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THERMODYNAMICS OF POLYMETHYLHYDROSILOXANE BASED ON 1,3,5,7-TETRAMETHYL-1,3,5,7-TETRAHYDROCYCLOTETRASILOXANE

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In an adiabatic vacuum calorimeter the temperature dependence of the heat capacity C_p^0 of 1,3,5,7-tetramethyl-1,3,5,7-tetrahydrocyclotetrasiloxane and polymethylhydrosiloxane on its basis was measured between 6 and 350 K mainly with accuracy of about 0.2%. Two-phase transitions corresponding, probably, to the fusion of *cis*- and *trans*-conformations of the monomer as well as the glass transition of the polymer were detected. The results obtained were used to calculate the thermodynamic functions C_p^0, $H^0(T)–H^0(0)$, $S^0(T)$, $G^0(T)–H^0(0)$ of the monomer and polymer in the range from $T\to0$ to T=340 K, and to estimate the zero entropy $S^0(0)$ of amorphous polymer. Standard entropies of formation ΔS_f^0 of the tested monomer and polymer at T=298.15 K as well as the entropy of synthesis of polymethylhydrosiloxane from 1,3,5,7-tetramethyl-1,3,5,7-tetrahydrocyclotetrasiloxane over the range from $T\to0$ to 340 K were estimated. The value of fractal dimension D in the heat capacity function of the multifractal variant of the Debye's theory of heat capacity was found to be 1.5 for polymer in the 18–35 K range, that testifies to its layer-chain structure.

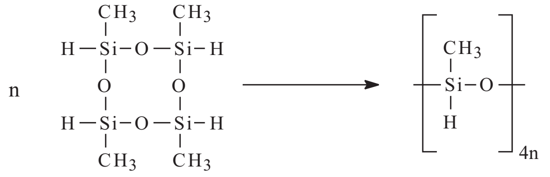
Keywords: *calorimetry, polymerization, polymethylhydrosiloxane, 1,3,5,7-tetramethyl-1,3,5,7-tetrahydrocyclotetrasiloxane, thermodynamic parameters*

Introduction

In reviews [1, 2] the dependences of thermodynamic characteristics and the parameters of the synthesis of organosilicon polymers possessing unique scientific and practical application properties [3] on their composition and structure, physical states and temperature were analyzed and attractive regularities were revealed.

The coauthors of the given article Zavin and Kotov recently succeeded in synthesizing polymethylhydrosiloxane (PMHS) based on 1,3,5,7-tetramethyl-1,3,5,7-tetrahydrocyclotetrasiloxane (TMTHCTS) and, therefore, it is of interest to study their properties for accumulating the appropriate data.

It is interesting to examine the thermodynamic properties of TMTHCTS and PMHS and the thermodynamic characteristics of the polymerization process:



with the purpose of optimizing technologies of the production and processing of this polymer.

For this reason we performed first the calorimetric study of the heat capacity of TMTHCTS and PMHS between 6 and 350 K and calculated the thermodynamic functions of the monomer and the polymer from the data obtained and the entropy of the process TMTHCTS→ PMHS in the above temperature interval.

Experimental

Samples

TMTHCTS was synthesized at A.N. Nesmeyanov Institute of Organoelement Compouds of RAS. The content of the main substance in the tested sample, according to analytical data, was more than 99 mol%. According to NMR-1H spectra [4], TMTHCTS exists as a statistical mixture of one *cis*- and three *trans*-conformations.

The initial monomer – 1,3,5,7-tetramethyl-1,3,5,7-tetrahydrocyclotetrasiloxane $[CH_3SiHO]_4$ – was prepared by hydrolysis of 30% solution of methylchlorosilane CH_3SiHCl_2 in sulfuric ether at temperature not above 283–288 K in the absence of an acceptor (in an acidic medium). After completing hydrolysis the ether solution of reaction products was washed with water to remove acidic impurities, separated from a water layer, dried over $CaCl_2$ during 24 h, further the ether was extracted and a residue was subject to fractional distillation. As a result, a fraction with boiling temperature 406–407.5 K/99.3 kPa ($n_D^{20}=1.3873$) was

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removed and it was found that its characteristics coincided with literature data [4].

Polymethylhydrosiloxane was synthesized by ionic polymerization of 1,3,5,7-tetramethylcyclotetrasiloxane $[CH_3SiHO]_4$ in the presence of a heterogeneous initiator, i.e. fluoropolymer sulfocationate of NAPHION type in H^+ form supplied by DUPONT firm. To prepare the initiator the starting fluoropolymer (copolymer of perfluoroethylene with 13% sodium salt of sulfonic acid perfluorovinyl ether) was activated with 20% HNO_3, thrice washed with distilled water and dried under vacuum (at 0.13 kPa, 353 K) for 3–4 days (till constant mass). The content of $-SO_3H$-groups in the initiator was determined by reverse titration of the polymer sample added in an excess of 0.1 N solution of alkali (NaOH). The sulfocationate in H^+ form was kept in a hermetically sealed container without access for air moisture.

Polymerization was conducted in the absence of solvents (in bulk) at 313–323 K. In a test tube previously calcined to remove moisture residue 4.00 g 1,3,5,7-tetramethylcyclotetrasiloxane was loaded and further argon was blown and 0.15 g NAPHION (1.87 mass% $-SO_3H$-groups) was added in argon flow. Then the test tube was placed in a thermostat preliminarily heated up to 313 K and was kept at the above temperature during 70 h. The monomer conversion and the composition of volatile products were controlled by GLC with using sampling. As previous experiments showed, the maximum yield of the polymer (95 mass%) was achieved in 60 h from the process beginning.

On completing the polymerization a transparent viscous product was separated from the heterogeneous initiator. The residue of cyclosiloxane was extracted from the polymer by evacuating at 313 K and pressure of 0.13 kPa during 10 h.

According to GPC data, the molecular mass of polymethylhydrosiloxane is equal to 162000, M_m/M_n=1.18.

The elemental analysis data for TMTHCTS and PMHS conformed to the formula composition within to analytical uncertainties. According to our calorimetric data, TMTHCTS was totally crystalline while PMHS was completely amorphous.

Methods

To study the heat capacity in the range 6 to 350 K a BKT-3 thermophysical device – a completely automatic adiabatic vacuum calorimeter – was employed. Its design and the measurement procedure of the heat capacity and temperatures of physical transformations were similar to those described earlier [5, 6]. The iron–rhodium thermometer used was calibrated by IST-90. The reliability of the calorimeter operation was checked by measuring the heat capacity of special-purity copper, standard synthetic corundum and benzoic acid of K-2 grade prepared at metrological institutions of the State Standard of the Russian Federation. From the calibration and test results of the calorimeter it was established that the measurement uncertainty of the heat capacity C_p^0 for the substances in a condensed state at helium temperatures was within ±2%; with rising temperature up to 40 K it decreased to ±0.5% and became equal to ±0.2% at T>40 K. The uncertainty of the determination of physical transformation temperatures was found to be ±0.02 K and enthalpies of physical transitions ±0.5%.

Results and discussion

Heat capacity

The heat capacity of TMTHCTS was measured from 6 to 350 K and of PMHS over the range 6 to 340 K. The masses of the monomer and the polymer placed in a calorimetric ampoule of the adiabatic vacuum calorimeter were 0.7405 and 0.4484 g, respectively. The pressure of a heat exchange gas (helium of special purity) in the ampoule with the polymer was 8 kPa at room temperature. In 6 series of the heat capacity measurements 244 experimental points of C_p^0 were obtained for the monomer and 161 values of C_p^0 in 5 series of measurements for the polymer. In the whole examined temperature range the heat capacity for the monomer was on the average 52% of the summary heat capacity of the calorimetric ampoule with the substance and as to the polymer, it made up 31%. A computer-assisted averaging of the experimental C_p^0 values was made by means of semi-logarithmic polynomials in the general form as a $\ln C_p^0 = \ln(a+bT+cT^2+dT^3+eT^4+fT^5+gT^6)$. The root-mean-square deviation of C_p^0 values from the corresponding smoothed $C_p^0 = f(T)$ curves did not exceed 0.35% between 6 and 80 K, 0.15% from 80 to 200 K and 0.1% in the interval 200 to 350 K. The molar mass of the object studied was calculated from the IUPAC table of atomic masses [7].

The experimental C_p^0 values for the monomer and the polymer and the smoothed $C_p^0 = f(T)$ plots are illustrated in Figs 1 and 2, respectively. As seen in Fig. 1, the heat capacity of the monomer increases gradually as temperature rises from 6 to 162 K. Besides, a sharp increase in the values C_p^0 is seen above 165 K and two first-order endothermic transitions with maximum C_p^0 at 196.6 K (BDF section, Fig. 1) and 211.2 K (FGL section, Fig. 1), respectively, occur. As TMTHCTS is a statistical mixture of one *cis*- and three *trans*-conformations [4], the avail-

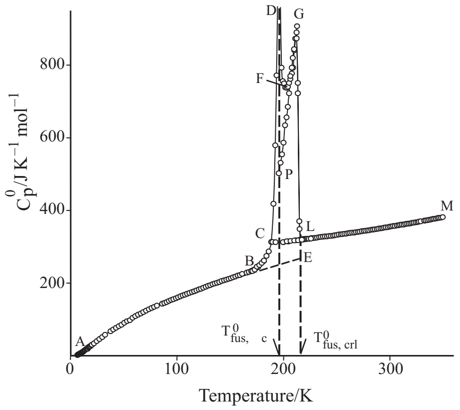

Fig. 1 Heat capacity of 1,3,5,7-tetramethyl-1,3,5,7-tetrahydrocyclotetrasiloxane: ABE – crystalline, LM – liquid, CL – overcooled liquid, BDFGL – the apparent heat capacity in the interval of phase transitions, $T^0_{\text{fus, crII}}$ – the melting temperature of crII crystals (*cis*-conformation), $T^0_{\text{fus, crI}}$ – the melting temperature of crI crystals (*trans*-conformation)

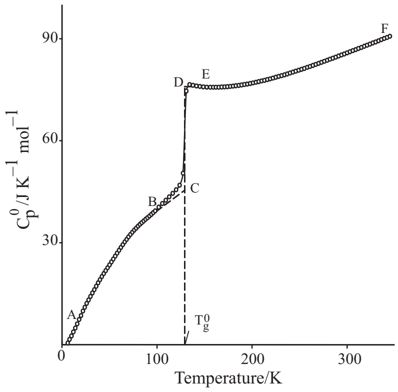

Fig. 2 Heat capacity of polymethylhydrosiloxane: ABC – glassy, EF – high elasticity, BE – the heat capacity in the interval of devitrification, CD – the increase of heat capacity on devitrification at glass transition temperature T^0_g

ability of the first endothermic peak can be explained by the fusion of *cis*-conformation (crII) and of the second peak by the fusion of three *trans*-conformations (crI). The last crystals disappear at 216.6 K and this temperature is regarded by us as the melting temperature T^0_{fus} of TMTHCTS because of the overlapping of the above mentioned transitions. At a temperature more than 216.6 K the heat capacity of the liquid monomer smoothly grows with rising temperature. On stepwise slow cooling the liquid monomer one succeeded in measuring its C_p^0 in an overcooled liquid-state in the range from T^0_{fus} to a temperature lower by 30 K than T^0_{fus} (section CL, Fig. 1). Afterwards a spontaneous crystallization took place. Besides, after annealing crystals crI at 205 K during 20 h the measurement of C_p^0 of the crystals crI on stepwise gradual cooling till 195 K turned out well (PF section, Fig. 1) while on subsequent cooling a spontaneous energy release resulted from the transition of crystals crI to crystals crII was observed.

The polymer devitrification was seen in the range 100–150 K on the $C_p^0 = f(T)$ plot (section BE, Fig. 2). In other respects, the temperature dependence of the heat capacity of the polymer did not exhibit any peculiarities.

For PMHS the estimation of the fractal dimension D [8], the most important value in the fractal variant of the Debye theory of the heat capacity for solid bodies [8, 9], seems to be of interest. The D value allows the judgement about the character of the solid body heterodynamics. The value of D can be obtained from the plot lnC_v *vs.* ln$T$ that follows from the expression [9]:

$$C_v=3D(D+1)kN\gamma(D+1)\xi(D+1)(T/\theta_{\max})^D \quad (1)$$

where k is the Boltzmann constant, N is the number of a repeating monomer unit of a polymer, $\gamma(D+1)$ is the γ-function, $\xi(D+1)$ is the ξ-function of Riemann and $\theta_{\max}$ is the maximum characteristic temperature. For a concrete solid body $3D(D+1)kN\gamma(D+1)\xi(D+1)=A$ is the constant and Eq. (1) can be written as:

$$\lg C_v = \ln A + D\ln(T/\theta_{\max}) \quad (2)$$

It can be assumed without a noticeable uncertainty that at T<50 K for PMHS, like other monomeric and polymeric compounds [10], $C_p^0 = C_v$ and then, using the experimental data on the heat capacity, we can calculate first D as a slope of the straight line described with Eq. (2) and further $\theta_{\max}$ from Eq. (1) by means of a special computer program.

For PMHS in the range 18 to 35 K D=1.5 and the maximum characteristic temperature $\theta_{\max}$ was determined to be 161 K. As demonstrated in [11], the D value indicates the heterodynamics of solids: D=1 corresponds to bodies of a chain structure, D=2 – of a layer one and D=3 to bodies of a spatial structure. Fractional values of D point to mixed heterodynamic structures. In the temperature interval under consideration for the polymethylhydrosiloxane D=1.5 that testifies to its layer-chain structure. The increase in the D value with lowering temperature is quite natural due to the enhancement of the intermolecular interaction as temperature drops. At the lowest temperatures for solid bodies of any structure D=3 that corresponds to the Debye T^3-law.

Thermodynamic parameters of monomer fusion

As was mentioned above, TMTHCTS has two first-order phase transitions with the maximum C_p^0 values at 196.6 and 211.2 K in the range 162 to 216.6 K. Because of the overlapping of these transitions we did not attempt to separately determine the values of enthalpies of the transitions. For TMTHCTS the summary enthalpy of fusion $\Delta H^0_{\mathrm{fus}}$ =12.2±0.2 kJ mol^{-1} was measured calorimetrically in three experiments (the $\Delta H^0_{\mathrm{fus}}$ values are 11.96, 12.17 and 12.35 kJ mol^{-1}) by continuous energy input with using the procedure demonstrated elsewhere [12]. The entropy of fusion $\Delta S^0_{\mathrm{fus}}$ =56.1±0.9 J K^{-1} mol^{-1} was calculated from the values of the enthalpy of fusion and the melting temperature (T^0_{fus} =216.6 K):

$$\Delta S^0_{\mathrm{fus}} = \Delta H^0_{\mathrm{fus}} / T^0_{\mathrm{fus}} \qquad (3)$$

Parameters of glass transition and glassy state of polymer

In Table 1 are given the parameters of glass transition and glassy state of PMHS. Temperatures of the onset and the termination of the glass transition were determined from the $C^0_{\mathrm{p}} = f(T)$ plot (Fig. 2). The glass transition temperature T^0_{g} was obtained from the relation $S^0(T)$ *vs*. T by the method described earlier [13]. The configurational entropy S^0_{conf} of the glass was estimated with using the equation [14]:

$$S^0_{\mathrm{conf}} = \Delta C^0_{\mathrm{p}}(T^0_{\mathrm{g}}) \ln(T^0_{\mathrm{g}} / T^0_2) \qquad (4)$$

where $\Delta C^0_{\mathrm{p}}(T^0_{\mathrm{g}})$ is the increase of the heat capacity on devitrification determined graphically (section CD, Fig. 2), T^0_2 is Kautsmann temperature [15], the value of T^0_{g} / T^0_2 for monomeric and polymeric glasses is equal to 1.29±0.13 [14]. In [14, 16] it was noted that the numerical value of S^0_{conf} is close to that of the zero entropy $S^0_{\mathrm{gl}}(0)$ and it can be taken to estimate absolute values of the entropy $S^0_{\mathrm{gl}}(T)$ of glassy substances on assumption that $S^0_{\mathrm{gl}}(0) = S^0_{\mathrm{conf}}$.

Thermodynamic functions

To calculate the thermodynamic functions (Tables 2 and 3) the temperature dependences of the heat capacity for the monomer and the polymer were extrapolated from the temperature of the measurement onset down to 0 K by the Debye function for the heat capacity:

$$C^0_{\mathrm{p}} = nD(\theta_{\mathrm{D}} / T) \qquad (5)$$

Table 1 Parameters of glass transition and glassy state of polymethylhydrosiloxane

Devitrification interval/K	T^0_{g} /K	$\Delta C^0_{\mathrm{p}}(T^0_{\mathrm{g}})$ /J K^{-1} mol^{-1}	S^0_{conf} /J K^{-1} mol^{-1}	$S^0_{\mathrm{gl}}(0)$ /J K^{-1} mol^{-1}
100–150	129	29.4	7.5	7.5

Table 2 Thermodynamic functions of 1,3,5,7-tetramethyl-1,3,5,7-tetrahydrocyclotetrasiloxane (*M*=240.511 g mol^{-1}; *p*=101.325 kPa)

Temperature/K	C^0_{p} /J K^{-1} mol^{-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}
		crystalline state		
0	0	0	0	0
5	1.14	0.0014	0.381	0.000505
10	8.02	0.0217	2.92	0.00752
15	18.86	0.0880	8.143	0.03415
20	30.22	0.2115	15.18	0.09203
25	41.47	0.3893	23.06	0.1872
30	52.30	0.6232	31.56	0.3236
40	72.18	1.253	49.55	0.7287
50	89.72	2.061	67.51	1.314
60	107.6	3.047	85.43	2.079
70	123.0	4.203	103.2	3.022
80	136.3	5.500	120.5	4.142
90	148.2	6.923	137.3	5.431
100	159.7	8.463	153.5	6.886
150	213.5	17.83	228.7	16.47
200	262.6	29.74	296.9	29.64
216.6	278.9	34.23	318.4	34.74
		liquid state		
216.6	319.0	46.39	374.6	34.74
250	332.6	57.28	421.3	48.05
298.15	354.4	73.80	481.7	69.82
300	355.4	74.45	483.9	70.71
340	376.1	89.07	529.6	90.99
350	384.6	92.87	540.6	96.34

Table 3 Thermodynamic functions of polymethylhydrosiloxane (M=60.128 g mol^{-1}; p=101.325 kPa)

Temperature/K	C_p^0 /J K^{-1} mol^{-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}
glassy state				
0	0	0	7.5	0
5	0.385	0.00053	7.6	0.0376
10	2.60	0.0072	8.47	0.0775
15	5.524	0.0275	10.08	0.1236
20	8.570	0.0630	12.09	0.1789
25	11.59	0.1139	14.35	0.2450
30	14.21	0.1784	16.70	0.3226
40	19.13	0.3455	21.47	0.5134
50	23.51	0.5590	26.22	0.7519
60	27.78	0.8155	30.88	1.037
70	31.73	1.114	35.47	1.369
80	34.87	1.447	39.92	1.746
90	37.38	1.809	44.18	2.167
100	39.88	2.195	48.24	2.629
129	47.90	3.470	59.40	4.192
high elasticity state				
129	77.30	3.470	59.40	4.192
150	75.81	5.074	70.92	5.564
200	76.95	8.877	92.79	9.681
250	80.8	12.81	110.3	14.77
298.15	85.64	16.82	125.0	20.44
300	85.84	16.98	125.5	20.68
340	90.17	20.50	136.5	25.92

where D denotes the Debye function of the heat capacity, n and θ_D are special parameters. With n=3 and θ_D=75.2 Equation (5) describes the experimental values of the heat capacity for TMTHCTS in the range 6 to 11 K with an uncertainty ca. 1.4% and with n=3 and θ_D=80.6 in the case of PMHS within to about 1.3%. It was assumed that at T<6 K Eq. (5) reproduces the C_p^0 values with the same error.

The enthalpy $H^0(T)$–$H^0(0)$ and entropy $S^0(T)$ were calculated by integrating the corresponding relationships $C_p^0 = f(T)$ and $C_p^0 = f(\ln T)$ and Gibbs function $G^0(T)$–$H^0(0)$ was estimated by the formula:

$$G^0(T)-H^0(0)=[H^0(T)-H^0(0)]-TS^0(T) \qquad (6)$$

The calculation of the functions was described in detail earlier [16].

Standard entropy of formation

The standard entropies of formation of the liquid monomer ΔS_f^0(TMTHCTS, l)= –1070.8 ±3.0 J K^{-1} mol^{-1} and highly elastic polymer ΔS_f^0(PMHS, h.e)=–263.1±0.7 J K^{-1} mol^{-1} at 298.15 K and p=101.325 kPa were evaluated from the values of their absolute entropy (Tables 2 and 3) as well as from literature data [17] on the absolute entropies of gaseous hydrogen and oxygen, crystalline carbon in the form of graphite and silicon. The above values are related to the processes:

$$4C(cr, gr)+8H_2(g)+2O_2(g)+4Si(cr)\rightarrow C_4H_{16}Si_4O_4(l)$$

$$C(cr, gr)+2H_2(g)+0.5O_2(g)+Si(cr)\rightarrow –CH_4SiO–(h.e.)$$

In brackets the physical states of reagents are given: cr – crystalline, h.e. – high elasticity, g – gaseous, l – liquid, gr – graphite.

Entropy of polymerization

The values of the entropy of polymerization ΔS_{pol}^0 of TMTHCTS

$$0.25C_4H_{16}Si_4O_4\rightarrow –CH_4SiO– \qquad (7)$$

over the range 0 to 340 K (Table 4) were determined from the absolute entropies of reagents listed in Tables 2 and 3. In the whole temperature range under study the entropies of polymerization of TMTHCTS are small positive magnitudes that encourages reaction (7).

Table 4 Entropy of polymerization of 1,3,5,7-tetramethyl-1,3,5,7-tetrahydrocyclotetrasiloxane in bulk (p=101.325 kPa)

Temperature/K	Physical states of monomer and polymer[a]	ΔS_{pol}^0 / J K^{-1} (mol polymer)$^{-1}$
0	cr; gl	7.5
100	cr; gl	9.9
200	cr; h.e	18.6
298.15	l; h.e	4.6
340	l; h.e	4.1

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