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Synthesis of polymethylsiloxane molecular brushes

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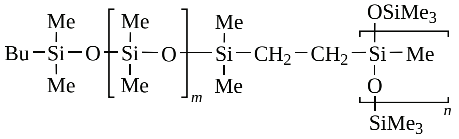
Dense purely methylsiloxane molecular brushes with high molecular masses were obtained by the 'grafting to' method. Vinyl groups of poly(vinyldimethylsiloxy)methylsiloxane were converted into (chlorodimethylsilyl)ethyl ones whose active chlorine atoms were replaced by monofunctional dimethylsiloxane oligomers having OLi terminal group to arrange side arms of the product. The molecular brushes thus prepared were characterized using physicochemical methods of analysis.



$$\mathrm{Bu{-}\underset{Me}{\overset{Me}{Si}}{-}O{-}\left[\underset{Me}{\overset{Me}{Si}}{-}O\right]_m{-}\underset{Me}{\overset{Me}{Si}}{-}CH_2{-}CH_2{-}\left[\underset{\underset{SiMe_3}{O}}{\overset{OSiMe_3}{Si}}{-}Me\right]_n}$$

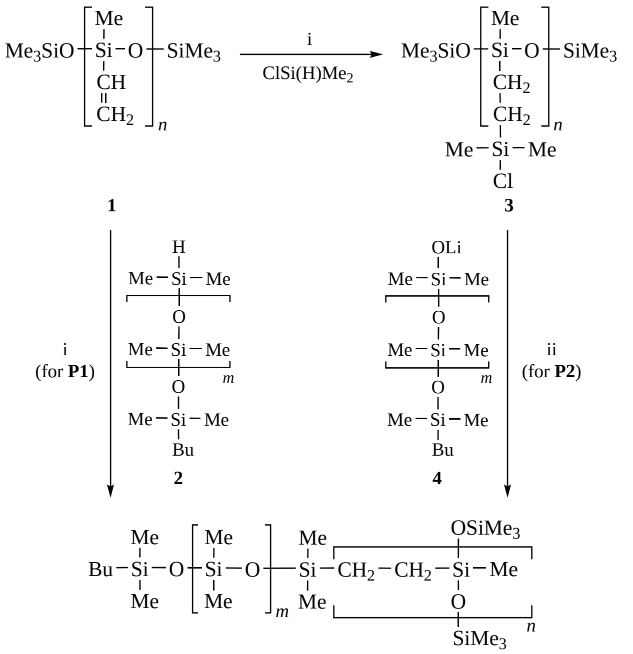
Keywords: polysiloxanes, molecular brushes, hydrosilylation, 'grafting to' method, polyfunctional matrix.

Polymethylsiloxane polymers represent a well-studied and widely used class of polymers with a set of practically valuable characteristics. At the same time, the architecture of the macromolecule gives the polymer a number of new properties that determine the range of applications for each specific type of structures. At present, much attention is being paid to polymers with dense macromolecule structures, in which their properties approach the ones of solid particles and which were distinguished into a separate class of 'macromolecules-particles'.[1] Such objects include dendrimers, hyperbranched polymers, nanogels, multi-arm stars and dense molecular brushes also known as 'bottle-brushes'. The structure, and hence, properties of molecular brushes can vary considerably depending on the grafting density of the side chains, as well as the length and flexibility of the side and main chains. The specific features of these structures provide a material with a number of unusual practically valuable properties, primarily for application as components of functional materials.[2–5] The most interesting are dense 'bottle-brush' structures with a lateral arm at each unit of the main chain, which leads to an expanded comb-like conformation due to steric repulsion of tightly grafted side chains[6–7] determining the specific rheological properties of such structures.

To obtain macromolecule particles with specific parameters, it is necessary to be able to finely tune the structure of the 'brush' during its synthesis. To date, three approaches to molecular brushes are known, *viz*., 'grafting through', 'grafting to' and 'grafting from'. Each of them has its own advantages and drawbacks. The term emphasizes the direction in which the grafted chains are formed. Aside from general problems, the preparation of polydimethylsiloxane brushes also encounters additional problems due to the high sensitivity of the siloxane bond to ionic reagents, without which it is rather difficult to synthesize comb-like polymers, and due to the high liability of a flexible siloxane chain to undergo cyclization during the synthesis. Siloxane brushes with a methylsilsesquioxane main chain and dimethylsiloxane side arms were obtained in very few studies and were explored insufficiently. Irregular and unstable siloxane brushes were obtained by silylation of a hydro-functional methylsiloxane chain[8] and more efficiently by addition of a monofunctional silanol to a hydromethylsiloxane linear matrix by the Piers–Rubinsztajn reaction.[9] However, the difficulty of obtaining a defect-free high-molecular hydride methylsiloxane is a challenge in this case.

A drawback in the preparation of methylsiloxane molecular brushes by polycondensation of macromonomers[10,11] and by grafting of arms to a sodium oxymethylsiloxane matrix[12] was that the main chain had rather low molecular mass. Taking into account that some properties of polymers, in particular rheological ones, are especially pronounced at high molecular masses, the development of a method for synthesizing comb-like polysiloxanes with high molecular masses appears to be a relevant goal. In the case of siloxane structures, grafting of monofunctional dimethylsiloxane oligomers onto a polyfunctional matrix appeared to be the most promising method for the preparation of molecular brushes. In this case, the key point is the presence of a high-molecular mass polyfunctional linear matrix of regular structure with reactive groups at each unit. Moreover, the addition reaction should not be accompanied by side processes of the macromolecule's siloxane skeleton cleavage.

In this work, we initially tested the popular in organosilicon chemistry hydrosilylation reaction of available high-molecular mass polymethylvinylsiloxane **1** as the polyfunctional linear matrix with hydrosilane oligomer **2** (Scheme 1, preparation of **P1**). Although this one-step synthesis seemed to be the optimal, in fact the reaction gave a crosslinked product. It could be assumed that with such a highly functional matrix, the formation of a small percentage of defective units occurred due to possible exchange of Si–H and Si–CH=CH_2 (*cf*. ref. 13) resulting in the cross-linking of chains. Altering the medium polarity and type of the platinum catalyst failed to give a soluble polymer. In view of this, a scheme was improved, namely, vinyl groups in starting



P1 (M_n = 390000)
or
P2 ($M_n = 1.5 \times 10^6$)

Scheme 1 *Reagents and conditions*: i, [Pt] (Karstedt's catalyst), toluene, room temperature, 24 h; ii, hexane, room temperature, 3 h.

material **1** were transformed into chloro(dimethyl)silylethyl ones of intermediate **3** (see Scheme 1).

In this case, the silylation of polyvinylmethylsiloxane **1** with low molecular weight $ClSi(H)Me_2$ occurred without violation of the main chain regularity. It is known[13] that the presence of a stronger electron-withdrawing substituent at the silicon atom with a Si–H bond increases the hydrosilylation rate, and it may be assumed that in this case the side processes of exchange of functional groups do not occur so readily. The completion of the formation of intermediate **3** was confirmed by the absence of signals of vinyl protons (δ = 6.0 ppm) in the ^{1}H NMR spectrum of the reaction mixture (see Online Supplementary Materials, Figure S1). Using this polyfunctional matrix **3**, a scheme for the synthesis of a dense comb-shaped polymethylsiloxane was finalized. The side branches were grafted by the reaction of chlorosilyl groups in the synthesized polyfunctional matrix with lithiumoxy functional oligomer **4**. Siloxide **4** was obtained by the BuLi induced non-equilibrium polymerization of hexamethylcyclotrisiloxane, with the number of dimethylsiloxane units in an arm being n ~ 15 (see Scheme 1, preparation of **P2**).

Side arms were grafted using polyfunctional matrices with molecular masses of 70,000 kD (**P1**) and 300,000 kD (**P2**). According to GPC data, the resulting polymethylsiloxanes with a 'bottle-brush' structure had a rather wide monomodal molecular mass distribution. ^{1}H NMR and ^{29}Si NMR data showed that the conversion of chlorosilyl groups was ~80% (see Online Supplementary Materials, Figure S2). The ^{1}H NMR spectrum of material **P2** contained minor signals of ethoxy groups at 1.15 and 3.6 ppm. Such groups could be formed in the course of reprecipitation with ethanol from a hexane solution followed by evacuation at 40 °C. This may indicate the incomplete conversion of chlorosilyl groups in the main chain during the grafting, which amounted to ~20% (^{1}H NMR data).

Table 1 Molecular mass characteristics of brush-like polymers determined by dynamic light scattering.

Parameter	**P1**	**P2**
M_{peak} of the original linear matrix (GPC)	0.07×10^6	0.3×10^6
M_n	0.39×10^6	1.5×10^6
M_w	0.68×10^6	4.0×10^6
M_p	0.42×10^6	1.6×10^6
M_w/M_n	1.8	2.6
Rg (nm)	30	81.1

The molecular mass characteristics of polymers **P1** and **P2** derived from dynamic light scattering are shown in Table 1.

To conclude, the silylation of a vinyl-functional methylsiloxane chain with a mono-hydro functional polydimethylsiloxane oligomer does provide preparation of brush-like polymer. An alternative grafting comprising reaction between chlorodimethylsilylethyl and lithium siloxide reactants affords molecular brushes containing ~80% of the target units, the rest being the defective ones.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.09.037.

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