

Thermodynamics of carbosilane dendrimers with diundecylsilyl and diundecylsiloxane terminal groups

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Abstract In this study for the first time the temperature dependences of the heat capacity C_p^0 and enthalpies of physical transitions of carbosilane dendrimers with diundecylsilyl and diundecylsiloxane terminal groups of the fifth generation have been measured using the methods of precision adiabatic vacuum calorimetry and differential scanning calorimetry over the range from 6 to 580 K. In the above temperature ranges the physical transformations have been detected and their thermodynamic characteristics were estimated and analyzed. The standard thermodynamic functions: heat capacity $C_p^0(T)$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T) - S^\circ(0)$, and free Gibbs energy $G^\circ(T) - H^\circ(0)$ and standard entropies of formation of dendrimers at $T = 298.15$ K have been calculated over the range from $T \rightarrow 0$ K to 580 K. The thermodynamic properties of studied dendrimers have been compared.

Keywords Carbosilane dendrimers · Adiabatic vacuum calorimetry · Differential scanning calorimetry · Glass transition · Heat capacity · Thermodynamic functions · Standard thermodynamic functions

Introduction

Dendritic macromolecules have been intensively studied in the past decade owing to their unique structure and a set of specific characteristics. The synthesis, modification, physicochemical properties, and possible application areas of diverse dendrimers and hyperbranched polymers have been intensively studied [1–5].

At present, particular attention is paid to the characterization of dendrimers since this information is necessary for gaining insight into the structure–properties relationship for these compounds. The dependence of different properties of dendrimers, such as the density, viscosity in solution and bulk, and glass transition temperature, on different parameters of dendritic molecules, primarily, on the nature of terminal groups, has been described in the literature [6–8]. So, to the present time by the methods of precision adiabatic vacuum calorimetry and differential scanning calorimetry standard thermodynamic properties various dendrimers had been investigated in a wide range of temperatures [9–15], in some cases [10–13] their dependences on composition and structure had been revealed and analyzed. Detection of the second high-temperature relaxation transformation for carbosilane dendrimers of high generations became the result of systematic research [13, 14]. The appearance of this transition suggests changes in the character of interactions between dendrimers with an increase in their generation number. It should be noted that the appearance of the second relaxation transition upon passage from the fifth to sixth generation coincides with a change in the aggregation state of dendrimers; that is, dendrimers of the first to the fifth (inclusive) generation are transparent liquids with different viscosities, while from the sixth generation, they have a waxlike consistency.

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The densification of the surface layer might lead to formation of the physical network between dendrimers. The determination of standard thermodynamic characteristics and its analysis are actual and significant for representatives of new class of macromolecules, i.e., dendrimers.

This research is a part of complex investigations of thermodynamic properties of different homologous series carbosilane dendrimers. It is interesting to evaluate the difference in studying dendrimers structure and composition, notably introduction of siloxane fragment, which insures more mobility of terminal alkyl groups and to begin to systematic investigation of the nature. This gradual variation in the nature of the surface layers enables us to initiate the systematic study of the nature of the second (high-temperature) transition in the temperature dependence of heat capacity.

The aim of this study is to calorimetrically study the temperature dependence of heat capacity of the carbosilane dendrimers with diundecylsilyl and diundecylsiloxane terminal groups of fifth generation in the range 6–(550–580) K, determine of glass transition thermodynamic characteristics and interpret them in terms of physical chemistry, to calculate the standard thermodynamic functions $C_p^0(T)$, $H^0(T) - H^0(0)$, $S^0(T) - S^0(0)$ and $G^0(T) - H^0(0)$ over the temperature range from $T \rightarrow 0$ to (550–580) K and standard entropies of formation of dendrimers in amorphous (devitrified) state at $T = 298.15$ K, to compare the thermodynamic properties of studied samples.

Experimental

Samples

Studied in this work samples of the carbosilane dendrimers with diundecylsilyl and diundecylsiloxane terminal groups of the fifth generation (gross-formulas $\text{Si}_{253}\text{C}_{3824}\text{H}_{8156}$, $M = 61255.8 \text{ g mol}^{-1}$, $\text{Si}_{381}\text{C}_{4080}\text{H}_{8924}\text{O}_{128}$, $M = 7074.75 \text{ g mol}^{-1}$, respectively) were synthesized at N.S. Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Science by the method described in detail elsewhere [16].

The structure of samples and the scheme of their synthesis are presented on Fig. 1.

Under normal conditions the dendrimers are transparent colorless waxy substance. In this study were used samples cleaned by the methods of preparative gel permeation chromatography. The composition and structure of studied samples were confirmed by elemental analysis and methods of NMR ^1H -spectroscopy [a “Bruker WP-200 SY spectrometer” (200.13 MHz, a standard is tetramethylsilane)] and IR-spectroscopy (a “Bruker ISF-110” device).

The carbosilane dendrimers with diundecylsilyl and diundecylsiloxane terminal groups of fifth generation were marked as **I** and **II**, respectively.

Apparatus and measurement procedure

Heat capacity of studied samples was measured over the range 6–350 K in a BKT-3.0 fully automatic adiabatic

Fig. 1 Structure of carbosilane dendrimers with diundecylsilyl and diundecylsiloxane terminal groups of the fifth generation and scheme of their synthesis

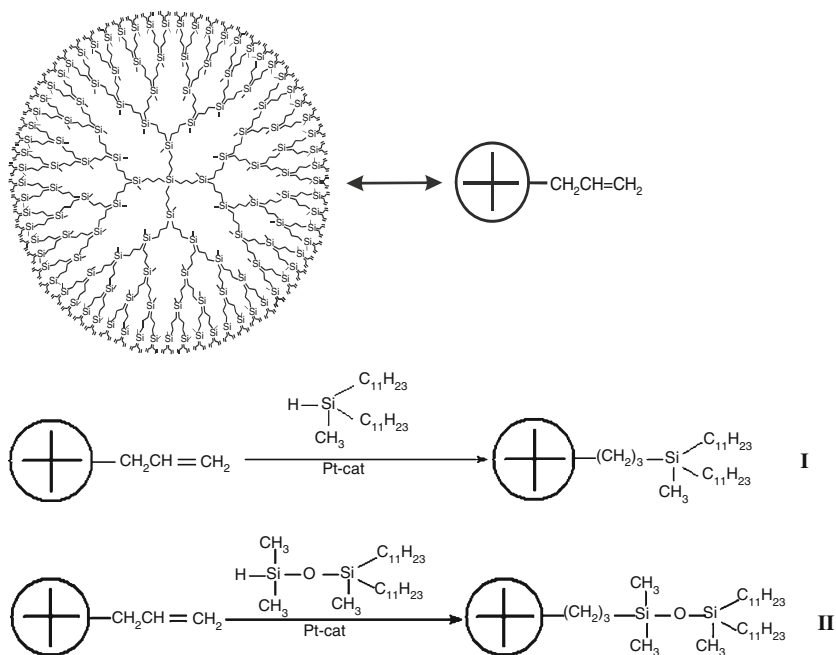


Table 2 continued

T/K	C_p^0	T/K	C_p^0
60.00	31.82	189.11	97.84
62.91	33.55	192.44	109.2
65.38	35.07	195.36	132.7
67.84	36.46	198.28	162.1
70.31	37.92	201.25	197.1
72.2	38.99	204.28	229.0
74.8	40.49	207.26	268.3
77.72	42.14	210.45	146.1
80.60	43.65	213.69	137.6
83.10	45.14	216.70	136.2
Series 2		219.70	135.0
80.36	43.40	222.69	134.1
82.30	44.96	225.68	133.6
85.20	46.20	230.84	133.3
87.30	47.38	237.88	133.1
89.50	48.50	244.32	133.0
92.69	50.16	250.75	133.3
96.16	51.79	257.17	133.7
99.10	53.13	263.57	134.1
102.1	54.48	269.95	134.2
105.7	56.03	276.21	134.2
109.24	57.59	276.33	134.3
112.20	58.72	278.76	134.0
115.16	59.78	281.31	134.1
118.64	61.27	283.83	134.2
122.02	62.50	286.34	134.3
124.99	63.60	288.78	134.4
127.96	64.73	291.13	134.5
130.93	65.76	293.41	134.6
133.90	67.01	295.6	134.7
130.93	65.76	297.69	134.8
139.84	69.42	283.83	134.2
142.81	70.46	286.34	134.3
146.22	71.84	299.68	134.9
149.19	73.06	301.59	135.0
152.56	74.36	303.4	135.1
155.97	75.97	305.12	135.1
159.34	77.38	306.76	135.2
162.32	78.72	308.33	135.3
165.30	79.86	309.84	135.3
168.28	81.22	311.3	135.4
171.26	82.78	312.71	135.5
174.25	84.26	314.09	135.5
177.24	85.80	315.47	135.6
180.22	87.50	316.84	135.6
182.36	88.88	318.23	135.7
184.10	89.95	319.65	135.7
186.18	91.86	321.12	135.8

Table 2 continued

<i>T</i> /K	<i>C_p⁰</i>
484.2	150.2
486	150.5
487.8	150.7
490.3	151.5
492.1	152.2
493.3	152.5
495.1	153.0
496.9	153.5
484.2	150.2
486.0	150.5
487.8	150.7
490.3	151.5
492.1	152.2
493.3	152.5
495.1	153.0
496.9	153.5
498.7	154.1
500.5	154.6
502.3	154.8
504.2	155.6
506	156.1
507.8	156.6
509.7	157.4
511.5	157.9
513.4	158.7
515.2	159.5
517.1	160.0
518.9	161.2
520.7	161.7
522.5	162.5
524.4	163.3
526.0	164.1
528.0	164.8
529.8	166.1
531.7	166.9
533.5	167.9
535.3	169.2
537.2	170.2
539.0	171.0
540.8	171.8
542.6	172.3
544.4	173.0
546.2	173.8
548.0	174.8
549.8	175.1
551.6	176.1
553.5	176.3
555.3	177.2

Table 2 continued

<i>T</i> /K	<i>C_p⁰</i>
557.1	177.4
558.9	177.9
560.7	178.6
562.5	179.1
564.3	178.9
566.1	180.0
567.9	179.6
569.7	179.9
571.5	180.1
573.3	180.3
575.1	180.3
576.8	179.8
578.6	179.3
580.4	177.7

M = 70747.50 g mol⁻¹, *p*^o = 0.1 MPa

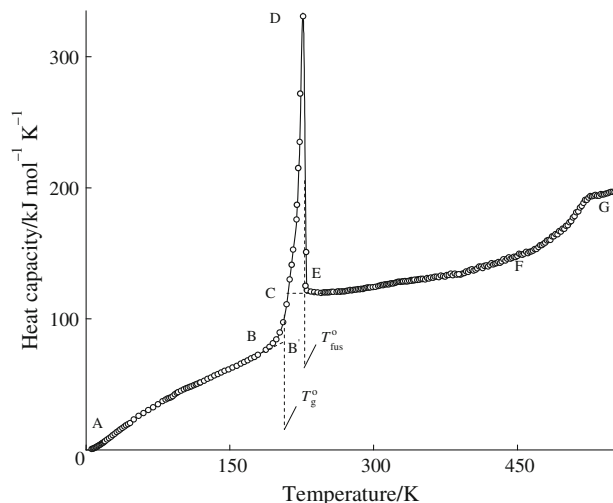


Fig. 2 Heat capacity of carbosilane dendrimer of the fifth generation with diundecylsilyl terminal groups: *ABB'* amorphous part in glassy state, *BCDE* apparent heat capacity in the interval of devitrification of the amorphous part and melting of crystalline dendrimer part, *EFG* devitrified state

the dendrimers was everywhere between 15 and 50% of the overall heat capacity of the calorimetric ampoule with the substance. The experimental *C_p⁰* values were smoothed by means of a computer program in the form of degree and semi-logarithmic polynomials. As an example, the polynomials with the corresponding coefficients for ranges from 6 to 13 K and from 225 to 346 K are cited below. For **II** in the interval between 6 and 13 K, the equation *C_p⁰*(*T*) = -1.10542 × 10² + 2.14308 × 10³(*T*/30) - 1.74246 × 10⁴(*T*/30)² + 7.77548 × 10⁴(*T*/30)³ - 2.06761 × 10⁵(*T*/30)⁴ + 3.31179 × 10⁵(*T*/30)⁵ - 2.98584 × 10⁵(*T*/30)⁶

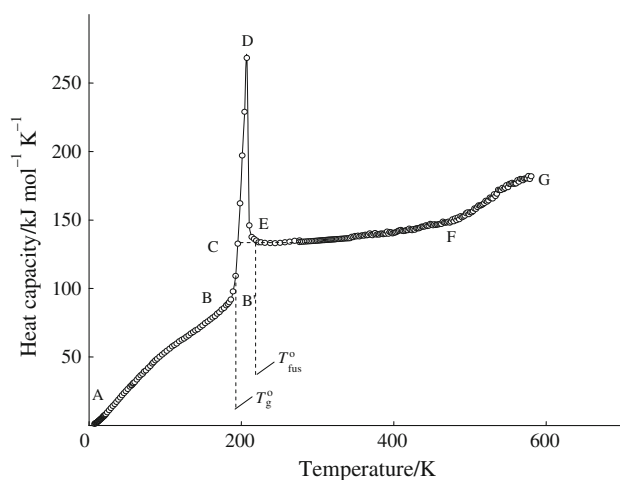


Fig. 3 Heat capacity of carbosilane dendrimer of the fifth generation with diundecylsiloxane terminal groups

+ $1.17637 \times 10^5 (T/30)^7$ as well as the equation $C_p^0(T) = -1.7409054 \times 10^5 + 1.3729883 \times 10^5 (T/30) - 4.6048614 \times 10^4 (T/30)^2 + 8.5233573 \times 10^3 (T/30)^3 - 9.4061029 \times 10^2 (T/30)^4 + 6.1906776 \times 10 (T/30)^5 - 2.2505345 (T/30)^6 + 3.4870097 \times 10^{-2} (T/30)^7$ in the range from 225 to 346 K were used. In these equations, C_p^0 is in $\text{kJ mol}^{-1} \text{K}^{-1}$ and temperature is in K. The root-mean-square deviation of the C_p^0 points from the corresponding smoothed curve $C_p^0 = f(T)$ was $\pm 0.20\%$ over the range 6–13 K, $\pm 0.50\%$ from 10 to 40 K, $\pm 0.20\%$ between 30 and 100 K, in the ranges 90–186 and 225–346 K the root-mean-square deviation was ± 0.40 and $\pm 0.40\%$ in the interval from 330 to 486 K.

The heat capacity of **I** smoothly and quite regularly changes with temperature increase in the range 6–195 K. There is anomalous changing the heat capacity with temperature rise on the temperature dependence $C_p^0 = f(T)$ in the ranges 195–235 and 461–532 K (Fig. 2). Since 195 K the heat capacity is sharply increased with growth of temperature, achieving the maximal meaning $C_{p,\text{max}}^0 = 330.8 \text{ kJ mol K}^{-1}$ at 226.48 K (Fig. 2, the point D), then sharply decreases up to $119.1 \text{ kJ mol K}^{-1}$ at 235.07 K. The above transformation is presumably related to devitrification of the amorphous part of the polymer, which smoothly passes to melting of its crystalline part.

It should be noted that the temperature of devitrification for studied sample is much higher in comparison with investigated earlier dendrimers of the sixth [13], seventh, and ninth [14] generations with terminal butyl groups and dendrimers by first–fifth generations with terminal allyl groups [11]. Probably, it is caused by a various nature of terminal groups, and also ability of undecyl fragments to form the ordered crystal areas, as well as in the case of methoxyphenyl benzoate-terminated liquid crystalline dendrimers [15].

In the range 461–532 K there is the second transformation on a curve $C_p^0 = f(T)$ reminding on the form the glass transition. The similar jump of the heat capacity was observed for studied earlier carbosilane dendrimers with terminal butyl groups: in range 370–470 K for the sixth generation (G-6 (Bu)₂₅₆) [13] and in an interval 390–490 K for seventh (G-7 (Bu)₅₁₂) and ninth (G-9 (Bu)₂₀₄₈) generations [14]. It is visible that the observable transition as well as the glass transition come at higher temperatures than for compared dendrimers. The assignment of the transition undoubtedly requires more extensive thermophysical, thermomechanical, and rheological experiments. Its physicochemical interpretation and assignment to a specific group according to thermodynamic classification likewise needs additional studies. However, the shift of the second transition toward higher temperatures with an increase in the size of terminal groups from butyl to undecyl is consistent with our hypothesis that there is a physical network that is similar to the entanglement network arising in classical polymers.

The temperature dependence of the heat capacity $C_p^0 = f(T)$ for **II** (Fig. 3) is similar considered for **I**; however, the glass transition and melting temperature (Table 3) are lower for the dendrimer containing the silicone spacer than those for the poly(undecyl) dendrimer. This situation is most likely related to the presence of the flexible siloxane spacer between the alkyl decoration and the dendrimer core. The jump of the heat capacity, corresponding to the second transformation, is somewhat lower, than in the case of **I**.

Low-temperature heat capacity ($20 \leq (T/\text{K}) \leq 50$) of the dendrimers under study is linear function versus temperature. This indicates on chain (linear) topology structure of compounds [22, 23].

Table 3 Glass transition and glassy state characteristics of polyundecylcarbosilane and polyundecylcarbosilane dendrimer with siloxane fragments of the fifth generation ($p = 0.1 \text{ MPa}$)

Dendrimer	Gross-formulae	$M/\text{g mol}^{-1}$	$T_g^0 \pm 0.5/\text{K}$	$\Delta C_p^0 \pm 0.5/\text{kJ K}^{-1} \text{mol}^{-1}$	$S_{\text{conf}}^0 \pm 0.5/\text{kJ K}^{-1} \text{mol}^{-1}$	$S^0(0) \pm 0.5/\text{kJ K}^{-1} \text{mol}^{-1}$
I	$\text{Si}_{253}\text{C}_{3824}\text{H}_{8156}$	61256.13	209.0	23.5	6.0	6.0
II	$\text{Si}_{381}\text{C}_{4080}\text{H}_{8924}\text{O}_{128}$	70747.5	190.1	26.5	6.8	6.8

The glass transition and glassy state

The thermodynamic characteristics of devitrification and glassy state of the dendrimers are listed in Table 3. The glass transition temperature T_g^0 was determined by the Alford and Dole method [24–26] from the inflection of the plot of the temperature dependence of entropy of heating. The devitrification intervals and an increase in the heat capacity on devitrification were determined graphically. The configuration entropy was calculated by Eq. 1:

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

where T_2^0 is Kauzmann temperature [27], the ratio T_g^0/T_2^0 is equal to (1.29 ± 0.14) [28] and [29]. It is suggested that the ratio is valid also for all dendrimers under study. It was shown [28] and [30] that the value S_{conf}^0 is close to the $S^0(0)$ value. Taking this into account it was assumed quite normally that $S^0(0) = S_{\text{conf}}^0$ [29] to evaluate the absolute value of the absolute entropy.

Melting

In Table 4 are represented the thermodynamic quantities of melting. The melting temperature of a crystalline part of samples accepted equal to temperature of the end of transformation (Figs. 2, 3, point D). The enthalpies of melting were determined as a difference of integrals on temperature under curves apparent (BCDEB) and normal (BB'CEB, extrapolational) heat capacity, respectively, in the interval of transformation.

Standard thermodynamic functions

To calculate the standard thermodynamic functions (Tables 5, 6) of **I** and **II**, their C_p^0 values were extrapolated from 6 K to zero temperature consistently with the Debye law in the low-temperature limit [30]:

$$C_p^0 = nD(\theta_D/T), \tag{2}$$

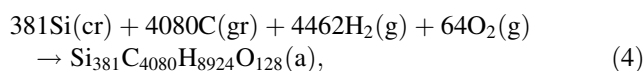
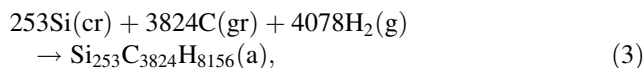
where D denotes Debye function of the heat capacity, n and θ_D are specially selected parameters (with $n = 3$,

$\theta_D = 51.7$ and 63.9 K for **I** and **II**, respectively). Equation 2 with these parameters describes the experimental C_p^0 values of the compound between 6 and 12 K with the error of $\pm 1.5\%$. In calculating the functions, it was assumed that Eq. 2 reproduced C_p^0 values of **I** and **II** at $T < 6$ K with the same error.

The calculation of enthalpy and entropy was made by the numerical integration of $C_p^0 = f(T)$ and $C_p^0 = \ln f(T)$ curves, respectively. The free Gibbs energy was calculated with Gibbs–Helmholtz equation from the enthalpies and entropies at the corresponding temperatures [31]. It was suggested that the error of the function values was $\pm 2\%$ at $T < 15$ K, $\pm 0.5\%$ between 15 and 40 K, $\pm 0.2\%$ in the range from 40 to 350 K, and $\pm 2\%$ from 330 to 580 K.

Standard entropies of formation of dendrimers at 298.15 K

From the absolute values of entropies (Tables 5, 6) of studied dendrimers at 298.15 K and the absolute entropies of simple substances [C(gr), Si(cr)] [32] and [H₂(g), O₂(g)] [33] at $T = 298.15$ K it was found that the standard entropies of formation of dendrimers are -418.9 , -466.3 kJ/(K mol), respectively. The values conform to the equations:



where the physical states of the reagents are indicated in parentheses (gr stands for graphite, g for gas, cr for crystal, and a for amorphous). The large negative $\Delta_f S^0$ values are related apparently to binding of 4078 and 4462 mol of gaseous hydrogen in the reaction of formation of dendrimers from simple substances.

Comparison of thermodynamic properties of studied dendrimers

It was interesting to compare thermodynamic characteristics of studied dendrimers. The values of glass transition and fusion temperature (Tables 3, 4) for dendrimer with siloxane outer layer are lower than for poly(undecyl) dendrimer. Most probably it is connected with presence in structure of this dendrimer flexible silicone spacer between alkyl decoration and dendrimer core. This small difference in structure of studied dendrimers imparts higher mobility to terminal alkyl groups owing to the presence of a more

Table 4 The thermodynamic characteristics of fusion for studied dendrimers ($p = 0.1$ MPa)

Dendrimer	$T_g^0 \pm 0.3/\text{K}$	$C_{p,\text{max}}^0 \pm 0.5/\text{kJ K}^{-1} \text{mol}^{-1}$	$\Delta_{\text{fus}}H^0/\text{kJ K}^{-1} \text{mol}^{-1}$
I	235.1	330.8	1393
II	220.0	268.3	1066

Table 5 Standard thermodynamic functions of carbosilane dendrimer of the fifth generation with diundecylsilyl terminal groups

T/K	$C_p^0/kJ\ mol^{-1}\ K^{-1}$	$H^\circ(T) - H^\circ(0)/kJ\ mol^{-1}$	$S^\circ(T) - S^\circ(0)/kJ\ mol^{-1}\ K^{-1}$	$-[G^\circ(T) - H^\circ(0)]/kJ\ mol^{-1}$
Amorphous part in glassy state				
5	0.350	0.429	0.118	0.149
10	1.80	5.57	0.776	2.17
15	4.04	20.0	1.91	8.69
20	6.619	46.49	3.421	21.91
25	9.403	86.49	5.193	43.32
30	12.27	140.7	7.161	74.13
40	17.72	291.2	11.46	167.0
50	23.21	492.9	15.93	303.8
60	28.06	750.4	20.62	486.5
80	37.04	1401	29.91	991.9
90	45.46	2225	39.07	1682
100	51.71	3196	47.91	2553
120	58.55	4299	56.39	3596
140	37.04	1401	29.91	991.9
160	65.24	5537	64.65	4807
180	72.73	6913	72.75	6181
200	85.35	8476	80.97	7717
Amorphous part in devitrified state				
250	120.1	15,611	112.6	12,549
270	121.1	18,021	122.0	14,896
290	123.1	20,463	130.6	17,422
298.15	124.1	21,470	134.1	18,501
310	125.7	22,950	138.9	20,118
330	128.4	25,492	146.9	22,977
350	129.9	28,075	154.5	25,991
370	131.7	30,690	161.7	29,154
390	133.9	33,344	168.7	32,459
410	138.0	36,061	175.5	35,901
430	142.1	38,860	182.2	39,478
450	147.3	41,755	188.8	43,188
470	153.3	44,756	195.3	47,028
490	164.4	47,929	201.9	51,000
510	178.4	51,340	208.7	55,106
530	193.9	55,104	216.0	59,352
550	196.8	59,007	223.2	63,743

$$M = 61256.13\ g\ mol^{-1}$$

flexible linkage between the surface structure and the dendrimer core. The jump of the heat capacity corresponding to second transition is somewhat lower than in the case of dendrimer **I**, while molecular mass is noticeably higher owing to incorporation of siloxane spacers. Take into account that dendrimers **I** and **II** have similar cores

and nature of outer layers it is possible to state that the strength of entanglements depends on the flexibility of outer structural fragments. In other words, the incorporation of flexible siloxane spacers does not change the chemical nature of outer layers but changes their flexibility and thus makes the entanglements less efficient.

Table 6 Standard thermodynamic functions of carbosilane dendrimer of the fifth generation with diundecylsiloxane terminal groups

T/K	$C_p^0/kJ\ mol^{-1}\ K^{-1}$	$H^\circ(T) - H^\circ(0)/kJ\ mol^{-1}$	$S^\circ(T) - S^\circ(0)/kJ\ mol^{-1}\ K^{-1}$	$-[G^\circ(T) - H^\circ(0)]/kJ\ mol^{-1}$
Amorphous part in glassy state				
5	0.331	0.400	0.111	0.138
10	2.04	5.900	0.800	2.120
15	4.42	22.00	2.074	9.082
20	7.08	50.70	3.703	23.36
25	10.08	93.40	5.599	46.54
30	13.28	151.8	7.722	79.83
40	19.85	317.2	12.43	180.2
50	25.93	546.7	17.53	329.8
60	31.83	835.4	22.78	531.2
80	43.38	1589	33.54	1094
100	53.56	2563	44.36	1873
120	61.73	3718	54.86	2866
140	69.36	5028	64.95	4065
160	77.64	6497	74.74	5462
180	87.36	8142	84.42	7054
190	100.4	9062	89.39	7922
Amorphous part in devitrified state				
240	133.0	16,590	124.7	13,341
260	133.8	19,258	135.4	15,944
280	134.3	21,939	145.3	18,752
298.15	134.8	24,379	153.8	21,467
300	134.8	24,629	154.6	21,752
320	135.8	27,336	163.3	24,933
340	136.7	30,059	171.6	28,283
360	138.8	32,817	179.5	31,794
380	139.9	35,605	187.0	35,459
400	140.9	38,412	194.2	39,272
420	142.6	41,246	201.1	43,226
440	144.8	44,120	207.8	47,316
460	147.0	47,039	214.3	51,537
480	149.5	50,002	220.6	55,886
500	155.0	53,050	226.8	60,360
520	163.2	56,232	233.1	64,959
540	171.7	59,575	239.4	69,683
560	176.6	63,073	245.7	74,534
580	181.0	66,669	252.0	79,512

$$M = 70747.50\ g\ mol^{-1}$$

Conclusions

- The heat capacities of carbosilane dendrimers with diundecylsilyl and diundecylsiloxane terminal groups of the fifth generation have been measured over the range from 6 to (550–580) K.
- From experimental data the standard thermodynamic functions of studied carbosilane dendrimers, namely, the heat capacity $C_p^0(T)$, enthalpy $H^\circ(T) - H^\circ(0)$,

entropy $S^\circ(T) - S^\circ(0)$, and Gibbs function $G^\circ(T) - H^\circ(0)$ have been calculated over the range from $T \rightarrow 0$ to (550–580) K, and the values of standard thermodynamic functions of formation of studied dendrimers at $T = 298.15$ K have been calculated.

- The standard thermodynamic properties of studied dendrimers have been compared; as a result some dependences thermodynamic properties on composition and structure were obtained.

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References

1. Tomalia DA, Naylor AM, Goddard WA. Starburst dendrimers: molecular-level control of size, shape, surface chemistry, topology, and flexibility from atoms to macroscopic matter. *Angew Chem Int Ed Engl.* 1990;29:138–75.
2. Newkome GR. *Advances in dendritic macromolecules.* Greenwich: JAI Press; 1994.
3. Astruc D, Chardac F. Dendritic catalysts and dendrimers in catalysis. *Chem Rev.* 2001;101:2991–3023.
4. Muzafarov AM, Rebrov EA, Papkov VS. Three-dimensionally growing polyorganosiloxanes. Possibilities of molecular construction in highly functional systems. *Russ Chem Rev.* 1991;60:807–14.
5. Beletskaya IP, Chuchuryukin AV. Synthesis and properties of functionalized dendrimers. *Russ Chem Rev.* 2000;69:639–60.
6. Lorenz K, Mulhaupt R, Frey H, Rapp U, Mayer-Posner F.J. Carbosilane-based dendritic polyols. *Macromolecules.* 1995;28:6657–61.
7. Wooley KL, Hawker CJ, Pochan JM, Frechet GMJ. Physical properties of dendritic macromolecules: a study of glass transition temperature. *Macromolecules.* 1993;26:1514–9.
8. Lorenz K, Frey H, Stuhn B, Mulhaupt R. Carbosilane dendrimers with perfluoroalkyl end groups. Core-shell macromolecules with generation-dependent. order macromolecules. 1997;30:6860–8.
9. Lebedev BV, Smirnova NN, Ryabkov MV, Ponomarenko SA, Makeev EA, Boiko NI, Shibaev VP. Thermodynamic properties of carbosilane dendrimer of the first generation with terminal methoxyundecylenate groups in the range 0–340 K. *Polym Sci Ser A.* 2001;43:323–31.
10. Ryabkov MV, Kulagina TG, Lebedev BV. Thermodynamic properties of carbosilane dendrimers of the first and second generations with terminal allyl groups in the range 0–340 K. *Russ J Phys Chem.* 2001;75:1988–96.
11. Lebedev BV, Ryabkov MV, Tatarinova EA, Rebrov EA, Muzafarov AM. Thermodynamic properties of the first to fifth generations of carbosilane dendrimers with allyl terminal groups. *Russ Chem Bull.* 2003;52:545–51.
12. Smirnova NN, Lebedev BV, Khranova NM, Tsvetkova LYa, Tatarinova EA, Myakushev VD, Muzafarov AM. The thermodynamic properties of carbosilane dendrimers of the sixth and seventh generations with terminal groups in the temperature range 6–340 K. *Russ J Phys Chem.* 2004;78:1369–74.
13. Smirnova NN, Stepanova OV, Bykova TA, Muzafarov AM, Tatarinova EA, Myakushev VD. Thermodynamic properties of carbosilane dendrimers of the third to the sixth generations with terminal butyl groups in the range from $T \rightarrow 0$ to 600 K. *Thermochim Acta.* 2006;440:188–94.
14. Smirnova NN, Stepanova OV, Bykova TA, Markin AV, Tatarinova EA, Muzafarov AM. Thermodynamic properties of carbosilane dendrimers of the seventh and ninth generations with terminal butyl groups in the temperature range from $T \rightarrow 0$ to 600 K. *Russ Chem Bull.* 2007;56:1991–5.
15. Lebedev BV, Kulagina TG, Ryabkov MV, Ponomarenko SA, Makeev EA, Boiko NI, Shibaev VP, Rebrov EA, Musafarov AM. Carbosilane dendrimer of second generation with terminal methoxyundecylenate groups. *J Therm Anal Calorim.* 2003;71:481–92.
16. Tereshchenko AS, Tupitsyna GS, Tatarinova EA, Bystrova AV, Muzafarov AM, Smirnova NN, Markin AV. Carbosilane dendrimers with diundecylsilyl, diundecylsiloxane, and tetrasiloxane terminal groups: synthesis and properties. *Polym Sci Ser B.* 2010;52:41–8.
17. Varushchenko RM, Druzhinina AI, Sorkin EL. Low-temperature heat capacity of 1-bromoperfluorooctane. *J Chem Thermodyn.* 1997;29:623–7.
18. Malyshev VM, Milner GA, Sorkin EL, Shibakin VF. Automatic low-temperature calorimeter. *Pribery i Tekhnika Eksperimenta.* 1985;6:195–7.
19. Paukov IE, Kovalevskaya YA, Kiseleva IA, Shuriga TN. A low-temperature heat capacity study of natural lithium micas. *J Therm Anal Calorim.* 2010;992:709–12.
20. Yagfarov MSh. Novii metod izmerenia teploemkosti i teplovih effektov. *Zh Fiz Khimii.* 1969;43:1620–5.
21. Kabo AG, Diky VV. Details of calibration of a scanning calorimeter of the triple heat bridge type. *Thermochim Acta.* 2000;347:79–84.
22. Lazarev VB, Izotov AD, Gavrichev KS, Shebershneva OV. Fractal model of heat capacity for substances with diamond-like structures. *Thermochim Acta.* 1995;269–270:109–16.
23. Tarasov VV. Theory of heat capacity of chain and layer structures. *Zhurnal fizicheskoi khimii.* 1950;24:111–28.
24. Alford S, Dole M. Specific heat of synthetic high polymers. VI. Study of the glass transition in polyvinyl chloride. *J Chem Soc.* 1955;77:4774–7.
25. Smirnova NN, Lebedev BV, Bykova TA, Markin AV, Tur DR. Thermodynamic properties of poly-[bis(trifluoroethoxy)-phosphazene] in the range from $T \rightarrow 0$ to 620 K. *J Therm Anal Calorim.* 2009;95:229–34.
26. Wunderlich B. Thermodynamic description of condensed phases. *J Therm Anal Calorim.* 2010;102:413–24.
27. Kauzmann W. The Nature of the glassy state and the behavior of liquids at low temperatures. *Chem Rev.* 1948;43:219–56.
28. Adam G, Gibbs JU. On the temperature dependence of cooperative relaxation properties in glass-forming liquids. *J Chem Phys.* 1965;43:139–46.
29. Bestul A, Chang SS. Excess entropy at glass transformation. *J Chem Phys.* 1964;40:3731–3.
30. Rabinovich IB, Nistratov VP, Telnoy VI, Sheiman MS. *Thermochemical and thermodynamic properties of organometallic compounds.* New York: Begell House Inc. Publishers; 1999.
31. Lebedev BV. *Thermodynamics of polymers.* Gorky: Gorky State University; 1989.
32. Cox JD, Wagman DD, Medvedev VA. *Codata key values for thermodynamics.* New York; 1984. Database <http://webbook.nist.gov/chemistry/>.
33. Chase MW Jr. *NIST-JANAF thermochemical tables.* 4th ed. *J Phys Chem Ref Data Monogr.* 1998;9:1951. Database <http://webbook.nist.gov/chemistry/>.