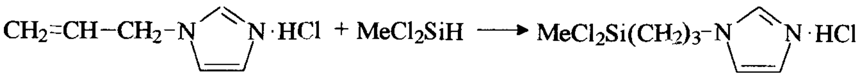
The polymer present in the water phase was regained by evaporation and extraction of residue with methylene chloride. The extract and the organic layer were combined, solvent evaporated and polymer dissolved in THF. ^{29}Si NMR disclosed considerable amount of cyclic oligomers in the polymer (about 40%). The polymer was purified on a silica gel column (silica gel 60x120 mesh, THF-heptane 1:1 v/v as eluent). Cyclics were separated by dissolving the polymer in methylene chloride and precipitation it in a large volume of pentane. 2.8 g. of the polymer was obtained, $\overline{M}_n$=2200, ^1H NMR ppm 0.05 (m, 3H, $SiC\underline{H}_3$), 0.4 (b.m., 2H, $SiC\underline{H}_2$), 1.5 (b.m., 2H, $SiCH_2C\underline{H}_2$), 3.85 (b.m., 2H, $CH_2C\underline{H}_2N$), 6.85, 7.0, 7.4 (b.m., 3H, Im). ^{13}C NMR ppm -0.8 (m, 1C, $SiCH_3$), 13.7 (m, 1C, $Si\underline{C}H_2$), 24.5 (m, 1C, $SiCH_2\underline{C}H_2$), 49.1 (1C, $\underline{C}H_2N$), 118.6, 128.3, 136.5 (m, 3C, Im). ^{29}Si NMR ppm -22.8 (b.m., 1Si).

Analyses

^{29}Si NMR spectra were made with a Bruker MSL-300 using INEPT technique. ^1H and ^{13}C NMR spectra were taken with a Bruker AC-200. All spectra were made in a $CDCl_3$ solution. Number average molecular weight was measured with a Knauer vapour pressure osmometer in CH_2Cl_2 at 26°C.

Results and discussions

Complexing of allylimidazole with hydrogen chloride blocks the base centre of the imidazole group, thus, preventing the formation of its complex with methyldichlorosilane interfering with the hydrosilylation process. At the same time the coordination of imidazole to the transition metal centre poisoning the catalyst is suppressed. The hydrosilylation goes smoothly under mild conditions leading to almost theoretical yield of the addition product. The process proceeds selectively to the anti-Markovnikov γ-addition isomer according to equation (1).

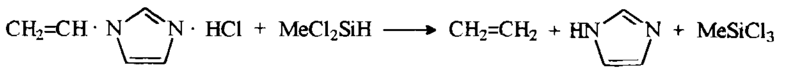


(1)

2 **1**

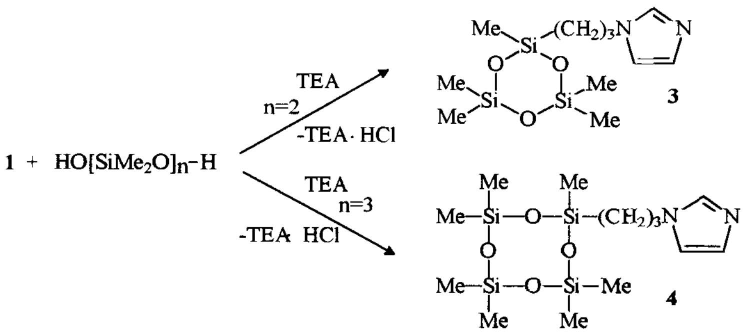
The yield of the β-adduct is not significant. It does not exceed 5% as judged from the inspection of the NMR spectra. The olefin isomerization process, which very often accompanies the hydrosilylation of allyl derivatives(31), does not occur in this case. Compound **1** appears as viscous honey like liquid. It is well soluble in methylene chloride and in some other chlorinated hydrocarbons.

Attempts to use this approach to hydrosilylation of N-vinylimidazole were not successful. The reaction of its hydrochloride proceeded slowly at room temperature while the process at elevated temperatures performed in the toluene suspension of the N-vinylimidazole complex led to a gaseous product and imidazole implying that β-elimination occurred under these conditions, equation (2).



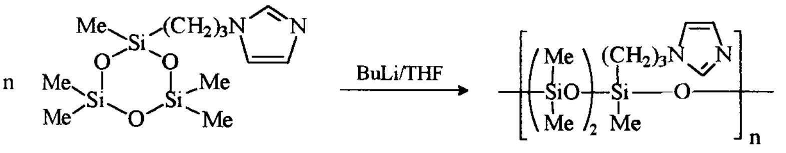
(2)

The protonated imidazole group in compound 1 is the electronegative substituent withdrawing electrons from silicon making 1 to be very reactive towards nucleophilic substitution at silicon. Heterofunctional polycondensation of 1 with silanols under catalysis with triethylamine (TEA) proceeds, as expected, smoothly and selectively. TEA acts here as a base receiving proton from silanol attacking the Si-Cl grouping(13). Homofunctional polycondensation cannot compete with heterofunctional one in this system. Slow addition of a solution of α,ω-siloxanodiol in TEA into a solution of 1 or reversely makes favourable conditions for the formation of cyclic condensation product according to reaction (3):



(3)

Compounds 3 and 4 are monomers for the synthesis of [γ-(N-imidazolo)propyl]methylsiloxane-dimethylsiloxane copolymers on the ring-opening homopolymerization routes, equation (4). The presence of dimethylsiloxane units in polysiloxanes modified in side groups may be highly desired as they permit the copolymer to retain precious properties of polydimethylsiloxane related to a high mobility of its siloxane chain. Monomer 3 is particularly suitable for the generation of these copolymers. Due to ring strain its anionic polymerization may occur in a selective way with little chain redistribution and back biting. Thus, if quenched in a proper moment, it leads to a high yield of the copolymer with low content of cyclic oligomers. Imidazole groups in the copolymer obtained on this route are evenly distributed along the copolymer chain and between the copolymer chains. The NMR spectra of the copolymer are shown on Figure 1.



(4)

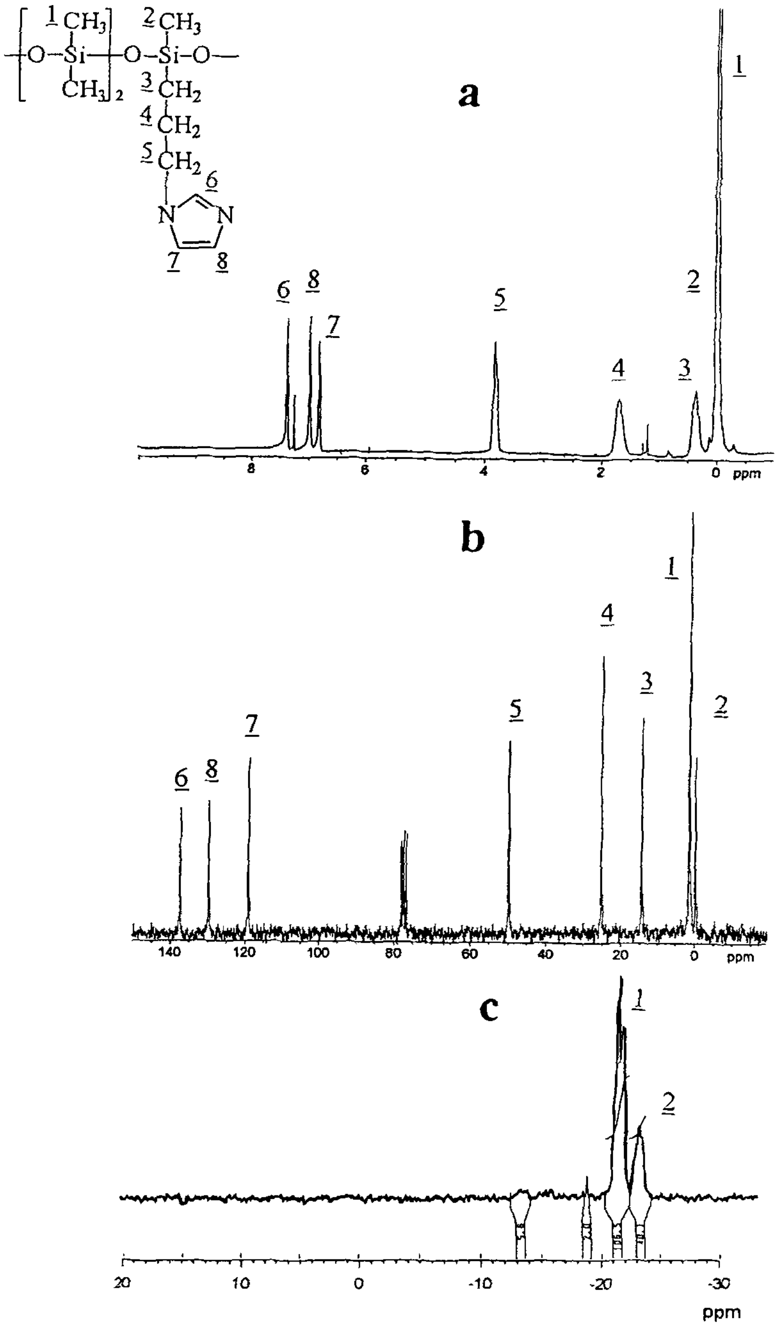
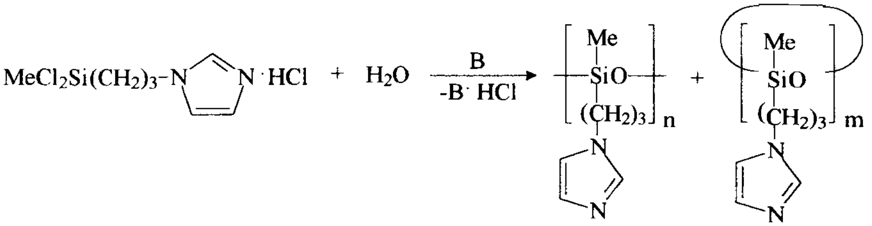


Figure 1. NMR spectra of [γ-(N-imidazolo)propyl]methylsiloxane-co-dimethylsiloxane obtained by anionic polymerization of **3**: **a** ^{1}H NMR, **b** ^{13}C NMR, **c** ^{29}Si NMR.

Serious problem in the polymerization of monomers bearing basic groups such as imidazole is association with water which decreases molecular weight producing end groups. Classical method of the water removal exploiting metal hydrides or alkali metal mirrors cannot be used for the purification of reactive monomers such as **3**. Thus **3** was purified only by distillation. A small amount of 1,4-di-t-butylpyridine was introduced to the polymerization system to decrease the activity of traces of water(33). This procedure was proved to be efficient in the anionic polymerization of some cyclic siloxanes(34). The polymerization was quenched at about 95-97% of the monomer conversion. Thus, the copolymer contained certain amount of monomer which was removed by heating of the polymer in vacuum. Usual procedure of the separation of cyclics from linear polysiloxanes, i.e. precipitation in methanol cannot be used here, as the copolymer itself is well soluble in methanol.

Homopolymers, i.e. poly[γ-(N-imidazolo)propyl]methylsiloxane, were obtained by hydrolytic polycondensation of **1** according to equation (5).



(5)

Reaction leads to considerable amounts of cyclic oligomers, mostly tetramer, which were separated from the linear polymer fraction by precipitating the polymer from methylene solution with an excess of pentane.

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