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Mendeleev Commun., 2017, **27**, 570–571

Mendeleev
Communications

The Suzuki modification of functional polydimethylsiloxanes

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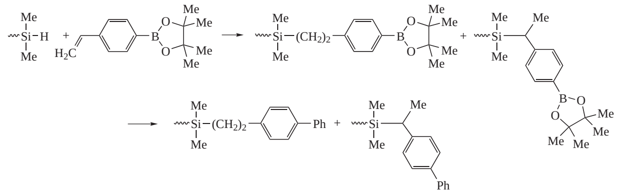
DOI: 10.1016/j.mencom.2017.11.010

Polydimethylsiloxanes with Si–H bond were coupled with 4-boronated styrene to produce α- and β-regioisomers, whose organoboron moiety was subjected to Suzuki reaction with bromobenzene to afford promising biphenyl-capped polysiloxanes.

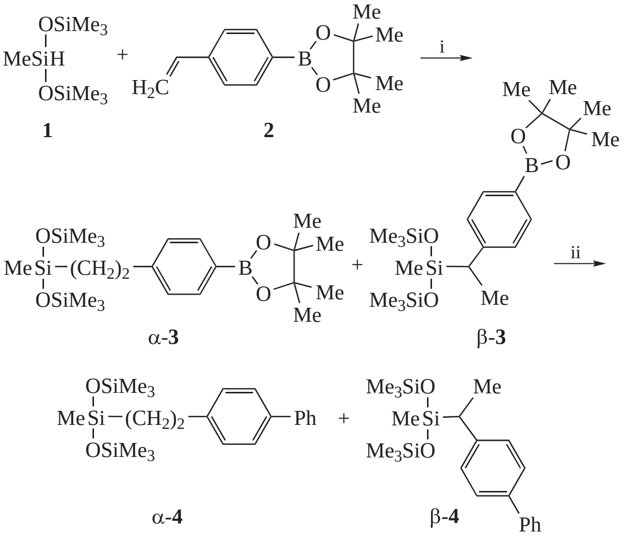


Among different classes of polymers, polydimethylsiloxanes (PDMS) have received a great deal of attention due to their wide operating temperature range, chemical and thermal stability, fire resistance, high gas permeability and biocompatibility. They find application as lubricating oils, silicone resins, hydrophobic and foam control agents in electronics, cosmetology, pharmaceutical, paper and fuel industry.[1,2] Nevertheless, during the past few decades some new approaches of PDMS modification have been developed, which allow one to adjust some of silicone propeties to specific needs as surfactants,[3] biodegradable block-copolymers,[4] copolymers with low surface energy[5] and polymers with non-linear optical properties.[6,7] There is also growing interest to PDMS as a matrix for drug delivery systems[8,9] and fluorescent bioimaging.[10] Also, some attempts were made to increase cohesive forces of polydimethylsiloxanes by introduction of terminal bulk groups.[11]

Currently, a number of approaches towards PDMS synthesis and modification with different substituents are known.[12] However, some problems can arise if the modifier has a complex alicyclic or heterocyclic structure, or if specific functional groups are present. To avoid this limitation, Suzuki cross-coupling reaction was successfully employed.[13,14] Until now, a few examples of using the Suzuki reaction have been reported for introduction of aromatic units into carbosilane dendrimers structure,[15] or functionalization thereof with aromatic ‘endcapping’ groups.[16] However, almost none of the publications concerned applicability of the Suzuki reaction in the presence of PDMS substrates, except di- or trisiloxane derivatives.[17,18]

In this study, we report on new two-step strategy of PDMS functionalization. The first step involves the introduction of arylborolane functional group into polysiloxanes chain. Secondly, the Suzuki cross-coupling is carried out between arylborolane functionalized polysiloxanes and an aryl halide. The cornerstone of this method is fairly stringent for siloxane bonds conditions of the Suzuki reaction (Pd-catalyst, base and microwave irradiation), which could lead to destructions or crosslinking of Si–O–Si fragments of PDMS during the reaction.

Starting from model monofunctional 1,1,1,3,5,5,5-heptamethyltrisiloxane **1** we synthesized borolane derivative α,β-**3** using hydrosilylation reaction between **1** and boronated styrene **2** (Scheme 1). Acording to NMR data, a mixture of α- and β-regioisomers of **3** in 70 : 30 ratio is thereby formed.[†] The Suzuki reaction between α,β-**3** and bromobenzene was then performed under typical conditions [Pd(PPh_3)$_4$, Na_2CO_3 2 M aqueous solution, toluene–water). The reaction mixture was heated to reflux using microwave (MW) irradiation (see Scheme 1).[‡] The completeness of the reaction was monitored by GPC (Figure 1), which also revealed shift of λ_{max} from 234 nm (reactant **3**) to 276 nm (product **4**) as the instrument was equipped with diode array as a detector (*cf.* ref. 19).



Scheme 1 *Reagents and conditions:* i, [Pt], toluene, 50 °C; ii, PhBr, Pd(PPh_3)$_4$, Na_2CO_3, toluene–water, MW.

[†] *Hydrosilylation (general procedure).* The Karsted’s catalyst (0.1 vol%) was added to a stirred 20% solution of siloxane **1**, **5** or **8** in dry dioxane under argon atmosphere and compound **2** (1 equiv. per each Si–H group). The mixture was heated at 50 °C for 6 h. After the reaction was complete, the mixture was passed through a thin layer of silica, and the solvent was evaporated. The products **3**, **6** or **9** were dried *in vacuo*.

[‡] *The Suzuki reaction (general procedure).* A mixture of silyloxy styryl borolane (1 equiv.), bromobenzene (2.5 equiv.), 2 M aq. Na_2CO_3 (5 equiv.) and toluene (10 ml) was purged with argon. Then, Pd(PPh_3)$_4$ (5 mol%) was added and purging with argon was continued for 10 min. The reaction vessel was sealed and irradiated in a MW reactor (110 °C, 150 W) for 2–3 h. Then the mixture was diluted with toluene, the organic phase was washed with brine and water. The solution was dried (Na_2SO_4) and the solvent was evaporated. The products **4**, **7**, **10** were obtained as colourless liquids.

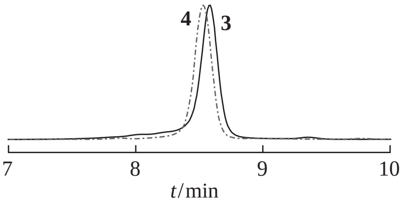
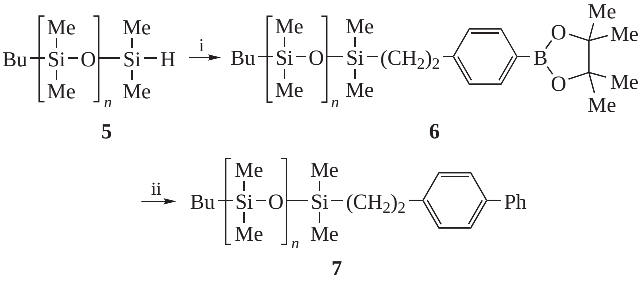


Figure 1 GPC chromatograms of reactant **3** and product **4**.

Further, we extended the developed strategy onto monofunctional PDMS with M_n = 900, which was prepared by BuLi-initiated anionic living polymerization of octamethylcyclotetrasiloxane. Capping with dimethylchlorosilane allowed us to obtain monofunctional polysiloxane **5** with Si–H group. The hydrosilylation of **2** with **5** (Scheme 2)[†] leads to product **6** (α,β-mixture, 60 : 40). The following Suzuki coupling with bromobenzene affords substance **7**.[‡] Similarly to model compounds **3** and **4**, polymers **6** and **7** also differ in their retention times during GPC analysis [Figure 2(*a*)], although the difference is smaller.



Scheme 2 *Reagents and conditions:* i, **2**, [Pt], toluene, 50 °C; ii, PhBr, $Pd(PPh_3)_4$, Na_2CO_3, toluene–water, MW.

The absorption maximum of product **7** is shifted bathochromically by *ca.* 20 nm as compared to reactant **6** (see Online Supplementary Materials). In this case, the value of λ_{max} is smaller than that for product **4**, apparently, because of hirdered rotation around Ar–Ar bond caused by polymer chain.

We also subjected PDMS **8** (M_n = 4900) with two telehelic Si–H groups to the developed transformations (Scheme 3).[†,‡] In this case, hydrosilylation can afford three types of regioisomers, αα, αβ and ββ in the statistic ratio of 1 : 2 : 1. NMR spectra confirmed that αβ regioisomers predominate over αα and ββ ones.

The profiles of GPC curves of reactant **9** and product **10** [Figure 2(*b*)] did not significantly change, as in the previous case, what indirectly proves the stability of siloxane chain towards the Suzuki conditions. The absorption maximum of product **10** also shifted bathochromically as compared with reactant **9**, exactly as in the case of compound **7** (see Online Supplementary Materials).

In conclusion, 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-styrene is a convenient reagent to introduce an aryl borolane function into the siloxane chain by the hydrosilylation reaction, giving α,β-isomeric mixture. Further Suzuki coupling with bromobenzene proceeds completely. The siloxane chain was proved intact under the Suzuki reaction conditions. The proposed strategy reveals new opportunities of polysiloxane functionalization to access biaryl-capped polymers.

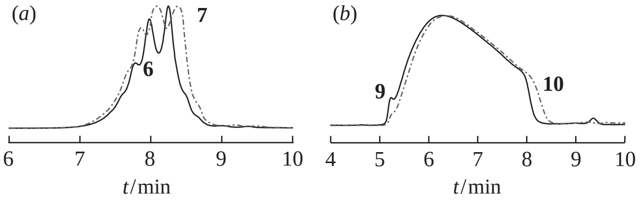
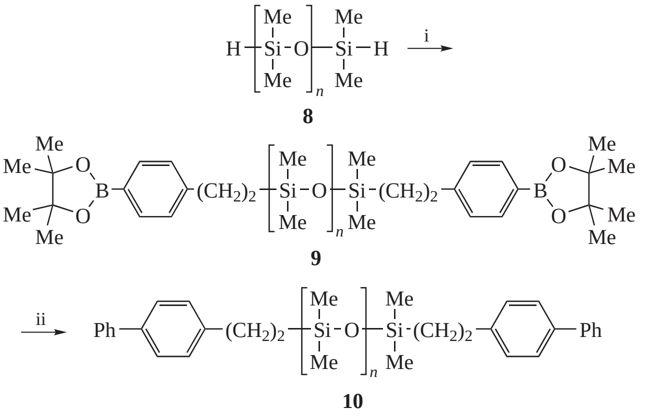


Figure 2 GPC chromatograms of (*a*) reactant **6** and product **7** and (*b*) reactant **9** and product **10**.



Scheme 3 *Reagents and conditions:* i, **2**, [Pt], toluene, 50 °C; ii, PhBr, [Pd], Na_2CO_3, toluene–water, MW.

This work was supported by the Russian Foundation for Basic Research (project no. 17-03-01037A).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2017.11.010.

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Received: 13th February 2017; Com. 17/5175