

CHEMICAL THERMODYNAMICS  
AND THERMOCHEMISTRY

## Thermodynamic Properties of First- and Third-Generation Carbosilane Dendrimers with Terminal Phenyldioxolane Groups

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**Abstract**—The heat capacities of first- and third-generation carbosilane dendrimers with terminal phenyldioxolane groups are studied as a function of temperature via vacuum and differential scanning calorimetry in the range of 6 to 520 K. Physical transformations that occur in the above temperature range are detected and their standard thermodynamic characteristics are determined and analyzed. Standard thermodynamic functions  $C_p^0(T)$ ,  $[H^0(T) - H^0(0)]$ ,  $[S^0(T) - S^0(0)]$ , and  $[G^0(T) - H^0(0)]$  in the temperature range of  $T \rightarrow 0$  to 520 K for different physical states and the standard entropies of formation of the studied dendrimers at  $T = 298.15$  K are calculated, based on the obtained experimental data.

**Keywords:** dendrimers, thermodynamics, heat capacity, glass transition temperature

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### INTRODUCTION

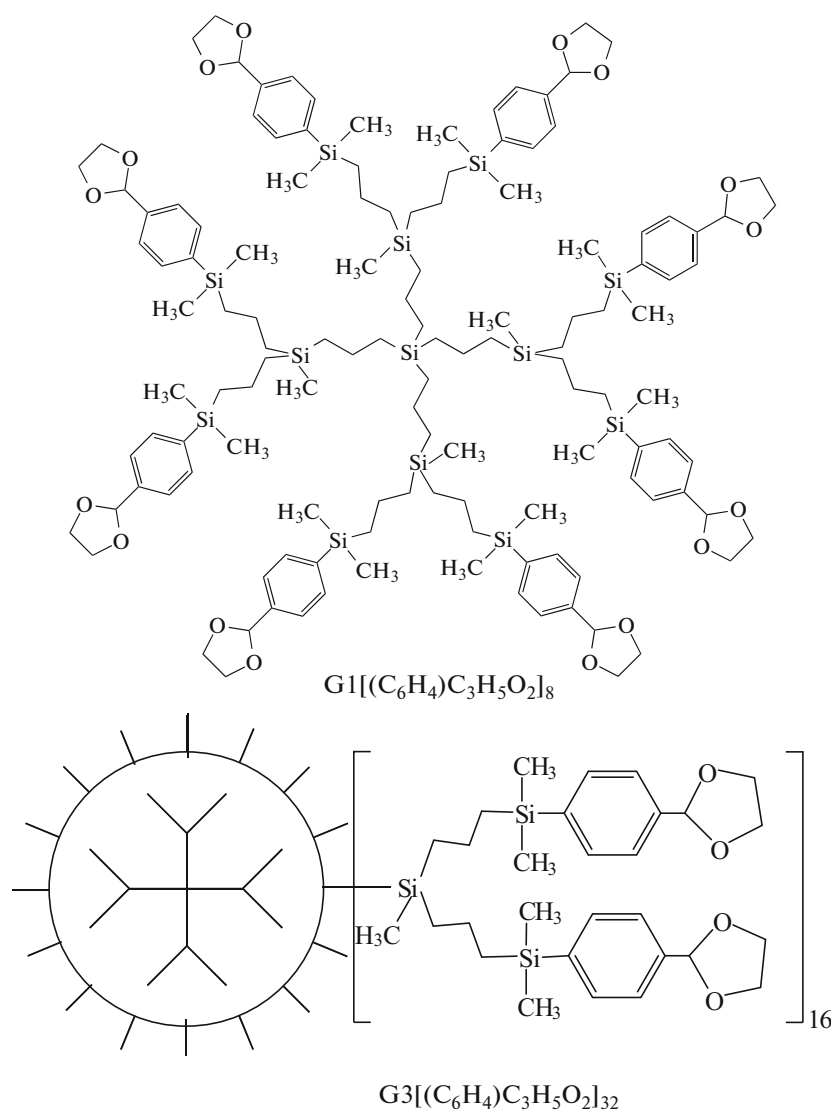
Dendrimers are monodisperse globular macromolecules with regular hyperbranched architectures [1–4]. They are characterized by good solubility in a wide spectrum of organic solvents and low viscosity of solutions, compared to linear polymers with equivalent molecular weight. Due to their unique structure, dendrimer molecules are capable of self-assembly. One feature of dendrimer synthesis is a great number of terminal groups forming the external sphere of a molecule and governing its behavior to a considerable degree [4], allowing us to control the properties of such objects. This and the variety of dendrimers of different chemical natures make the design of new materials with valuable commercial properties very promising.

Dendrimers are now being tested in the development and production of high-tech nanomaterials with unique magnetic, electrochemical, and photochemical properties. Carbosilane dendrimers are thermodynamically and kinetically stable, due to the low polarity and great strength of Si–C bonds. Considering the high degree of external sphere functionality, such molecules can be used to immobilize catalytically active species in designing reusable catalysts. The most promising field of dendrimer application is medicine [5, 6]. The authors of [7] showed dendrimer molecules to be capable of including up to 30 vol % of a solvent, suggesting their high potential for the encapsulation of

low-molecular-weight objects within the structure. They can carry chemically, optically, and biologically active species, especially different pharmaceutical substances, thereby facilitating their transport and reducing their toxicity. The pharmaceutical agent, contained in the inner sphere of a dendrimer when entering affected tissue, is released due to the change in the pH of the medium.

The acquisition and study of thermodynamic data on dendrimers, along with knowledge of important patterns of changes in their properties depending on composition and structure, are important and highly relevant lines of research. Studying the standard thermodynamic properties of carbosilane dendrimers via precision adiabatic vacuum and differential scanning calorimetry in a wide range of temperatures allowed us to determine and analyze their dependences on composition and structure [8–15]. This work continues our studies of thermodynamic properties of carbosilane dendrimers.

The aims of this work were to study the temperature dependences of the heat capacities of first- and third-generation carbosilane dendrimers with terminal phenyldioxolane groups via calorimetry in the range of 6 to 520 K; to detect possible physical transformations upon their heating and cooling, and to determine their thermodynamic characteristics; to calculate standard thermodynamic functions  $C_p^0(T)$ ,  $[H^0(T) - H^0(0)]$ ,



**Fig. 1.** Schematic representation of the samples of first- ( $G1[(C_6H_4)C_3H_5O_2]_8$ ) and third-generation ( $G3[(C_6H_4)C_3H_5O_2]_{32}$ ) carbosilane dendrimers with terminal phenyldioxolane groups.

$[S^\circ(T) - S^\circ(0)]$ , and  $[G^\circ(T) - H^\circ(0)]$  for the range of  $T \rightarrow 0$  to 520 K, and the standard entropies of formation of dendrimers in an amorphous (devitrified) state at  $T = 298.15$  K; and to compare the standard thermodynamic properties of the studied dendrimers.

## EXPERIMENTAL

### Sample Characteristics

Figure 1 shows schematic representations of the investigated carbosilane dendrimer samples. GX denotes the generation number of the allyl functional dendrimer on whose basis the compounds were obtained, and the structural formula in square brackets is the fragment of the terminal group of the dendrimer surface layer.

The dendrimer samples studied in this work were synthesized at the Enikolopov Institute of Synthetic Polymeric Materials of Russian Academy of Sciences [16]. Under normal conditions, the first-generation dendrimer was a transparent colorless viscous liquid, while the third-generation dendrimer was a transparent wax-like substance. Both samples were very soluble in organic solvents. The composition and structure of our samples were confirmed via elemental analysis,  $^1H$  NMR spectroscopy (Bruker WP-200 SY spectrometer; 200.13 MHz; internal standard tetramethylsilane), and IR spectroscopy (Bruker ISF-110 Fourier-transform spectrometer).

### Measuring Apparatus and Procedure

The heat capacities of the dendrimers in the range of 6 to (324–345) K were measured using a BKT-3

automated adiabatic vacuum calorimeter (Termis, Russia). The operational reliability of the calorimeter was verified by measuring the heat capacities of reference substances, K-2 grade benzoic acid, and corundum. The data from calibrating the calorimeter showed the error in measuring heat capacity to be no more than  $\pm 2\%$  up to 15 K;  $\pm 0.5\%$  in the range of 15–40 K; and  $\pm 0.2\%$  in the range of 40–345 K. The error in measuring the glass transition temperature was  $\pm 1$  K. The calorimeter design and operating procedure were described in detail in [17, 18].

The calorimetric ampule was a thin-walled cylindrical titanium vessel with a volume of  $1.5 \times 10^{-6}$  m<sup>3</sup>. The ampules with the investigated samples were filled at room temperature with dry helium of extra pure grade acting as the heat exchange gas up to a pressure of 5 kPa. The cooling agents were liquid helium and nitrogen.

The heat capacity in the range of 320–520 K was studied using a DSC 204 *F1 Phoenix* differential scanning calorimeter (NETZSCH Gerätebau, Germany). The calorimeter design and operating procedure were described in [19, 20]. The calorimeter was calibrated by determining the heat capacities of corundum and the melting points and enthalpies of melting of *n*-heptane, mercury, indium, tin, lead, bismuth, and zinc in the range of 170–700 K. The calorimeter calibration data showed that the apparatus and procedure allowed us to determine the phase transition temperature with an error of  $\pm 0.5$  K and the enthalpies of transitions with an error of  $\pm 1\%$ . The error in measuring  $C_p^0$  by the above means was not more than  $\pm 2\%$ . All measurements were performed in an argon stream at a rate of heating the crucible containing the substance of 5 K/min.

Calorimetric ampules of BKT-3 and DSC were loaded with G1[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>8</sub> (0.2510 g and 22.3 mg) and G3[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>32</sub> (0.2432 g and 31.8 mg), respectively. The heat capacity of the investigated dendrimers in the range of 6 to 520 K was 25–55% of the total heat capacity of the calorimetric ampule containing the substance. The experimental  $C_p^0$  points in the region where no transformation occurred were fitted as power and semilogarithmic polynomials, with the corresponding coefficients being selected by special computer programs. For each investigated sample, the heat capacity was measured in five series (Tables 1 and 2). The first four series (197 experimental  $C_p^0$  values) were obtained using the adiabatic vacuum calorimeter; the  $C_p^0$  values of series 5 were obtained by means of DSC. The molecular weights of the investigated dendrimers were calculated using the standard atomic weight table recommended by IUPAC [21].

## RESULTS AND DISCUSSION

### Heat Capacity

The experimental  $C_p^0$  values and smoothed curves for G1[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>8</sub> and G3[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>32</sub> are shown in Fig. 2. Upon cooling the samples from room temperature to the initial measurement temperature of  $\sim 6$  K at a rate of 0.02 K/s under the conditions of our apparatus, they underwent supercooling and vitrification. Subsequent heating while measuring the heat capacity in the range of 50–80 K for G1[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>8</sub> and 45–85 K for G3[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>32</sub> resulted in anomalous changes in the heat capacities (sections BCD and B'C'D' in Fig. 2), expressed as positive deviations from the normal (interpolated) course of the curves. The anomalies were reproduced each time we cooled and subsequently measured  $C_p^0$  in this temperature range. Similar anomalies in the same temperature ranges were observed for carbosilane dendrimers with other terminal groups, typically of less than the fifth generation [22]. The emergence of such anomalies in identical temperature ranges was systemic and did not depend on the nature of terminal groups; rather, it was determined by the number of the dendrimer's generation. These anomalies were due to the excitation of vibrations of eclipsed groups of repeating fragments (e.g., methyl fragments) in the macromolecules upon their heating and freezing, as was confirmed by the data from studying the IR spectrum of a third-generation dendrimer with terminal ethylene oxide groups [12]. In thermodynamic terms, the anomalies observed in the investigated dendrimers must be attributed to the order  $\rightleftharpoons$  disorder equilibrium relaxation transition in McCullough's classification [23]. The thermodynamic characteristics of the detected anomalies are given in Table 3. The procedure for determining them was described in [24].

The dendrimers devitrified upon further heating. The glass transition occurred each time they were cooled to temperatures below the glass transition point  $T_g^0$  and subsequently heated with repeated measurements of  $C_p^0$ . The characteristics of the process did not change when measured repeatedly after cooling from the devitrified state.

Excluding the anomalous regions, the dendrimers' heat capacities changed smoothly and in a fairly regular manner as the temperature rose. As might be expected,  $C_p^0$  grew more slowly as the temperature rose in the devitrified state. The third-generation dendrimer devitrified at a relatively higher temperature, since the first-generation dendrimer was a low-molecular weight compound with a regular branched structure.

In [14], we presented a diagram for the glass transition temperatures  $T_g^0$  of carbosilane dendrimers with different types of terminal groups as a function of the

**Table 1.** Experimental heat capacity ( $\text{kJ K}^{-1} \text{mol}^{-1}$ ) of the first-generation carbosilane dendrimer with terminal phenyldiolane groups  $\text{G1}[(\text{C}_6\text{H}_4)\text{C}_3\text{H}_5\text{O}_2]_8$ ,  $M(\text{Si}_{13}\text{C}_{128}\text{H}_{204}\text{O}_{16}) = 2363.90 \text{ g/mol}$ 

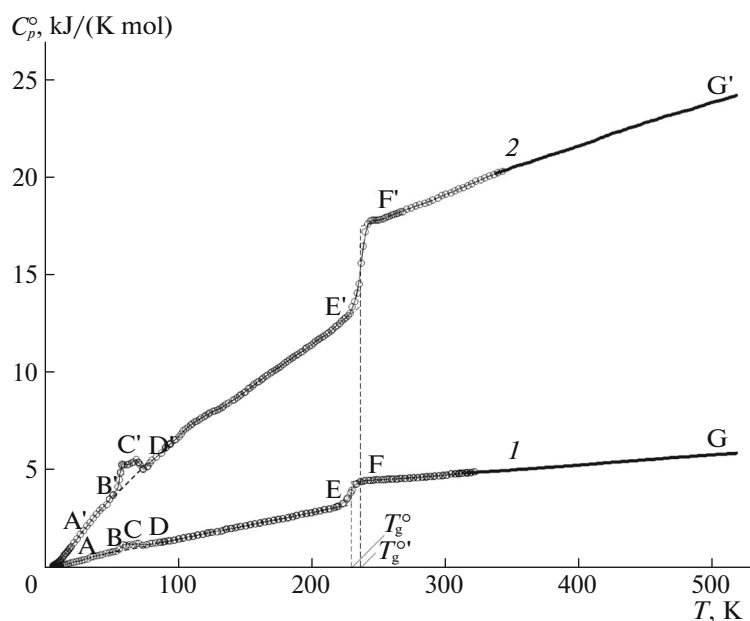
$T, \text{K}$	$C_p$	$T, \text{K}$	$C_p$	$T, \text{K}$	$C_p$	$T, \text{K}$	$C_p$	$T, \text{K}$	$C_p$	$T, \text{K}$	$C_p$
Series 1		36.65	0.5744	210.48	2.986	108.45	1.586	264.67	4.579	390.2	5.21
6.01	0.0189	46.24	0.6501	213.90	3.026	112.08	1.636	267.92	4.595	393.2	5.23
6.97	0.0364	41.42	0.7352	220.67	3.168	115.67	1.691	271.19	4.605	396.2	5.24
7.99	0.0384	51.16	0.8274	224.09	3.313	119.23	1.742	274.39	4.626	399.2	5.26
8.93	0.0416	53.65	0.8647	227.50	3.501	122.89	1.793	277.64	4.631	402.2	5.28
9.66	0.0515	59.02	1.194	230.88	3.858	126.44	1.846	281.40	4.652	405.2	5.29
10.26	0.0626	63.80	1.189	235.08	4.309	130.04	1.884	284.56	4.669	408.2	5.31
10.86	0.0699	68.65	1.251	238.40	4.425	134.70	1.934	287.18	4.690	411.2	5.32
11.33	0.0756	73.77	1.184	240.73	4.480	137.23	1.967	290.37	4.707	414.2	5.34
11.63	0.0783	78.85	1.222	243.83	4.499	139.60	2.000	293.54	4.723	417.2	5.36
12.13	0.0863	83.96	1.265	247.10	4.503	145.10	2.071	296.67	4.740	420.2	5.38
17.91	0.2080	86.80	1.303	250.29	4.525	147.94	2.109	299.81	4.759	423.2	5.39
21.45	0.2827	89.06	1.324	253.22	4.532	151.51	2.154	302.55	4.770	426.2	5.41
25.55	0.3522	Series 3		256.35	4.541	154.70	2.203	305.64	4.796	429.2	5.43
29.83	0.4326	86.80	1.303	259.43	4.558	155.07	2.210	308.71	4.818	432.2	5.44
34.34	0.5279	89.97	1.334	261.40	4.562	158.64	2.258	311.75	4.829	435.2	5.46
39.03	0.6123	93.20	1.370	262.56	4.574	161.78	2.301	314.80	4.851	438.2	5.47
43.80	0.6924	97.21	1.423	265.66	4.574	165.74	2.354	317.82	4.870	441.2	5.49
48.69	0.7801	100.83	1.475	268.81	4.595	169.29	2.399	320.84	4.889	444.2	5.50
51.16	0.8274	104.46	1.530	271.95	4.610	172.83	2.451	323.86	4.903	447.2	5.52
56.15	0.9640	108.08	1.581	275.04	4.618	175.50	2.485	Series 5		450.2	5.53
61.31	1.182	111.70	1.633	278.22	4.638	176.35	2.496	318.2	4.89	453.2	5.55
66.17	1.204	115.31	1.685	280.85	4.647	179.88	2.541	321.2	4.90	456.2	5.56
70.62	1.232	118.76	1.733	284.06	4.669	182.94	2.586	324.2	4.91	459.2	5.58
76.31	1.194	122.53	1.787	287.72	4.695	183.38	2.588	327.2	4.91	462.2	5.59
81.39	1.248	124.80	1.820	290.87	4.707	186.89	2.640	330.2	4.93	465.2	5.61
86.51	1.298	129.73	1.875	294.00	4.728	189.89	2.683	333.2	4.94	468.2	5.63
Series 2		133.32	1.922	297.12	4.744	190.40	2.692	336.2	4.95	471.2	5.65
5.95	0.0189	136.90	1.964	300.24	4.766	193.89	2.737	339.2	4.97	474.2	5.67
6.48	0.0334	140.80	2.016	303.16	4.782	197.31	2.782	342.2	4.98	477.2	5.68
7.47	0.0376	143.20	2.045	306.22	4.796	200.79	2.825	345.2	4.99	480.2	5.69
8.48	0.0396	147.57	2.106	309.26	4.817	204.27	2.879	348.2	5.00	483.2	5.71
9.33	0.0465	151.13	2.152	312.29	4.839	211.20	2.990	351.2	5.02	486.2	5.72
9.99	0.0574	158.24	2.248	315.28	4.846	214.65	3.031	354.2	5.04	489.2	5.74
10.57	0.0668	162.19	2.310	318.25	4.870	218.10	3.085	357.2	5.05	492.2	5.75
11.11	0.0734	165.32	2.348	321.18	4.893	220.00	3.120	360.2	5.07	495.2	5.76
11.59	0.0774	168.84	2.399	Series 4		221.54	3.172	363.2	5.08	498.2	5.78
11.88	0.0818	172.37	2.444	83.96	1.265	224.96	3.357	366.2	5.09	501.2	5.80
13.04	0.104	179.42	2.541	86.51	1.298	228.38	3.572	369.2	5.10	504.2	5.81
14.66	0.1430	186.45	2.639	89.06	1.324	231.76	4.019	372.2	5.12	507.2	5.82
16.27	0.1812	193.30	2.737	90.37	1.339	237.48	4.442	375.2	5.14	510.2	5.83
19.61	0.2431	196.81	2.776	94.60	1.390	241.71	4.491	378.2	5.16	513.2	5.85
23.48	0.3174	200.19	2.825	97.62	1.430	248.33	4.520	381.2	5.17	516.2	5.86
27.67	0.3877	203.62	2.870	101.26	1.483	254.85	4.541	384.2	5.18	518.2	5.87
32.07	0.4822	207.03	2.915	104.91	1.537	261.40	4.562	387.2	5.20	521.2	5.89

In series 1 and 2, the heat capacity values correspond to the amorphous glass state of the dendrimer; in series 3 and 4, the heat capacity values correspond to the amorphous glassy state of the dendrimer in the ranges of 86.80–230.88 and 83.96–231.76 K, and to the amorphous devitrified state of the dendrimer in the ranges of 230.88–321.18 and 231.76–323.86 K, respectively; in series 5, the heat capacity values correspond to an amorphous devitrified state of the dendrimer (every third experimental  $C_p$  value is given).

**Table 2.** Experimental heat capacity ( $\text{kJ K}^{-1} \text{mol}^{-1}$ ) of the third-generation carbosilane dendrimer with terminal phenyldiolane groups  $\text{G3}[(\text{C}_6\text{H}_4)\text{C}_3\text{H}_5\text{O}_2]_{32}$ ,  $M(\text{Si}_{61}\text{C}_{560}\text{H}_{924}\text{O}_{64}) = 10393.68 \text{ g/mol}$ 

$T, \text{K}$	$C_p$	$T, \text{K}$	$C_p$	$T, \text{K}$	$C_p$	$T, \text{K}$	$C_p$	$T, \text{K}$	$C_p$	$T, \text{K}$	$C_p$
Series 1		17.42	0.8880	164.56	9.749	308.85	19.37	192.87	11.07	394.2	21.5
5.85	0.0890	19.10	1.036	167.86	9.901	312.10	19.46	196.12	11.21	397.2	21.5
6.66	0.123	21.83	1.260	171.17	10.08	315.35	19.55	199.38	11.37	400.2	21.6
7.36	0.158	26.72	1.742	174.47	10.21	318.60	19.65	202.64	11.55	403.2	21.7
8.22	0.201	31.60	2.139	177.76	10.37	321.85	19.74	205.89	11.72	406.2	21.7
9.11	0.244	36.53	2.557	181.06	10.54	325.11	19.84	209.15	11.87	409.2	21.8
10.02	0.296	41.41	2.945	184.34	10.70	328.37	19.93	212.42	11.99	412.2	21.9
10.99	0.361	46.52	3.287	187.62	10.85	331.64	20.02	215.68	12.17	415.2	22.0
12.08	0.442	48.98	3.517	190.89	11.00	334.93	20.12	218.94	12.38	418.2	22.1
13.55	0.573	51.74	3.763	194.16	11.12	338.24	20.20	222.20	12.57	421.2	22.1
15.11	0.7012	56.05	4.541	197.43	11.28	341.56	20.30	225.46	12.76	424.2	22.2
16.67	0.8239	56.97	4.933	200.69	11.44	344.91	20.39	228.73	12.95	427.2	22.3
18.26	0.9644	58.26	5.327	203.95	11.63	Series 4		231.99	13.39	430.2	22.4
19.93	1.111	61.88	5.301	207.21	11.78	90.87	6.171	235.26	14.10	433.2	22.4
24.30	1.485	65.35	5.405	210.48	11.92	91.63	6.205	238.52	15.65	436.2	22.5
29.14	1.941	68.66	5.552	213.74	12.05	94.24	6.356	241.76	17.27	439.2	22.6
34.07	2.336	70.88	5.409	217.01	12.25	94.99	6.397	245.01	17.81	442.2	22.6
38.97	2.762	73.87	5.092	220.28	12.46	98.71	6.611	248.28	17.85	445.2	22.7
43.86	3.100	76.82	5.211	223.56	12.65	102.55	6.893	251.57	17.87	448.2	22.8
48.76	3.503	79.29	5.409	226.83	12.84	106.54	7.142	254.85	17.93	451.2	22.8
51.22	3.715	84.16	5.699	230.12	13.07	109.90	7.329	258.13	18.03	454.2	22.9
54.92	4.145	Series 3		233.41	13.67	113.26	7.503	261.42	18.12	457.2	23.0
56.83	4.861	90.96	6.168	236.68	14.59	116.62	7.625	264.71	18.20	460.2	23.0
58.00	5.254	94.32	6.330	239.95	16.51	119.97	7.765	267.99	18.29	463.2	23.1
59.72	5.319	97.69	6.559	243.21	17.65	123.32	7.907	Series 5		466.2	23.2
63.81	5.335	101.06	6.756	246.49	17.84	126.67	8.022	340.2	20.3	469.2	23.2
66.50	5.451	104.43	7.027	249.78	17.85	130.02	8.125	343.2	20.3	472.2	23.3
70.35	5.449	107.79	7.232	253.08	17.90	133.37	8.252	346.2	20.4	475.2	23.3
71.85	5.303	111.16	7.407	256.38	17.98	136.71	8.399	349.2	20.5	478.2	23.4
74.36	5.074	114.52	7.561	259.69	18.08	142.76	8.649	352.2	20.6	481.2	23.4
77.32	5.246	117.88	7.691	263.00	18.17	146.73	8.844	355.2	20.6	484.2	23.5
80.74	5.506	121.24	7.829	266.30	18.23	150.05	9.005	358.2	20.7	487.2	23.6
87.58	5.904	124.59	7.956	269.61	18.32	153.37	9.177	361.2	20.7	490.2	23.6
Series 2		127.94	8.071	272.91	18.42	156.68	9.321	364.2	20.8	493.2	23.7
6.25	0.103	131.29	8.186	276.22	18.50	159.99	9.532	367.2	20.9	496.2	23.7
7.01	0.142	134.63	8.315	279.52	18.58	163.29	9.688	370.2	21.0	499.2	23.8
7.86	0.181	137.98	8.448	282.81	18.66	166.60	9.829	373.2	21.0	502.2	23.9
8.67	0.220	141.32	8.594	286.09	18.73	169.89	10.01	376.2	21.1	505.2	23.9
9.56	0.269	144.65	8.754	289.37	18.80	173.19	10.16	379.2	21.2	508.2	24.0
10.49	0.323	147.98	8.907	292.63	18.89	176.48	10.28	382.2	21.2	511.2	24.1
11.52	0.396	151.30	9.067	295.88	19.00	179.76	10.46	385.2	21.3	514.2	24.1
12.84	0.508	154.62	9.229	299.13	19.10	183.05	10.61	388.2	21.4	517.2	24.2
14.36	0.637	157.93	9.427	302.38	19.19	186.33	10.78	391.2	21.4	521.2	24.3
15.78	0.7554	161.25	9.593	305.62	19.27	189.61	10.92				

In series 1 and 2, the heat capacity values correspond to the amorphous glassy state of the dendrimer; in series 3 and 4, the heat capacity values correspond to the amorphous glassy state of the dendrimer in the ranges of 90.96–239.95 and 90.87–238.52 K, and to the amorphous devitrified state of the dendrimer in the ranges of 239.95–344.91 and 238.52–267.99 K, respectively; in series 5, the heat capacity values correspond to the amorphous devitrified state of the dendrimer (every third experimental  $C_p$  value is given).



**Fig. 2.** Heat capacities of the G1[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>8</sub> (1) and G3[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>32</sub> (2) dendrimers as functions of temperature: AE and A'E' are glassy states; BCD and B'C'D' are abnormal changes in the heat capacity; FG and F'G' are devitrified states; EF and E'F' are changes in the heat capacity in the ranges of the glass transition:  $T_g^0$  and  $T_g^{0'}$  are the temperatures of the glass transition.

corresponding generation's number. The glass transition temperature of dendrimers was found to depend on the generation's number (up to the fourth or fifth generation). With a further increase in the number of dendrimer generations,  $T_g^0$  remained virtually constant. It should be noted that the structure and chemical nature of a dendrimer's external layer are the most important factors when determining their  $T_g^0$  values. A change in the structure of a dendrimer's surface layer is thus an effective tool for controlling its properties.

#### *Standard Thermodynamic Characteristics of the Glass Transition and the Glassy State*

The thermodynamic characteristics of the glass transition and the glassy state for the investigated dendrimers are given in Table 4. The glass transition temperature  $T_g^0$  was determined according to Alford and Dole [25], from the intercept of the temperature dependence of the entropy of heating. The range of the glass transition and the increase in the heat capacity upon the glass transition  $\Delta C_p^0(T_g^0)$  were determined by

graphic means. Configuration entropy  $S_{\text{conf}}^0$  was calculated using Eq. (1), proposed in [26]:

$$S_{\text{conf}}^0 = \Delta C_p^0(T_g^0) \ln(T_g^0/T_2^0), \quad (1)$$

where  $T_2^0$  is the Kauzmann temperature [27] and the  $(T_g^0/T_2^0)$  ratio according to [25–27] is 1.29. This relation was also assumed to be true for the investigated dendrimers. As was shown in [28], the  $S_{\text{conf}}^0$  value is close to  $S^0(0)$ . We may therefore logically assume that  $S^0(0) = S_{\text{conf}}^0$  when estimating the absolute entropy.

As Table 4 shows,  $T_g^0$  for the investigated dendrimers changes upon moving from G1[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>8</sub> to G3[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>32</sub>, due to the change in the free volume of dendrimer molecules with an increase in the number of generation.

#### *Standard Thermodynamic Functions*

To calculate the standard thermodynamic functions (Tables 5 and 6) of the investigated dendrimers, heat capacities  $C_p^0$  were extrapolated from the initial

**Table 3.** Standard thermodynamic characteristics of anomalies for the carbosilane dendrimers under study

Dendrimer	$\Delta T$ , K	$\Delta_{\text{an}}H^0$ , kJ mol <sup>-1</sup>	$\Delta_{\text{an}}S^0$ , J K <sup>-1</sup> mol <sup>-1</sup>
G1[(C <sub>6</sub> H <sub>4</sub> )C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> ] <sub>8</sub>	50–80	3.15 ± 0.03	41.9 ± 0.5
G3[(C <sub>6</sub> H <sub>4</sub> )C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> ] <sub>32</sub>	45–85	17.1 ± 0.2	189 ± 3

**Table 4.** Standard thermodynamic characteristics of the glass transition and the glassy state for the investigated carbosilane dendrimers

Dendrimer	$\Delta T$ , K	$T_g^o \pm 1$ , K	$\Delta C_p^o(T_g^o)$ , kJ K <sup>-1</sup> mol <sup>-1</sup>	$S_{\text{conf}}^o$	$S^o(0)$
				J K <sup>-1</sup> mol <sup>-1</sup>	
G1[(C <sub>6</sub> H <sub>4</sub> )C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> ] <sub>8</sub>	200–260	231	1.18 ± 0.01	301 ± 3	301
G3[(C <sub>6</sub> H <sub>4</sub> )C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> ] <sub>32</sub>	210–260	238	4.07 ± 0.04	1036 ± 10	1036

**Table 5.** Standard thermodynamic functions of the first-generation carbosilane dendrimer with terminal phenyldioxolane groups G1[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>8</sub>,  $M(\text{Si}_{13}\text{C}_{128}\text{H}_{204}\text{O}_{16}) = 2363.90$  g/mol

$T$ , K	$C_p^o(T)$ , kJ K <sup>-1</sup> mol <sup>-1</sup>	$[H^o(T) - H^o(0)]$ , kJ/mol	$[S^o(T) - S^o(0)]$ , J K <sup>-1</sup> mol <sup>-1</sup>	$-[G^o(T) - H^o(0)]$ , kJ/mol
Amorphous (glassy) state				
5	0.0164	0.0215	5.76	0.00732
10	0.0689	0.226	32.1	0.0949
20	0.3272	2.247	160.3	0.9594
50	0.8421	20.34	675.6	13.43
100	1.524	84.26	1549	70.61
150	2.166	176.9	2292	166.8
200	2.825	302.3	3008	299.4
231	3.252	396.6	3446	399.7
Amorphous (devitrified) state				
231	4.436	396.6	3446	399.7
250	4.558	482.0	3801	468.2
298.15	4.764	705.3	4617	671.3
300	4.775	714.2	4647	679.9
350	5.02	959.5	5403	931.5
400	5.27	1216	6089	1219
450	5.54	1487	6724	1539
500	5.79	1770	7321	1891
520	5.88	1887	7550	2040

measured temperature to 0 K using the Debye heat capacity function:

$$C_p^o = n\mathbf{D}(\theta_D/T), \quad (2)$$

where  $\mathbf{D}$  is the Debye function and  $n$  and  $\theta_D$  are specially selected parameters. In the range of 7 to 10 K, the values of  $n$  and  $\theta_D$  were 3 and 81.0 K for G1[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>8</sub>, and 16 and 79.0 K for G3[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>32</sub>. Equation (2) with the above parameters describes the experimental  $C_p^o$  values of the investigated dendrimers in the range of 7 to 10 K with an error of ±1.5%. In calculating the functions, we assumed that Eq. (2) reproduced the  $C_p^o$  values at  $T \leq 7$  K with the same error.  $[H^o(T) - H^o(0)]$  and  $[S^o(T) - S^o(0)]$  were calculated by numerically integrating curves  $C_p^o = f(T)$  and  $C_p^o = f(\ln T)$ , respectively;

Gibbs function  $[G^o(T) - H^o(0)]$  was calculated from the enthalpy and entropy values at corresponding temperatures. The calculation procedure was described in [24, 29]. The error in the calculated function values was assumed to be ±2% at  $T < 20$  K; ±0.6% in the range of 20–80 K; ±0.3% in the range of 80–350 K; and ±2% in the range of 350–520 K.

Standard entropies of formation  $\Delta_f S^o$  of the dendrimers in the amorphous (devitrified) state were calculated from the  $[S^o(T) - S^o(0)]$  values of the investigated dendrimers at  $T = 298.15$  K (Tables 5 and 6), their zero entropies (Table 4), and the absolute entropies of their elemental substances (C<sub>(gr)</sub>, Si<sub>(c)</sub>, H<sub>2(g)</sub>, and O<sub>2(g)</sub>) [30, 31] at the same temperature. The  $\Delta_f S^o$  values, calculated per corresponding moles of the macromolecules for each dendrimer, were (−11013 ±

**Table 6.** Standard thermodynamic functions of the third-generation carbosilane dendrimer with terminal phenyldioxolane groups G3[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>32</sub>,  $M(\text{Si}_{61}\text{C}_{560}\text{H}_{924}\text{O}_{64}) = 10\,393.68$  g/mol

$T, \text{K}$	$C_p^0(T),$ $\text{kJ K}^{-1} \text{mol}^{-1}$	$[H^0(T) - H^0(0)],$ $\text{kJ/mol}$	$[S^0(T) - S^0(0)],$ $\text{J K}^{-1} \text{mol}^{-1}$	$-[G^0(T) - H^0(0)],$ $\text{kJ/mol}$
Amorphous (glassy) state				
5	0.0577	0.0746	19.6	0.0246
10	0.286	0.895	124	0.350
20	1.115	7.792	569.7	3.601
50	3.596	79.55	2590	49.94
100	6.692	351.4	6267	275.3
150	9.008	748.0	9454	670.1
200	11.42	1260	12381	1217
238	13.47	1731	14533	1728
Amorphous (devitrified) state				
238	17.54	1731	14533	1728
250	17.82	1943	15403	1908
298.15	19.06	2831	18647	2729
300	19.11	2866	18765	2763
350	20.5	3857	21818	3779
400	21.6	4910	24628	4941
450	22.8	6021	27244	6239
500	23.8	7187	29700	7663
520	24.2	7668	30642	8266

97)  $\text{J K}^{-1} \text{mol}^{-1}$  for G1[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>8</sub> and  $(-51\,539 \pm 410) \text{ J K}^{-1} \text{mol}^{-1}$  for G3[(C<sub>6</sub>H<sub>4</sub>)C<sub>3</sub>H<sub>5</sub>O<sub>2</sub>]<sub>32</sub>.

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