



# INVESTIGATION OF THE SURFACE ACTIVITY AND INTERFACE BEHAVIOR OF HYBRID CARBOSILANE–CYCLOSILOXANE DENDRIMERS

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## Abstract

This work deals with hybrid carbosilane–cyclosiloxane dendrimers featuring variable tension of rings in the outer layer. The presence of a siloxane bond in the shell of these dendrimers, due to its surface activity, allows the formation of monolayers at the interface. The interfacial energies at a water–hexane interface, measured by the spinning drop method, indicate change in the mechanism of emulsion stabilization with an increase in the generation number of the dendrimers explored.

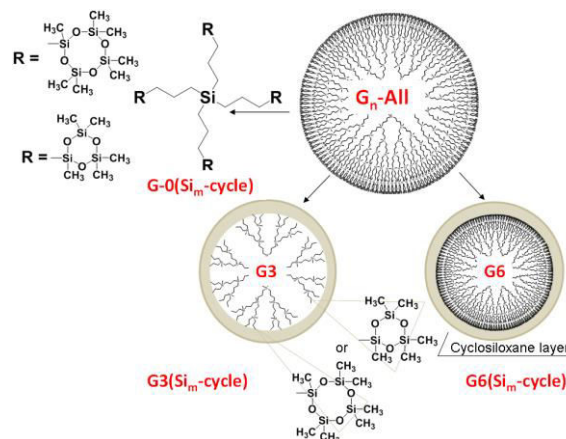
**Key words:** carbosilane dendrimers, amphiphilicity, Langmuir monolayers, interfacial energy, Pickering emulsions.

## Introduction

Dendrimers are polymers that exhibit a number of features due to their regular branched structure: monodispersity, high functionality of the outer layer, and compact sizes. High-generation dendrimers feature a principally different nature of intermolecular interactions, which is confirmed by at least two phenomena: a sharp increase in the viscosity on passing to higher generations and the ability to order into a crystal lattice of the plastic crystal type (the effect of the long-range order and the absence of the short-range order) [1–10].

Investigations on the properties of macromolecules with complex chemical structures, such as dendrimers, is of great importance both for establishing the structure–property relationships and for understanding the physical nature of self-organization. The presence of a siloxane component in hybrid carbosilane–siloxane dendrimers determines their unique chemical and physical properties. The surface properties inherent to them due to the presence of a siloxane bond in their structure play a special role; their amphiphilic nature makes them potentially suitable for practical use as surfactants and also allows them to form stable monomolecular layers on the surface of the water–air interface. The study of the properties of these systems will allow us to determine the area of their use, both for practical applications and as model compounds in molecular design.

This work is concerned with the dendrimers of the zero, third and sixth generations, consisting of a hydrophobic carbosilane skeleton and a polar cyclosiloxane shell. The outer layer of the dendrimers contains dimethylcyclosiloxane groups



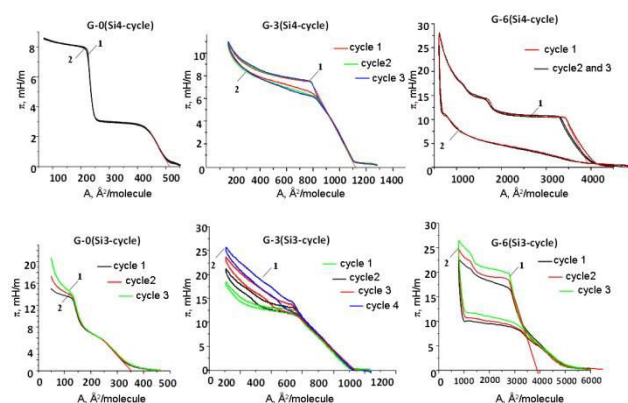
of variable tension, namely, pentamethylcyclotrisiloxane ( $G_n(\text{Si}_3\text{-cycle})$ , where  $n$  is the generation number) and heptamethylcyclotetrasiloxane ( $G_n(\text{Si}_4\text{-cycle})$ ). The synthesis of these dendrimers and their main physicochemical properties were described in Ref. [11]. Herein, we present the results of investigations on the surface-active properties of these versatile models.

## Results and discussion

Carbosilane–cyclosiloxane dendrimers are amphiphilic systems with different polarity of the core and shell. Earlier it was established that, to understand the behavior of a homologous series of dendrimers, it is not necessary to study the properties of all representatives of the series. The minimum required set is low generations for the development of a synthetic scheme, medium generations, which manifest the polymeric properties, as well as representatives of higher generations with special properties that are characteristic only of dendrimers [11]. In our case, these are the zero, third and sixth generations. The presence of a polar siloxane shell in the dendrimers under consideration allows the formation of monolayers at the water–air interface and their study by the Langmuir method.

Figure 1 depicts the surface pressure isotherms of the dendrimers explored.

Despite the similarity of the chemical compositions, the dendrimers of different generations behave differently at the interface. A detailed study of the behavior of these systems at the interface will be considered in a separate report. Herein, we



**Figure 1.** Langmuir surface pressure isotherms for G-n(Sim-cycle), where  $n = 0, 3, 6$ ;  $m = 3, 4$ ; compression mode (1), decompression (2).

consider only some features necessary to explain their surface-active properties.

Dendrimers of the zero generation G-0(Sim-cycle) ( $m$  is the number of -SiO- units in the outer shell of the dendrimer;  $m = 3$  or 4) demonstrate a two-step surface pressure isotherm under compression and reversible expansion. This shape of the isotherm can be explained by intramolecular rearrangements in the region of the first plateau. Third-generation dendrimers G-3 (Sim-cycle) demonstrate a single-step isotherm during layer compression and a small hysteresis during expansion. The isotherm shape indicates the formation of a monolayer with the subsequent collapse. For dendrimers of the sixth generation G-6 (Sim-cycle), the type of isotherms has a stepped character. This allows us to assume the formation of multilayer structures during compression. In the compression–expansion cycle, significant hysteresis is observed. This type of isotherms is characteristic of high-generation dendrimers and can be explained by the special intermolecular organization of macromolecules, which manifests itself in the formation of a network of entanglements [12]. For dendrimers with strained pentamethylcyclotrisiloxane groups in the shell, G-n(Si3-cycle), an increase in the pressure in the collapse region is observed with each subsequent compression–expansion cycle for all the studied generations, which allows us to assume that hydrolysis of cyclosiloxane groups occurs at the water–air interface, as a result of which the formed hydroxy groups interact with the water surface.

The nature of amphiphilic dendrimers is such that the surface-active properties they exhibit make them promising objects for use in various fields, not only due to amphiphilicity as such, but mainly because it is combined in these objects with a changing shape of molecules, their rigidity with a virtually unchanged chemical composition. While for low generations of dendrimers, one can expect the classical behavior, for example, as emulsion stabilizers in emulsion polymerization processes [13], then with an increase in the generation number and obvious difficulties in intramolecular rearrangements at the interface, one should expect a significant change in the surface activity. To determine the effectiveness of surfactants, various methods for measuring surface tension are used.

To determine the interfacial energy of the carbosilane–cyclosiloxane dendrimers, the spinning drop method was used. For two series of the carbosilane–cyclosiloxane dendrimers with

pentamethylcyclotrisiloxane and heptamethylcyclotetrasiloxane groups in the shell, the values of interfacial energy at the hexane–water system (interfacial tension of the hexane–water system is 50 mN/m) were obtained. The results are summarized in Table 1.

**Table 1.** Interfacial energies for two series of the hybrid carbosilane–cyclosiloxane dendrimers featuring different tensions of cyclosiloxane groups in the outer shell at the water–hexane interface

G-n	CS:CyS, <sup>a</sup> wt %		Interfacial energy, mN/m (water–hexane)		
	G-n (Si3-cycle)	G-n (Si4-cycle)	C, mg/mL	G-n (Si3-cycle)	G-n (Si4-cycle)
G-0	2:8	1,5:8,5	0.1	44.5	44.1
			1	35.0	32.6
			5	28.9	33.3
G-3	4:6	3:7	0.1	34.8	42.0
			1	22.4	33.6
			5	20.6	33.7
G-6	4:6	3:7	0.1	36.3	39.2
			1	18.7	35.2
			5	15.1	28.6

<sup>a</sup> ratio of the carbosilane (CS) and cyclosiloxane (CyS) parts.

From the data in Table 1 it is evident that, as the solution concentration increases, the interfacial energy decreases for the dendrimers of all generations. With an increase in the generation number, a decrease in the interfacial energy values is observed in both series, respectively.

Considering that at low generations the content of the siloxane part is higher and the siloxane part has a lower surface energy, it was expected that the minimum of the surface energy values would be at low generations. However, the results obtained showed the opposite picture.

For the dendrimers of the third and sixth generations, with an almost unchanged ratio of the carbosilane and siloxane parts, the smallest value of the interfacial energy falls on the largest dendrimer, which has the properties of a macromolecule-particle. Probably, when using these systems as emulsion stabilizers, a stabilization mechanism similar to the Pickering principle is realized [14, 15], *i.e.*, the dendrimer exhibits particle properties.

It is also important to note that, with a similar tendency to a decrease in the interfacial energy for the parallel series of dendrimers, differing only in the size of the siloxane cycle, we see significant differences in the values of the interfacial energy for the same generations. So, if we consider the systems with the same dendrimer concentration (for example, 1%), the values of the interfacial energy change by 20–25% in the case of Gn-(Si4-cycle) series and by 30–50% in the case of Gn-(Si3-cycle) series.

This phenomenon is likely to be associated with the fact that in dendrimers with strained pentamethylcyclotrisiloxane groups in the shell at the interface, the cyclosiloxanes in the outer layer of the dendrimer open, resulting in the formation of hydroxy groups. Their appearance increases the amphiphilicity of the molecules, which leads to a decrease in the values of the interfacial energy. The compression isotherms of the monolayers shown in Fig. 1 illustrate the above-mentioned.

## Experimental section

The surface pressure isotherms were obtained using a Langmuir bath (612D, Nima, England). The bath was made from Teflon, its sizes were 20×30 cm. The subphase was distilled water, deionized on an Aquilon D-301 setup (specific resistance 18 MOhm/cm). The dendrimers explored were dissolved in chloroform with a concentration of 1 mg/mL. The barrier movement rate was 50 cm<sup>2</sup>/min. The accuracy of the surface pressure determination was 0.1 mN/m.

The interfacial tension between the aqueous and oil phases was determined by the spinning drop method on a Krüss SDT tensiometer at 25 °C.

## Conclusions

The investigations on the interfacial energy showed that, in the case of the amphiphilic carbosilane–cyclorosiloxane dendrimers, we deal with the new objects with adjustable surface activity, up to a possible change in the mechanism of emulsion stabilization when moving from low to high generations.

The selected models also allowed us to show the possibilities of regulating the properties depending on the reactivity of cyclorosiloxanes in the surface layer of the molecular structure.

Thus, due to the fact that the synthetic schemes of carbosilane systems allow us to regulate the density of the core within one generation and the chemical nature of the surface layer, then, taking into account the fact that the carbosilane dendrimers are represented by a wide range of generations, they can be considered as a new versatile platform for creating surfactants with ample opportunities for controlling the operational properties of such objects.

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