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Polydimethylsiloxanes with bulk end groups: synthesis and properties

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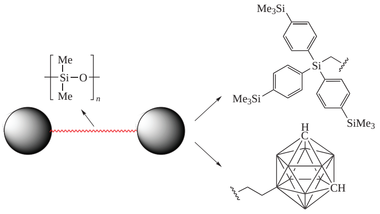
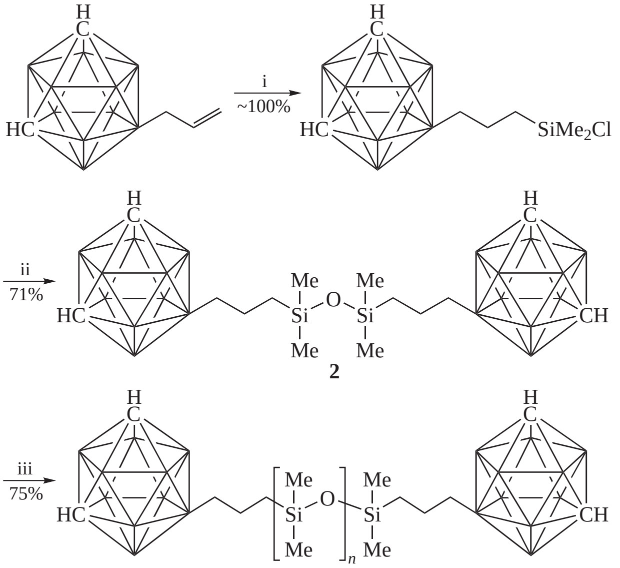
New polydimethylsiloxanes containing bulk terminal groups such as carboranyl and tris(4-trimethylsilylphenyl)silyl moieties have been synthesized and their thermophysical and rheological properties have been examined.



Polydimethylsiloxanes (PDMS) find broad application[1–5] due to their valuable properties such as low glass transition temperatures, heat stability, water resistance, resistance to oxidation, stability at high and low temperatures, great molecular flexibility, high impact resistance, good electrical insulation, oxygen permeability, biocompatibility, low surface energy, and relative insensitivity to UV light. The only their disadvantage is that they do not form strong fibers and films because of low cohesive forces.

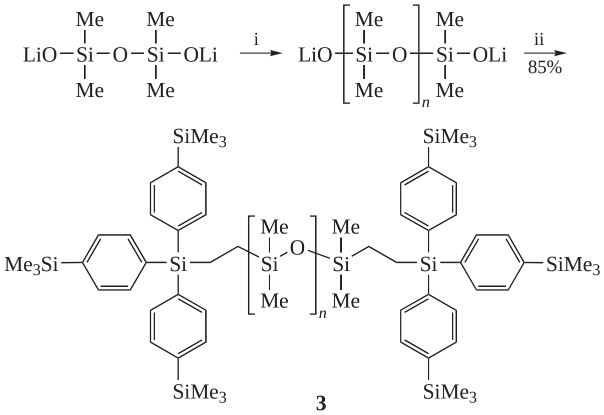
The aim of our study was to increase cohesive forces of polydimethylsiloxanes by introduction of terminal bulk groups. Here, we report preparation and characterization of new PDMS containing bulky carboranyl[6] and tris(4-trimethylsilylphenyl)silyl[7] at *termini* of the chain.

The carboranyl-substituted PDMS **1** was synthesized by equilibrium polymerization of octamethylcyclotetrasiloxane with 1,3-bis-[3-(*m*-carboran-9-yl)propyl]tetramethyldisiloxane **2** in the presence of CF_3SO_3H as a catalyst (Scheme 1). Carboranyldisiloxane **2**, in turn, was obtained in two steps.



Scheme 1 *Reagents and conditions*: i, Me_2SiClH, the Karstedt's [Pt] catalyst; ii, H_2O; iii, cyclo-$(OSiMe_2)_4$, CF_3SO_3H.

The preparation of polydimethylsiloxane containing tris(4-trimethylsilylphenyl)silyl terminal groups (**3**) was performed by anionic polymerization of hexamethylcyclotrisiloxane in the presence of dilithium tetramethyldisiloxandiolate with subsequent *in situ* treatment of the living polymer with 1-(chlorodimethylsilyl)-2-[tris(4-trimethylsilylphenyl)silyl]ethane (Scheme 2).

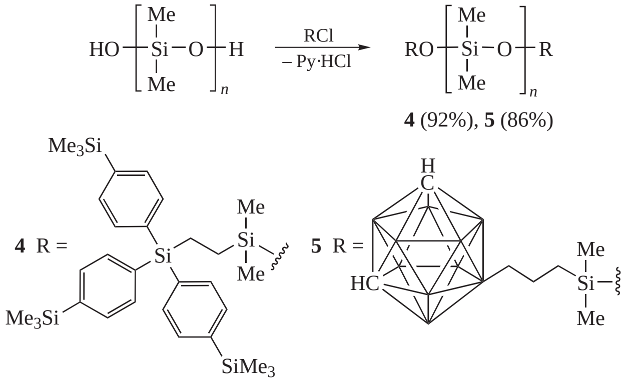


Scheme 2 *Reagents and conditions*: i, cyclo-$(OSiMe_2)_3$; ii, $(4\text{-}Me_3SiC_6H_4)_3$-$SiCH_2CH_2SiMe_2Cl$.

The structures of new compounds have been confirmed by GPC, NMR, IR spectroscopy and elemental analysis.

To study the effect of bulk end groups on properties of PDMS with higher molecular masses, two other polymers (**4**, MM = = 34000, p = 1.64; and **5**, MM = 35000, p = 1.70) containing the same bulk end groups were prepared by heterofunctional condensation of PDMS bearing OH end groups (MM = 33000, p = 1.6) with corresponding bulky chlorosilanes (Scheme 3).

The PMDS **1** and **3** containing two different types of bulk terminal groups have close values of molecular masses (MM = 7000 and 6900), while as can be expected polydispersity index of polymer **1** prepared by cationic polymerization (p = 1.51) is higher



Scheme 3

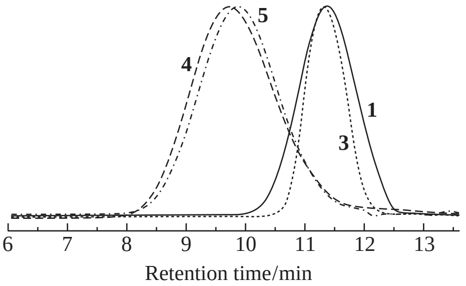


Figure 1 GPC data for polymers **1**, **3**, **4** and **5**.

than that of polymer **3** (p = 1.21) obtained by anionic polymerization (Figure 1).

Differential scanning calorimetry (DSC) study of polymers **1** and **3** of low molecular masses (MM = 7000 and 6900) has shown that end-capping of polymer chain with their bulky groups differently affects thermophysical properties of PDMS (Figure 2). DSC curve obtained on heating for non-capped PDMS (curve *1*) demonstrates full set of thermal transitions typical of low-molecular-weight polydimethylsiloxanes: glass transition at –123 °C, a cold crystallization exotherm at –82 °C and a bimodal endotherm at –45 °C corresponding to the melting of a crystalline phase. End-capping (curves *2* and *3*) leads to suppression of the crystallization of PDMS. Glass transition temperature of **1** increases in comparison with PDMS, its value is –117 °C (curve *2*), whereas for **3** a glass transition temperature remains almost unchanged (–122 °C, curve *3*). A reversible endotherm appears at –10 °C (4 J g^{-1}) on DSC curve for **3** in addition to a glass transition.

We can conclude that PDMS chain and carbornyl end groups form a common amorphous phase in the case of polymer **1** that leads to an increase in glass transition temperature. The tris(4-trimethylsilylphenyl)silyl end groups form a separate crystalline phase in polymer **3** due to steric hindrance. However, in comparison with melting point of (4-$Me_3SiC_6H_4)_3SiCH_2CH_2SiMe_2Cl$ (158 °C) this crystalline phase melts at significantly lower temperature (–10 °C).

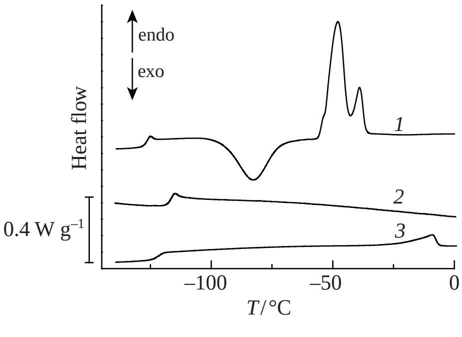


Figure 2 DSC curves for (*1*) pure PDMS (MM = 5000), (*2*) **1** and (*3*) **3**. Heating rate 10 K min^{-1}.

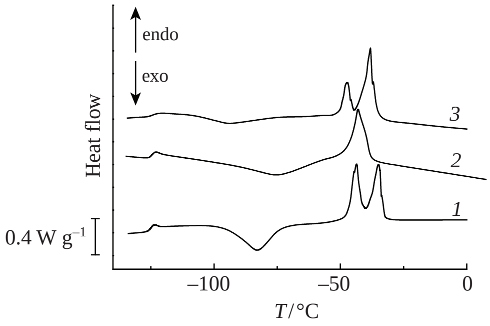


Figure 3 DSC curves for (*1*) pure PDMS (MM = 33 000), (*2*) **4** and (*3*) **5**. Heating rate 10 K min^{-1}.

DSC study of PDMS **4** and **5** has revealed that the used bulky end groups have no effect on thermophysical properties of the polymers upon increase in weight to 34 000–35 000 (Figure 3). The polymers demonstrate thermal transitions specific for PDMS. However, it should be noted that introduction of tris(4-trimethylsilylphenyl)silyl end groups to polymer **4** makes difficult the formation of crystalline phase of PDMS. In this case the cold crystallization proceeds at higher temperatures, as compared to individual PDMS, and the heat of cold crystallization is equal to the heat of melting (23 J g^{-1}), therefore the melting peak is monomodal. One can conclude that in case of individual PDMS and polymer **5** the melting peaks are bimodal caused by the fact that PDMS partially crystallizes in the course of cooling and the high-temperature peak on DSC curve belongs to melting of PDMS crystals created under such conditions. Introduction of carboranyl end groups to polymer **5** works both ways (see Figure 3, curve *3*). On the one hand, the tendency of PDMS to crystallization increases, which is evidences by essentially large area of high-temperature melting peak and the reduced temperature of exothermic peak of cold crystallization. On the other hand, the temperatures of endothermic melting peaks are displaced to the area of lower temperatures in comparison with initial PDMS (see Figure 3, curve *1*). This is in a good agreement with the data obtained for low-molecular polymer **1**, when the large carboranyl group forms with PDMS a common amorphous phase with higher glass temperatures as compared to PDMS. When PDMS weight grows up to 34 000–35 000 the bulky end groups have no effect on glass temperature.

Flow curves of the polymers under study are presented in Figure 4. Viscosity (η) of **1**, **3**, **4**, **5** does not depend on shear rate ($\dot{\gamma}$). The polymers obtained are Newtonian liquids. Polymer **1** containing carboranyl groups demonstrates lower values of η than polymer **3** with tris(4-trimethylsilylphenyl)silyl end groups (curves *1* and *2*). Polymers **4** and **5** possessing higher molecular masses exhibit higher value of viscosity (curves *3* and *4*).

Viscous flow energy values E_a obtained from temperature dependences of viscosity (see Online Supplementary Materials) are 18, 27, 18 and 15 kJ mol^{-1} for **1**, **3**, **4** and **5**, respectively. As can be seen, both the type of the end groups and their molar concentration affect the value of E_a.

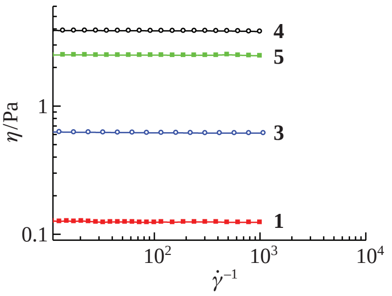


Figure 4 Flow curves of **1**, **3**, **4** and **5** obtained at room temperature.

In general, an introduction of bulk terminal groups to a polymeric chain increases the sizes of chain segment and causes increase in E_a.[8] Polymers with carboranyl end groups (**1** and **5**) have lower values of viscosity than polymers **3** and **4** with tris(4-trimethylsilylphenyl)silyl end groups. Thus, the presence of a small amount of carboranyl end groups has no effect on the chain segment value and, as a result, on the value of E_a.

In conclusion, the presence of carboranyl and tris(4-trimethylsilylphenyl)silyl end groups in PDMS suppresses the crystallization in cases of low molecular masses. In the case of tris(4-trimethylsilylphenyl)silyl terminal groups the higher effect on thermophysical and rheological properties has been observed, especially for low molecular polymer **3**.

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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.2016.11.022.

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