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Synthesis and rheological properties of star-shaped polydimethylsiloxanes based on carbosilane dendrimers

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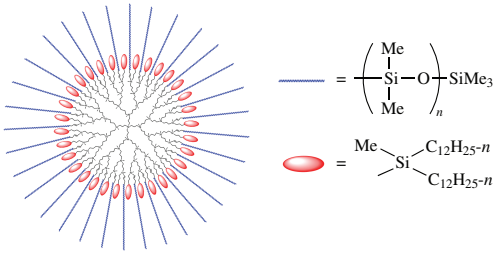
The rheological measurements of star-shaped polydimethylsiloxanes with 8, 32 and 128 arms synthesized from carbosilane dendrimers of 2nd, 4th and 6th generations, respectively, revealed the Newtonian character of flow in the systems with 8 or 32 arms and a pseudoplastic character of flow in the 128-arm one. The activation energy of viscous flow was found to be 18.5 kJ mol^{-1} for all the objects.



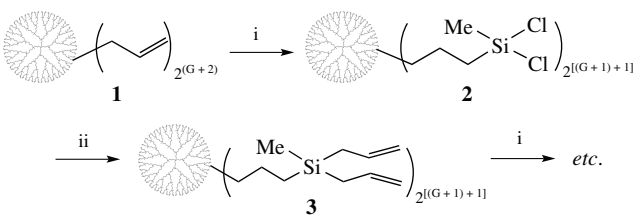
Star-shaped polymers possess all the properties inherent in classical polymeric objects, and differ in lower viscosities of melts and solutions in comparison with linear ones with similar molecular masses. Multi-armed star-shaped polymeric systems demonstrated a qualitative change in properties, namely, a transition to the properties of a macromolecular particle that differ significantly from ordinary polymer characteristics.

The specifics of multi-armed star-shaped structures is that the system consists of a dense central core, a middle zone close to a semi-diluted solution, and an outer layer where the polymer arms would acquire free conformations.[1–4] Star-shaped polymers with a number of arms $f \leqslant 32$ behave as classical liquids at all arm lengths. With an increase in f parameter, it is assumed that at a certain critical number of arms and, accordingly, structure density, the properties jump from classical to anomalous close to those of a solid sphere. Available data show that if the number of arms is small ($f < 20$), the coefficients in the Mark–Kuhn–Houwink equation are $\alpha = 0.6–0.7$,[5] which corresponds to the coil-like conformation of the polymer. At $f > 100$, α value approaches 0.06, which conforms to hard spherical objects. Melts of multi-armed stars also differ from classical polymer melts and have a well-ordered structure similar to that of dense colloidal systems.[6] Multi-armed system was also described as a model of a soft 'hybrid' sphere that includes a polymer (arms) and colloid (core) parts with non-uniform density of links.[7] The structural complexity and, accordingly, the dynamics of the molecule manifest themselves as a combination of polymeric and colloidal behaviours. A theoretical description of the relaxation process of star-shaped polymers was suggested,[8–10] according to which two factors are of decisive importance: (*1*) the molecular mass of the polymer involved in the entanglement process and (*2*) the friction coefficient of a monomeric unit, while the rheology of dendrimers and hyperbranched polymers where Newtonian behaviour was retained even at high molecular masses.[11,12] The modern common views on star-shaped polymers were formulated,[13] when their properties were intermediate between linear polymers and solid spheres, and were characterized by two separate relaxation processes, arm relaxation, which did not depend on the number of arms, and structural relaxation, or center of mass relaxation, that was a function of the number of arms and their size.

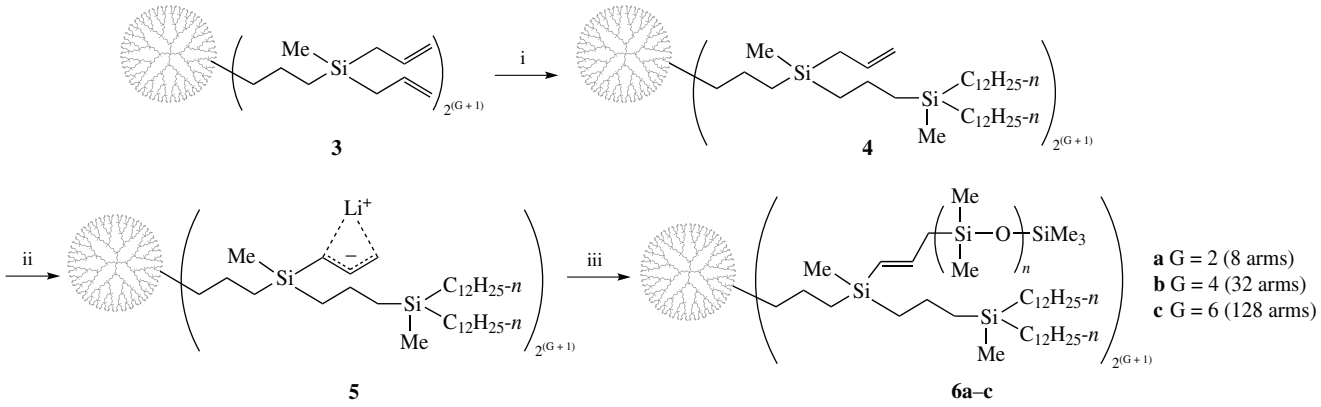
Previous studies of such objects in solutions revealed that with an increase in the number of arms, star-shaped macromolecules would undergo self-organization into a block up to the formation of a column-type mesophase.[14] This work was aimed at a rheological study of a number of polydimethylsiloxane multi-armed systems with 2nd, 4th and 6th generation carbosilane dendrimers as a center of branching.

The divergence (core-first) method is most efficient for synthesizing multi-armed star-shaped polydimethylsiloxanes with regular structure, in which the arms are grown from a multifunctional initiating nucleus by ionic polymerization.[15,16] The other options to perform the synthesis, namely, convergent (arm-first), *i.e.* the addition of monofunctional live linear polymers to the multifunctional center[17,18] or linking the terminal groups of monofunctional oligomers,[19] suffer significant drawbacks: in the first case, it is impossible to obtain truly multi-armed systems, and in the second case, the reaction product is statistical by nature.

To obtain star-like polydimethylsiloxane structures, polyfunctional lithium initiators of anionic polymerization were synthesized from 2nd, 4th and 6th generation carbosilane dendrimers. The choice of the counter-ion was determined by the fact that only the lithium active center allows non-equilibrium



Scheme 1 *Reagents and conditions*: i, $Cl_2Si(Me)H$, [Pt] (the Karstedt's catalyst), hexane, toluene; ii, AllMgCl, THF. G and G + 1 are the generation numbers of the starting and obtained dendrimers, respectively.



Scheme 2 *Reagents and conditions*: i, $(n\text{-}C_{12}H_{25})_2Si(Me)H$, [Pt] (the Karstedt's catalyst), toluene; ii, BuLi, TMEDA, hexane; iii, *cyclo*-$(OSiMe_2)_3$, THF, then $ClSiMe_3$.

polymerization of cyclotrisiloxane without a chain transfer reaction to be performed, which provides multi-armed structures on the basis of the core-first method.

The starting carbosilane dendrimers with diallyl(methyl)silyl functional groups in the outer shell **3** were synthesized classically[20] *via* hydrosilylation of initial dendrimer **1** followed by the Grignard reactions of chloro dendrimers **2** (Scheme 1).

GPC data after purification of all the dendrimer generations synthesized showed that monomodal, narrowly dispersed products were obtained. Their structure were in good agreement with the ^{1}H NMR spectra [Online Supplementary Materials, Figure S1(*a*)].

The following transformations of carbosilane dendrimers with allyl functional shell into star-shaped polydimethylsiloxanes are outlined in Scheme 2. The possibility to obtain polyfunctional lithium dendritic compounds ensures creating an external hydrocarbon layer (see Scheme 2, compound **4**) in which the intermolecular aggregation of lithium atoms does not occur thus providing dissolution of these organolithium derivatives in organic solvents[21] [Figure S1(*b*)].

In earlier studies on the synthesis of such compounds,[22] the presence of double bonds in lithiated compounds was noted, so the possibility of their complete lithiation remained unclear. In view of this, the lithiation of the allyl group was simulated in a model monomeric system, namely, the reaction between allyl(trimethyl)silane and butyllithium in the presence of TMEDA. ^{1}H NMR spectroscopy of the reaction mixture confirmed the structure of the carbanion formed in the complex with TMEDA (Figure S2), which agrees with the mechanism of lithiation of allylsilanes.[23] Upon quenching the resulting lithium-containing compound with trimethylchlorosilane, the double bond migrated from α-position to the β one (signals at δ 5.5 and 6.1), which explains the preservation of unsaturated bonds upon complete formation of lithium centers, as follows from the number of trimethylsilyl groups added for blocking (Figure S3).

Therefore, the formation of dendrimer polylithium carbanion derivative **5** with a protective didodecylsilyl layer (see Scheme 2) was confirmed by the termination with trimethylsilyl groups. The growth of Si–Me signal intensity in ^{1}H NMR spectrum upon blocking compared with the starting reactant was the evidence for the formation of lithium carbanions (Figure S4).

A series of polylithium macroinitiators were obtained on 2nd, 4th and 6th generation dendrimers containing 8, 32 and 128 centers of anionic polymerization, respectively. Anionic polymerization of hexamethylcyclotrisiloxane using the initiators synthesized gave star-shaped polydimethylsiloxanes **6a–c** (see Scheme 2 and Figures S5–S7).

The density of compounds synthesized and its increase with an increase in the number of arms are manifested in a growing difference between the molecular masses measured by GPC and ^{1}H NMR spectroscopy, $M_{n(GPC)}/MW_{(NMR)}$. The presence of a known number of protons of didodecylsilyl groups of the branching center in the structure of the compounds makes it possible to calculate the average molecular mass of the macromolecule and the arm length from ^{1}H NMR spectral data. The data on the characteristics of obtained star-shaped polydimethylsiloxanes (PDMSs) (Table 1) show that the molecular mass $M_{n(GPC)}$, *viz.*, based on the macromolecule size in solution, practically does not change with an increase in the number of arms. However, the actual molecular mass $MW_{(NMR)}$ grows very strongly, and the $M_{n(GPC)}/MW_{(NMR)}$ ratio that characterizes the increasing structure density changes by an order of magnitude with an increase in f value. In this case, as mentioned above, the coefficient α in the Mark–Kuhn–Houwink equation, which is 0.6–0.7 for the coil-like polymer conformation, equals $\alpha = 0.06$ at $f > 100$, which characterizes multi-armed systems as rigid spherical objects. This explains the significant difference in the molecular masses obtained by different methods.

The difference in the properties of the PDMS stars with variation of the number of arms manifests itself in the rheological behaviour of samples. Star-shaped PDMS containing 8 arms is a transparent viscous liquid, while 32- and 128-armed ones are viscous white substances. It follows from the flow curves at 20 °C in viscosity (η)–shear rate (γ) coordinates when the polymer viscosity increases with the number of arms having the same length. Polymers containing 8 or 32 arms are Newtonian liquids (η does not depend on γ), whereas the polymer containing 128 arms is a pseudoplastic liquid (η decreases with increasing γ) (Figure 1).

An important parameter describing the properties of a polymeric object is the activation energy of viscous flow (E_a), which is a physical characteristic of intermolecular interaction. PDMS has the smallest E_a value among the polymers, namely,

Table 1 Characteristics of obtained star-shaped polydimethylsiloxanes.

Sample	Number of arms (f)	M_n (based on GPC[a])	MWD[a]	MW (based on ^{1}H NMR)	Arm length (number of units)	$M_{n(GPC)}/MW_{(NMR)}$
6a	8	23800	1.34	36700	53	0.65
6b	32	26400	1.23	176200	65	0.15
6c	128	29600	1.19	649100	59	0.05

[a] Based on polystyrene standards.

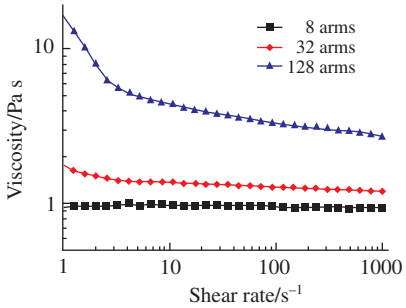


Figure 1 Flow curves of star-shaped PDMSs with 8, 32 and 128 arms at 20 °C.

15 kJ mol^{-1}. The E_a value is quite sensitive to the existence of branching and functional groups in linear polymer chains.

The activation energy of viscous flow was calculated by the Arrhenius equation $\eta = Ae^{Ea/RT}$ (where η is the viscosity, R is the universal gas constant, and T is the temperature expressed in K) based on flow curves of star-shaped PDMSs at various temperatures (Figure S8).

The temperature *vs*. viscosity plots in coordinates of the Arrhenius equation (Figure 2) are straight lines, which made it possible to determine the E_a for all the samples as 18.5 kJ mol^{-1}. It is slightly higher than the E_a for linear PDMS (E_a = 15 kJ mol^{-1}).[24] This result shows that the rheology of star-shaped PDMSs with the specified number of arms and the arm length of about 60 units is determined by the nature of the arms and is close to that of linear PDMS, while increasing the number of arms does not affect the level of intermolecular interaction.

The above data show the specificity of the properties of multi-armed star-shaped structures. The anomalously low viscosity that is characteristic of low-armed structures grows insignificantly with an increase in the number of arms, while the actual molecular weight of the macromolecule (Table 2) determined from ^{1}H NMR increases greatly. The viscosity of the linear PDMS analogue with the similar molecular mass grows very significantly, by several orders of magnitude. It was suggested to describe the properties of such structures using the so-called branching coefficient $g' = A_{star}/A_{lin}$ that equals the ratio of the parameters of a star-shaped polymer and its linear analogue with similar molecular mass.[26] Previously, for PDMS stars with the number of arms from 12 to 48, the g' coefficient obtained from characteristic viscosities decreased *ca*. twofold,[27] while in the case of dynamic viscosities and the number of arms in the same range, the g' coefficient decreased twofold, but it decreased by three orders at f = 128. Note that in this case, the activation energy of viscous flow remains the same and almost equals the E_a of linear PDMS.

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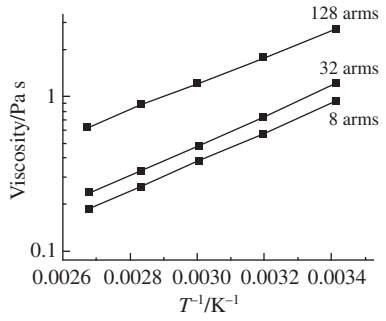

Figure 2 Temperature dependences of the viscosity of star-shaped PDMSs in coordinates of the Arrhenius equation.

Table 2 Properties of star-shaped PDMSs with arms lengths of n ~ 60.

f	M_n (GPC)	MW (^{1}H NMR)	η_{star}[a]/ Pa s	$\eta_{lin.analog}$[b]/ Pa s	$g' = \eta_{star}/\eta_{lin.}$	E_{act}/ kJ mol^{-1}
8	23800	36700	0.96	2.19	4.4×10^{-1}	18.5
32	26400	176200	1.28	270	4.8×10^{-3}	18.5
128	29600	649100	3.30	39810	4.0×10^{-4}	18.5

[a] At 20 °C and a shear rate of 100 s^{-1}. [b] Linear PDMS with a molecular mass analogous to that of a star, at 20 °C.[25]

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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.2019.11.006.

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