



Investigation of thermodynamic properties of liquid-crystalline carbosilane dendrimers with methoxyphenylbenzoate terminal groups



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ABSTRACT

The temperature dependences of the heat capacity of liquid-crystalline carbosilane dendrimers of the first to the fourth generations with methoxyphenylbenzoate terminal groups have been measured by the method of adiabatic vacuum calorimetry over the range from $T = (6 \text{ to } 370) \text{ K}$ in the present investigation. The phase transformations have been detected and their thermodynamic characteristics have been estimated and analyzed in the above temperature range. The standard thermodynamic functions, namely, the heat capacity $C_p(T)$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T) - S^\circ(0)$ and potential Φ_m° , for the range from $T \rightarrow (0 \text{ to } 370) \text{ K}$ and the standard entropy of formation of dendrimers in different physical states at $T = 298.15 \text{ K}$ have been calculated based on the experimental values. The standard entropies of hypothetical synthesis of studied compounds were estimated. The linear dependences of changing the corresponding thermodynamic properties of the dendrimers on their molecular weight and the number of mesogenic groups on the outer layer have been obtained.

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1. Introduction

Dendrimers are represented monodisperse macromolecules with regular and highly branched three-dimensional architecture [1–5]. The construction of dendrimers can be realized by two basic ways: by a divergent approach, in which the molecule is growing from the core to the periphery, and a convergent approach, when the dendrimer molecule is built starting from the periphery fragments. The choice of the synthetic methods is determined by the available chemical reactions, requirements toward the dendrimer molecules and the other factors [6].

The basic features of dendrimers are hyper-branched topology; a low polydispersity, the absence of linking which are specific for long macromolecules and the large number of terminal groups. In addition, they are commonly characterized by low values of glass transition temperature, high solubility, and low viscosity in solutions [7–10]. The combination of dendrimers structural perfection and the possibilities of their groups' modification are specified their application as functional nanosized materials with unique electronic, optical, magnetic and chemical properties that are required for the elaboration of modern nanotechnology.

Liquid-crystalline (LQ) dendrimers take a special position among a wide variety of dendritic molecules due to their specific molecular structure combined flexible spherical dendritic architecture with rigid rod-like mesogenic groups capable of anisotropic LC mesophase formation. The induction and the control of the mesomorphic properties (phase type and stability) in dendrimers can be achieved by a dedicated molecular design which depends on the chemical nature and structure of both the functional groups and the dendritic matrix. Nowadays, different LC dendrimers on the base of polyorganosiloxane, carbosilane, polyimine and other dendritic structure were synthesized [11–16].

This research is continued the complex investigations of thermodynamics of liquid-crystalline carbosilane dendrimers with methoxyphenylbenzoate terminal group. Earlier the thermodynamic properties of liquid-crystalline carbosilane dendrimers of the second and the fourth generations with methoxyphenylbenzoate terminal groups have been examined by us [17]. In this connection it seems interesting to find the dependences of changing the corresponding thermodynamic properties of the dendrimers on their structural parameters.

Thus, the goal of the present investigation is to study the thermodynamic properties of liquid-crystalline carbosilane dendrimers of the first to the fourth generations with methoxyphenylbenzoate terminal groups in the temperature range from $(6 \text{ to } 370) \text{ K}$ by adiabatic vacuum calorimetry and to reveal the dependences of thermodynamic properties on dendrimers composition and structure.

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2. Experimental

2.1. Samples

The synthesis and structure of liquid-crystalline carbosilane dendrimers of the first and the third generations with terminal methoxyphenyl benzoate groups are represented in figures 1 and 2. As regards the others dendrimers, these data were published in reference [17].

The samples of dendrimers under study have been synthesized in Moscow State University at the Laboratory of Polymers Chemical Transformations of High-molecular Compounds by the method described in detailed elsewhere [18]. Derived samples were cleaned by the methods of preparative gel permeation chromatography (a «KNAUER» device, column Waters 8 · 300 on ultrasilicagel with pore size (dimension) 100 nm, THF as an eluent, detector is the refractometer Waters R-410). The purity and individuality of studied dendrimers were approved by gel permeation chromatography (GPC) and NMR ^1H – spectroscopy (a Bruker WP-200 and WP-250 spectrometer in CCl_4 and CDCl_3 solutions).

NMR ^1H data for **G-1(Und-MPhB)₈**: (CCl_4 , 200 MHz): $\delta = 0.1$ (s, 12H), 0.2 (s, 96H), 0.8 (m, 64H), 1.5 (m, 124H), 1.9 (m, 16H), 2.8 (t, 16H), 7.1 (d, 16H), 7.3 (d, 32H), 7.4 (d, 16H), 8.4 (d, 16H).

G-2(Und-MPhB)₁₆: (CCl_4 , 200 MHz): $\delta = 0.1$ (s, 36H), 0.2 (s, 192H), 0.7 (m, 112H), 1.4 (m, 268H), 1.8 (m, 32H), 2.6 (m, 32H), 3.9 (t, 48H), 7.0 (d, 32H), 7.2 (d, 32H), 7.3 (d, 32H), 8.3 (d, 32H).

G-3(Und-MPhB)₃₂: (CDCl_3 , 250 MHz): $\delta = -0.08$ (s, 84H), 0.03 (s, 384H), 0.54 (m, 240H), 1.28 (m, 568H), 1.73 (m, 64H), 2.55

(m, 64H), $\delta = 3.79$ (t, 96H), 6.90 (d, 64H), 7.09 (d, 64H), 7.19 (d, 64H), 8.18 (d, 64H).

G-4(Und-MPhB)₆₄: (CDCl_3 , 250 MHz): $\delta = -0.08$ (s, 180H), 0.03 (s, 768H), 0.54 (m, 624H), 1.27 (m, 268H), 1.72 (m, 128H), 2.54 (m, 128H), $\delta = 3.78$ (t, 196H), 6.89 (d, 28H), 7.08 (d, 128H), 7.18 (d, 128H), 8.18 (d, 128H).

The polarizing microscopic investigations were performed using a Mettler FP-800 central processor equipped with a hot stage Mettler FP-82 and control unit in conjunction with a Lomo R-112 polarizing microscope. X-ray diffraction measurements were made using $\text{CuK}\alpha$ -radiation ($\lambda = 1.542 \text{ \AA}$) from 1.5 kW sealed tube. Monodispersity of compounds was confirmed by GPC analysis.

The information for all studied dendrimers is listed in table 1 as phase behavior and structure was published in detail in reference [19].

2.2. Apparatus

A precision automatic adiabatic vacuum calorimeter (BCT-3) with discrete heating was used to measure heat capacities over the temperature range from (6 to 370) K. The liquid helium and nitrogen were used as cooling reagents. The principle and structure of the adiabatic calorimeter are described in detail elsewhere [20,21]. The all measurements were performed with a computer-controlled measuring system comprising of an analogue-to-digital converter, a digital-to-analogue converter, and a switch. The calorimetric cell is a thin-walled cylindrical vessel made from titanium. The sensitivity of the thermometric circuit was

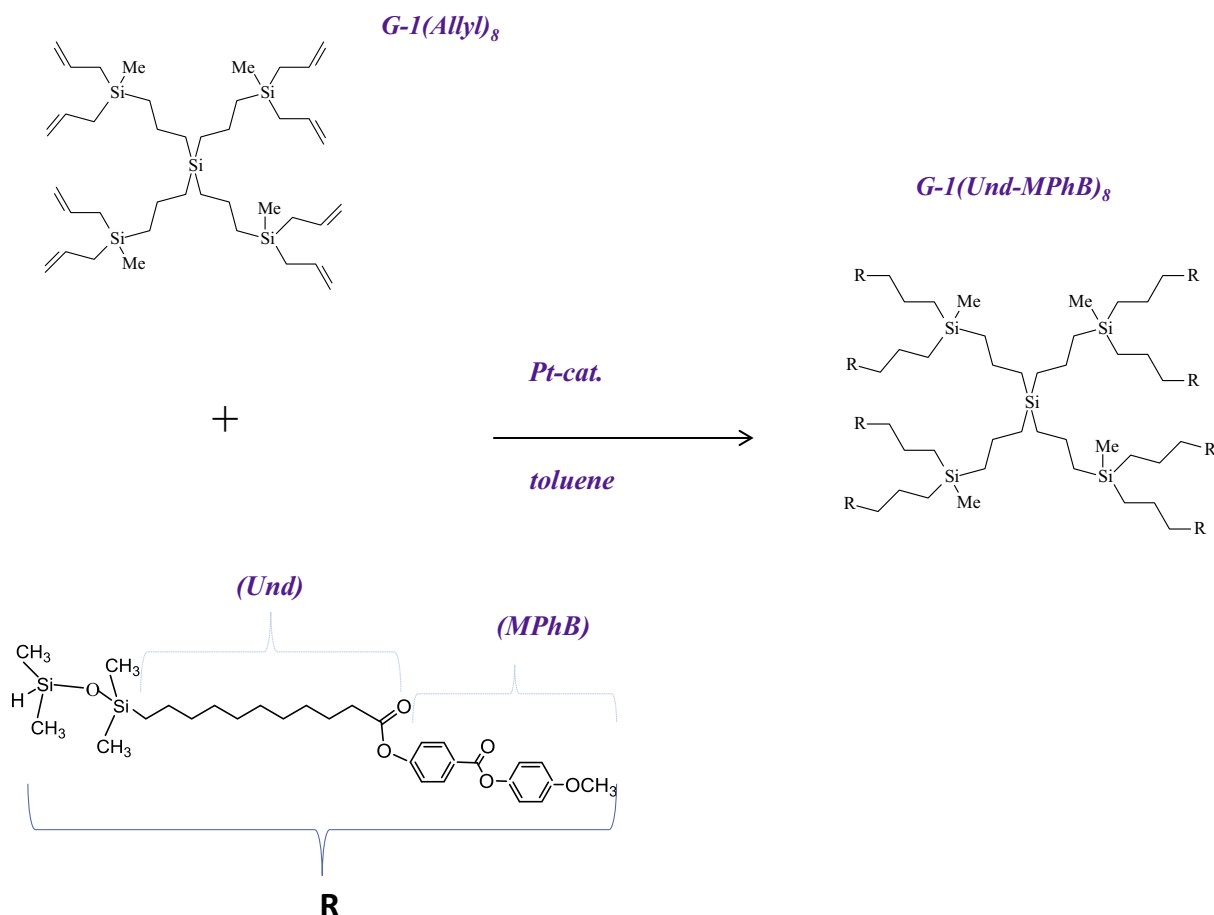


FIGURE 1. The scheme of synthesis and structure of liquid-crystalline carbosilane dendrimer of the first generation with terminal methoxyphenylbenzoate groups **G-1(Und-MPhB)₈**.

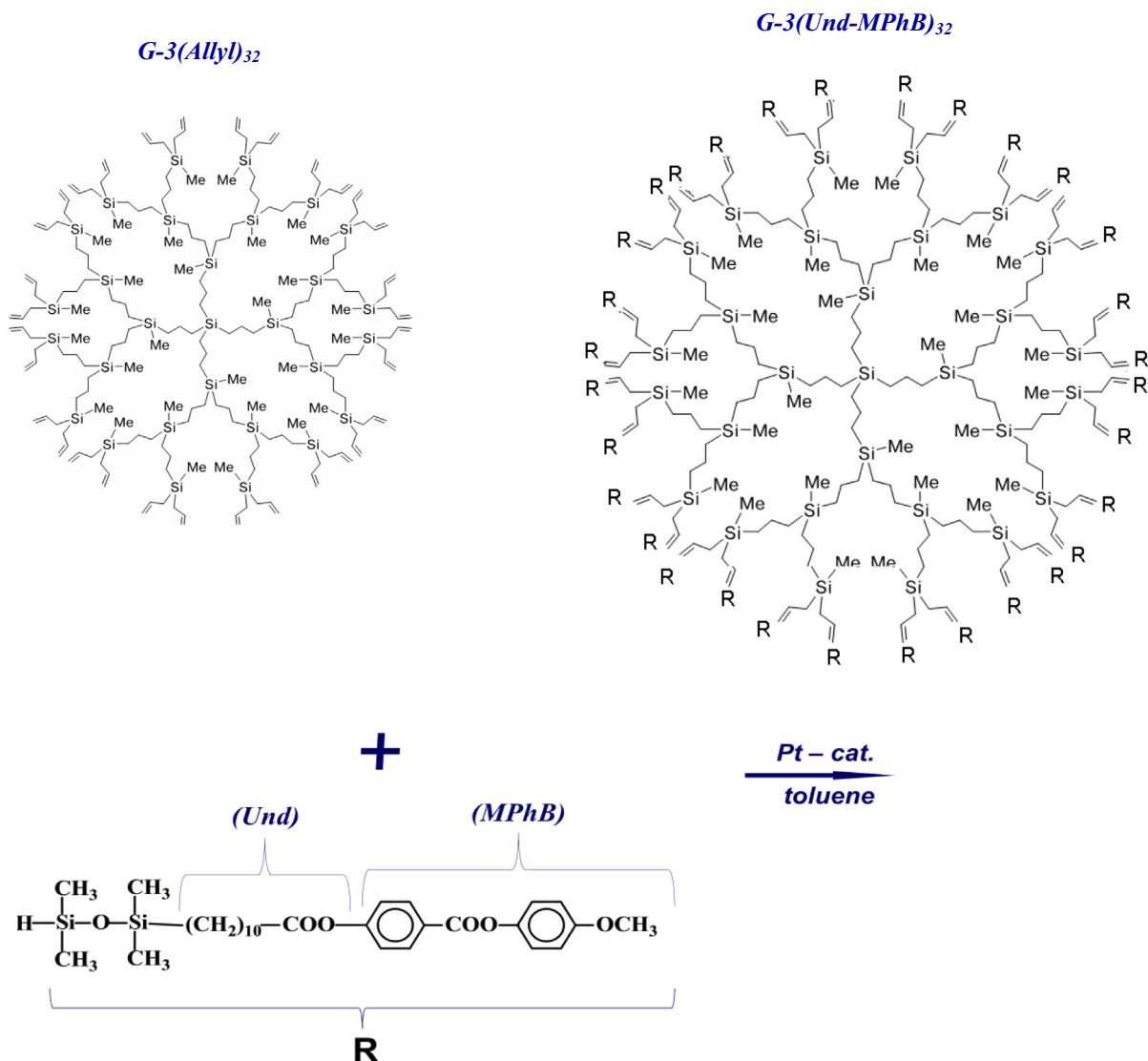


FIGURE 2. The scheme of synthesis and structure of liquid-crystalline carbosilane dendrimer of the third generation with terminal methoxyphenylbenzoate groups G-3(Und-MPhB)₃₂.

$T = 0.001$ K, and the sensitivity of the analogue-to-digital converter was $0.1 \mu\text{V}$. The energy introduced into the sample cell and the equilibrium temperature of the cell after the energy input were automatically recorded and processed online by a computer.

The calorimeter was tested by the measuring of heat capacity of special purity copper and reference samples of synthetic corundum and K-2 benzoic acid. The measurement uncertainty of heat capacity of the tested substances at helium temperatures was within $2 \cdot 10^{-2} C_p$, with rising temperature up to 40 K it decreased down to $0.5 \cdot 10^{-3} C_p$ and was equal to $2 \cdot 10^{-3} C_p$ in the range from $T = (40 \text{ to } 370) \text{ K}$. The phase transformations temperatures have been measured with the standard uncertainty $u(T) = 0.02 \text{ K}$.

3. Results and discussion

3.1. Heat capacity

The temperature dependences of heat capacity of the investigated liquid-crystalline carbosilane dendrimers are represented in figure 3.

The experimental data were smoothed using least squares polynomial fits as follows:

$$C_{p,m} = \begin{cases} \sum_{i=0}^7 A_i \ln \left(\frac{T}{30} \right)^i, & 6 \text{ K} \leq T \leq 40 \text{ K} \\ \sum_{i=0}^6 B_i \ln \left(\frac{T}{30} \right)^i, & 40 \text{ K} \leq T \leq 370 \text{ K} \end{cases},$$

where A_i and B_i are polynomial coefficients.

The tested substances under conditions of our apparatus were cooled from the room temperature to the temperature of measurement onset with the rate $0.01 \text{ K} \cdot \text{s}^{-1}$ that is attended by their supercooling and then vitrification. On subsequent heating during the process of heat capacity measuring it was observed the devitrification of dendrimers amorphous part (the region BC on figure 3) over the range from $T = (230 \text{ to } 275) \text{ K}$. The crystalline part of the samples underwent physical transformations since $T = 280 \text{ K}$. The transition of semi-crystalline state crIII to crystals crII (the range CFGH, curve 4 on figure 3), which formed liquid crystals crI (the range HGIK, curve 4 on figure 3) was detected in case of G-4(Und-MPhB)₆₄. The formation of liquid-crystalline state was less

TABLE 1
Samples information.

Sample	Source	State	Mole fraction purity	Purification and analysis methods
G-1(Und-MPhB) ₈	Present work	Semicrystalline	0.99	Gel permeation chromatography (GPC) NMR ¹ H –spectroscopy, X-ray diffraction analysis
G-2(Und-MPhB) ₁₆	[17]	Liquid-crystalline	0.99	GPC NMR ¹ H –spectroscopy, X-ray diffraction analysis
G-3(Und-MPhB) ₃₂	Present work	Liquid-crystalline	0.99	GPC NMR ¹ H –spectroscopy, X-ray diffraction analysis
G-4(Und-MPhB) ₆₄	[17]	Liquid-crystalline	0.99	GPC NMR ¹ H –spectroscopy, X-ray diffraction analysis

complicated in the conditions of thermodynamic equilibrium experiment for the other samples (the plots CFGH, curves 1, 2, 3 on figure 3). The overcooled liquid crystals were obtained for the G-1(Und-MPhB)₈ (the plot HH'). For all dendrimers under study, it was observed the fusion of liquid crystals crI with the formation of isotropic liquid I in the temperature interval from 345 to 355 K (the plots LMNO and IJK on curve 4 and curves 1, 2, 3 correspondingly, figure 3). Otherwise the temperature dependences of heat capacity of compounds under consideration hadn't any features. Heat capacities smoothly increased with the temperature rise and following relation $C_p^\circ[\text{G-1(Und-MPhB)}_8] < C_p^\circ[\text{G-2(Und-MPhB)}_{16}] < C_p^\circ[\text{G-3(Und-MPhB)}_{32}] < C_p^\circ[\text{G-4(Und-MPhB)}_{64}]$ (figure 3) takes place always.

3.2. Thermodynamic characteristics of phase transformations

3.2.1. Glass transition and glassy state

The thermodynamic characteristics of the glass transition and glassy state for dendrimers under study are listed in table 2. The

glass transition temperature T_g° was determined by the Alford and Dole method [22–24] from the inflection of the plot of $S^\circ(T) = f(T)$. The devitrification interval and the increase of the heat capacity on devitrification $\Delta C_p^\circ(T_g^\circ)$ were determined graphically. The configuration entropy was calculated from the following equation [25–27]:

$$S_{\text{conf}}^\circ = \Delta C_p^\circ(T_g^\circ) \cdot \ln 1.29, \quad (1)$$

where $1.29 = (T_g^\circ/T_2^\circ)$ and T_2° is the Kauzmann temperature. It was suggested that this ratio is also valid for the investigated dendrimers. It was assumed that $S_{\text{conf}}^\circ \approx S^\circ(0)$ [25,28].

3.2.2. Phase transformations

The parameters of phase transformations, including in liquid-crystalline state, are listed in table 3. The transition $\text{crIII} \rightleftharpoons \text{crII}$ is connected with formation of liquid-crystalline state for G-4(Und-MPhB)₆₄, which is undergoing the rearrangement of crystals crII to crI on further heating. This transformation didn't observe for the other dendrimers and the formation of liquid-crystalline state

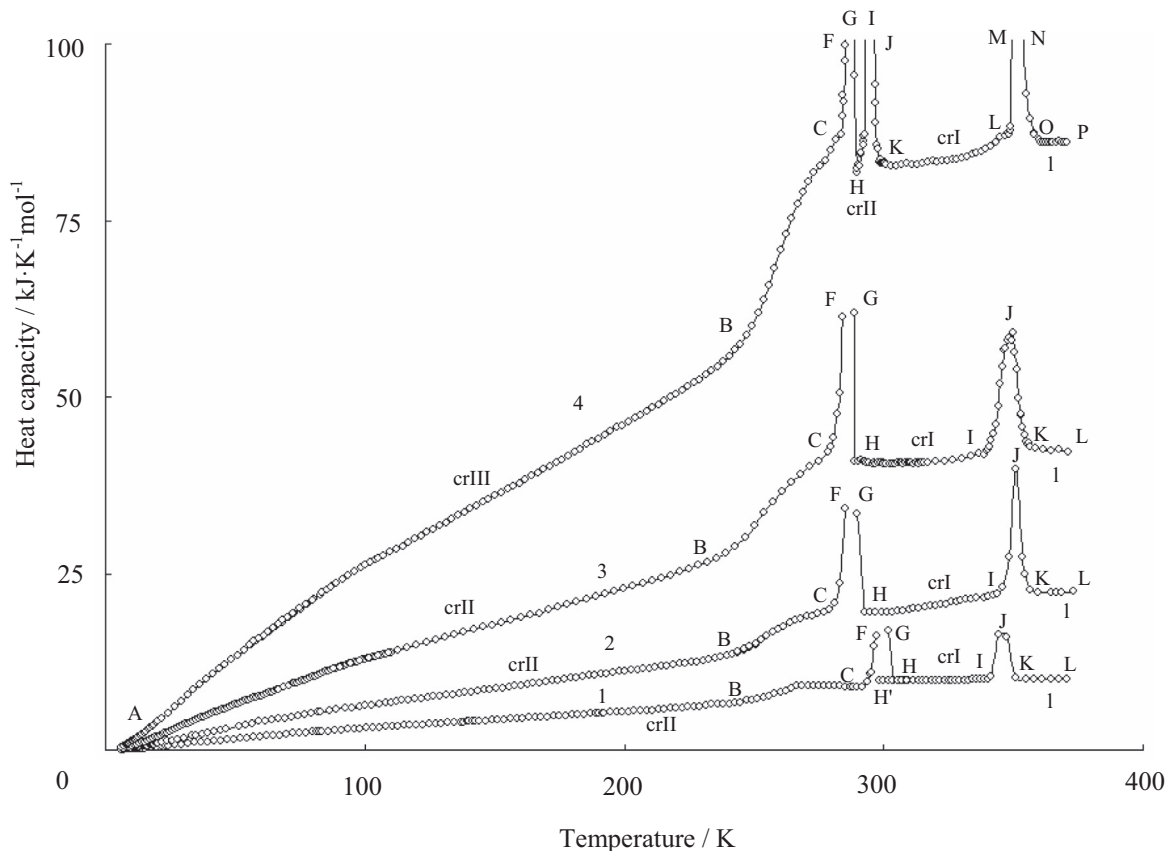


FIGURE 3. Temperature dependences of the heat capacity of liquid-crystalline carbosilane dendrimers of the first to the fourth generation with terminal methoxyphenylbenzoate groups: 1 – G-1(Und-MPhB)₈; 2 – G-2(Und-MPhB)₁₆ [17]; 3 – G-3(Und-MPhB)₃₂; 4– G-4(Und-MPhB)₆₄ [17].

TABLE 2

Glass transition and glassy state characteristics of studied liquid-crystalline carbosilane dendrimers with methoxyphenylbenzoate terminal groups at pressure $p = 0.1$ MPa.^a

Dendrimer	Gross-formulae	$M/\text{g} \cdot \text{mol}^{-1}$	$T_g^\circ \pm 1/\text{K}$	$\Delta C_p^\circ(T_g^\circ)/\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$S_{\text{conf}}^\circ/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$S^\circ(0)/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
G-1(Und-MPhB) ₈	C ₂₇₂ H ₄₂₈ Si ₂₁ O ₄₈	5056	259	2.07 ± 0.02	525 ± 6	525
G-2(Und-MPhB) ₁₆ [17]	C ₅₆₀ H ₈₉₂ Si ₄₅ O ₉₆	10424	254	3.65 ± 0.04	929 ± 10	930
G-3(Und-MPhB) ₃₂	C ₁₁₃₆ H ₁₈₂₀ Si ₉₃ O ₁₉₂	21160	250	6.30 ± 0.07	1604 ± 17	1604
G-4(Und-MPhB) ₆₄ [17]	C ₂₂₈₈ H ₃₆₇₆ Si ₁₈₉ O ₃₈₄	42634	258	15.7 ± 0.2	3998 ± 40	4000

^a Standard uncertainty u is $u(p) = 10$ kPa; reported uncertainties correspond to the combined expanded uncertainties for 0.95 level of confidence ($k \approx 2$).

TABLE 3

Thermodynamic characteristics of phase transformations for liquid-crystalline carbosilane dendrimers samples at pressure $p = 0.1$ MPa.^a

Dendrimer	Transitions								
	crIII \rightleftharpoons crII			crII \rightleftharpoons crI			crI \rightleftharpoons l		
	$T_{\text{tr}}^\circ/\text{K}$	$\Delta_{\text{tr}}H^\circ/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{tr}}S^\circ/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$T_{\text{tr}}^\circ/\text{K}$	$\Delta_{\text{tr}}H^\circ/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{tr}}S^\circ/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$T_{\text{tr}}^\circ/\text{K}$	$\Delta_{\text{tr}}H^\circ/\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_{\text{tr}}S^\circ/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
G-1(Und-MPhB) ₈				300.1 ± 0.2	66.42 ± 0.30	221.4 ± 1.5	347.5 ± 0.2	40.50 ± 0.21	116.5 ± 0.8
G-2(Und-MPhB) ₁₆ [17]				287.2 ± 0.2	166.8 ± 1.8	581.2 ± 5.8	351.1 ± 0.1	69.76 ± 0.71	198.7 ± 2.0
G-3(Und-MPhB) ₃₂				286.1 ± 0.2	371.0 ± 3.2	1297 ± 12	349.8 ± 0.1	117.5 ± 0.94	335.9 ± 4.0
G-4(Und-MPhB) ₆₄ [17]	287.2 ± 0.2	412 ± 4	1433 ± 15	294.6 ± 0.2	110.2 ± 1.0	373.4 ± 3.8	351.2 ± 0.1	174.2 ± 1.8	496.1 ± 5.0

^a Standard uncertainty u is $u(p) = 10$ kPa; reported uncertainties correspond to the combined expanded uncertainties for 0.95 level of confidence ($k \approx 2$).

is designated as a transition $\text{crII} \rightleftharpoons \text{crI}$. The transition $\text{crII} \rightarrow \text{crI}$ can be attributed to a crystal-smectic mesophase transition that was confirmed by X-ray diffraction. At subsequent heating all dendrimers were melting with the formation of isotropic liquid l. The phase behavior and phase transition temperatures of the dendrimers previously were determined by polarizing optical microscope (POM) with LOMO P-112 polarizing microscope equipped by Mettler TA-400 heating stage [19].

The transition temperatures have been taken the temperatures, responding the maximal apparent heat capacity values in transition intervals.

Phase transition enthalpies have been calculated as areas, which are limited responding figures, e.g. for the transition $\text{crI} \rightleftharpoons \text{l}$ is IJKI for G-2(Und-MPhB)₁₆ (figure 3). Phase transition entropies were evaluated by the second law of thermodynamics with using enthalpies and temperatures values. It should be noted that phase transitions thermodynamic characteristics in liquid-crystalline state were reproduced by repeated heating and cooling.

The samples of dendrimers form inclined type smectic crystals [29] in liquid-crystalline state. The structure of dendrimers was confirmed by means of X-ray diffraction investigations. WAXS results showed one diffuse peak with intermesogenic distance about 0.5 nm, that slightly raises with the increase of the generation number (the values of D are (0.485, 0.489, 0.492 and 0.494) nm for G-1(Und-MPhB)₈–G-4(Und-MPhB)₆₄ correspondingly). SAXS measurements revealed two sharp reflections being first and second order from the layer spacing ($d = 4.27$ and 4.66 nm respectively). They also increase with the growth of the generation number. These results suggest the existence of orthogonal disordered smectic A mesophase for compounds in question. As a result, the dendrimers possess lamellar structure where the layers of mesogenic groups alternate with the layers of dendritic cores.

3.2.3. Standard thermodynamic functions

The heat capacity values of liquid-crystalline carbosilane dendrimers with methoxyphenylbenzoate terminal groups were extrapolated from the initial temperature of measurements to $T \rightarrow 0$ K based on Debye model of heat capacity to calculate the standard thermodynamic functions [30]:

$$C_p^\circ = nD(\Theta_D/T), \quad (2)$$

where D is the symbol of the Debye function, n and Θ_D are specially selected parameters. For the investigated dendrimers $n = 6$ and Θ_D were equal to $T = (50.2, 61.3, 63.7, 77.4)$ K correspondingly.

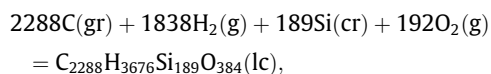
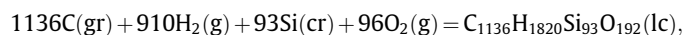
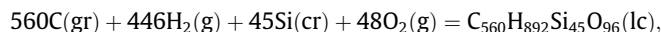
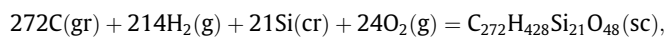
The standard thermodynamic functions of G-1(Und-MPhB)₈–G-4(Und-MPhB)₆₄ dendrimers are given in table 4.

The calculations of $H^\circ(T) - H^\circ(0)$ and $S^\circ(T) - S^\circ(0)$ were made by the numerical integration of the $C_p^\circ(T)$ and $C_p^\circ(\ln T)$ curves, respectively. The potential Φ_m° was computed from the enthalpies and entropies at the corresponding temperatures. The calculation technique was described in elsewhere [28].

The standard entropies of formation $\Delta_f S^\circ$ of dendrimers under study in different physical states at $T = 298.15$ K were calculated based on their $S^\circ(T) - S^\circ(0)$ values at $T = 298.15$ K (table 4) and the absolute entropies of elementary substances [C(gr), Si(cr)] [31] and [H₂(g), O₂(g)] [32]. The calculated $\Delta_f S^\circ$ values are:

$$\begin{aligned} \Delta_f S^\circ(\text{G-1(Und-MPhB)}_8) &= -(26419 \pm 207) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}, \\ \Delta_f S^\circ(\text{G-2(Und-MPhB)}_{16}) &= -(54235 \pm 426) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}, \\ \Delta_f S^\circ(\text{G-3(Und-MPhB)}_{32}) &= -(109864 \pm 974) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}, \\ \Delta_f S^\circ(\text{G-4(Und-MPhB)}_{64}) &= -(222541 \pm 1746) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}. \end{aligned}$$

The obtained $\Delta_f S^\circ$ values correspond to the following reactions:



where the physical states of the reagents are indicated in parentheses (gr stands for graphite, g for gas, cr for crystal, sc for semi-crystalline and lc for liquid-crystalline).

It seems rational to make the hypothetical synthesis of liquid-crystalline carbosilane dendrimer G- n (Und-MPhB) _{n} from appropriate carbosilane dendrimers with terminal allyl groups [G- n (All) _{n}] and appropriate substituted silane [33,34] and to calculate its entropy at different temperatures and standard pressure.

TABLE 4

The thermodynamic functions of G-1(Und-MPhB)₈–G-4(Und-MPhB)₆₄ liquid-crystalline carbosilane dendrimers with methoxyphenylbenzoate terminal groups at pressure $p = 0.1 \text{ MPa}$.^a

T/K	$C_p^\circ(T)/\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$H^\circ(T) - H^\circ(0)/\text{kJ} \cdot \text{mol}^{-1}$	$S^\circ(T) - S^\circ(0)/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$-\Phi_m^\circ/\text{kJ} \cdot \text{mol}^{-1}$
<i>G-1(Und-MPhB)₈</i>				
<i>Semicrystalline state crII</i>				
5	0.0269	0.0342	9.13	0.0115
10	0.130	0.415	57.5	0.161
15	0.274	1.41	136	0.636
20	0.4695	3.220	239.2	1.562
25	0.6590	6.047	364.6	3.068
50	1.574	34.19	1108	21.23
100	3.083	152.5	2688	116.3
150	4.253	336.3	4162	288.1
200	5.443	578.9	5550	531.1
250	7.115	874.9	6864	841.1
298.15 ^c	9.002	1293	8390	1208
300.1 ^c	9.000	1310	8446	1224
<i>Liquid-crystalline state crI</i>				
300.1 ^c	9.795	1376	8667	1224
347.5 ^c	10.00	1846	10,120	1671
<i>Liquid state I</i>				
347.5 ^c	10.00	1886	10,236	1671
370 ^c	10.08	2112	10,866	1908
<i>G-2(Und-MPhB)₁₆ [17]</i>				
<i>Semicrystalline state crII</i>				
5	0.0463	0.0583	15.5	0.0195
10	0.262	0.798	110	0.297
15	0.546	2.79	267	1.22
20	0.9111	6.392	472.0	3.049
25	1.321	11.98	719.7	6.012
50	3.268	69.46	2238	42.41
100	6.284	313.0	5495	236.5
150	8.651	686.8	8494	587.3
200	11.16	1183	11,330	1083
250	14.89	1810	14,115	1719
287.2 ^c	19.50	2481	16,612	2287
<i>Liquid-crystalline state crI</i>				
287.2 ^c	19.50	2648	17,194	2287
298.15	19.60	2866	17,938	2482
350 ^c	22.15	3944	21,267	3499
351.1 ^c	22.15	3967	21,331	3520
<i>Liquid state I</i>				
351.1 ^c	22.15	4037	21,530	3520
370	22.31	4459	22,702	3941
<i>G-3(Und-MPhB)₃₂</i>				
<i>Semicrystalline state crII</i>				
5	0.0956	0.120	32.0	0.0401
10	0.569	1.661	226	0.598
15	1.185	5.9817	569	2.55
20	1.944	13.72	1009	6.453
25	2.621	25.07	1513	12.75
50	6.432	140.1	4552	87.49
100	12.853	625.5	11,021	476.7
150	17.791	1394	17,184	1184
200	22.942	2410	22,997	2189
250	31.75	3713	28,779	3482
286.1 ^c	40.50	5082	33,882	4608
<i>Liquid-crystalline state crI</i>				
286.1 ^c	40.50	5453	35,178	4608
298.15	40.54	5945	36,863	5046
300	40.55	6020	37,114	5114
349.8 ^c	40.90	8048	43,368	7122
<i>Liquid state I</i>				
349.8 ^c	42.40	8165	43,704	7122
370	42.50	9022	46,085	8029
<i>G-4(Und-MPhB)₆₄ [17]</i>				
<i>Semicrystalline state crIII</i>				
5	0.191	0.239	63.9	0.0799
10	1.18	3.42	463	1.21
15	2.46	12.4	1175	5.23
20	4.032	28.45	2088	13.31
25	5.458	52.12	3138	26.34

TABLE 4 (continued)

T/K	$C_p^\circ(T)/\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$H^\circ(T) - H^\circ(0)/\text{kJ} \cdot \text{mol}^{-1}$	$S^\circ(T) - S^\circ(0)/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$-\Phi_m^\circ/\text{kJ} \cdot \text{mol}^{-1}$
60	15.91	435	12,058	288.4
100	26.12	1281	22,642	982.8
160	37.90	3202	37,467	2793
200	46.14	4882	46,808	4479
240	55.45	6903	55,991	6535
287.2 ^c	82.97	10,321	68,894	9482
<i>Liquid-crystalline state crll</i>				
287.2 ^c	82.97	10,733	70,327	9482
294.6 ^c	82.97	11,329	72,374	9994
<i>Liquid-crystalline state crl</i>				
294.6 ^c	82.97	11,439	72,748	9994
298.15	82.97	11,731	73,736	10,253
350 ^c	85.17	16,074	87,158	14,432
351.2 ^c	85.23	16,176	87,450	14,536
<i>Liquid state l</i>				
351.2 ^c	85.23	16,350	87,946	14,536
370	86.65	17,963	92,419	16,232

^a Standard uncertainty of temperature $u(T) = 0.01$ K. Combined expanded relative uncertainties for the heat capacity $U_{C_p}(C_p^\circ)$ are 0.02, 0.005, 0.002 and 0.002; the combined expanded relative uncertainties $U_{C_p}[H^\circ(T) - H^\circ(0)]$ are 0.022, 0.007, 0.005 and 0.015; $U_{C_p}[S^\circ(T) - S^\circ(0)]$ are 0.023, 0.008, 0.006 and 0.017; $U_{C_p}[G^\circ(T) - H^\circ(0)]$ are 0.03, 0.01, 0.009 and 0.019 in the ranges $6 \text{ K} \leq T \leq 15 \text{ K}$, $15 \text{ K} \leq T \leq 40 \text{ K}$, $40 \text{ K} \leq T \leq T_{tr}^\circ$ and $T_{tr}^\circ \leq T \leq 370 \text{ K}$ respectively for 0.95 level of confidence ($k \approx 2$).

^b $\Phi_m^\circ = [H^\circ(T) - H^\circ(0)] - T[S^\circ(T) - S^\circ(0)]$.

^c Extrapolated.

In table 5 are listed the standard entropies of synthesis of G-1 (Und-MPhB)₈-G-4(Und-MPhB)₆₄ dendrimers per mole of methoxyphenylbenzoate ester of 11-tetramethyldisiloxyundecanoic acid to reveal the dependence of dendrimers thermodynamic properties on the nature of terminal groups and generation number. As it can be seen, ΔS_r° for the dendrimers under study take the close values. Thus, the conclusion that thermodynamic parameters of dendrimers synthesis do not depend on number generation and are defined by the nature of terminal groups was made. Besides the fusion temperatures T_{fus}° and also the temperatures of polymorphous transformations (table 3) for compared dendrimers take the close values. This fact indicates that thermodynamic properties are more specified by the nature of terminal groups rather than generation number. Such consequence was obtained by us earlier at systematic investigation of carbosilane dendrimers [35,36].

3.2.4. The dependences of dendrimers thermodynamic properties on their composition and structure

The determination of dependences between the thermodynamic properties of dendrimers under study and their molecular mass M and also the number of mesogenic (terminal) groups m on the outer layer at different temperatures seems interesting for us. It appears that the isotherms have a linear character:

$$C_p^\circ(298.15) = 1.9676M - 972.53, \quad (3)$$

$$C_p^\circ(298.15) = 1320.5m - 1587.8, \quad (4)$$

$$H^\circ(298.15) = 0.2771M - 33.553, \quad (5)$$

$$S^\circ(298.15) = 1.7371M - 198.29. \quad (6)$$

TABLE 5

Standard entropies of synthesis of liquid-crystalline carbosilane dendrimers at different temperatures and pressure $p = 0.1$ MPa.^a

T/K	G-n(All)m [33]	H-Si-Und-MPhB [34]	G-n(Und-MPhB)m	$-\Delta S_r^\circ/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
<i>G-1(All)₈ + 8 H-Si-Und-MPhB → G-1(Und-MPhB)₈</i>				
100	oc	cr	sc	1624 (203)
200	h.e.	cr	sc	1766 (221)
298.15	h.e.	cr	sc	1780 (223)
340	h.e.	l	lc	2060 (258)
<i>G-2(All)₁₆ + 16H-Si-Und-MPhB → G-2(Und-MPhB)₁₆ [17]</i>				
100	g	cr	sc	3541 (221)
200	h.e.	cr	sc	4097 (256)
298.15	h.e.	cr	lc	3239 (202)
340	h.e.	l	lc	4222 (264)
<i>G-3(All)₃₂ + 32H-Si-Und-MPhB → G-3(Und-MPhB)₃₂</i>				
100	g	cr	sc	7531 (235)
200	h.e.	cr	sc	8148 (255)
298.15	h.e.	cr	lc	6400 (200)
340	h.e.	l	lc	8469 (265)
<i>G-4(All)₆₄ + 64H-Si-Und-MPhB → G-4(Und-MPhB)₆₄ [17]</i>				
100	g	cr	sc	13916 (217)
200	h.e.	cr	sc	15194 (237)
298.15	h.e.	cr	lc	12798 (200)
340	h.e.	l	lc	16802 (262)

^a Standard uncertainty of temperature $u(T) = 0.01$ K. Combined expanded relative uncertainties for the entropy of synthesis $U_{C_p}(\Delta S_r^\circ)$ are 0.015, for 0.95 level of confidence ($k \approx 2$); where the physical states of the reagents are indicated in parentheses (oc – overcooled, g for glassy, cr – crystal, h.e. – high-elastic, sc – semi-crystalline, lc – liquid-crystalline, and l for liquid).

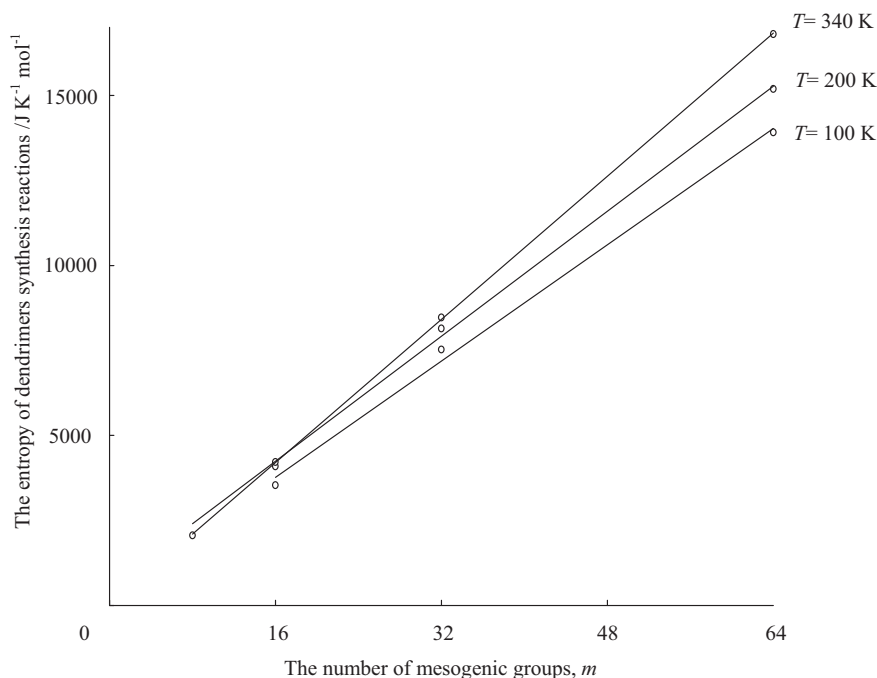


FIGURE 4. The dependence of dendrimers synthesis reactions entropy on the number of mesogenic groups m on the outer layer at $T = (100, 200 \text{ and } 340) \text{ K}$.

In equations (3)–(6) the heat capacity values are given in $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, enthalpy in $\text{kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and entropy $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. There are also the linear dependence of entropy of dendrimers synthesis reactions on the number of mesogenic groups m on the outer sphere (figure 4) at $T = (100, 200 \text{ and } 340) \text{ K}$. As it can be seen from figure 4 the experimental points corresponds to average curves with adequate accuracy. The reliability of approximation $R^2 = 1$. The equations of isothermal dependences are cited below:

$$\Delta S_r(100 \text{ K})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 213.77m + 348.5, \quad (7)$$

$$\Delta S_r(200 \text{ K})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 229.62m + 574, \quad (8)$$

$$\Delta S_r(340 \text{ K})/\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} = 262.92m + 0.5652. \quad (9)$$

The significance of the dependences obtained is associated with the possibility of prediction of thermodynamic properties for dendrimers not investigated. In addition the linear relation between properties and M , m values denotes additive contributes of dendrimer units to appropriate properties. This fact is pointed to constancy of intermolecular forces in dendrimers with their upsizing, i.e. with the generation number growth.

4. Conclusions

The temperature dependences of heat capacity for liquid-crystalline carbosilane dendrimers of the first to the fourth generations with methoxyphenylbenzoate terminal groups have been measured over the range from $T = (6 \text{ to } 370) \text{ K}$ by adiabatic calorimetry. Within the above temperature interval the phase transformations have been revealed and their thermodynamic characteristics have been revealed and analyzed. Specifically, the phase transitions in liquid crystalline state have been detected and their thermodynamic quantities were interpreted with structural parameters.

From the experimental values, the standard thermodynamic functions of the dendrimers investigated, namely, the heat capacity

$C_p^\circ(T)$, enthalpy $H^\circ(T) - H^\circ(0)$, entropy $S^\circ(T) - S^\circ(0)$ and potential Φ_m° have been calculated over the range from $T \rightarrow (0 \text{ to } 370) \text{ K}$ and entropies of formation of dendrimers in different physical states at $T = 298.15 \text{ K}$ have been calculated. The linear dependences of changing the corresponding thermodynamic properties of the dendrimers on their molar mass and the number of mesogenic groups on the outer layer have been obtained. It was found that thermodynamic properties of dendrimers are more specified by the nature of outer layer than generation number.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jct.2016.02.019>.

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