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Thermodynamic properties of carbosilane dendrimers of the third to the sixth generations with terminal butyl groups in the range from $T \to 0$ to 600 K

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Abstract

In the present work temperature dependences of heat capacity of carbosilane dendrimers with butyl terminal groups of the third and the fourth generations as well as of the fifth and the sixth generations have been determined first in the range from 6 to 340 K and between 6 and 600 K, respectively, by precision adiabatic vacuum and dynamic calorimetry. In the above temperature ranges the physical transformations have been detected and their thermodynamic characteristics have been estimated and analyzed. The experimental data were used to calculate standard thermodynamic functions, namely the heat capacity $C_p^o(T)$, enthalpy $H^o(T) - H^o(0)$, entropy $S^o(T) - S^o(0)$ and Gibbs function $G^o(T) - H^o(T)$, for the range from $T \to 0$ to (340–600) K. Linear dependences of changing the corresponding thermodynamic functions of the dendrimers on their molecular weight and the number of butyl groups on an outer sphere have been determined.

Keywords: Carbosilane dendrimers; Adiabatic vacuum calorimetry; Heat capacity; Thermodynamic functions; Devitrification

1. Introduction

The synthesis and the examination of physicochemical properties of polymers of a virtually new type—dendrimers—are one of the most promising and sufficiently developing directions of up-to-date chemistry [1–7]. Those are a particular class of high-molecular compounds containing regular branches in a monomeric unit the number of which increases in a geometric progression from the molecule center to periphery [8,9]. According to the last classification [9], 1, 2, 3 and *n* generations of dendrimers are distinguished depending on the number of sphere branches. At present, the studies of the dendrimer synthesis [10–12], their individual physicochemical characteristics [13–15] and the quest for fields of their practical application [1–16] are actively performed. Nevertheless, published works on the study of thermodynamic properties of dendrimers are not numerous. Most of available works are devoted to the investigation of the thermal behavior of dendrimers, i.e. the determination of temperatures of their devitrification and decomposition. Only in a few papers [17–23] the data on low-temperature dependences of the heat capacity and the values of thermodynamic functions calculated based on them are presented.

It is obvious that a highly urgent task is the accumulation of precise thermodynamic values for the compounds of the given class and the determination of the most general qualitative and quantitative dependences of the change in their thermodynamic properties on the composition and structure. It is known [8–10] that the dendrimers combine the properties of macromolecules and individual molecular species. In this connection, it is natural to analyze the interrelation between the composition and structure of the dendrimers and their thermodynamic functions for a consistent comparison with similar characteristics of classic polymers.

The goal of the given work is to calorimetrically determine the temperature dependence of the heat capacity $C_p^o = f(T)$ of the carbosilane dendrimers of the third and the fourth generations

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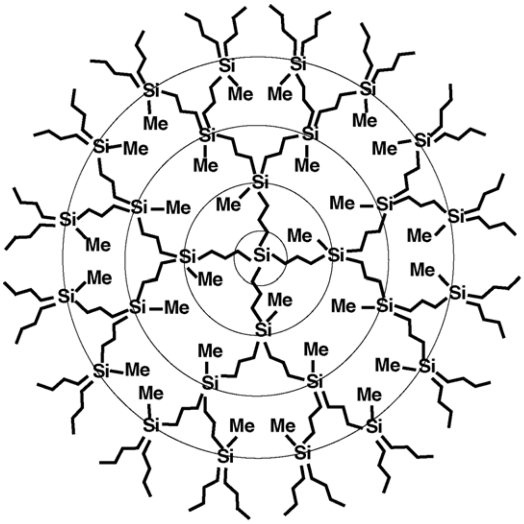
between 6 and 340 K and of the fifth and the sixth generations from 6 to 600 K, to detect their possible physical transformations on heating and cooling and to interpret them in terms of physical chemistry, to calculate the standard thermodynamic functions $C_p^o(T)$, $H^o(T) - H^o(0)$, $S^o(T) - S^o(0)$ and $G^o(T) - H^o(0)$ in the range from $T \rightarrow 0$ to (340–600) K and to elucidate the dependences of thermodynamic characteristics of the compounds on their composition and structure.

2. Experimental

2.1. Sample

The structure of the carbosilane dendrimer of the third generation with terminal butyl groups {G-3(Bu)$_{32}$} is shown as an example below.



G-3(Bu)$_{32}$

For higher generations the conventional designations are the following: G-4(Bu)$_{64}$, G-5(Bu)$_{128}$, G-6(Bu)$_{256}$, G-*n*(Bu)$_m$, where G is the generation, $n = 1, 2, 3, \ldots$ are the generation numbers, *m* is the number of butyl groups on the outer sphere of the dendrimer molecules.

The samples of the carbosilane dendrimers were synthesized at N.S. Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Science by the method described in detail elsewhere [24]. Under normal conditions the dendrimers of 3, 4, 5 generations are transparent colorless viscous liquids while the dendrimer of the sixth generation is a transparent waxy substance. The composition and structure of the samples were confirmed by elemental analysis and methods of NMR ^{1}H-spectroscopy {a “Bruker WP-200 SY spectrometer” (200.13 MHz, a standard is tetramethylsilane)} and IR-spectroscopy (a “Bruker ISF-110” device).

2.2. Apparatus and measurement procedure

To measure the heat capacity C_p^o of the tested substances in the range from 6 to 340 K a BKT-3.0 automatic precision adiabatic vacuum calorimeter with discrete heating was used. The calorimeter design and the operation procedure were described earlier [25,26]. The calorimeter was tested by measuring the heat capacity of special-purity copper (OSCH) and reference samples of synthetic corundum and K-2 benzoic acid. The analysis of the results showed that an uncertainty of measurements of the heat capacity of the substances at helium temperatures was within to ±2%, with rising temperature up to 40 K it decreased down to ±0.5% and was equal to ±0.2% at $T > 40$ K. Temperatures of physical transformations can be determined with an uncertainty of ±0.02 K and their enthalpy with an error of ±0.5%.

To measure the heat capacity of the substances between 300 and 600 K an automatic thermoanalytical complex—a dynamic calorimeter operating by the principle of triple thermal bridge—was employed [27,28]. The device design and the measurement procedure of the heat capacity, temperatures and enthalpies of physical transformations were demonstrated in detail in the same works. The reliability of the calorimeter operation was checked by measuring the heat capacity of the standard sample of synthetic corundum as well as the thermodynamic characteristics of fusion of indium, tin and lead. As a result, it was found that the calorimeter and the measurement technique allow one to obtain the heat capacity values of the substances in solid and liquid states with a maximum uncertainty of ±1.5% and the physical transformation temperatures within to ca. ±0.5 K. Since the heat capacity of the examined compounds was also measured between 300 and 350 K in the adiabatic vacuum calorimeter with an uncertainty of ±0.2% and the conditions of measurements in the dynamic device were chosen so that in the above temperature interval the C_p^o values, measured with employing both calorimeters, coincided it was assumed that at $T > 350$ K the heat capacity was determined with an uncertainty of 0.5–1.5%. The data on the heat capacity of the objects under study were obtained in the range from 300 to 600 K at an average rate of heating of the calorimeter and the substance of 0.0133 K/s.

3. Results and discussion

3.1. Heat capacity

All experimental C_p^o points and averaging curves are illustrated in Figs. 1 and 2. The main characteristics of experiments on the heat capacity measurement for the carbosilane dendrimers are listed in Table 1. The tested substances under conditions of our apparatus were cooled from room temperature to the temperature of the measurement onset (∼6 K) at a rate of 0.01 K/s. On subsequent heating all the dendrimers underwent devitrification over the range from 175 to 195 K that is practically the same for all samples being studied in the present work. The transition parameters for the dendrimers are summarized in Table 2. According to the data, the behavior of the substances in the low-temperature interval in no way practically differs from that of systems having an allyl frame at silicon atoms [21] and is similar for polybutylcarbosilane dendrimers of various generations. The temperature ranges where the devitrification of all dendrimers occurs lie between 20 and 35 K. The devitrification temperature T_g^o increases on going from the third generation of

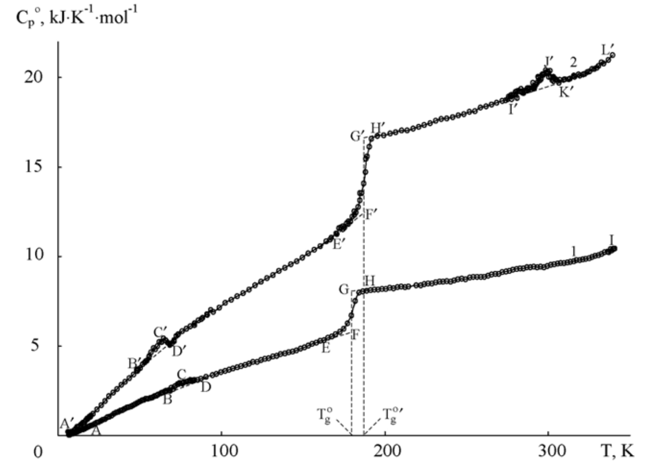


Fig. 1. Temperature dependence of heat capacity of carbosilane dendrimers with terminal butyl groups of: 1—the third generation, 2—the fourth generation; AF, A′F′—the glassy state; GL, G′L′—the high-elastic state; EH, E′H′—temperature dependences of heat capacity in the devitrification interval; FG, F′G′—the increase in heat capacity on devitrification; BCD, B′C′D′, I′J′K′—the heat capacity anomalies as a positive deviation from the normal trend of curve; BD, B′D′, I′K′—the normal trend of heat capacity (a dashed line) in the interval of its anomalous dependence.

dendrimer to the fourth one. On further growing the generation number it remains substantially invariable. For all samples the devitrification was reproduced every time on cooling down to a temperature below T_g^o and on subsequent heating when the repeated measurement of C_p^o was performed. Besides, the process characteristics did not change when the measurement cycle was conducted after cooling the compound in a high-elastic state at different rates. Thus, no crystallization of the dendrimer samples with butyl terminal groups occurred, those existed in glassy and high-elastic states in the temperature interval considered.

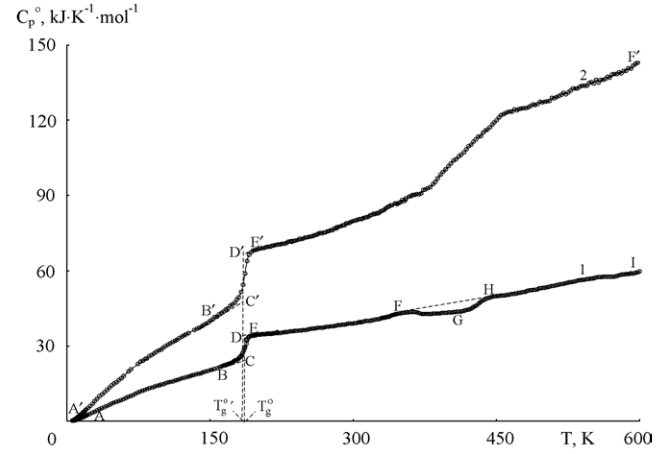


Fig. 2. Temperature dependence of heat capacity of carbosilane dendrimers with terminal butyl groups of: 1—the fifth generation, 2—the sixth generation; AC, A′C′—the glassy state; DI, D′F′—the high elasticity state; BE, B′E′—temperature dependences of heat capacity in devitrification interval; CD, C′D′—the increase in heat capacity on devitrification; FGH—the anomaly of heat capacity for G-5(Bu)$_{128}$ as a negative deviation from the normal trend of curve; FH—the normal trend of heat capacity of G-5(Bu)$_{128}$ (a dashed line) in the interval of its anomalous dependence.

Table 1
The characteristics of experiments on measuring of the heat capacity of the G-3(Bu)$_{32}$–G-6(Bu)$_{256}$ carbosilane dendrimers with butyl terminal groups

Dendrimer	m[a] (g)	z[b]	N[c]	ΔT[d]	RMSD for C_p^o (%)[e]
G–3(Bu)$_{32}$	0.1375	4	196	6–90	0.07
				70–230	0.05
				210–340	0.03
G–4(Bu)$_{64}$	0.1565	6	224	6–90	0.07
				70–230	0.05
				210–340	0.03
G–5(Bu)$_{128}$	0.3026	4	229	6–90	0.07
				70–230	0.05
				210–350	0.03
				340–420	0.15
				400–600	0.15
G–6(Bu)$_{256}$	0.2013	4	188	6–90	0.07
				70–230	0.05
				210–350	0.03
				340–420	0.15
				400–600	0.15

[a] Weight of sample placed in calorimetric ampoule in adiabatic vacuum calorimeter.

[b] Number of test series.

[c] Number of experimental points for C_p^o in adiabatic vacuum calorimeter.

[d] Temperature range for heat capacity measurements.

[e] Root-mean-square deviation of the experimental C_p^o values from the corresponding smoothed $C_p^o = f(T)$ curves.

For all the dendrimers, except G-6(Bu)$_{256}$, with rising temperature the regions of an anomalous variation of the heat capacity are seen on the $C_p^o = f(T)$ plots as a positive deviation from a normal (interpolation) trend of the curve for G-3(Bu)$_{32}$ and G-4(Bu)$_{64}$ and a negative deviation in the case of G-5(Bu)$_{128}$. The temperature ranges of these anomalies and their thermodynamic characteristics are given in Table 3. It is worth of note that those were reproduced always on cooling and further measuring the C_p^o values in the above intervals. The nature of the anomalies is not quite clear and requires additional investigations. They are likely to be brought about by the excitation of oscillations of shielded atomic groups of repeating fragments in macromolecules on their heating and by freezing on cooling. Probably, the anomalies in the tested dendrimers should be attributed to equilibrium relaxation λ-transitions of order ↔ disorder type. The similar anomalies in the same ranges as in the case of G-3(Bu)$_{32}$ and G-4(Bu)$_{64}$ were observed too in carbosilane dendrimers with terminal allyl groups and this conforms with the fact that the same atomic groups, e.g. methyl groups, of the dendrimers of both rows took part in the given process.

The heat capacity of the dendrimers smoothly and fairly regularly changed as temperature rose and, besides as it is expected, the heat capacity more gradually increased with rising temperature in the high-elastic state and the following sequence always remained:

$C_p^o[\mathrm{G}-3(\mathrm{Bu})_{32}] < C_p^o[\mathrm{G}-4(\mathrm{Bu})_{64}] < C_p^o[\mathrm{G}-5(\mathrm{Bu})_{128}] < C_p^o[\mathrm{G}-6(\mathrm{Bu})256]$ (Figs. 1 and 2). At $T < 340$ K the heat capacity of G-3(Bu)$_{32}$ is lower than that of G-4(Bu)$_{64}$, G-5(Bu)$_{128}$ and G-6(Bu)$_{256}$ by 50–55%, 70–80% and 85–90%,

Table 2
Glass transition and glassy state characteristics of the G-3(Bu)$_{32}$—G-6(Bu)$_{256}$ carbosilane dendrimers with butyl terminal groups ($p = 0.1$ MPa)

Dendrimer	Gross-formulae	M (g/mol)	$T_g^o \pm 0.5$ (K)	ΔC_p^o (kJ/(K mol))	S_{conf}^o (kJ/(K mol))	$S^o(0)$ (kJ/(K mol))
G–3(Bu)$_{32}$	$C_{240}H_{540}Si_{29}$	4241.4	179.8	1.904	0.485	0.485
G–4(Bu)$_{64}$	$C_{496}H_{1116}Si_{61}$	8795.5	186.0	3.82	0.973	0.973
G–5(Bu)$_{128}$	$C_{1008}H_{2268}Si_{125}$	17903.8	186.5	9.29	2.366	2.366
G–6(Bu)$_{256}$	$C_{2032}H_{4572}Si_{253}$	36120.3	186.2	17.26	4.395	4.395

respectively. An essential difference in the behavior showed itself at higher temperatures. So, while the behavior of the dendrimers of the third to fifth generations was identical the dendrimer of the sixth generation displayed the second transition on the $C_p^o = f(T)$ plot between 370 and 470 K. The appearance of the second jump of the heat capacity for the sixth generation dendrimer over the range from 370 to 470 K calls for a separate consideration. Moreover, the availability of such transition is noteworthy because it can be associated with the mobility of the molecular structure as postulated earlier difference in the mobility of internal and external spheres of the molecular structure [29] that affects the total mobility of the dendrimer molecule. Apparently, it is not accidental starting from the sixth generation the dendrimers of this homolytical row stop flowing without load. It is clear that the objective explanation of the observed transition needs a wide variety of experiments such as thermophysical ones with using new objects distinguished by the structure of the outer and inner spheres of the molecular structure and experiments with applying thermomechanical and rheological methods.

In the temperature range from 340 to 600 K the differences in the heat capacities of G-5(Bu)$_{128}$ and G-6(Bu)$_{256}$ are 50–60%.

3.2. *Thermodynamic characteristics of physical transformations*

Characteristics of devitrification and glassy state of the dendrimers are listed in Table 2. The glass transition temperature T_g^o was determined by Alford and Dole method [30]—from the inflection of a plot of the temperature dependence of entropy of heating. The devitrification intervals and an increase in the heat capacity on devitrification $\Delta C_p^o(T_g^o)$ were determined graphically [31]. The configuration entropy S_{conf}^o was calculated by Eq. (1) [32]:

$$S_{conf}^o = \Delta C_p^o(T_g^o) \ln \frac{T_g^o}{T_2^o}, \tag{1}$$

where T_2^o is Kauzmann temperature [33], the ratio T_g^o/T_2^o is equal to (1.29 ± 0.14) [32,34]. It is suggested that the ratio is valid also for all dendrimers under study. It was shown [32,35] that the S_{conf}^o value is close to the magnitude of $S^o(0)$ and taking this into account one may assume quite normally that $S^o(0) = S_{conf}^o$ [35] in order to evaluate the absolute value of the entropy $S^o(T)$.

The anomaly characteristics are given in Table 3. The temperature intervals of the anomalies were determined graphically from the $C_p^o = f(T)$ curves and temperatures corresponding to the maximum deviation of the heat capacity from the normal trend of curves were taken as the temperatures of anomalies T_{an}^o. The enthalpies and entropies of anomalies were calculated as the difference of areas of the relations C_p^o versus T and C_p^o versus $\ln T$, respectively, under the heat capacity curves in the anomaly intervals (Figs. 1 and 2).

3.3. *Thermodynamic functions*

To calculate the standard thermodynamic functions (Table 4) of the dendrimers their C_p^o values were extrapolated from the temperature of the measurement beginning to 0 K by Debye's function of heat capacity:

$$C_p^o = nD\left(\frac{\theta_D}{T}\right), \tag{2}$$

where D is the symbol of Debye's function, n and θ_D are specially selected parameters. In the range from 6 to 13 K for the dendrimers of the third, fourth, fifth and sixth generations n and θ_D are 120 and 82, 245 and 82, 325 and 69, 841 and 76, respectively. Eq. (2) with the above parameters describes the experimental C_p^o values of the compounds between 7 and 13 K with an uncertainty of ±0.6%. On calculating the functions it was assumed that Eq. (2) reproduces the C_p^o values of the dendrimers at $T < 6$ K with the same uncertainty. The calculations of $H^o(T) - H^o(0)$ and $S^o(T) - S^o(0)$ were made by the numerical integration of $C_p^o = f(T)$ and $C_p^o = f(\ln T)$ curves and the

Table 3
The thermodynamic characteristics of observed anomalies for studied dendrimers samples

Dendrimer	ΔT_{an} (K)	$T_{an}^o \pm 0.5$ (K)	$C_{p,exc}^o$ [a] (kJ/(K mol))	ΔH_{an}^o (kJ/(K mol))	ΔS_{an}^o (kJ/(K mol))
G–3(Bu)$_{32}$	68–90	76.4	0.16	1.397	0.0129
G–4(Bu)$_{64}$	50–70	63.4	0.48	5.997	0.0816
	289–306	298.3	0.78	6.359	0.0212
G–5(Bu)$_{128}$	365–445	420.1	−3.59	−186.0	−0.494

[a] $C_{p,exc}^o$—the molar exceed heat capacity into the anomalous interval.

Table 4
The thermodynamic functions of studied dendrimers at a standard pressure

T (K)	$C_p^o(T)$ (kJ/(K mol))	$H^o(T) - H^o(0)$ (kJ/mol)	$S^o(T) - S^o(0)$ (kJ/(K mol))	$-[G^o(T) - H^o(0)]$ (kJ/mol)
G-3(Bu)$_{32}$				
Glassy state				
5	0.0175	0.0219	0.00583	0.00729
10	0.129	0.340	0.0456	0.116
15	0.3150	1.438	0.1319	0.5414
20	0.5160	3.510	0.2499	1.488
25	0.6986	6.620	0.3878	3.076
50	1.755	37.55	1.204	22.64
100	3.280	166.2	2.925	126.3
150	4.551	362.3	4.499	312.5
179.8	5.449	511.9	5.406	460.1
High elastic state				
179.8	7.353	511.9	5.406	460.1
200	7.618	663.4	6.204	577.4
250	8.156	1053	7.941	932.3
298.15	8.801	1462	9.434	1351
340	9.662	1844	10.63	1771
G-4(Bu)$_{64}$				
Glassy state				
5	0.0362	0.0453	0.0121	0.0151
10	0.268	0.837	0.114	0.301
15	0.6294	3.090	0.2913	1.279
20	1.033	7.190	0.5246	3.302
25	1.447	13.36	0.7979	6.589
50	3.414	75.73	2.449	46.71
100	6.697	342.1	6.022	260.2
150	9.230	740.8	9.221	642.4
186.0	11.37	1111	11.43	1014
High elastic state				
186.0	15.19	1111	11.43	1014
200	15.55	1326	12.54	1182
250	16.70	2131	16.13	1901
298.15	18.91	2973	19.20	2752
340	19.72	3760	21.67	3608
G-5(Bu)$_{128}$				
Glassy state				
5	0.080	0.100	0.0268	0.0335
10	0.530	1.479	0.2000	0.5209
15	1.229	5.803	0.5407	2.307
20	2.049	13.85	0.9986	6.121
25	2.815	26.30	1.551	12.47
50	6.856	148.6	4.781	90.39
100	13.59	670.7	11.74	503.3
150	18.64	1830	21.42	1383
186.5	22.40	2580	25.88	2246
High elastic state				
186.5	31.69	2580	25.88	2246
200	31.98	3009	28.10	2611
250	33.70	5442	38.72	4236
298.15	35.94	7118	44.84	6251
340	38.91	8675	49.72	8230
400	40.0	11100	56.2	11400
450	46.0	13200	61.2	14300
500	49.1	15600	66.2	17500
550	52.6	18100	71.0	21000
600	54.9	20800	75.7	24600

Table 4 (*Continued*)

T (K)	$C_p^o(T)$ (kJ/(K mol))	$H^o(T)-H^o(0)$ (kJ/mol)	$S^o(T)-S^o(0)$ (kJ/(K mol))	$-[G^o(T)-H^o(0)]$ (kJ/mol)
G-6(Bu)$_{256}$				
Glassy state				
5	0.153	0.192	0.0511	0.0639
10	1.08	2.91	0.391	0.999
15	2.568	11.94	1.102	4.590
20	4.154	28.59	2.050	12.41
25	5.817	53.52	3.155	25.35
50	13.89	304.7	9.793	185.0
100	26.78	1354	23.81	1027
150	36.84	2947	36.59	2542
186.2	45.08	4428	45.41	4026
High elastic state				
186.2	62.34	4428	45.41	4026
200	63.28	5295	49.90	4684
250	67.65	8561	64.46	7553
298.15	73.22	11940	76.80	10958
340	79.18	15124	86.79	14383
400	93.6	20218	101	20003
450	111	25334	113	25329
500	117	31100	125	31300
550	125	37200	136	37800
600	132	43500	147	44900

Gibbs function $G^o(T)-H^o(0)$ was estimated from the enthalpies and entropies at the corresponding temperatures [36]. It was suggested that the uncertainty of the function values is ±1% at $T < 30$ K, ±0.5% between 30 and 80 K, ±0.2% in the range from 80 to 350 K and ±1.5% between 350 and 600 K.

3.4. *Standard entropies of formation of dendrimers at 298.15 K*

From the absolute values of entropies (Tables 2 and 4) of the carbosilane dendrimers at 298.15 K and the absolute entropies of simple substances [C(gr), H_2(g), Si(cr)] it was found at $T = 298.15$ K [37,38] that the standard entropies of formation of G-3(Bu)$_{32}$–G-6(Bu)$_{256}$ dendrimers are -27.2 ± 0.1, -56.7 ± 0.1; -108.9 ± 0.1; -228.9 ± 0.1 kJ/(K mol), respectively. The values conform to the equations:

$$240\mathrm{C_{gr}} + 270\mathrm{H_{2\,g}} + 29\mathrm{Si_{cr}} = \mathrm{C_{240}H_{540}Si_{29\,h.e.}},$$

$$496\mathrm{C_{gr}} + 558\mathrm{H_{2\,g}} + 61\mathrm{Si_{cr}} = \mathrm{C_{496}H_{1116}Si_{61\,h.e.}},$$

$$1008\mathrm{C_{gr}} + 1134\mathrm{H_{2\,g}} + 125\mathrm{Si_{cr}} = \mathrm{C_{1008}H_{2268}Si_{125\,h.e.}},$$

$$2032\mathrm{C_{gr}} + 2286\mathrm{H_{2\,g}} + 253\mathrm{Si_{cr}} = \mathrm{C_{2032}H_{4572}Si_{253\,h.e.}},$$

where the physical states of the reagents are the following: gr—graphite, g—gas, cr—crystalline, h.e.—high elasticity.

3.5. *Dependence of thermodynamic functions of dendrimers on their composition and structure*

Using the data from Table 4, the relations between the thermodynamic functions and the molecular mass of the dendrimers at some temperatures were plotted. It turned out that the isotherms have a linear character in the chosen temperature intervals. Fig. 3 illustrates the isotherms ($T = 100$, 200, 298.15 and 340 K) of the relations C_p^o against M (the molecular mass) of the carbosilane dendrimers of the third to the sixth generations with terminal butyl groups, the dendrimers being in similar physical states. As seen in Fig. 3, the experimental points correspond well to the averaging curves, the reliability of approximations R^2 is 0.9996–0.9999. The maximum arithmetic-mean error of the deviation of the experimental points from the appropriate curves is ±(0.5–2.0)%. Below are given equations of relations between the thermodynamic functions of the tested objects and their molecular mass M at certain temperatures T:

$$C_p^o(100) = 0.0007368M + 0.2558, \tag{3}$$

$$C_p^o(200) = 0.001747M + 0.3409, \tag{4}$$

$$C_p^o(298.15) = 0.002008M + 0.6086, \tag{5}$$

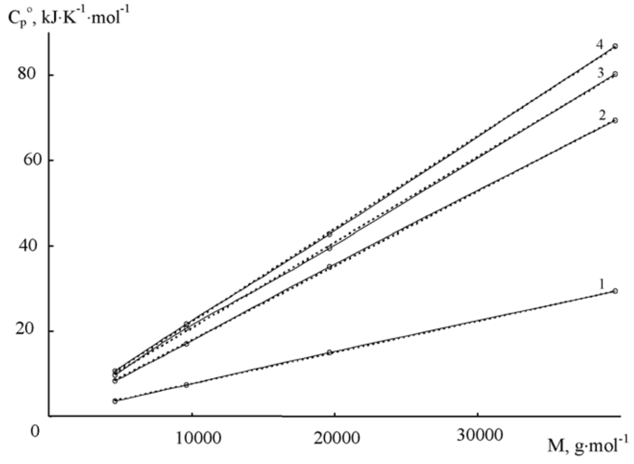


Fig. 3. Dependence of isotherms of heat capacity on molecular mass of carbosilane dendrimers of the third to the sixth generations: 1—$T = 100$ K, 2—$T = 200$ K, 3—$T = 298.15$ K, 4—$T = 340$ K.

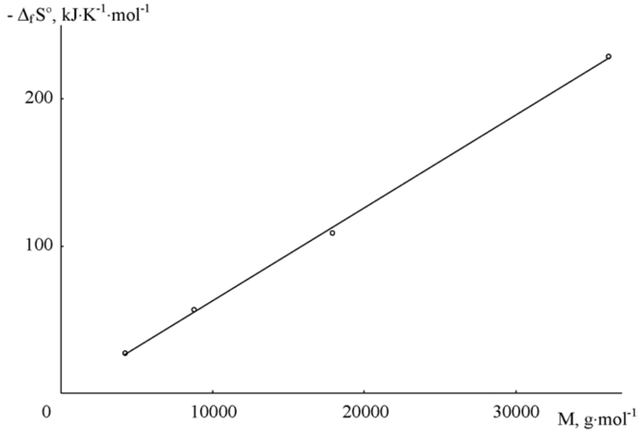


Fig. 4. Dependence of entropy of formation $\Delta_f S^o$ of dendrimers of the third to the sixth generations with terminal butyl groups at 298.15 K on molecular mass *M*.

$$C_p^o(340) = 0.002178M + 0.3928, \tag{6}$$

$$H^o(298.15) - H^o(0) = 0.3285M + 87.248, \tag{7}$$

$$S^o(298.15) - S^o(0) = 0.002111M + 0.5996, \tag{8}$$

$$G^o(298.15) - H^o(0) = 0.3010M + 90.848. \tag{9}$$

In Eqs. (3)–(9) the heat capacity and the entropy are given in kJ/(K mol) while the enthalpy and Gibbs function in kJ/mol.

From the data of the present work the relation between the formation entropy and the molecular mass (M) and the number of butyl groups (k) on the outer sphere of the dendrimers at 298.15 K was constructed. Isotherms $\Delta_f S^o$ versus M and k are straight lines (for example, Fig. 4; the reliability of the approximations chosen is 0.9992) described by linear equations (Eqs. (10) and (11)) with an uncertainty of 0.5%:

$$\Delta_f S^o\,(298.15\,\mathrm{K}) = -0.8978k + 2.3004, \tag{10}$$

$$\Delta_f S^o\,(298.15\,\mathrm{K}) = -0.0063M + 0.3274, \tag{11}$$

where the entropy of formation is given in kJ/(K mol). The dependences derived allow the estimation of $\Delta_f S^o$ of the higher generation dendrimers with terminal butyl groups.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tca.2005.11.009.

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