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Thermodynamic properties of the first to fifth generations of carbosilane dendrimers with allyl terminal groups*

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Temperature dependences of the specific heats, characteristic temperatures, and enthalpies of physical transformations of the first to fifth generations of carbosilane dendrimers with allyl terminal groups were studied using an adiabatic vacuum calorimeter in the temperature range 6—340 K. The error of measurements was, as a rule, about 0.2%. Thermodynamic characteristics of physical transformations of the dendrimers were determined and their thermodynamic functions $C_p^\circ(T)$, $H^\circ(T)-H^\circ(0)$, $S^\circ(T)-S^\circ(0)$, and $G^\circ(T)-H^\circ(0)$ were calculated for the temperature range 0—340 K. The thermodynamic functions of the dendrimers are linearly related to their molecular weights, the number of allyl groups on their outer spheres, and the number of moles of diallylmethylsilane per mole of the dendrimers formed. Additive dependence of the properties of the dendrimers on their chemical composition and structure indicates that the energy of interaction between structural fragments of the dendrimers is independent of the dendrimer generation number. The fractal dimensions, D, of all dendrimers studied in this work are 1.2—1.3 in the temperature range 30—50 K, thus indicating a chain-layered structure of the dendrimer glasses.

Key words: carbosilane dendrimers with allyl terminal groups, generation, specific heat, calorimetry, thermodynamics.

Dendrimers combine the properties of macromolecules and individual molecular species and represent a new form of organization of polymeric structures.[1] One of the most important aspects of studies of these compounds is to elucidate interrelations between their structure and thermodynamic properties.[1—3] The synthesis, physicochemical characteristics, and practical applications of dendritic polymers have been the subject of intensive research.[2—7] Nevertheless, their thermodynamic properties are still poorly studied. Only few calorimetric studies[8—13] of the thermodynamic characteristics of dendritic polyperfluorophenylgermane[8—10] and the G-1 and G-2 carbosilane dendrimers with methoxyundecylene terminal groups[11—13] have been reported. An unquestionable advantage of calorimetric studies of dendrimers is the possibility of obtaining quantitative data on the thermodynamic properties over a wide temperature range, which permits elucidation of interrelations between the thermodynamic properties and the chemical composition and molecular structure of these compounds.

The aim of this work was (i) to carry out calorimetric measurements of the temperature dependences of the specific heats of G-1(All)$_8$—G-5(All)$_{128}$ carbosilane dendrimers with allyl terminal groups in the temperature range 6—340 K, (ii) to reveal physical transformations of these compounds on heating and on cooling in this temperature range and to determine their thermodynamic characteristics, (iii) to calculate the thermodynamic functions (for the temperature range 0 K < $T \le$ 340 K) and the standard entropies of formation of the dendrimers from elementary substances at 298.15 K, and (iv) to elucidate interrelations between the thermodynamic characteristics of these compounds and their chemical composition and structure, physical states, and temperature.

Experimental

Dendrimer samples. The structures of the first three generations of carbosilane dendrimers with allyl terminal groups stud-

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* Dedicated to Academician I. P. Beletskaya on the occasion of her anniversary.

† Deceased.

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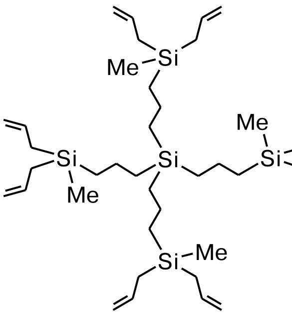
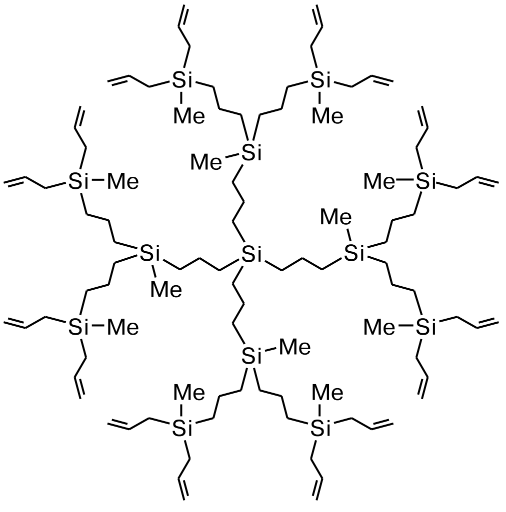
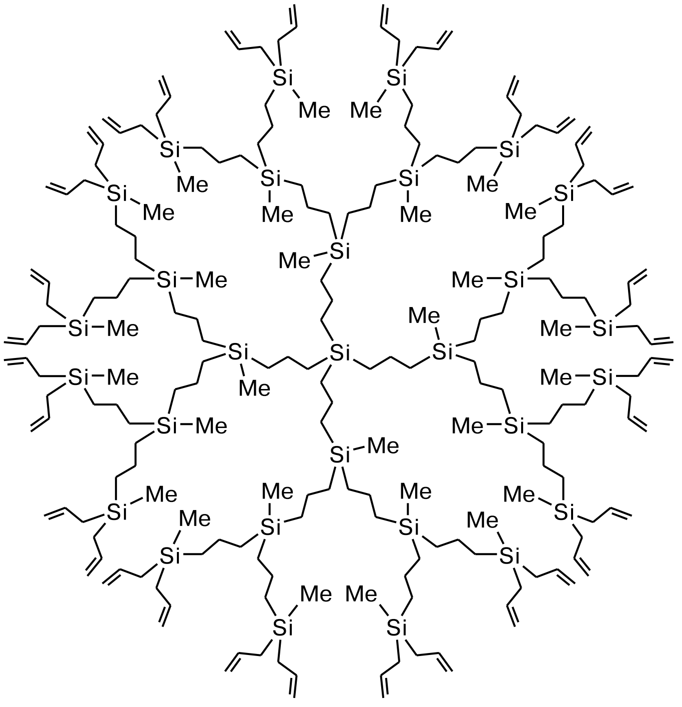


G-1(All)$_8$



G-2(All)$_{16}$



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

ied in this work, namely, G-1(All)$_8$, G-2(All)$_{16}$, and G-3(All)$_{32}$ are shown above.

Conventional notations of the dendrimers are given with the structural formulas. The fourth and fifth dendrimer generations are denoted in a similar way, namely, G-4(All)$_{64}$ and G-5(All)$_{128}$, respectively. A common notation for a dendrimer generation has the form G-n(All)$_m$,[14] where G the abbreviation of the term "generation;" n = 1, 2, 3,... is the dendrimer generation number; and m is the number of allyl groups on the outer sphere of the dendrimer molecules ($m = 2^{n+2}$).

Samples of G-1(All)$_8$—G-5(All)$_{128}$ dendrimers were prepared at the N. S. Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences (Moscow) following the known procedure.[14] All compounds was purified using HPLC (a KNAUER preparative chromatograph with a Vertex column). All compounds are bright-yellow viscous liquids under normal conditions. The structures of the samples were confirmed by ^{1}H NMR spectroscopy (spectra were recorded on a Bruker WP-250 instrument) and IR spectroscopy (spectra were recorded on a Bruker ISF-110 spectrometer).[14]

Experimental techniques and measurement procedure. The specific heats (C_p°), temperatures, and enthalpies of physical transformations were measured on a BKT-3 thermal-physics setup (an automated adiabatic vacuum calorimeter). The design of the calorimeter and the experimental procedure were similar to those reported earlier.[15,16] Based on the results of calibrations and tests of the calorimeter, we found that the error of measurements of the specific heat at helium temperatures lies within 2%. As the temperature increased to 40 K, the error of measurements reduced to 0.5% and then down to ~0.2% for the temperature range 40—340 K. The phase transition temperatures were determined with an error of up to 0.02 K, while the accuracy of determination of the phase transition enthalpies was 0.5%.

The most important parameters of the experiments on measuring the specific heats of the dendrimers are listed in Table 1. All experimental points for C_p° and the smoothed curves are shown in Fig. 1.

Results and Discussion

Specific heat. On cooling from room temperature down to ~5—6 K at a rate of ~0.01 K s^{-1} the compounds under study experienced a transition to the supercooled state and then to the glassy state. On heating in the course of specific heat measurements all dendrimers, except for the G-2(All)$_{16}$ dendrimer, exhibited an anomaly in the temperature range 60—80 K, which manifested itself as positive deviation of the temperature dependence of the specific heat from its normal behavior. On further heating all dendrimers experienced devitrification. A continuation

Table 1. Characteristics of experiments on measuring the specific heats (C_p°) of the G-1(All)$_8$—G-5(All)$_{128}$ carbosilane dendrimers with allyl terminal groups

Dendrimer	m^a/g	z^b	N^c	ΔT^d /K	RMSD for C_p° (%)^e
G-1(All)$_8$	0.1513	7	383	6—50	0.07
				80—220	0.05
				240—340	0.02
G-2(All)$_{16}$	0.2518	3	250	6—80	0.07
				80—220	0.05
				240—340	0.02
G-3(All)$_{32}$	0.1964	5	264	6—50	0.07
				80—220	0.05
				240—340	0.03
G-4(All)$_{64}$	0.2683	5	250	6—50	0.07
				80—220	0.05
				240—340	0.04
G-5(All)$_{128}$	0.2696	4	237	6—50	0.07
				80—220	0.05
				240—340	0.03

[a] Weight of the sample placed in calorimetric ampule.

[b] Number of test series.

[c] Number of experimental points for C_p°.

[d] Temperature range for specific heat measurements.

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

of the specific heat measurements of supercooled liquids formed at $T < 160$ K led to spontaneous crystallization of the G-1(All)$_8$ dendrimers only, which began at $T \approx 175$ K (detected by intense heat release). After completion of crystallization and cooling of the crystals obtained down to the initial measuring temperature (~6 K) they were reheated and the C_p° *vs.* T dependences exhibited melting detected by sharp endotherm in curve *1*. Other dendrimers did not exhibit crystallization upon heating; moreover, crystallization was also not observed in the experiments with variable heating/cooling rates.

The enthalpy difference between the glassy state ($H°_{\text{glass}}(0)$) and the crystalline state ($H°_{\text{cryst}}(0)$) of the G-1(All)$_8$ dendrimers calculated for $T = 0$ K is 17.6 kJ mol^{-1}, while the zero-point entropy, $S°(0)$, in the glassy state is 58 J K^{-1} mol^{-1}.[12] The temperature dependences of the specific heats of the compounds under study exhibited no features, that is, the C_p° values smoothly increased with an increase in the temperature and were ordered as follows: C_p°[G-1(All)$_8$] < C_p°[G-2(All)$_{16}$] < < C_p°[G-3(All)$_{32}$] < C_p°[G-4(All)$_{64}$] < C_p°[G-5(All)$_{128}$] at the same temperatures throughout the temperature range studied (see Fig. 1). It should be noted that the specific heats of the G-1(All)$_8$ dendrimers in the glassy and crystalline states coincide within the limits of experimental errors. Usually, this is typical of polymeric systems only.

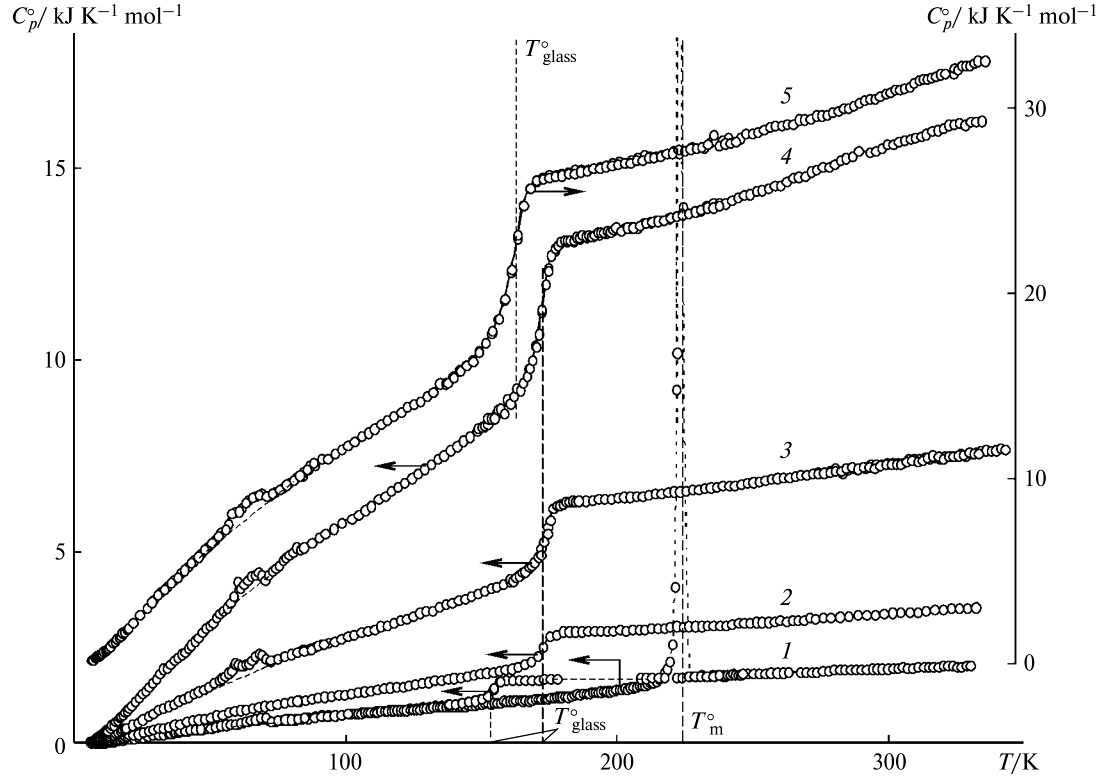


Fig. 1. Specific heats of the G-1(All)$_8$—G-5(All)$_{128}$ carbosilane dendrimers with allyl terminal groups: G-1(All)$_8$ (*1*); G-2(All)$_{16}$ (*2*); G-3(All)$_{32}$ (*3*); G-4(All)$_{64}$ (*4*); and G-5(All)$_{128}$ (*5*). $T°_{\text{glass}}$ is the glass transition temperature; $T°_{\text{m}}$ is the melting temperature of G-1(All)$_8$.

In the temperature range T°_{glass}—T°_{m} the specific heat, C_p°, of the G-1(All)$_8$ supercooled liquid is appreciably (by ~25—30%) larger than the specific heat in the crystalline state.

The thermodynamic characteristics of melting of this dendrimer have been studied in detail.[12] Their numerical values are as follows: T°_{m} = 222.8 K, $\Delta H^{\circ}_{\text{m}}$ = 39.2±1.2 kJ mol^{-1}, and $\Delta S^{\circ}_{\text{m}}$ = 176±5 J K^{-1} mol^{-1}.

It was of interest to determine the fractal dimension, D, of the dendrimers under study, which is the most important parameter in the multifractal version of the Debye theory of specific heat of solids.[17,18] It allows assessment of the character of the heterodynamics of solids.[19] The D values can be found[17] from the $\ln C_V$—$\ln T$ plot, as follows from the formula

$$C_V = 3D(D+1)kN\gamma(D+1)\xi(D+1)(T/\Theta_{\max})^D, \qquad (1)$$

where k is the Boltzmann constant, N is the number of atoms in the molecule, $\gamma(D+1)$ is the γ-function, $\xi(D+1)$ is the Riemann ξ-function, and $\Theta_{\max}$ is the maximum characteristic temperature. For a particular solid the parameter $\mathrm{A} = [3D(D+1)kN\gamma(D+1)\xi(D+1)]/\Theta^D_{\max}$ is a constant, and Eq. (1) can be written as follows

$$\ln C_V = \ln \mathrm{A} + D\ln T. \qquad (2)$$

It is known that for all solids and, probably, for the dendrimers under study one gets $C_p^{\circ} \approx C_V$ at $T < 50$ K. Using the experimental data on the specific heats of the G-1(All)$_8$—G-5(All)$_{128}$ dendrimers, we obtained that D = 1.2—1.3 in the temperature range 30—50 K. With these D values and the corresponding characteristic temperatures $\Theta_{\max}$ (264.5, 461.0, 305.3, 299.2, and 444.1 K, respectively) the specific heats of the dendrimers under study can be calculated using Eq. (1) with an error of ±0.5%. The D value lies between 1.8 and 1.9 in the temperature range 15—30 K and equals 3 at $T < 10$ K. An increase in D on cooling seems to be due to diminution of the volume of the compound and to strengthening of intermolecular interactions. At $T > 30$ K, these factors have an insignificant or even negligible effect on the parameter D. The D values found (D = 1.2—1.3) suggest that the dendrimer glasses studied in this work have a chain-layered structure.

Glass transition and glassy state parameters. The glass transition and glassy state parameters of the compounds under study are listed in Table 2. The temperature ranges for glass transitions, the glass transition temperatures (T°_{glass}), and the increase in the specific heat upon devitrification, $\Delta C_p^{\circ}(T^{\circ}_{\text{glass}})$, were determined graphically.[20] The configuration entropies, S°_{conf}, were calculated using the formula[21]:

$$S^{\circ}_{\text{conf}} = \Delta C_p^{\circ}(T^{\circ}_{\text{glass}})\ln T^{\circ}_{\text{glass}}/T_2^{\circ}, \qquad (3)$$

where T_2° is the Kauzman temperature.[22] Usually, the $T^{\circ}_{\text{glass}}/T_2^{\circ}$ ratio for monomeric and polymeric glasses is 1.29±0.14.[21,23] It is thought to hold for all the dendrimers under study. It was shown[21,24] that the numerical value of S°_{conf} is close to that of the $S^{\circ}(0)$ parameter and, in principle, the configuration entropy can be used for estimating the absolute values of entropies, $S^{\circ}(T)$, of glassy substances by setting $S^{\circ}(0) = S^{\circ}_{\text{conf}}$.[24] However, the $S^{\circ}(0)$ entropy of the G-1(All)$_8$ dendrimers is nearly by a factor of 1.3 greater than the S°_{conf} value. Probably, this is due to specific features of the first dendrimer generation, which is a low-molecular-weight compound.

Table 2. Glass transition and glassy state parameters of the G-1(All)$_8$—G-5(All)$_{128}$ carbosilane dendrimers with allyl terminal groups (p = 101.325 kPa)

Dendrimer	ΔT_{glass}	T°_{glass}	k*	$\Delta C_p^{\circ}(T^{\circ}_{\text{glass}})$	S°_{conf}
	K			J K^{-1} mol^{-1}	
G-1(All)$_8$	150—160	154±1	35	405	44
G-2(All)$_{16}$	170—180	172±1	70	810	206
G-3(All)$_{32}$	170—180	173±1	140	1640	417
G-4(All)$_{64}$	170—180	172±1	310	3660	931
G-5(All)$_{128}$	160—170	162±1	680	7922	2016

* The number of "beads."

Analysis of the data listed in Table 2 shows that all dendrimers undergo devitrification in very narrow temperature ranges (~10 K), which is usually typical of monomeric compounds). The temperature range for glass transition on heating in chain polymers is, as a rule, several times wider (usually, 20—30 K). The G-2(All)$_{16}$—G-4(All)$_{64}$ dendrimers undergo devitrification in the same temperature range, whereas for the G-1(All)$_8$ and G-5(All)$_{128}$ dendrimers this range is shifted toward lower temperatures. The G-2(All)$_{16}$—G-4(All)$_{64}$ dendrimers also have nearly the same glass transition temperature (173±1 K), while the T°_{glass} values for the G-1(All)$_8$ and G-5(All)$_{128}$ dendrimers are 20 and 10 K lower, respectively. The lower T°_{glass} value of the G-1(All)$_8$ dendrimers is quite reasonable,[25] since this is a low-molecular-weight compound with more disordered molecular structure. A decrease in the T°_{glass} value for the G-5(All)$_{128}$ dendrimers was first observed and can be due to a decrease in the contribution of intermolecular interactions owing to an increase in the distances between allyl groups on the dendrimer sphere. The dependence of T°_{glass} on the molecular weight M, which is typical of chain polymers (an increase in T°_{glass} with increasing M), was not observed for the dendrimers under study.

It was shown[26] that an increase in the specific heat upon devitrification, $\Delta C_p^{\circ}(T^{\circ}_{\text{glass}})$, is due to excitation of the vibrations of the atoms or atomic groups capable of executing individual motions (the so-called "beads"). Analysis of the $\Delta C_p^{\circ}(T^{\circ}_{\text{glass}})$ values for many polymers showed[26] that "beads" make an additive contribution to the specific heat, namely, 11.7 J K^{-1} mol^{-1} per mole of "beads". This allows determination of the number of "beads," k, in each dendrimer under study using the formula $k = \Delta C_p{}^\circ(T^\circ_{\text{glass}})/11.7$ (see Table 2). It is noteworthy that the number of "beads" in the first three dendrimer generations is doubled on going from G-1 to G-2 and then from G-2 to G-3. Passage from G-3 to G-4 and then from G-4 to G-5 causes the number of "beads" to increase by nearly a factor of 2.2. We believe that the narrow temperature range for the devitrification and close values of the glass transition temperatures of the dendrimers under study are due to the fact that they are determined by excitation of vibrations of "beads" of the same nature and chemical composition in identical intermolecular force fields. A decrease in T°_{glass} on going from the fourth to the fifth dendrimer generation can probably be attributed to a decrease in the density of the G-5 dendrimer and, hence, to an increase in the free volume.

Thermodynamic characteristics of the specific heat anomalies. All dendrimers, except for the G-2(All)$_{16}$ dendrimer, exhibited specific heat anomalies in the glassy state on heating and on re-heating after cooling to temperatures below the lowest temperature at which the anomaly could be detected. The G-1(All)$_8$ dendrimer exhibited a specific heat anomaly in both the glassy and crystalline states. The characteristics of the specific heat anomalies are listed in Table 3. The temperature ranges for the anomalies were determined graphically and the temperatures corresponding to the maximum specific heats ($C^\circ_{p,\max}$) in these temperature ranges were taken as the specific heat anomaly temperatures, T°_{an}. The enthalpies were calculated as the differences between the areas under the $C_p{}^\circ(T)$ curves with and without the specific heat anomaly (points and dashed lines, respectively). The entropies were calculated analogously using the corresponding $C_p{}^\circ(\ln T)$ curves. The nature of the specific heat anomaly is still to be clarified; however, reproducibility of this phenomenon suggests that it originates from the excitation of vibrations of particular atomic groups in the molecules on heating and on freezing and can be attributed to relaxation phase transitions of the order $\rightleftharpoons$ disorder type in the dendrimers under study.

Thermodynamic functions. To calculate the thermodynamic functions (Table 4), the temperature dependences of the specific heats of the G-(All)$_8$—G-5(All)$_{128}$ dendrimers were extrapolated from the initial measuring temperature (~6 K) down to 0 K using the Debye formula for the specific heat

$$C_p{}^\circ = nD(\Theta_D/T), \tag{4}$$

where D is Debye's specific heat function and n and Θ_D are parameters. In the temperature range 7—16 K the n and Θ_D values found for the G-1(All)$_8$—G-5(All)$_{128}$ dendrimers are respectively 10 and 61.08; 39 and 72.74; 80 and 73.01; 183 and 74.85; and 350 and 70.96. The thermodynamic functions were calculated assuming that the specific heats of the compounds under study at $T < 6$ K can be determined using formula (4) with nearly the same error as that typical of the temperature ranges for which the n and Θ_D values were obtained.

Table 3. Characteristics of specific heat anomalies in carbosilane dendrimers under study

Dendrimer	ΔT_{an}	T°_{an}	$C^\circ_{p,\max}$	$\Delta S^\circ_{\text{an}}$	$\Delta H^\circ_{\text{an}}$ /J mol^{-1}
	K		J K^{-1} mol^{-1}		
G-1(All)$_8$	62—73	69.10	477.7	6.0	414.2
G-3(All)$_{32}$	55—72	67.87	2354	35.4	2422
G-4(All)$_{64}$	56—70	67.59	4472	57.7	3537
G-5(All)$_{128}$	51—72	69.56	9207	83.4	5806

The $H^\circ(T) - H^\circ(0)$ and $S^\circ(T) - S^\circ(0)$ functions were calculated by numerical integration of the dependences $C_p{}^\circ = f(T)$ and $C_p{}^\circ = f(\ln T)$, respectively, while the Gibbs functions, $G^\circ(T)—H^\circ(0)$, of the compounds were determined using the enthalpies and entropies at the corresponding temperatures.

Dependence of thermodynamic functions of dendrimers on the chemical composition and molecular structure. Using the data listed in Table 4, we plotted the dependences of the thermodynamic functions of the dendrimers under study on their molecular weights at different temperatures. The corresponding isotherms were found to be linear.

Figure 2 presents the dependences of the specific heat isotherm ($C_p{}^\circ$) on the molecular weight of the G-1(All)$_8$—G-5(All)$_{128}$ carbosilane dendrimers at T = 100, 200, 298.15, and 340 K (at these temperatures the dendrimers are in identical physical states). As can be seen, the smoothed lines fit well the experimental data. Reliability of the approximation R^2 = 1. The

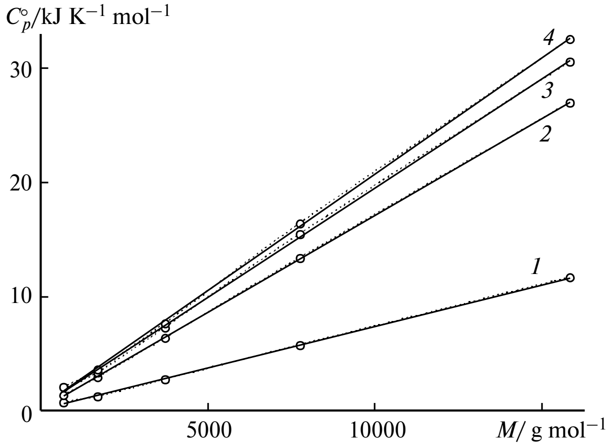


Fig. 2. Dependences of the specific heat isotherm ($C_p{}^\circ$) on the molecular weight (M) of the G-1(All)$_8$—G-5(All)$_{128}$ carbosilane dendrimers at different temperatures: 100 (*1*); 200 (*2*); 298.15 (*3*); and 340 K (*4*).

Table 4. Thermodynamic functions of carbosilane dendrimers at a standard pressure

T/K	$C_p^\circ(T)$	$S^\circ(T)-S^\circ(0)$	$H^\circ(T)-H^\circ(0)$	$-[G^\circ(T)-H^\circ(0)]$
	J K^{-1} mol^{-1}		kJ mol^{-1}	
G-1(All)$_8$				
Glassy state				
5	2.56	0.852	0.0032	0.00107
10	21.6	7.295	0.0554	0.01759
15	49.86	20.94	0.2286	0.08549
20	85.08	40.26	0.5685	0.2367
25	118.1	62.68	1.074	0.4929
50	289.2	200.5	6.279	3.745
100	536.9	482.4	27.25	20.99
154	728.1	751.5	61.27	54.46
Supercooled liquid				
154	1134	751.5	61.27	54.46
200	1186	1055	114.7	96.26
222.8	1212	1184	142.0	121.8
Crystalline state				
5	2.56	0.852	0.0032	0.00107
10	21.6	7.295	0.0554	0.01759
15	49.86	20.94	0.2286	0.08549
20	85.08	40.26	0.5685	0.2367
25	118.1	62.68	1.074	0.4929
50	289.2	200.5	6.280	3.745
100	536.9	482.4	27.25	20.99
200	903.8	963.8	98.82	93.95
222.8	991.7	1066	120.4	117.1
Liquid				
222.8	1212	1242	159.6	117.1
298.15	1355	1615	256.4	225.2
340	1429	1798	314.8	296.6
G-2(All)$_{16}$				
Glassy state				
5	8.20	2.74	0.0103	0.0034
10	57.0	19.8	0.1479	0.0501
15	123.8	55.06	0.5941	0.2318
20	205.2	101.8	1.415	0.6201
25	282.5	155.6	2.645	1.247
50	690.2	480.7	14.92	9.112
100	1286	1162	65.80	50.44
172	2085	2047	185.8	166.3
Rubbery state				
172	2895	2047	185.8	166.3
200	2955	2488	267.6	229.9
298.15	3381	3740	576.9	538.2
340	3568	4197	722.5	704.4
G-3(All)$_{32}$				
Glassy state				
5	16.7	5.58	0.021	0.0070
10	115	44.18	0.326	0.1158
15	264	118.5	1.269	0.5095
20	441	217.9	3.016	1.342
25	626	336.3	5.686	2.721
50	1503	1043	32.40	19.74
100	2763	2555	144.6	110.9
173	4680	4501	409.8	368.8
Rubbery state				
173	6290	4501	409.8	368.8
200	6408	5420	581.0	503.0
298.15	7277	8130	1250	1174
340	7658	9110	1563	1535
G-4(All)$_{64}$				
Glassy state				
5	35.3	11.79	0.044	0.0147
10	251	81.25	0.609	0.2033
15	560	241.0	2.634	0.9817
20	921	450.2	6.310	2.694
25	1300	696.9	11.87	5.548
50	3100	2152	66.90	40.70
100	5803	5259	298.3	227.6
172	9312	9258	840.7	751.7
Rubbery state				
172	12970	9258	840.7	751.7
200	13394	11246	1210	1039
298.15	15564	16961	2622	2435
340	16358	19061	3291	3189
G-5(All)$_{128}$				
Glassy state				
5	107	36.3	0.136	0.046
10	530	235	1.682	0.666
15	1202	574.9	5.993	2.630
20	1963	1024	13.89	6.594
25	2743	1545	25.63	12.99
50	6424	4600	140.9	89.09
100	12225	10932	611.8	481.5
162	17949	18090	1543	1396
Rubbery state				
162	25871	18090	1543	1396
200	27009	23574	2534	2180
298.15	30632	34963	5346	5079
340	32680	39126	6673	6630

maximum mean deviation of the experimental points from corresponding straight lines is ~0.5% for the G-1(All)$_8$—G-4(All)$_{64}$ dendrimers and ~5% for the G-5(All)$_{128}$ dendrimer. Listed below are the equations of the isotherms of the thermodynamic functions of the carbosilane dendrimers under study on their molecular weights M.

$$C_p^\circ(100) = 0.7373M + 30.261, \tag{5}$$

$$C_p^\circ(200) = 1.7037M + 49.777, \tag{6}$$

$$C_p^\circ(298.15) = 1.9352M + 123.9, \tag{7}$$

$$C_p^\circ(340) = 2.0653M + 49.191; \tag{8}$$

$$H^\circ(100) - H^\circ(0) = 0.0386M + 0.0908, \tag{9}$$

$$H^\circ(200) - H^\circ(0) = 0.1598M - 9.1161, \tag{10}$$

$$H^\circ(298.15) - H^\circ(0) = 0.3367M + 7.0193, \tag{11}$$

$$H^\circ(340) - H^\circ(0) = 0.4205M + 10.631; \tag{12}$$

$$S^\circ(100) = 0.6872M + 0.8578, \tag{13}$$

$$S^\circ(200) = 1.4845M + 61.498, \tag{14}$$

$$S^\circ(298.15) = 2.2032M + 28.265, \tag{15}$$

$$S^\circ(340) = 2.4663M + 17.328. \tag{16}$$

In equations (5)—(16) the specific heat is given in J K^{-1} mol^{-1}, the enthalpy is given in kJ mol^{-1}, and the entropy is given in J K^{-1} mol^{-1}. We found that similar dependences can be obtained using the number of allyl groups (m) on the outer sphere of the dendrimers and the number of moles of diallylmethylsilane (q) per mole of the dendrimers formed. The dependences of the corresponding thermodynamic functions on m at 298.15 K are as follows:

$$C_p^\circ\,(298.15) = 244.42m - 481.25, \tag{17}$$

$$H^\circ(298.15) - H^\circ(0) = 42.51m - 98.246, \tag{18}$$

$$S^\circ(298.15) = 278.2m - 717.17. \tag{19}$$

Assuming that these dependences also hold for higher dendrimer generations (G > 5), one can evaluate their thermodynamic functions using corresponding equations. In addition, linear dependences of the properties on M, m, and q indicate additive contributions of structural fragments of the dendrimers under study to the corresponding properties. This, in turn, points to invariance of the intermolecular forces in dendrimers with respect to an increase in their size (generation number).

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