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# CARBOSILANE DENDRIMER OF SECOND GENERATION WITH TERMINAL METHOXYUNDECYLENATE GROUPS

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## Abstract

The thermodynamic properties of carbosilane dendrimer of second generation with terminal methoxyundecylene groups were studied between 6 and 340 K by adiabatic vacuum calorimetry: the temperature dependence of the molar heat capacity $C_p^0$ was measured, the physical transformations were established and their thermodynamic characteristics were obtained. The experimental data were used to calculate the thermodynamic functions $C_p^0(T)$, $H^0(T)–H^0(0)$, $S^0(T)$, $G^0(T)–H^0(0)$ of the compound in the range 0 to 340 K. From the relation $C_p^0(T)$ the fractal dimension of the dendrimer was experimentally determined. The heat capacity of the dendrimer was compared with the corresponding additive values calculated from the properties of its constituents – a dendritic matrix (carbosilane dendrimer of second generation) and the corresponding amount of moles of methyl ester of 11-(tetramethyldisiloxy)undecanoic acid serving as terminal groups.

**Keywords**: carbosilane dendrimer of second generation with terminal methoxyundecylenate groups, dendritic matrix of second generation, entropy of formation, fractal dimension, heat capacity, methyl ester of 11-(tetramethylsiloxy)undecanoic acid, thermodynamic functions

## Introduction

Although the investigations of the synthesis, various physico-chemical characteristics and a practical application of dendritic polymers [1–5] are widely carried out, their thermodynamic properties are not still studied well. A detailed calorimetric study of the thermodynamic characteristics of a dendritic polyperfluorophenyl germane [6–8] and the carbosilane dendrimer of first generation with terminal methoxyundecylenate groups [9]

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was fulfilled only in works [6–9]. The calorimetric data make it possible to obtain the combination of a wide variety of quantitative characteristics of dendrimers offering scope for the discovery of their relations with the composition and structure, the physical state and temperature of the objects under study.

The goal of the present work was to synthesize and to perform the calorimetric study of the thermodynamic properties for the carbosilane dendrimer of second generation having terminal methoxyundecylenate groups, i.e. to measure the temperature dependence of the heat capacity $C_p^0$ between 0 and 340 K, to show up the physical transformations on heating and cooling the dendrimer in the above temperature interval and to obtain their thermodynamic characteristics, to calculate the thermodynamic functions in the range 0 to 340 K, to compare the thermodynamic properties of the dendrimer with the corresponding additive values calculated from the heat capacities of its constituents – a dendritic matrix of second generation and the corresponding quantity of methyl ester of 11-(tetramethylsiloxy)undecanoic acid, namely methoxyundecylenate groups, and to estimate the entropies of formation of the carbosilane dendrimer via the hydrosilylation reaction of the carbosilane dendritic matrix of second generation with methyl ester of 11-(tetramethylsiloxy)undecanoic acid.

# Experimental

## *Synthesis procedure of dendrimer with terminal methoxyundecylenate groups*

### Methyl ester of undecylenic acid (compound I)

Undecylenic acid (10 g) was dissolved in methyl alcohol (19 mL) and concentrated $H_2SO_4$ (0.5 mL) was added. A reaction mixture was boiled with mixing on a magnetic stirrer during 10 h. Then an excess of methanol was distilled off, the mixture was washed with water and the product formed was isolated with ethyl ether. An ester extract was washed with $NaHCO_3$ solution and further with water to pH=7 and dried overnight over anhydrous $CaCl_2$. The ester was distilled off on a vacuum rotary evaporator. A crude product was purified by column chromatography on silica gel (Merck 40/60) using toluene as an eluent. The yield was 91%.

### Methyl ester of 11-(dimethylchlorosilyl)undecanoic acid (compound II)

Dimethylchlorosilane (12 mL) and toluene (8 mL) were added in methyl ester of undecylenic acid (8 mL). A reaction mixture was purged with argon and 2 drops of RS-072 Pt-catalyst were added. The reaction was conducted in a closed vessel for 7 days at 35°C. The completion of the reaction was checked by $^1$H NMR spectroscopy.

### Methyl ester of 11-(tetramethyldisiloxy)undecanoic acid (compound III)

A mixture of pyridine (22.6 mL), $H_2O$ (4 mL) and THF (25 mL) was slowly added dropwise on cooling and with continuous mixing to a solution of compound II (3 g) in dimethylchlorosilane (60 mL). Further $H_2O$ (50 mL), chloroform (200 mL) were added to a reaction mixture and the mixture was washed with water till a neutral reaction. The mixture was dried over $MgSO_4$ and evaporated under vacuum. The product was purified by column chromatography on silica gel (Merck 40/60) using toluene-ethyl acetate (30:1) mixture as an eluent. The yield was 80%. $^1$H NMR ($CDCl_3$, 250 MHz), δ, ppm: 0.041 {s, 6H, $HSi(CH_3)_2OSi(CH_3)_2$; 0.145 (d, 6H, $J$=2.4 Hz, $HSi(CH_3)_2OSi(CH_3)_2$; 0.508 ($t$, 2H, $J$=7.3 Hz, $SiCH_2$); 1.2–1.4 {m, 16H, $(CH_2)_8$; 1.52–1.67 (m, 2H, $CH_2CH_2COO$); 2.288 ($t$, 2H, $J$=7.3 Hz, $CH_2CH_2COO$); 3.652 (s, 3H, $COOCH_3$); 4.660 {m, 1H, $HSi(CH_3)_2$}.

Dendrimer G-2(Und-Me)$_{16}$ (compound IV)

Compound III (1.4 g), toluene (5 mL) and 2 drops of RS-072 Pt-catalyst were added to dendrimer G-2(All)$_{16}$ (0.244 g) [11]. The reaction was conducted in argon flow with mixing on a magnetic stirrer at 35°C for 15 days. Toluene was distilled off on the vacuum rotary evaporator. The dendrimer was purified by preparative gel-permeation chromatography (GPC). The yield was 40%. $^1$H NMR ($CDCl_3$, 250 Hz), δ, ppm: 0.092 (s, 36H, $SiCH_3$); 0.014 (s, 192H, {$(CH_3)_2SiOSi(CH_3)_2$}); 0.42–0.66 (m, 144H, $SiCH_2$); 1.2–1.4 (m, 300H, $CH_2$); 1.51–1.67 (m, 32H, $CH_2CH_2COO$); 2.285 ($t$, 32H, $J$=7.3 Hz, $CH_2CH_2COO$); 3.648 (s, 48H, $COOCH_3$).

### *Apparatus and measurement procedure*

$^1$H NMR spectra were recorded with a Bruker WP-250 instrument. For the analysis 3% solutions of the substances in $CDCl_3$ were taken. The analytical and preparative GPC were carried out with a Knauer device on Waters columns (8×300 and 19×300 mm) packed with Ultrastyragel having pore sizes 1000 Å. THF as an eluent, a Waters R-410 refractometer as a detector.

To study the temperature dependence of the heat capacity, temperatures and enthalpies of physical transitions in the range 5 to 340 K a BKT-3 thermophysical device – an adiabatic vacuum calorimeter – was employed; its design and the operational procedure were similar to those described earlier [12, 13]. From the calibration and test results of the calorimeter it was established that the measurement uncertainty of the heat capacity for the substances at helium temperatures was within 2%; with rising temperature up to 40 K it decreased to 0.5% and became equal to *ca.* 0.2% from 40 to 340 K.

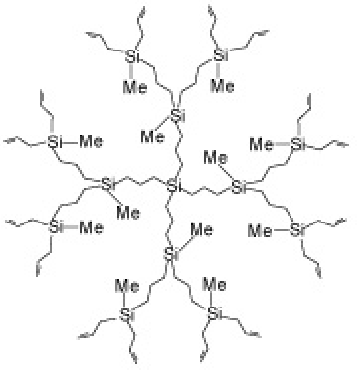
### *Synthesis of dendrimer*

The sample of the carbosilane dendrimer of second generation was prepared according to the procedure first demonstrated in [10]. The synthesis was performed by the following equation:

$$\text{G-2(All)}_{16}+16\text{H-Si-Und-Me}\rightarrow\text{G-2(Und-Me)}_{16}$$

where G-2(All)$_{16}$ is the carbosilane dendrimer of second generation.

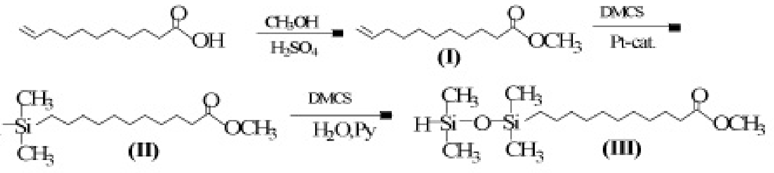
H-Si-Und-Me is methyl ester of 11-(tetramethylsiloxy)undecanoic acid, $H\text{-}Si(CH_3)_2\text{-}O\text{-}Si(CH_3)_2\text{-}(CH_2)_{10}COOCH_3$; G-2(Und-Me)$_{16}$ is the carbosilane



dendrimer of second generation with terminal methoxyundecylenate groups – the addition product of H-Si-Und-Me at double allyl C=C bonds of the carbosilane dendritic matrix of second generation G-2(All)$_{16}$.

The synthesis of initial carbosilane dendrimer of second generation G-2(All)$_{16}$ is described elsewhere [11]. Under usual conditions, the dendrimer is a transparent viscous liquid. The molecular mass of the dendrimer was calculated by its formula as 1707 g mol$^{-1}$.

Methyl ester of 11-(tetramethylsiloxy)undecanoic acid H-Si-Und-Me was synthesized by the scheme as follows:



where DMCS is dimethylchlorosilane.

Methyl ester of undecylenic acid (compound I) was formed by the standard procedure through the interaction of undecylenic acid with methyl alcohol in the presence of concentrated sulfuric acid. Methyl ester of 11-(dimethylchlorosilyl)undecanoic acid (compound II) was prepared via the hydrosilylation reaction in the presence of Pt-catalyst. The reaction was conducted till the double bond in a reaction mixture was totally ‘exhausted’, that was checked by the disappearance of proton signals in the region of 5.0 and 5.8 ppm on a $^1$H NMR spectrum. Compound III was a product of the cohydrolysis reaction with 40-fold mole excess of DMCS. The reaction proceeded with using pyridine to fix releasing HCl. The structure of compound III was proved by $^1$H NMR spectroscopy.

At the second stage, the coupling of compound (III) formed to the dendritic matrix was carried out by the scheme shown above. A 1.5-fold excess of III was used in the course of the hydrosilylation reaction to guarantee the substitution of all eight allyl groups of the dendritic matrix. $^1$H NMR spectroscopy was used to check up the completion of the reaction. The dendrimer was purified by GPC method and it was found that a total content of impurities was less than 0.1 mass%. The structure of dendrimer G-2(Und-Me)$_{16}$ was confirmed by $^1$H NMR spectroscopy. At room temperature the product was a light-brown waxy substance. The molecular mass of the dendrimer 7030 g mol$^{-1}$ was estimated by its formula.

*Calorimetric measurements*

The dendrimer (0.3060 g) was placed in a calorimetric ampoule. To improve heat exchange a previously evacuated ampoule with the substance was filled with special-purity helium up to a pressure of 40 Pa at room temperature. In 4 series of the heat capacity measurements reflecting the sequence of experiments 267 experimental points of $C_p^0$ were obtained in the range 6 to 340 K. The smoothing of the $C_p^0$ points was made on a computer. The scatter of experimental $C_p^0$ points from the smoothed curves did not exceed the uncertainty of the measurements.The root-mean-square deviation between 5 and 50 K was 0.07%, from 80 to 220 K 0.05% and in the range 240 to 335 K it was equal to 0.02%. All the experimental $C_p^0$ points and the averaged curves $C_p^0=f(T)$ are illustrated in Fig. 1. The experiments showed that in the temperature interval studied the dendrimer exists in two crystalline crII and crI states (the crystals are denoted by us), an overcooled liquid state (l') – a very unstable state – and a liquid (l) one. The overcooled liquid was formed on melting crystals crII and in the course of its formation, due to a high thermodynamic instability, the liquid crystal-

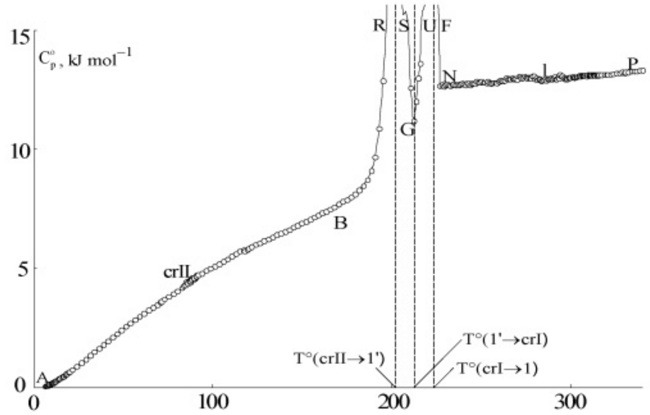


**Fig. 1** Temperature dependence of heat capacity of carbosilane dendrimer G-2(Und-Me)$_{16}$: AB – crystals crII; BRSGUFN – the apparent heat capacity in the temperature region of physical transformations (melting of crII with the formation of overcooled liquid l' crystallizing when it appears with the formation of crystals crI and melting of crystals crI); NP – liquid; $T^\circ$(crII→l') – the melting temperature of crystals crII; $T^\circ$(l'→crI) – the crystallization temperature of l'; $T^\circ$(crI→l) – the melting temperature of crystals crI

lized with the formation of crystals crI. The temperature ranges where the above physical states are observed are shown in Fig. 1.

## Results and discussion

### *Heat capacity*

As seen in Fig. 1, the heat capacity of crystals crII and liquid (l) (curves AB and NP) does not exhibit any peculiarities: it gradually increases with rising temperature, the increase in $C_p^0$ of crystals crII occurring substantially more rapidly than that of the liquid. The temperature dependence of the heat capacity in the region of physical transformations is illustrated in Fig. 2. Curve BR is the apparent heat capacity in the beginning of the melting range of crystals crII. The termination of the process of crII melting is masked with the onset of an exothermic process of crystallization of liquid l' formed when crystals crII melt. It is in an overcooled state and thermodynamically unstable and, therefore, the attempt to measure directly the heat capacity of the overcooled liquid was unsuccessful. It is, however, obvious that its heat capacity lies on the extended section of the temperature dependence of $C_p^0$ for liquid l (Fig. 2, curve NP) in the temperature interval between $T^0$(crII→l') and $T^{\mathrm{o}}$(l'→crI). Thus, if one succeeded in measuring $C_p^0$ of the overcooled liquid it would be described with curve DE. Curve SG is the apparent heat capacity which is, on the one hand, the consequence of the endothermic process of crystals crII melting being in progress and, on the other hand, of the exothermic process of the overcooled liquid crystallization. The

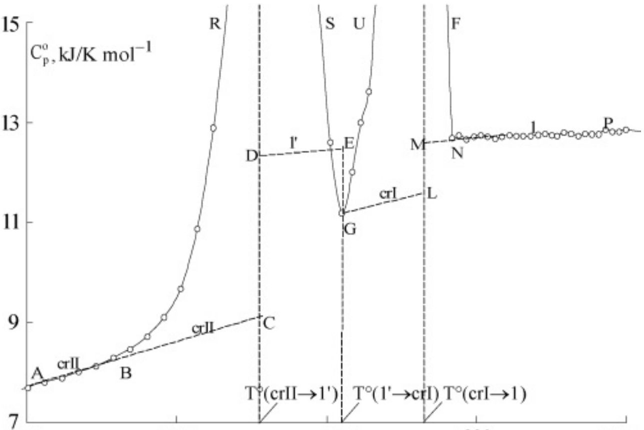


**Fig. 2** Temperature dependence of heat capacity of carbosilane dendrimer G-2(Und-Me)$_{16}$ in the physical transformation region: ABC – crystals crII; DE – overcooled (metastable) liquid (l'); GL – crystals crI; MNP – liquid (l); BRSG, GUFN – the apparent heat capacities in the region of melting of crystals crII, crystallization of l' and melting of crystals crI; $T^{\mathrm{o}}$(crII→l') – the melting temperature of crystals crII; $T^{\mathrm{o}}$(l'→crI) – the crystallization temperature of l' and $T^{\mathrm{o}}$(crI→l) – the melting temperature of crystals crI

availability of the exothermic process was judged from the heat release leading to a spontaneous heating of the calorimeter with the substance. Both simultaneously proceeding processes are completed at point G and just here the melting of crystals crI formed begins. The melting process of crystals crI terminates at point N. Curve GUFN is the apparent heat capacity in the melting region of crI. The normal heat capacity of crI is described with GL. Point L is obtained by the extrapolation of the heat capacity of crystals crI from point G to $T^{\circ}(\text{crI}\rightarrow\text{l})$, the trend of curve GL being chosen the same as that of BC in the case of crII since the temperature dependences of polymorphic crystals (crII and crI are crystals of this type) are usually similar. $T^{\circ}(\text{crII}\rightarrow\text{l'})$ corresponding to the maximum apparent heat capacity on melting crII, $\{C^0_{\text{p,max}}(\text{crII}\rightarrow\text{l'})=23.6\ \text{kJ K}^{-1}\ \text{mol}^{-1}\}$, was considered to be the melting temperature of crystals crII. It was suggested that the crystallization of l' was completed at point G and the temperature corresponding to it was regarded as the temperature of the exothermic crystallization process, $T^{\circ}(\text{l'}\rightarrow\text{crI})$. $T^{\circ}(\text{crI}\rightarrow\text{l})$ corresponding to the maximal apparent heat capacity in the melting interval, $\{C^0_{\text{p,max}}(\text{crI}\rightarrow\text{l})=31.3\ \text{kJ K}^{-1}\ \text{mol}^{-1}\}$, was taken as the melting temperature of crystals crI. A normal trend of the heat capacity for crII in the region of melting is shown with curve BC {the extrapolation of AB up to $T^{\circ}(\text{crII}\rightarrow\text{l'})$}.

The heat capacity of the dendrimer between 0 and 6 K is described by the Debye function for the heat capacity:

$$C^0_{\text{p}}=nD(\theta_{\text{D}}/T) \qquad (1)$$

where $D$ denotes the Debye function of the heat capacity, $n$ and $\Theta_{\text{D}}$ are special parameters.

For the dendrimer under study $n$=148.2 and $\Theta_{\text{D}}$=73.15 K are selected from the experimental $C^0_{\text{p}}$ values in the range 9 to 17 K. In this interval with these parameters Eq. (1) reproduces the experimental values of $C^0_{\text{p}}$ within 2%. It was assumed that at $T$<9 K this expression reproduces the $C^0_{\text{p}}$ values with the same uncertainty. Hence, over the range 0 to 18 K the relation $C^0_{\text{p}}\sim T^3$ occurs. In the fractal variant of the Debye theory of the heat capacity [14] the exponent of $T$ in the Debye function of the heat capacity is referred to as a fractal dimension and denoted $D$. With using the procedure demonstrated earlier [15], from the experimental data on $C^0_{\text{p}}$ by the plot $\ln C^0_{\text{p}}$ *vs*. $\ln T$ we determined the magnitudes of $D$ as the slope of the straight-line segments of the relation in the temperature intervals 18 to 30 K and 30 to 50 K and those were 1.7 and 1.4, respectively. Such procedure of the $D$ estimation is applicable for the temperature region where $C^0_{\text{p}}\approx C_{\text{v}}$. In fact, in the interval $T$<60 K it can be assumed without a noticeable uncertainty that the above equality exists. With lowering temperature from 30 to 0 K the value of $D$ increases from 1.4 to 3 at 17 K and further remains invariable. This shows the conformity to the $T^3$-Debye law [16] and holds true for bodies of any heterodynamic structure. At $T$>30 K $D$=1.4 and it is unchanged up to 50 K and, probably, for $C_{\text{v}}$ at higher temperatures as well. According to theories of the heat capacity of solid bodies [15, 17], $D$=3 corresponds to bodies of spatial (three-dimensional) structure, $D$=2 and $D$=1 to those of two-dimensional structure and chain one, respectively; fractal values of *D* indicate that the substances have combined structures. In particular, *D*=1.4 for the dendrimer studied implies that the latter, perhaps, has a planar-chain structure, i.e. it possesses a fractal dimension.

Figure 3 shows the temperature dependences of the heat capacity derived from the direct measurement data for the dendrimer (a solid curve) and calculated from the experimental $C_p^0$ values of the dendrimer constituents G-2(All)$_{16}$ and 16H-Si-Und-Me as additive values (a dotted line). It is seen that in the range of 0 to 200 K (the substances are in a crystalline state), the additive values of $C_p^0$ are larger than the experimental values and between 250 and 340 K (the substances are liquid) the additive $C_p^0$ values are smaller at $T$<300 K and larger at $T$>300 K. For the crystalline dendrimer, the differences in the heat capacities to be compared change from 22% at 25 K to 12% at 200 K traversing the minimum 4% at 100 K; with the liquid dendrimer, the differences decrease from 5% at 250 K to 2% at 340 K. At $T$ about 300 K the additive and measured values of $C_p^0$ coincide. The reason for the lower $C_p^0$ values of the dendrimer as compared with the additive ones for it between 0 and 200 K is likely to be the difference of molecular (lattice) contributions to the corresponding values of the heat capacity: For the dendrimer there are only six molecular vibrations but on calculating the additive values the number of the vibrations is 112 (6 for G-2(All)$_{16}$ and 96 in the case of H-Si-Und-Me). However, the difference of the molecular components should be very great. Nevertheless, this is not observed because of the fact that the difference is balanced out by the contributions to the heat capacity of atomic vibrations in the dendrimer which has much more such vibrations than the starting compounds such as G-2(All)$_{16}$ and H-Si-Und-Me. The distinction between the experimental and additive values of $C_p^0$ over the range 250 to 340 K is, on the whole, small and, therefore, no commentaries are needed.

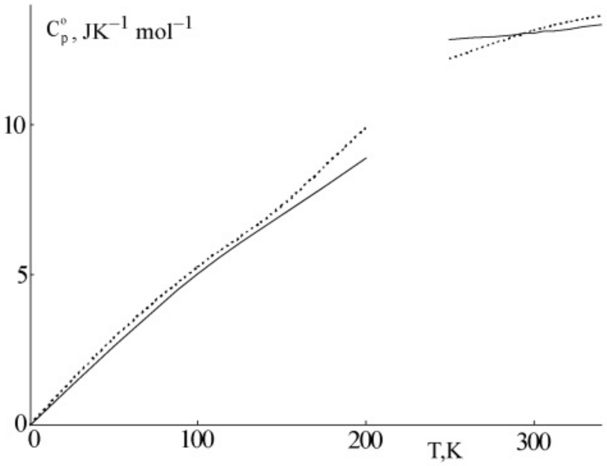


**Fig. 3** Heat capacity of the dendrimer; a solid line – from the data of direct measurements of the dendrimer; a dotted line – the additive values calculated as the sum of the heat capacities for G-2(All)$_{16}$ and H-Si-Und-Me

## *Thermodynamic parameters of physical transformations*

In Table 1 are given the thermodynamic characteristics of phase transitions in the dendrimer G-2(Und-Me)$_{16}$ obtained from our calorimetric data. The temperature intervals of the transitions were determined graphically by the procedure described above in the section 'Heat capacity'. The enthalpy of melting $\Delta H^{o}(\mathrm{crI}\to 1)$ was calculated as the area bounded with lines GUFNMLG. The area bounded by lines BRSG and BCDEG is the algebraic sum of the enthalpy of melting for crII $\Delta H^{o}(\mathrm{crII}\to 1')$ and the enthalpy of crystallization of l' $\Delta H^{o}(\mathrm{l}'\to\mathrm{crI})$, i.e. $\Delta H^{o}(\mathrm{crII}\to 1')+\Delta H^{o}(\mathrm{l}'\to\mathrm{crI})=78.74$ kJ mol$^{-1}$. According to the first thermodynamics law, $-\Delta H^{o}(\mathrm{l}\to\mathrm{crI})=\Delta H^{o}(\mathrm{crI}\to\mathrm{l})$. Without a great error it can be assumed that $\Delta H^{o}(\mathrm{l}\to\mathrm{crI})=\Delta H^{o}(\mathrm{l}'\to\mathrm{crI})$ and then

$$\Delta H^{o}(\mathrm{crII}\to 1')+\Delta H^{o}(\mathrm{l}\to\mathrm{crI})=\Delta H^{o} \tag{2}$$

Equation (2) allows the estimation of the value of $\Delta H^{o}(\mathrm{crII}\to\mathrm{l}')$. Substituting the $\Delta H^{o}(\mathrm{l}\to\mathrm{crI})$ and $\Delta H^{o}$ values into Eq. (2), the value of $\Delta H^{o}(\mathrm{crII}\to\mathrm{l}')$ was obtained (Table 1). Entropies of transitions were calculated from their enthalpies and temperatures. By comparing the entropies $\Delta S^{o}(\mathrm{crII}\to\mathrm{l}')$ and $\Delta S^{o}(\mathrm{crI}\to\mathrm{l})$ one finds that the first is about 2.4 time larger than the second. In this connection, it is suggested that crystals crII are common and crystals crI are of plastic character that is usually typical occurrence for globular molecules [18].

**Table 1** Thermodynamic characteristics of phase transitions in the dendrimer ($M$=7030 g mol$^{-1}$)

| Transitions* | Temperature interval of transition/K | $T_{\mathrm{tr}}$/K | $\Delta H^{0}$/ kJ mol$^{-1}$ | $\Delta S^{0}$/ J mol$^{-1}$ K$^{-1}$ |
|---|---|---|---|---|
| crII→1' | 190–210 | 200.6 | 148.6 | 741 |
| 1'→crI | 210–212 | 210.0 | –69.9 | –333 |
| crI→I | 212–229 | 223.0 | 69.9 | 313 |

*crII, crI – crystalline, 1:l'-overcooled liquid, 1-liquid

## *Thermodynamic functions*

From the temperature-dependent heat capacities, temperatures and enthalpies of physical transitions (Table 1), the thermodynamic functions were calculated in the range 0 to 340 K (Table 2). The enthalpy $H^{o}(T)-H^{o}(0)$ and entropy $S^{o}(T)$ were estimated by the numerical integration from the curves $C_{\mathrm{p}}^{0}=f(T)$ and $C_{\mathrm{p}}^{0}=f(\ln T)$, respectively, and the values of the corresponding phase transitions. Gibbs function $G^{o}(T)-H^{o}(0)$ was calculated from the enthalpy and entropy values of the dendrimer at the corresponding temperatures. A detailed description of the function calculation is given previously, for instance, in [19].

**Table 2** Thermodynamic functions of the dendrimer ($M$=7030 g mol$^{-1}$)

| $T$/K | $C_p^0$/ J mol$^{-1}$ K$^{-1}$ | $H^0(T)$–$H^0(0)$/ kJ mol$^{-1}$ | $S^0(T)$/ J mol$^{-1}$ K$^{-1}$ | –[$G^0(T)$–$H^0(0)$]/ kJ mol$^{-1}$ |
|---|---|---|---|---|
| | | crystals crII | | |
| 5 | 33.70 | 0.0480 | 13.43 | 0.0191 |
| 10 | 188.9 | 0.5593 | 77.87 | 0.2194 |
| 15 | 431.2 | 2.084 | 198.4 | 0.8921 |
| 20 | 708.9 | 4.925 | 359.9 | 2.270 |
| 25 | 1013 | 9.228 | 550.7 | 4.540 |
| 30 | 1332 | 15.07 | 763.0 | 7.816 |
| 35 | 1570 | 22.24 | 983.7 | 12.18 |
| 40 | 1885 | 30.88 | 1213 | 17.67 |
| 45 | 2195 | 41.08 | 1454 | 24.34 |
| 50 | 2488 | 52.80 | 1700 | 32.22 |
| 60 | 3033 | 80.43 | 2202 | 51.73 |
| 70 | 3558 | 113.4 | 2709 | 76.29 |
| 80 | 4073 | 151.6 | 3219 | 105.9 |
| 90 | 4571 | 194.8 | 3727 | 140.7 |
| 100 | 5039 | 242.9 | 4233 | 180.5 |
| 110 | 5470 | 295.4 | 4734 | 225.3 |
| 120 | 5863 | 352.1 | 5227 | 275.1 |
| 130 | 6225 | 412.6 | 5711 | 329.8 |
| 140 | 6570 | 476.6 | 6185 | 389.3 |
| 150 | 6916 | 544.0 | 6650 | 453.5 |
| 160 | 7284 | 614.9 | 7108 | 522.3 |
| 170 | 7693 | 689.8 | 7561 | 595.6 |
| 180 | 8091 | 768.9 | 8013 | 673.5 |
| 190 | 8495 | 851.9 | 8462 | 755.9 |
| 200 | 8880 | 939 | 8907 | 842.8 |
| | | overcooled liquid | | |
| 210 | 12660 | 1211 | 10254 | 941.8 |
| | | crystals crI | | |
| 210 | 10500 | 1142 | 9921 | 941.8 |
| 220 | 10860 | 1248 | 10418 | 1043 |
| | | liquid | | |
| 230 | 12751 | 1440 | 11272 | 1152 |
| 240 | 12774 | 1568 | 11816 | 1268 |
| 250 | 12828 | 1696 | 12339 | 1389 |

**Table 2** Continued

| $T$/K | $C_p^0$/ J mol$^{-1}$K$^{-1}$ | $H^0(T)–H^0(0)$/ kJ mol$^{-1}$ | $S^0(T)$/ J K$^{-1}$ mol$^{-1}$ | $–[G^0(T)–H^0(0)]$/ kJ mol$^{-1}$ |
|---|---|---|---|---|
| 260 | 12884 | 1824 | 12843 | 1515 |
| 270 | 12932 | 1953 | 13330 | 1646 |
| 280 | 12973 | 2083 | 13801 | 1781 |
| 290 | 13031 | 2213 | 14258 | 1922 |
| 298.15 | 13052 | 2319 | 14618 | 2039 |
| 300 | 13054 | 2343 | 14699 | 2066 |
| 310 | 13105 | 2474 | 15128 | 2215 |
| 320 | 13170 | 2605 | 15545 | 2368 |
| 330 | 13248 | 2737 | 15952 | 2526 |
| 340 | 13337 | 2870 | 16348 | 2687 |

### *Entropy of synthesis reaction (assembly) of dendrimer*

As shown above, G-2(Und-Me)$_{16}$ was prepared as follows. First, the carbosilane nucleus of the dendrimer G-2(All)$_{16}$ was formed by a divergent scheme [5]. Then long aliphatic tails H-Si-Und-Me were attached to it. The determination of the entropy change in the case of such assembly of the dendrimer was of interest. The process can be represented by the scheme:

$$\text{G-2(All)}_{16}\text{+16H-Si-Und-Me}\rightarrow\text{G-2(Und-Me)}_{16}$$

Its entropy $\Delta S^o$ was evaluated from the absolute entropies of the reagents. The entropy of G-2(Und-Me)$_{16}$ was determined in the present work (Table 2) and those of G-2(All)$_{16}$ and H-Si-Und-Me were calculated by us with using the data on the temperature dependences of the heat capacities, temperatures and enthalpies of physical transformations by the third thermodynamics law obtained also at the authors laboratory. The entropy values of the process under consideration are listed in Table 3. As it should be expected, in the whole temperature range $\Delta S^o$ has a negative magnitude as for any other reactions of component association.

**Table 3** Entropy of formation reaction of dendrimer G-2(Und-Me)$_{16}$

| $T$/K | Physical state of reagents* | | | $–\Delta_r S^0$/ |
|---|---|---|---|---|
| | G-2(All)$_{16}$ | H-Si-Und-Me | G-2(Und-Me)$_{16}$ | J mol$^{-1}$ K$^{-1}$ |
| 50 | gl | cr | crII | 573 |
| 100 | gl | cr | crII | 873 |
| 298.15 | l | l | l | 946 |
| 340 | l | l | l | 977 |

*gl-glassy, cr – crystalline, l – liquid

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