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Thermodynamics of fluorinated derivatives of carbosilane dendrimers of high generations*

A. V. Markin,[a]★ Ya. S. Samosudova,[a] N. N. Smirnova,[a] N. A. Sheremet´eva,[b] and A. M. Muzafarov[b]

[a]*Research Institute of Chemistry,*
N. I. Lobachevsky Nizhni Novgorod University,
23/5 prosp. Gagarina, 603950 Nizhni Novgorod, Russian Federation.
Fax: +7 (831) 434 5056. E-mail: smirnova@ichem.unn.ru
[b]*N. S. Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences,*
70 ul. Profsoyuznaya, 117393 Moscow, Russian Federation

The temperature dependences of the heat capacities of fluorinated derivatives of carbosilane dendrimers of high (4.5 and 7.5) generations were studied by adiabatic vacuum calorimetry in the range from 6 to 340 K for the first time. The standard thermodynamic characteristics of devitrification were estimated. The experimental results were used to calculate the standard thermodynamic functions $C_p°(T)$, $H°(T)—H°(0)$, $S°(T)—S°(0)$, and $G°(T)—H°(0)$ over the range from $T \to 0$ to 340 K and standard entropies of formation of dendrimers at T = 298.15 K. The low-temperature ($T \leq 50$ K) heat capacity was analyzed by using Debye´s heat capacity theory of solids and the multifractal model. The values of fractal dimensionality D were determined, and some conclusions about topology of the studied structures were made. The standard thermodynamic characteristics of the studied fluorinated derivatives of carbosilane dendrimers were compared.

Key words: carbosilane dendrimers, generation, chemical thermodynamics, heat capacity, devitrification, thermodynamic functions.

In the recent time dendrite macromolecules attract researchers´ attention due to a unique structure and a complex of specific physicochemical properties.[1,2] Dendrimers represent a new class of high-molecular compounds containing regular branchings in each monomeric unit arranged in such a way that their number increases in geometric progression from the center of the molecule to periphery. The methods developed for chemical modification of the external surface layer makes it possible to control the properties of dendrimers in a wide range. It is known that the introduction of fluorocarbon fragments imparts hydrophobicity, thermal stability, and enhanced lubricity to the dendrite systems compared to the non-modified analogs.[3—7] A combination of the external layer and silicon—hydrocarbon framework in the dendrimer structure allows one to consider these macromolecules as a core—shell system and provide broad possibilities of studying specific features of the behavior of dendrimers. However, in spite of serious progress in the field of studies of synthesis and proofs for the individual character of dendrimers, there is certain backwardness in measuring their main physicochemical characteristics, which restraints understanding of specific features of the physicochemical nature of dendrimers and search for areas of efficient practical application.

Complex thermodynamic studies of some carbosilane dendrimers were carried out by precision calorimetry up to the present time.[8—15] For example, in some cases,[10,14] the composition—property dependences were obtained and analyzed. This study is a continuation of works on studying the thermodynamic properties of various representatives of carbosilane dendrimers.

The purpose of the present work is the calorimetric study of dependences of the heat capacities on the temperature of carbosilane dendrimers of generations 4.5 and 7.5 with the fluorinated external layer in the range from 6 to 340 K, an analysis of these dependences in the range $T < 50$ K using the multifractal model, and revealing and determination of the thermodynamic characteristics of possible physical transformations on their heating and cooling. We also aimed at calculating the standard thermodynamic functions for the temperature range from 0 to 340 K and standard entropies of formation of dendrimers in the amorphous (devitrified) state at 298.15 K and at comparing the thermodynamic characteristics of the studied carbosilane dendrimers.

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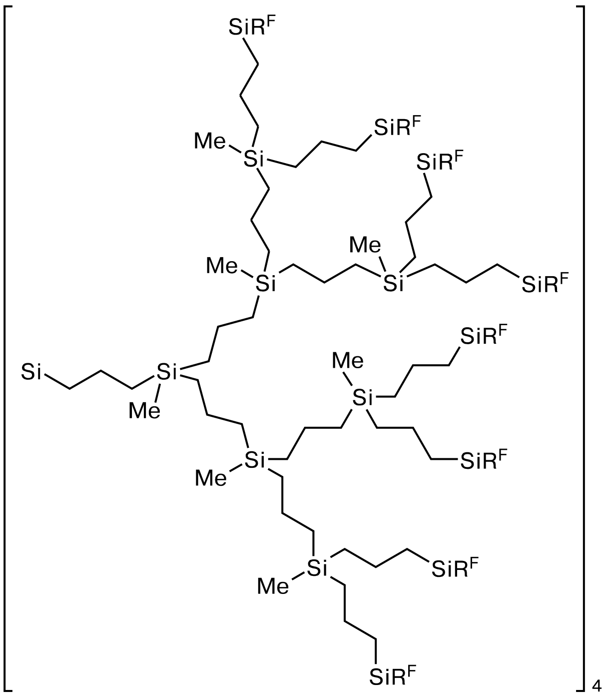
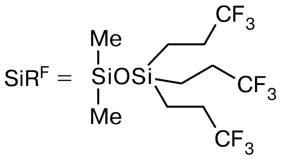
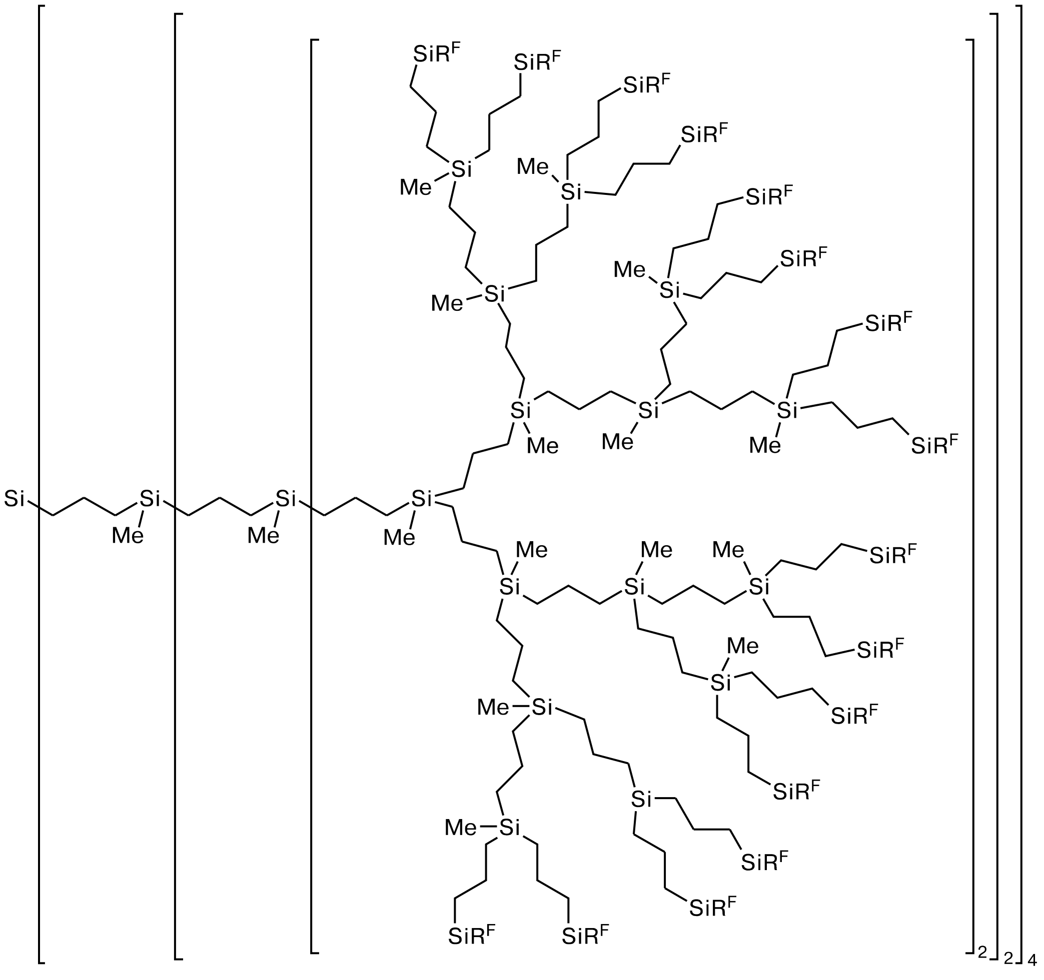


G-4.5(F)



$\mathrm{SiR^F} = \mathrm{SiMe_2OSi(CH_2CH_2CF_3)_3}$

G is generation of dendrimer,
4.5 and 7.5 are numbers of generation



G-7.5(F)

Experimental

Studied samples. Samples of carbosilane dendrimers G-4.5(F) and G-7.5(F) (empirical formulas $Si_{61}C_{560}H_{1020}F_{288}O_{32}$ and $Si_{765}C_{4592}H_{8412}F_{2304}O_{256}$, M = 16 349 and 132 987 g mol^{-1}, respectively) were synthesized by a procedure described in detail.[7,16]

Under standard conditions, the studied samples of dendrimers were transparent, colorless, and resinous substances highly soluble in organic solvents.

The composition and structure of the studied samples were confirmed by the data of elemental analysis, ^{1}H NMR spectroscopy (Bruker WP-200 SY spectrometer (200.13 MHz), tetramethylsilane as an internal standard), and FTIR spectroscopy (Bruker ISF-110).

The temperature dependences of the heat capacities of the samples in the range 6—340 K were measured by a known procedure using a BKT-3 automated adiabatic vacuum calorimeter.[17,18] The inaccuracy of measuring the heat capacity did not exceed ±2% near 10 K, ±0.5% in the range 15—40 K, and ±0.2% in the range 40—340 K. The temperatures of physical transformations were determined with an inaccuracy of ±0.2 K.

The weights of the studied substances placed in a BKT-3 calorimetric ampule were $0.2401 \cdot 10^{-3}$ and $0.2164 \cdot 10^{-3}$ kg, respectively. For the samples G-4.5(F) and G-7.5(F), 181 and 191 experimental values of heat capacity, respectively.

The heat capacity of the samples was always 10—50% of the total heat capacity of heat capacity of the calorimetric ampule with the substance. The experimental points of $C_p°$ were averaged in the form of power and semilogarithmic polynomials using special programs in such a way that their root-mean-square deviation from the averaged curve $C_p° = f(T)$ did not exceed the inaccuracy of measurements of heat capacity.

Results and Discussion

Heat capacity. The experimental data and smoothed dependences $C_p° = f(T)$ for dendrimers are shown in Fig. 1.

Under the experimental conditions, the studied substances were cooled from room temperature to the temperature of beginning of measurements equal to ~6 K with a rate of 0.02 K s^{-1}. Upon subsequent heating, the dendrimers were devitrified in the range from 195 to 235 K.

Devitrification was reproduced every time on cooling to the temperature below $T°_g$ and subsequent heating during repeated measurement of $C_p°$, and the characteristics of the process remained unchanged after the repeated measurement upon cooling from the devitrified state with another rate, 0.01 K s^{-1}. Thus, under our experimental conditions, no crystallization of the studied dendrimer samples was observed. Note that the same behavior was observed for the earlier studied dendrimers of the seventh generation with the terminal butyl groups G-7(Bu)$_{512}$[14] and G-7(Ph)(Bu)$_{384}$.[15]

A comparison of the data of this work and those for the starting carbosilane analogs ($T°_g$ ≈ 180 K)[12] suggests a substantial increase in the glassy transition temperature upon the introduction of fluorocarbon substituents into the surface layer of the molecular structure of the dendrimers. Thus, the glassy transition temperature of the carbosilane dendrimers depends on the nature of substituents and groups of the external layer. As should be expected, the introduction of the fluorocarbon fragments makes the dendrimer structure more rigid.

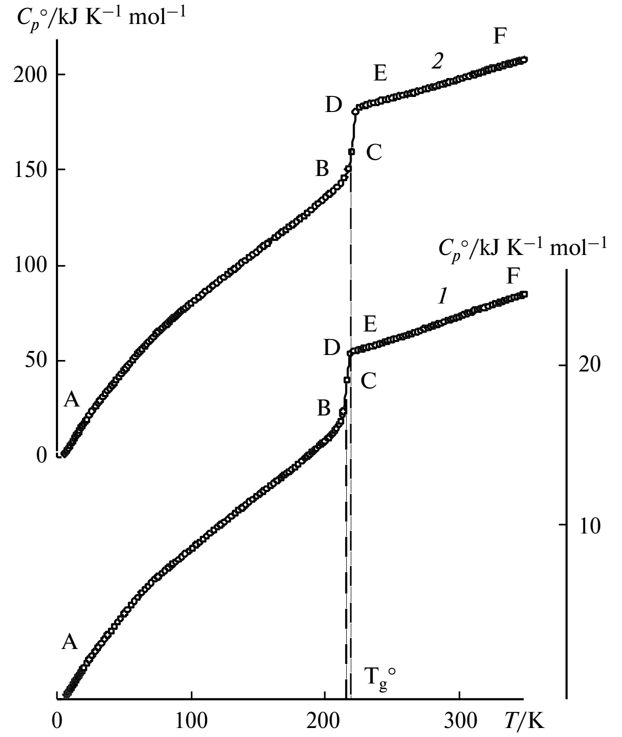


Fig. 1. Temperature dependences of the heat capacity of carbosilane dendrimers G-4.5(F) (*1*) and G-7.5(F) (*2*): AC is the glassy state, DF is the devitrified state, BE is the heat capacity over the devitrification range, CD is the heat capacity increased upon devitrification, and $T_g°$ is the glassy transition temperature.

It seemed interesting to examine the heat capacity of the studied samples in the low-temperature region ($20 \le T \le 50$ K) in terms of the multifractal model.[19,20] In this generalized model,[19] the exponent at T in the function of heat capacity is designated as D and named fractal dimensionality. The values of D make it possible to judge about the type of topology of solid structures. According to Tarasov's theory of heat capacity of solids,[21,22] for bodies of chain structure the dependence of $C_p°$ on T in the low-temperature region is proportional to T^1, for solids of layered structure it is proportional to T^2, and for solids of spatial structure the dependence is proportional to T^3; *i.e.*, for them the values of D are 1, 2, and 3, respectively. It seems possible to estimate the values of D by the experimental data of the low-temperature dependence of the heat capacity from the slope of the corresponding rectilinear regions of the plot of lnC_v on ln$T$. This follows, in particular, from the equation

$$C_v = 3D(D + 1)kN\gamma(D + 1)\xi(D + 1)(T/\theta_{\max})^D, \quad (1)$$

Table 1. Standard thermodynamic characteristics of devitrification and glassy state of carbosilane dendrimers G-4.5(F) and G-7.5(F)

Dendrimer	Empirical formula	M/g mol^{-1}	$T_g°±1$/K	$\Delta C_p°$	$S°_{conf}$
				/kJ K^{-1} mol^{-1}	
G-4.5(F)	$Si_{61}C_{560}H_{1020}F_{288}O_{32}$	16349	216	4.36	1.11
G-7.5(F)	$Si_{765}C_{4592}H_{8412}F_{2304}O_{256}$	132987	218	34.20	8.71

where N is the number of particles, k is the Bolzmann constant, $\gamma(D + 1)$ is the gamma function, $\xi(D + 1)$ is the Riemann function, θ_{max} is the characteristic temperature, and D is the fractal dimensionality.

It can be accepted without substantial error that at $T < 50$ K $C_p° = C_v$, then from the dependence of $\ln C_p°$ on $\ln T$ we find that in the range 20—50 K for the studied dendrimers the values of D and θ_{max} are 1.2 and 234.9 K; 1.2 and 206.2 K, respectively. With the found parameters Eq. (1) reproduced the values of $C_p°$ in the indicated temperature range with the inaccuracy about ±1%. Thus, the topological structure of the studied dendrimers can be considered as chain layered.

Standard thermodynamic characteristics of devitrification and glassy state. The thermodynamic characteristics of devitrification and glassy state are presented in Table 1.

The glassy transition state $T_g°$ was determined by the Alford and Dole method[23] from the inflection of the temperature plot of the entropy of heating. The range of devitrification and an increase in the heat capacity during devitrification $\Delta C_p°(T_g°)$ were determined graphically. The configurational entropy $S°_{conf}$ was calculated by earlier proposed[24] Eq. (2)

$$S°_{conf} = \Delta C_p°(T_g°)\ln T_g°/T_2°, \qquad (2)$$

where $T_2°$ is the Kauzmann temperature,[25] and the ratio $T_g°/T_2°$ equals 1.29±0.14 (see Refs 24 and 25). It was assumed that the presented ratio is fulfilled for the dendrimers studied as well. As has been shown earlier,[26] $S°_{conf}$ is close to $S°(0)$; taking this into account, we accepted that for the estimation of the absolute entropy $S°(0) = S°_{conf}$ (see Table 1).

Standard thermodynamic functions. For the calculation of the standard thermodynamic functions (Tables 2 and 3) of the studied dendrimers, the values of heat capacities $C_p°$ were extrapolated from the temperature of beginning of measurements to 0 K by the function of Debye´s heat capacity

$$C_p° = n\mathrm{D}(\theta_{\mathrm{D}}/T), \qquad (3)$$

where D is Debye´s function, and n and θ_{D} are specially selected parameters. In the range from 7 to 13 K for dendrimers G-4.5(F) and G-7.5(F), the values of n and θ_{D} are 3 and 58.9 K; 3 and 60.9 K, respectively. Equation (3) with these parameters describes the experimental values of $C_p°$ of the dendrimers in the indicated range with an inaccuracy of ±1.7%. It was accepted when calculating the functions that Eq. (3) reproduces the values of $C_p°$ at $T < 7$ K with the same inaccuracy. The enthalpy $H°(T)—H°(0)$ and entropy $S°(T)—S°(0)$ were calculated by the numerical integration of the curves $C_p° = f(T)$ and $C_p° = f(\ln T)$ with respect to T, respectively; the Gibbs function $G°(T)—H°(0)$ was calculated by the values of enthalpy and entropy at the corresponding temperatures. The calculation procedure was published, *e.g.*, in Ref. 26. It was assumed that the error of the calculated values of the functions was ±1% at $T < 30$ K, ±0.5% in the range 30—80 K, and ±0.2% in the range 80—340 K.

The standard entropies of formation $\Delta_f S°$ for G-4.5(F) and G-7.5(F) in the amorphous (devitrified) state were calculated from the values of absolute entropies of the carbosilane dendrimer (see Tables 2 and 3) and the corresponding simple substances [C(gr), Si(cr)] [27] and [H_2(g), O_2(g), F_2(g)] [28] at 298.15 K. The calculated values of $\Delta_f S°$ were −75.02±0.1 and −616.1±0.1 kJ K^{-1} mol^{-1}, respectively. They correspond to the equations

Table 2. Standard thermodynamic functions of carbosilane dendrimer G-4.5(F) (M = 16 349 g mol^{-1}) in the amorphous glassy and in the amorphous devitrified states

T/K	$C_p°(T)$	$S°(T)—S°(0)$	$H°(T)—H°(0)$	$-[G°(T)—H°(0)]$
	kJ K^{-1} mol^{-1}		kJ mol^{-11}	
		Glassy state		
5	0.118	0.0396	0.150	0.0496
10	0.685	0.274	2.01	0.732
20	2.060	1.176	15.79	7.726
50	5.523	4.453	130.8	91.86
100	9.679	9.688	520.2	448.6
160	13.80	15.15	1227	1197
200	16.66	18.53	1835	1871
216	17.80	19.85	2110	2178
		Devitrified state		
216	22.16	19.85	2110	2178
220	22.38	20.26	2199	2258
260	23.44	24.08	3115	3146
298.15	24.61	27.37	4031	4129
300	24.67	27.52	4077	4179
340	25.85	30.68	5088	5344

Table 3. Standard thermodynamic functions of carbosilane dendrimer G-7.5(F), (M = 132 987 g mol^{-1}) in the amorphous glassy and in the amorphous devitrified states

T/K	$C_p°(T)$	$S°(T)-S°(0)$	$H°(T)-H°(0)$	$-[G°(T)-H°(0)]$
	kJ K^{-1} mol^{-1}		kJ mol^{-1}	
		Glassy state		
5	0.962	0.322	1.21	0.403
10	5.78	2.29	16.8	6.11
20	17.19	9.827	132.1	64.42
50	45.66	37.12	1089	766.9
100	80.95	80.52	4321	3730
160	114.3	125.9	10190	9950
200	137.2	153.8	15204	15547
218	147.7	165.8	17710	18358
		Devitrified state		
218	181.9	165.8	17710	18358
220	182.4	167.8	18147	18759
260	190.2	198.9	25602	26104
298.15	198.1	225.4	33005	34206
300	198.6	226.7	33371	34624
340	207.2	252.1	41493	44205

$$61\ \mathrm{Si\ (cr)} + 560\ \mathrm{C\ (gr)} + 510\ \mathrm{H_2\ (g)} +$$

$$+\ 144\ \mathrm{F_2\ (g)} + 16\ \mathrm{O_2\ (g)} \rightarrow \mathrm{Si_{61}C_{560}H_{1020}F_{288}O_{32}\ (a)},$$

$$765\ \mathrm{Si\ (cr)} + 4592\ \mathrm{C\ (gr)} + 4206\ \mathrm{H_2\ (g)} +$$

$$+\ 1152\ \mathrm{F_2\ (g)} + 1280\ \mathrm{O_2\ (g)} \rightarrow \mathrm{Si_{765}C_{4592}H_{8412}F_{2304}O_{256}\ (a)},$$

where gr is graphite, g is gas, cr is crystal, and a is amorphous state.

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