

## **THE THERMAL PROPERTIES OF POLYSILOXANES POLY(DIMETHYL SILOXANE) AND POLY(DIETHYL SILOXANE)**

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New measurements and literature data on polysiloxanes covering heat capacities, transition parameters, enthalpies, entropies and Gibbs energies are presented and critically reviewed. The *ATHAS* computation method is used to bring heat capacities into agreement with an approximate frequency spectrum. The various crystal and mesophases are discussed. The *ATHAS* (1990) recommended data are as follows: For poly(dimethyl siloxane) the glass transition is at 146 K with an increase in heat capacity of 29.24 J/(K mol). The completely crystalline sample melts at about 219 K with a heat of fusion of 2.75 kJ/mol. For poly(diethyl siloxane) the glass transition is at 135 K with an increase in heat capacity of 34.48 J/(K mol). The completely crystalline sample changes to a condis crystal at 206.7 K with a heat of disordering of 2.72 kJ/mol. The transition to a poorly characterized "viscous crystal" with thermodynamic properties close to the melt occurs at 282.7 K with an enthalpy of transition of 1.84 kJ/mol. Final fusion occurs at 308.5 K and a small endotherm of about 231 J/mol. Tables of heat capacities, enthalpies, entropies and Gibbs energies are given from 0 K to 550 K.

Of the polysiloxanes only poly(dimethyl siloxane), PDMS, and poly(diethyl siloxane), PDES, have found major attention. In the 1980 *ATHAS* data bank of heat capacities of macromolecules [1] only few data on semicrystalline PDMS and PDES could be presented [2]. The follow-up analyses and fitting of the data in the solid state to approximate vibrational frequency spectra done with many other polymers [3] could not be carried out before because of lack of data and understanding of the phase behaviour. This paper, largely based on the experimental work of one of us (J.P.W.) [4] and the continuing *ATHAS* collection of thermal data, brings PDMS and PDES into the group of close to 100 well characterized polymers [5].

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Poly(diethyl siloxane) is known to exhibit multiple first-order transitions in the temperature range of 200–310 K. There have been several reports in the literature in which the nature of these transitions is described based on thermal techniques. Karasz in 1975 [6] and Lebedev in 1984 [7] used adiabatic calorimetry to estimate the thermodynamics of the transition from one crystal form to another and suggested that dimorphism exists in the crystalline portion of PDES. Although Turdakin [8] reported the specific heat capacity of PDES in the temperature range 55–300 K, no explanation was provided for the endotherm in the 170–210 K region. Differential scanning calorimetry of PDES with varying thermal history showed a series of transitions that suggested that a stable *condis* mesophase (a conformationally disordered and mobile state [9]) exists in the temperature range from about 200–280 K [10]. Recently Kögler et al. [11] supported the existence of the *condis* phase by solid state NMR data. In addition, molecular mechanics calculations suggested details about the nature of the low-energy rotational isomers [12]. Beyond the *condis* state a “viscous crystalline” or “liquid crystalline” state with only slightly different entropy and enthalpy than the liquid was reported, up to about 310 K [13]. Its nature is still not fully understood, but may be caused by a temperature-dependent fraction of rigid chain segments caused by intramolecular steric hindrance [12]. Additional DSC results were reported by Lee [14] and Papkov [15, 16]. While Lee had provided no interpretation of the results, Papkov proposed that two crystal polymorphs exist at low temperature ( $\alpha_1, \beta_1$ ). At high temperature these become  $\alpha_2$  and  $\beta_2$  polymorphs (*condis* crystals in our nomenclature). While the crystal polymorphs could also be verified by solid state NMR, there was only one *condis* spectrum [11].

Poly(dimethyl siloxane) is used as a related model-polymer that shows none of the mesophase complication of PDES. Based on a combination of computed and experimental heat capacities of PDMS for crystals and liquid, and of PDES for crystals, mesophase and liquid it is possible to recommend tables of heat capacity, enthalpy and free enthalpy (Gibbs function). The transition temperatures and thermodynamic parameters of the transitions are summarized and critically reviewed.

## Experimental

*Samples:* The sample of PDES was originally provided by Boyer (Midland Macromolecular Institute and Dow Chemical Company) and is the same sample that was characterized by Beatty and Karasz [6]. The molecular mass of this sample was reported to be  $\bar{M}_n = 112,000$ . The sample of PDMS used for reference

purposes was a commercial product, General Electric SF-96 (350) dimethyl silicone fluid without further known characterization.

*Equipment:* DSC measurements were made with a modified Mettler TA-2000 B instrument fitted with a TA-11 cell, TA-34 and TA-341 coolant controller and a ME-70329 liquid nitrogen evaporator. The TA-34 and TA-341 were modified to improve the low temperature stability of the instrument. The nitrogen coolant gas flow-valve was machined and hand fitted and the time constant for the liquid nitrogen evaporator was modified to provide a more gradual "turn-on" and reduce over-pressuring the Dewar vessel and surging. With these modifications a stable isotherm was obtained at 105 K. Both temperature and heat-flow scales were calibrated using the standard procedures and materials (naphthalene, benzoic acid, indium, *p*-terphenyl, tin and *n*-hexane for temperature and sapphire for heat capacity).

*Calibration and measurements:* For measurements of the heat capacity, the baselines of the empty pan and sapphire-reference were measured and compared to the heat-flow measurements of the PDES and PDMS samples. The repeatability of the sapphire ( $\text{Al}_2\text{O}_3$ ) heat capacity measurements was within  $\pm 0.1\%$ . The overall error was estimated to be about  $\pm 3\%$  [17]. Enthalpy calibrations were also carried out using benzoic acid, *p*-nitrotoluene, water, chloroform and *n*-hexane as secondary standards and were curve fitted to an inverse quadratic function. The standard heating rate was 10 K/min.

The temperature range for measurements of heat capacity was 110 to 343 K for PDES and 110 to 373 K for PDMS. Isothermal baselines were determined at the two extremes.

*Sample treatment:* Samples of different thermal histories were prepared. Isotropic liquids at 343 K and 373 K, respectively, were cooled at rates ranging between 1 to 30 K/min to get sample of varying crystallinities. For PDES, the crystallinity ranged between 34.1% and 58.5% and for PDMS the samples cooled at 1-2 K/min were highly crystalline (with 89-99% crystallinity) while sample cooled at 10 K/min had a low crystallinity of 6.2%. PDMS samples of intermediate crystallinity could not be prepared.

Amorphous PDES samples were prepared by quenching the melt from above 340 K with liquid nitrogen. The quenched sample was then quickly placed into the DSC cell, prior equilibrated at 105-108 K. It could not be avoided that small amounts of water condensed as frost on the sample in this procedure. The small amount of external water caused difficulties in the 270-280 K temperature region, with the heat of fusion of water superimposing on the PDES trace. Attempts were made to quench the mesophase of PDES (200-280 K). For this purpose, the mesophase was obtained by slowly cooling PDES from its isotropic liquid state to the rigid crystal and then reheating the sample through  $T_d$  to 240-243 K, where the

mesophase could be equilibrated. The mesophase was then quenched with liquid nitrogen. Isothermal annealing experiments were carried out in the temperature range from 258 K to 271 K for 1 hour each.

*Transitions:* The glass transition temperature,  $T_g$ , is chosen at half-devitrification when judged by the heat capacity increase. For the melting peaks, three characteristic temperatures that are usually considered are the onset, the peak (maximum), and the melting-end temperatures. In this paper, all melting peaks are characterized by their extrapolated onset temperature. The area of the melting peak above the heat capacity base-line was used to determine heat of fusion. The fraction crystallinity was determined from the equation:

$$w^c = \Delta H_{\text{trans}} / \Delta H_{\text{trans}}^0 \quad (1)$$

The limiting values for amorphous and 100% crystalline samples were obtained from experimental plots of  $\Delta C_p$  and  $\Delta H_{\text{trans}}$  for different crystallinities reported earlier [10].

## Results and discussion

### *Thermal analysis experiments*

(a) Poly(dimethyl siloxane) PDMS: The DSC curves on heating of PDMS crystallized at different cooling rates and the sample quenched from the isotropic melt are shown in Fig. 1. Amorphous PDMS (trace A) shows a glass transition at 146 K followed by a broad exotherm characterized by the onset temperature  $T_c$  of about 185 K. The onset of the melting transition peak,  $T_m$ , appears at 219 K. Samples cooled at 10 K/min (trace B) were found to be only about 6% crystalline (estimated from the heat of fusion) and showed a DSC trace similar to that for amorphous samples. The PDMS samples crystallized on slow cooling at 2 K/min (trace C) were highly crystalline (89–99%) and showed a sharp melting endotherm with a peak at  $T_m = 219$  K. A small glass transition was also detected and was attributed to the presence of a small amount of amorphous phase in these samples. Since either only highly crystalline or only amorphous samples were obtained, the analyzed poly(dimethyl siloxane) seems to need a well defined nucleation step so that samples of intermediate crystallinity could not be prepared. The glass transition and melting transition temperatures observed were close to those available in the *ATHAS* literature review of recommended experimental data [2]. Hence the recommended transition temperatures have not been altered by the new experiments.

(b) Poly(diethyl siloxane) PDES: The results of the DSC experiments with poly(diethyl siloxane) prepared with different sample histories have already been

described in an earlier publication [10]. PDES samples cooled from the isotropic liquid (crystallinities ranged between 34.1% to 58.5%) show a glass transition between 134–136 K, a disordering transition from the rigid-crystal to condiscrystal at  $T_d$  between 194–199 K, followed by the major melting transition ( $T_i = 258$ –269 K). As described above,  $T_m$  does not lead to the isotropic state, but to the little explored “viscous crystalline” state which at 300–310 K changes with a small and broad endotherm to the isotropic state (equilibrium melt).

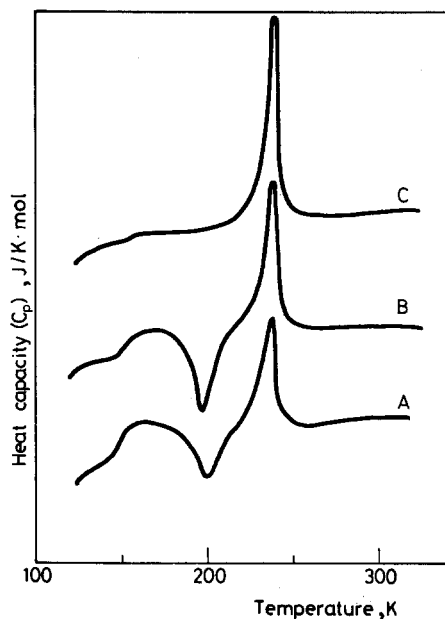


Fig. 1 DSC curves of poly(dimethyl siloxane) quenched to the amorphous state (A), cooled at 10 K/min (B) and slowly crystallized at 2 K/min (C)

At the slowest cooling rates the transition temperatures correspond to the upper ends of their reported ranges and sharper transitions are observed. Amorphous samples, obtained by quenching the liquid, show a cold crystallization exotherm for a supercooled liquid-to-mesophase transition at about 160 K. Annealing of PDES samples just below  $T_m$ , at temperatures ranging from 258–272 K for 1 hour, showed an increase in  $T_i$  from 255 K for an unannealed sample to 276 K for the sample annealed at 264.8 K [10]. Further increase in annealing temperature resulted in increasing fusion, which on cooling leads to recrystallization, and double melting peaks on renewed thermal analysis. The transition temperature  $T_d$  was found to increase from 197 to 206 K as the annealing temperature was increased to 264.8 K. This increase in  $T_d$  parallel with an increase in  $T_i$  is in direct conflict with the report

of a lower  $T_d$  transition correlating with the higher  $T_i$  [15]. A higher  $T_i$  can be produced solely by annealing the condis state.

In order to arrive at a recommended set of data for the transition parameters, the results of Kögler et al. [11] and Papkov et al. [15, 16] were critically reviewed and compared with the results obtained from our laboratory [10]. The data are listed in Table 1. The two transition peaks in the 200 K and the 270 K temperature region are listed separately whenever assigned to different polymorphs. The annealing behaviour just discussed and the solid state NMR results [11] suggest, however, that it is possible that at least the two condis phases differ only in perfection. In addition to these more recent data, the adiabatic calorimetry data of Beatty and Karasz [6] and Lebedev et al. [7] carried out on semicrystalline samples are also listed in Table 1. They showed the existence of only single first-order transitions. Also the X-ray diffractograms show only minor differences between the proposed different crystals. To arrive at a single set of recommended transition temperatures, an average of all reported transitions was taken and is listed in Table 1. Also listed are the reported transition enthalpies and estimates of the transition entropies gained by dividing the transition enthalpies by the observed (non-equilibrium) transition

**Table 1** Reported thermodynamic transitions of poly(diethyl siloxane)

	Beatty and Karasz [6]	Papkov et al. [15, 16]		Kögler et al. [11]		Wunder- lich et al. [10]	Lebedev et al. [7]	Recom- mended average
		$\alpha$ -form	$\beta$ -form	$\alpha$ -form	$\beta$ -form			
$\Delta H_x$ (kJ/mol)	—	—	0.276	—	0.186	—	—	0.2314
$\Delta S_x$ (J/mol)	small	0.9	0.9	0.6	0.6	small	—	0.75 <sup>c</sup>
$T_x$ (K)	293	319	319	310	310	~300	—	308.5 <sup>c</sup>
$\Delta H_i$ (kJ/mol)	1.02	1.73	2.14	1.79	1.85	1.72	2.62 <sup>a</sup>	1.840
$\Delta S_i$ (J/mol)	3.78	6.20	7.39	6.41	6.40	6.23	8.88 <sup>a</sup>	6.47 <sup>c</sup>
$T_i$ (K)	270	280	290	279	289	276	295	282.7 <sup>c</sup>
$\Delta H_d$ (kJ/mol)	3.37	2.86	2.65	2.97	2.88	1.69	2.63 <sup>a</sup>	2.72 <sup>c</sup>
$\Delta S_d$ (J/mol)	16.84	13.35	12.88	14.0	14.0	8.2	12.95 <sup>a</sup>	13.17 <sup>c</sup>
$T_d$ (K)	200	214	206	212	206	206	203	206.7 <sup>c</sup>
$\Delta C_p$ (J/K mol)	17.35	37.0	—	—	—	30.95	34.513 <sup>b</sup>	34.475 <sup>d</sup>
$T_g$ (K)	130	136	—	—	—	135	135	135

<sup>a</sup> Values recalculated using 78.6% as the corrected crystallinity.

<sup>b</sup> Obtained using calculated  $C_p$  data for solid (data agrees with author's data with an average and RMS deviation of  $-0.40 \pm 0.58\%$  from 40–120 K) and author's melt data.

<sup>c</sup> Values obtained by averaging the data reported by the various authors.

<sup>d</sup> Recommended value obtained from calculated solid data and the recommended experimental liquid data (ATHAS data bank, 1990).

temperature. The solutions to the questions of the transition temperatures for the two polymorphs  $\alpha_1$  and  $\beta_1$  and the existence of the condis polymorphs  $\alpha_2$  and  $\beta_2$  are left for future work.

#### *Equilibrium thermodynamic transitions*

(a) Poly(dimethyl siloxane) PDMS: The limited experimental data on  $\Delta C_p$  and  $\Delta H_m$  were best described by a linear function:

$$\Delta C_p = 25.90 - 9.421 \times 10^{-3} \Delta H_m \text{ [in J/(K mol)]} \quad (2)$$

and the limiting values of Eq. (2):  $\Delta C_p^0 = 25.90$  J/(K mol) and  $\Delta H_m^0 = 2.75$  kJ/mol, were used for completely amorphous and crystalline PDMS. As approximation of the transition temperatures 146 K was chosen as the glass transition and 219 K for the equilibrium melting temperature. The final *ATHAS* recommended  $\Delta C_p$  at 146 K for 29.24 J/(K mol) was obtained from the heat capacity difference calculated for solid PDMS using the calculation scheme, and the experimental data for the liquid.

(b) Poly(diethyl siloxane) PDES: To determine the limiting values of  $\Delta C_p$  and heat of transition for PDES, the experimental value for the various semicrystalline samples of PDES analyzed in our laboratory were fit into the linear function:

$$\Delta C_p = 30.65 - 18.12 \times 10^{-3} \Delta H_d \text{ [} (\pm 13.3\%) \text{ in J/(K mol)]} \quad (3)$$

$$\Delta C_p = 31.25 - 18.14 \times 10^{-3} \Delta H_i \text{ [} (\pm 12.6\%) \text{ in J/(K mol)]} \quad (4)$$

Both show only random deviations from linearity, thereby indicating the absence of a "rigid-amorphous fraction" in PDES [10]. The values of  $\Delta C_p^0$  obtained for completely amorphous sample from both equations were found to be in close agreement. This suggests that crystal order is set at the  $T_c/T_i$  transition and the ordering of the mesophase to the solid crystal is nearly complete. In addition, annealing near the 200 K ( $T_d$ ) transition had no effect on either  $T_d$  or  $T_i$ , supporting the above statement [10]. The average value of  $\Delta C_p = 30.95$  J/(K mol) at 135 K ( $T_g$ ) was taken as the experimental value and is compared with the results of other authors in Table 1. The reported  $T_g$  and  $\Delta C_p$  of PDES by Beatty and Karasz [6] were much lower and are apparently for a semicrystalline sample of unknown crystallinity. The final *ATHAS* recommended  $\Delta C_p$  at 135 K of 34.48 J/(K mol) was obtained from the heat capacity difference calculated for solid PDES using the calculation scheme, and the experimental data for the liquid (to be described below).

The low value of 1.69 kJ/mol of Eq. (3) for  $\Delta H_d^0$  of the transition from the rigid-crystal to the condis-crystal was compensated in the average of Table 1 by the value reported by Beatty and Karasz [6] which is most likely to high. The recommended

average is thus perhaps the best choice. Assuming the experimental peak temperatures not to be too far from the equilibrium transition temperatures, the entropy of transition is 13.17 J/(K mol). This is a value typical for a fully ordered to "conformationally disordered" crystal transition [9] and agrees well with a discussion of the possible motion in the condis state [12].

The average value of the  $\Delta H_i^0$ , the enthalpy of transition of the condis phase to the "viscous crystalline" state is less than  $\Delta H_d^0$  and the estimated entropy of transition  $\Delta S_i$  is, because of the higher transition temperature, about half of  $\Delta S_d$  (Table 1). The heat of transition to the ultimate, isotropic melt is only about 0.231 kJ/mol and the entropy change, about 0.75 J/(K mol).

#### *Heat capacities of PDMS and PDES*

a) Recommended experimental data: The newly measured heat capacity of Poly(dimethyl siloxane) for the molten state [4] agreed closely with the 1980 *ATHAS* data bank [2]:

$$C_p(\text{solid}) = \exp [0.0189189 (\ln T)^3 - 0.402175 (\ln T)^2 + 3.35144 (\ln T) - 4.78444] \text{ J/(K mol)} \quad (5)$$

$$C_p(\text{liquid}) = 0.1215 T + 81.55 \text{ J/(K mol)} \quad (6)$$

Equations (5) and (6) represent the PDMS heat capacity from 5 to 146 K ( $T_g$ ) and from 146 to 340 K, respectively.

The liquid-phase heat capacities for poly(diethyl siloxane) in the temperature range of 290 to 360 K were obtained by averaging the results of six new experiments. The averaged data points were fitted to the equation:

$$C_p = 0.2365 T + 93.75 [(\pm 2.3\%) \text{ in J/(K mol)}] \quad (7)$$

At lower temperatures the 1980 *ATHAS* data bank contained heat capacity data reported by Beatty and Karasz [6] and Turdakin et al. [8]. These differed by 2–9%, so that no recommendation had been made at that time. Since the Lebedev et al. [7] have reported on additional adiabatic calorimetry for a semicrystalline sample (recalculated to be 78.6% crystalline) from 10 to 330 K.

All these heat capacities of PDMS and PDES were again critically reviewed and combined to the recommended experimental heat capacity data (1990). The details of this will appear in a separate publication that represents the overall update of the 1980 *ATHAS* data bank and its expansion to almost 150 polymers [18]. The recommended experimental heat capacity data (*ATHAS* data bank 1990) of PDES from 10 to 360 K is listed in Table 2. As will be shown later, the use of the extrapolated melt data to represent the heat capacity of the mesophase is a reasonable approximation.



**Table 2** Recommended experimental heat capacity data of poly(diethyl siloxane)

Temp., K	$C_p$ , J/(K mol)
10.0	2.477
15.0	6.112
20.0	10.789
25.0	16.081
30.0	20.979
40.0	30.837
50.0	39.678
60.0	47.789
70.0	55.440
80.0	62.630
90.0	69.360
100.0	75.630
110.0	81.440
120.0	87.409
130.0	94.158
135.0 $T_g$	97.532
135.0 $T_g$	127.721
140.0	128.863
150.0	131.147
160.0	133.432
170.0	135.717
180.0	138.001
190.0	140.286
200.0	142.571
210.0	144.855
220.0	147.140
230.0	149.425
240.0	151.709
250.0	153.994
260.0	156.279
270.0	158.563
280.0	160.848
290.0	163.133
300.0	165.417
310.0	167.702
320.0	169.986
330.0	172.271
340.0	174.556
350.0	176.840
360.0	179.125

b) Computed data for the solid state: Heat capacities were calculated for solid PDMS and PDES using the available *ATHAS* (1990) recommended experimental data and the well established *ATHAS* computation scheme [19] as described in the last publication of this series [3c]. The reported vibrational spectrum of PDMS [20] was, as a first approximation, separated into 20 group and 10 skeletal vibrations ( $N_s$ ). For the skeletal vibrations two low frequency bending vibrations of each backbone atom and three of each of the methyl groups were considered. The group vibrations expressed in kelvin ( $1 \text{ K} = 0.695 \text{ cm}^{-1} = 2.08 \times 10^{-5} \text{ Hz}$ ;  $h\nu/k = \theta$ ) were based on the IR and Raman spectra of PDMS and are listed in Table 3. The experimental heat capacity from 10 to 25 K gave upon inversion to a Debye frequency spectrum a  $\theta_D$  that ranged between 132.41 and 199.01 K ( $N_s = 10$ ). The lowest value of  $\theta_D$  was chosen. The uncertainty in  $\theta_D$  is not expected to introduce large errors in  $\theta_3$  since the  $\theta_1$  and  $\theta_3$  is recalculated in the Tarasov approximation. Subtracting the group vibrational contribution of the heat capacity, as computed from the data in Table 3, the experimental skeletal heat capacity in the temperature range 40 to 110 K was well represented by a  $\theta_1 = 508.55 \pm 5.6 \text{ K}$  and  $\theta_3 = 67.55 \pm 0.36 \text{ K}$ . Using this approximation of 10 skeletal vibration, almost all of the experimental heat capacity below 110 K was found to be due to the 10 skeletal vibrations. In fact, even close to the glass transition temperature, at 130 K, only 2.5% of the heat capacity was attributable to the contributions of the group vibrations.

Since several of the thus chosen skeletal vibrations were reasonably well known from the IR and Raman data,  $\theta_1$  and  $\theta_3$  were recalculated using only 6 and 4 skeletal vibrations, i.e. adding 4 and 6 of the original skeletal vibrations to the group vibrations of Table 3. For  $N = 6$  two skeletal vibrations for each methyl group, of frequencies between 550 and 830 K, assumed to be close to C-Si-C bending vibrations, were added to the group vibrations. For  $N = 4$ , two additional vibrational modes at about 296 K (corresponding to  $\text{CH}_3$ -torsion) were added for each  $-\text{CH}_3$ . Values of  $\theta_1 = 307.1 \pm 14.2$  and  $\theta_3 = 66.96 \pm 1.56$  for the temperature range 15 to 60 K were obtained for  $N = 6$ . For  $N = 4$ , the variation in  $\theta_1$  and  $\theta_3$  was more erratic and the average for the narrow temperature range from 15 to 40 K was  $207.99 \pm 10.88$  and  $65.78 \pm 1.8 \text{ K}$ , respectively. Heat capacities  $C_v$  were calculated for all the three sets of computations. The  $C_p$  to  $C_v$  and  $C_v$  to  $C_p$  conversions were made using the modified Nernst-Lindemann equation with an average  $A_0$  value of  $3.9 \pm 10^{-3} \text{ (K mol)/J}$  [21]. Using 6 and 4 skeletal vibrations, the deviation of the calculated  $C_p$  from the experimental data of Table 2 was much higher than the experimental uncertainty of perhaps  $\pm 5\%$ . Heat capacity for solid PDMS was, therefore, calculated using the original choice of  $N_s = 10$  and  $\theta_1$  and  $\theta_3$  values of 508.55 K and 67.55 K, respectively, and the group vibrations of Table 3. The so-calculated  $C_p$  agrees with the experimental  $C_p$  in the temperature ranges

Table 3 Group vibration frequencies in kelvin ( $h\nu/k$ )<sup>a</sup>

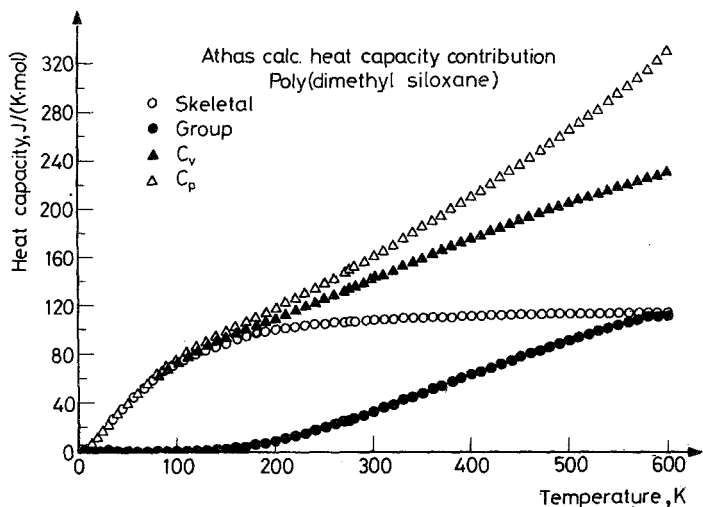
Polymer	Approximate vibrational mode	<i>N</i>	Frequency, K
Poly(dimethyl siloxane)	CH <sub>3</sub> as. stretch	4.00	4259
	CH <sub>3</sub> sym. stretch	2.00	4180
	CH <sub>3</sub> as. bend	4.00	2043
	CH <sub>3</sub> sym. bend	2.00	1813
	CH <sub>3</sub> rock	4.0	1273
	Si-CH <sub>3</sub> as. stretch	1.00	1158
	Si-CH <sub>3</sub> sym. stretch	1.00	1022
	Si-O asym. stretch	1.00	1540
	Si-O sym. stretch	1.00	712
Poly(diethyl siloxane)	CH <sub>3</sub> as. stretch	2.00	4262
	CH <sub>3</sub> as. stretch	2.00	4259
	CH <sub>3</sub> sym. stretch	2.00	4147
	CH <sub>3</sub> as. bend	2.00	2107
	CH <sub>3</sub> as. bend	2.00	2101
	CH <sub>3</sub> sym. bend	0.50	1987
		0.76	1973-1987
		0.74	1973
	CH <sub>3</sub> rock (+ CH <sub>2</sub> wag)	1.10	1453-1521
		0.90	1453
	CH <sub>3</sub> rock	1.30	1361-1393
		0.42	1333-1361
		0.28	1336
	CH <sub>2</sub> as. stretch	2.00	4213
	CH <sub>2</sub> sym. stretch	2.00	4085
	CH <sub>2</sub> bend	2.00	2094
	CH <sub>2</sub> wag	0.36	1876
		0.8	1842-1876
		0.8	1846
	CH <sub>2</sub> twist	0.66	1722-1791
	(CH <sub>3</sub> rock)	1.10	1695-1722
		0.24	1695
	CH <sub>2</sub> rock	1.04	1222-1295
		0.96	1289
	Si-CH <sub>2</sub> as. stretch	1.00	1158
	Si-CH <sub>2</sub> sym. stretch	1.00	1022
	Si-O asym. stretch	1.00	1540
Si-O sym. stretch	1.00	712	

<sup>a</sup> Sources of the listed approximate frequency ranges:

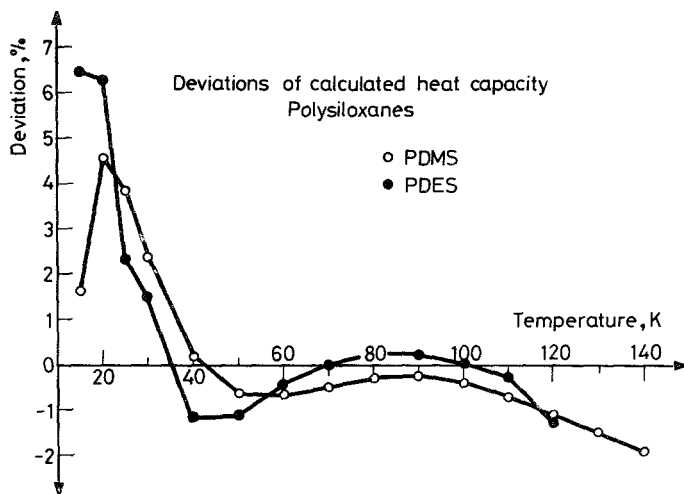
Poly(dimethyl siloxane) - From the IR and Raman spectra as evaluated in Ref. [20].

Poly(diethyl siloxane) - From the normal-mode calculation of polypropylene [3d] and from that of PDMS.

15–30 K and 40–120 K, with an average and RMS deviation of  $(3.10 \pm 1.16)\%$  and  $(-0.71 \pm 0.57)\%$ , respectively. Figure 2 shows the calculated heat capacities from 0.1 to 500 K. The deviation of the calculated  $C_p$  from the experimental  $C_p$  is depicted in Fig. 3.



**Fig. 2** Heat capacity of crystalline poly(dimethyl siloxane) computed from an approximate vibrational spectrum. Curves from bottom to top: 1. Group vibration contribution (frequencies given in Table 3). 2. Skeletal vibration contribution (Tarasov treatment  $\theta_3 = 67.55$  K and  $\theta_1 = 508.55$  K). 3. Heat capacity at constant volume and 4. Heat capacity at constant pressure



**Fig. 3** Heat capacity difference  $C_p(\text{calculated}) - C_p(\text{experiment})/C_p(\text{experiment})$ . Curve A is for PDMS (open circles) and curve B is for PDES (filled circles)

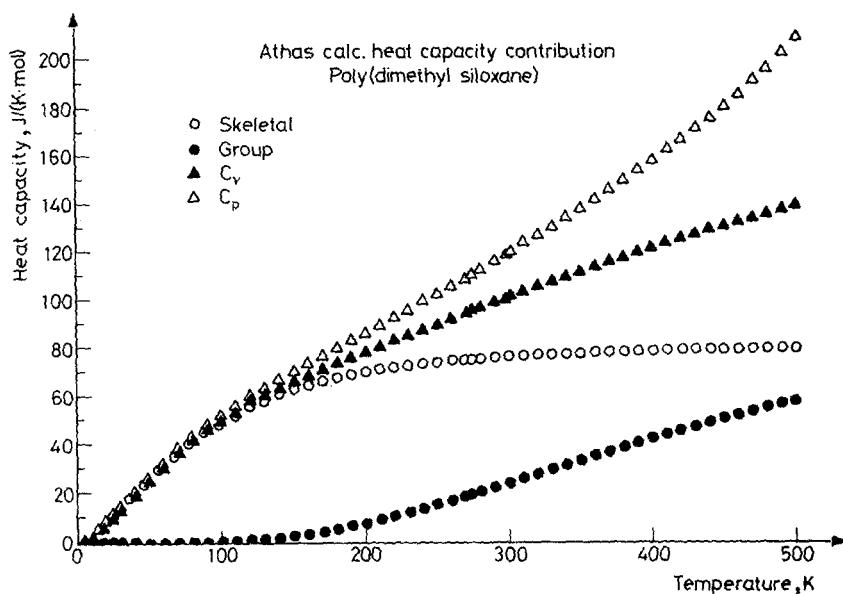


Fig. 4 Heat capacity of crystalline poly(diethyl siloxane) computed from an approximate vibrational spectrum. Curves from bottom to top: 1. Group vibrations contribution (frequencies given in Table 3). 2. Skeletal vibration contribution (Tarasov treatment  $\theta_3 = 87.4$  K,  $\theta_1 = 480$  K). 3. Heat capacity at constant volume and 4. Heat capacity at constant pressure

The heat capacity of the solid state was similarly calculated for poly(diethyl siloxane) using the newly recommended heat capacity data. Out of the total of 48 vibrational modes, 14 lower energy vibrations were assigned to the skeletal modes. The 34 group vibrations were retrieved from the vibrational spectrum of PDMS and normal-mode calculations of polypropylene [3d]. To evaluate the skeletal contributions to the heat capacity, the low temperature heat capacity from 10–25 K was approximated by an average value of  $\theta_D = 178.14$  K. Using this value of  $\theta_D$ , the experimental heat capacities in the temperature range 30–120 K upon fitting to a Tarasov function, gave a  $\theta_1 = 466.7 \pm 15.3$  K and  $\theta_3 = 110.05 \pm 1.86$  K. If, however, only the 10 K value of  $\theta_D = 154.32$  K was used, a relatively more constant  $\theta_1$  and  $\theta_3$  resulted. From 25–120 K,  $\theta_1 = 480 \pm 6.7$  K and  $\theta_3 = 87.4 \pm 0.6$  K. Using again, the universal  $A_0 = 3.9 \times 10^{-3}$  (K mol)/J, the calculated  $C_p$  shown in Fig. 4 agrees with the experimental  $C_p$  from 10–30 K with an average and RMS deviation of  $2.46 \pm 3.93\%$ . A much better fit was obtained over the temperature range 40–120 K (average and RMS deviation was  $-0.40 \pm 0.58\%$ ). The deviations as a function of temperature are also shown in Fig. 3.

The relatively larger deviations in calculated  $C_p$  in the low temperature region for PDMS and PDES are caused by errors in measurement of experimental heat capacities, which are typically greater than 5%. Variation in  $\theta_3$  (which is a measure of the intermolecularly coupled vibrations) from a value of 67.5 for PDMS to 87.4 for PDES having similar backbone structure, suggests the need of still lower  $C_p$  data to approximate the skeletal heat capacity contribution. In addition, it is necessary to establish the change in heat capacity with crystallinity that becomes substantial at lower temperature (below 50 K). The choice of  $\theta_1$  for the two polymers indicates that, as observed in the other polymers analyzed in the *ATHAS* laboratory, the group vibrations derived from normal-mode calculations or from IR and Raman spectra can well represent the heat capacity contribution of the intramolecular vibrations. The value of  $\theta_1$  is usually much less or not at all dependent on crystallinity. The  $\theta_1$  value of 480 K for PDES is lower than that of PDMS ( $\theta_1 = 508.5$  K) because of the larger mass. Assuming that the intramolecular force-constants do not change significantly between the polymers, the  $\theta_1$  value for PDES would be expected to be even lower (433 K) because of the larger mass. Although the experimental uncertainty in  $\theta_1$  is considerable, one can suggest that the relatively large value of  $\theta_1$  for PDES is due to its stiffer back-bone chain, caused by intramolecular steric hindrance [12].

c) Heat capacity of the mesophase of PDES: An attempt was made to determine the heat capacity in the mesophase region (210–250 K) of PDES. The crystallinity in this region was determined from the experimental  $\Delta H_d$  values [4].

$$X_m = \frac{\Delta H_d}{\Delta H_d^0} \quad (8)$$

$X_m$  was found to vary between 0.377 to 0.565 for the samples crystallized on slow cooling and were comparable to the crystallinities calculated from the heat of transition of the condic crystal to the viscous crystal ( $X_c = 0.341$ – $0.585$ ).

The contribution of the mesophase to the heat capacity was then obtained from the equation:

$$C_{p,m} = \frac{C_{p, \text{exp}} - (1 - X_c)C_{p,1}}{X_c} \quad (9)$$

Figure 5 shows that there is considerable scatter in the mesophase  $C_p$  data about the values for the liquid heat capacity extrapolated from the melt region. In all cases the mesophase heat capacity was considerably higher than the solid heat capacity calculated from the approximate vibrational spectrum. In Fig. 6 curve A is the DSC trace of the 264.8 K annealed sample of crystallinity  $X_m = 0.71$  over the total temperature region. One can assume that there is a latent heat contribution over the entire mesophase region. Curves B and C for PDES samples crystallized on cooling

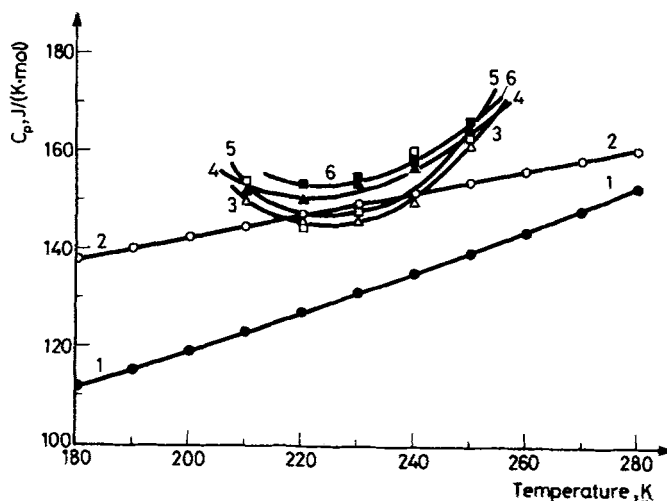


Fig. 5 Adjusted experimental heat capacity of PDES in the mesophase region calculated using Eq. (9). From bottom to top: 1. Crystal heat capacity (for reference). 2. Liquid heat capacity (for reference). 3. Sample of crystallinity 43.1%. 4. Sample of crystallinity 46.9%. 5. Sample of crystallinity 47.2%. 6. Sample of crystallinity 58.5%

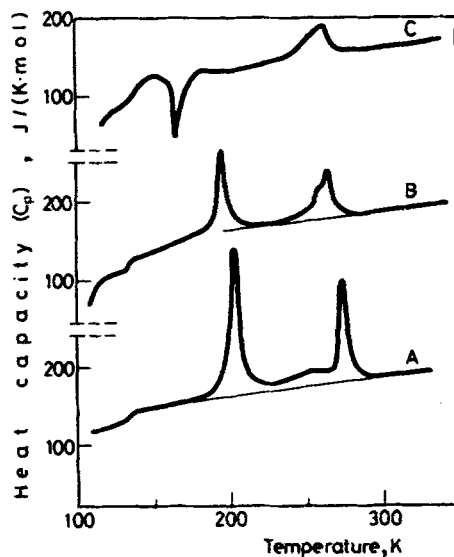


Fig. 6 DSC curves of PDES samples prepared under different conditions. Curve A: annealed at 264.8 K ( $w^c = 0.71$ ), curve B: cooled at 10 K/min ( $w^c = 0.49$ ) and curve C: quenched from the melt ( $w^c = 0$ )

**Table 4** Thermodynamic functions of crystalline poly(dimethyl siloxane)\*

Temp., K	$C_p$ , J/(K mol)	${}^cH_T - {}^cH_0$ , J/mol	${}^cS_0$ , J/(K mol)	${}^cH_0 - G$ , J/mol
0.10	0.000	0.00	0.000	0.00
0.20	0.000	0.00	0.000	0.00
0.30	0.000	0.00	0.000	0.00
0.40	0.000	0.00	0.000	0.00
0.50	0.000	0.00	0.000	0.00
0.60	0.001	0.00	0.000	0.00
0.70	0.001	0.00	0.000	0.00
0.80	0.001	0.00	0.000	0.00
0.90	0.002	0.00	0.001	0.00
1.00	0.003	0.00	0.001	0.00
1.20	0.005	0.00	0.002	0.00
1.40	0.008	0.00	0.003	0.00
1.60	0.011	0.01	0.004	0.00
1.80	0.016	0.01	0.005	0.00
2.00	0.022	0.01	0.007	0.00
3.00	0.075	0.06	0.025	0.02
4.00	0.179	0.18	0.060	0.06
5.00	0.349	0.44	0.116	0.15
6.00	0.600	0.90	0.201	0.30
7.00	0.936	1.67	0.318	0.56
8.00	1.357	2.81	0.469	0.95
9.00	1.855	4.41	0.657	1.51
10.00	2.414	6.54	0.881	2.27
15.00	5.662	26.57	2.464	10.39
20.00	9.021	63.34	4.552	27.69
25.00	12.244	116.48	6.908	56.22
30.00	15.331	185.41	9.403	96.68
40.00	21.268	368.60	14.640	217.02
50.00	27.057	610.36	20.016	390.47
60.00	32.700	909.27	25.452	617.83
70.00	38.125	1263.40	30.899	899.53
80.00	43.298	1670.86	36.336	1236.00
90.00	48.153	2128.49	41.723	1626.54
100.00	52.669	2632.84	47.031	2070.27
110.00	56.862	3180.58	52.246	2566.43
120.00	60.792	3769.12	57.367	3114.97
130.00	64.506	4395.87	62.384	3714.10
140.00	68.009	5058.60	67.293	4362.38
146.00	70.052	5472.61	70.184	4774.33
150.00	71.394	5755.60	72.100	5059.39
160.00	74.686	6486.13	76.816	5804.38
170.00	77.914	7249.20	81.439	6595.42
180.00	81.103	8044.12	85.978	7431.91
190.00	84.276	8871.11	90.452	8314.83



Table 4 Cont.

Temp., K	$C_p$ , J/(K mol)	${}^cH_T - {}^cH_0$ , J/mol	${}^cS_0$ , J/(K mol)	${}^cH_c - G$ , J/mol
200.00	87.450	9729.80	94.858	9241.86
210.00	90.638	10620.26	99.200	10211.83
219.00	93.528	11448.80	103.059	11121.16
220.00	93.851	11542.58	103.490	11225.28
230.00	97.094	12497.35	107.736	12281.95
240.00	100.374	13484.68	111.936	13379.88
250.00	103.693	14504.80	116.095	14519.04
260.00	107.054	15558.59	120.232	15701.74
270.00	110.457	16646.18	124.338	16925.20
273.15	111.538	16995.84	125.624	17318.36
280.00	113.904	17767.79	128.411	18187.25
290.00	117.396	18924.34	132.473	19492.84
298.15	120.274	19892.90	135.769	20586.58
300.00	120.932	20116.03	136.513	20837.87
310.00	124.513	21343.05	140.532	22221.79
320.00	128.142	22606.36	144.546	23648.46
330.00	131.819	23906.21	148.548	25114.67
340.00	135.547	25243.01	152.537	26619.47
350.00	139.328	26617.17	156.515	28163.22
360.00	143.168	28029.66	160.498	29749.73
370.00	147.070	29480.89	164.477	31375.43
380.00	151.041	30971.40	168.449	33039.36
390.00	155.088	32501.81	172.420	34742.00
400.00	159.221	34073.34	176.403	36487.72
410.00	163.449	35686.70	180.388	38272.59
420.00	167.786	37342.78	184.377	40095.63
430.00	172.249	39042.68	188.372	41957.47
440.00	176.855	40788.14	192.389	43863.04
450.00	181.628	42580.49	196.419	45808.09
460.00	186.598	44421.45	200.463	47791.63
470.00	191.801	46313.07	204.527	49814.46
480.00	197.284	48258.29	208.626	51882.15
490.00	203.110	50260.04	212.755	53990.15
500.00	209.363	52322.01	216.919	56137.56
510.00	216.151	54448.91	221.126	58325.45
520.00	223.686	56647.39	225.399	60560.14
530.00	232.256	58926.17	229.742	62837.00
540.00	242.426	61297.87	234.173	65155.49
550.00	255.518	63784.12	238.730	67517.38

\* The significant figures in this table are purely for computational reasons and do not reflect the precision of the data (see text).

at 2 K/min ( $X_m = 0.491$ ) and quenched from the melt with cold crystallization, respectively, show mesophase heat capacities closer to the extrapolated liquid data. Hence, it was assumed that the heat capacity for mesophase of PDES can be approximated by the heat capacity of the liquid, extrapolated to the mesophase temperature region (Eq. (7)). Similar high heat capacities have also been observed for condensation crystals of other molecules [3i]. The high heat capacity seems to be coupled to the large amplitude molecular motion in the mesophase that approaches the level of the liquid. While X-ray diffraction studies [16] indicate that positional order of the mesophase is high, both nuclear magnetic resonance [11, 22] and dielectric constant measurements indicate considerable molecular motion and a volume increase in the mesophase [23].

d) Thermodynamic functions: Thermodynamic functions (enthalpy, entropy and Gibbs function) were determined for all phases of PDMS and PDES by integration of the recommended heat capacities. The results are listed in Tables 4–7. Below the glass transition, calculated crystalline heat capacities were assumed to be the same as the glassy heat capacities. Usually below 50 K the amorphous heat capacities are higher than the crystalline values. For example, in the case of polyethylene,  $\theta_3$ , which describes the intermolecular contribution to the heat capacities, varies from 80 K for the amorphous state to 158 K for the crystalline state [3d]. The value of  $\theta_1$  which, in turn, is a measure of the intramolecular heat capacity, remains constant at 519 K. This variation in heat capacity at low temperature is, however, not expected to affect the integral values significantly since absolute heat capacities are small in this temperature range.

For PDMS the enthalpy for the solid crystal was evaluated from the equation:

$${}^cH_T - {}^cH_0 = \int_0^{T_m} C_{pc} dT + \Delta H_m + \int_{T_m}^T C_{pa} dT \quad (10)$$

while for PDES which shows multiple phase transitions, the enthalpy of the various states was represented by

$$\begin{aligned} {}^cH_T - {}^cH_0 = & \int_0^{T_d} C_{pc} dT + \Delta H_d + \int_{T_d}^{T_i} C_{pa} dT + \Delta H_i + \\ & + \int_{T_i}^{T_x} C_{pa} dT + \Delta H_x + \int_{T_x}^T C_{pa} dT \end{aligned} \quad (11)$$

where  $C_{pc}$  is the calculated crystalline heat capacity and  $C_{pa}$  is the recommended experimental liquid heat capacity.

To determine the residual entropy of amorphous materials at 0 K the crystalline heat capacity for PDMS and the mesophase heat capacity for PDES up to the temperature of isotropization to the melt were integrated. The residual entropy is

Table 5 Thermodynamic functions of amorphous poly(dimethyl siloxane)\*

Temp., K	$C_p$ , J/(K mol)	${}^aH_T - {}^cH_0$ , J/mol	${}^aS_0$ , J/(K mol)	${}^cH_0 - G$ , J/mol
0.10	0.000	1154.32	3.496	-1153.97
0.20	0.000	1154.32	3.496	-1153.62
0.30	0.000	1154.32	3.496	-1153.27
0.40	0.000	1154.32	3.496	-1152.92
0.50	0.000	1154.32	3.496	-1152.57
0.60	0.001	1154.32	3.496	-1152.22
0.70	0.001	1154.32	3.496	-1151.87
0.80	0.001	1154.32	3.496	-1151.52
0.90	0.002	1154.32	3.497	-1151.17
1.00	0.003	1154.32	3.497	-1150.82
1.20	0.005	1154.32	3.498	-1150.12
1.40	0.008	1154.32	3.499	-1149.42
1.60	0.011	1154.33	3.500	-1148.73
1.80	0.016	1154.33	3.501	-1148.03
2.00	0.022	1154.33	3.503	-1147.32
3.00	0.075	1154.38	3.521	-1143.81
4.00	0.179	1154.50	3.556	-1140.28
5.00	0.349	1154.76	3.612	-1136.70
6.00	0.600	1155.22	3.697	-1133.04
7.00	0.936	1155.99	3.814	-1129.29
8.00	1.357	1157.13	3.965	-1125.41
9.00	1.855	1158.73	4.153	-1121.35
10.00	2.414	1160.86	4.377	-1117.09
15.00	5.662	1180.89	5.960	-1091.49
20.00	9.021	1217.66	8.048	-1056.70
25.00	12.244	1270.80	10.404	-1010.70
30.00	15.331	1339.73	12.899	-952.76
40.00	21.268	1522.92	18.136	-797.48
50.00	27.057	1764.68	23.512	-589.08
60.00	32.700	2063.59	28.948	-326.71
70.00	38.125	2417.72	34.395	-10.07
80.00	43.298	2825.18	39.832	361.38
90.00	48.153	3282.81	45.219	786.90
100.00	52.669	3787.16	50.527	1265.54
110.00	56.862	4334.90	55.742	1796.72
120.00	60.792	4923.44	60.863	2380.12
130.00	64.506	5550.19	65.880	3014.21
140.00	68.009	6212.92	70.789	3697.54
146.00	70.052	6626.93	73.680	4130.35
146.00	99.289	6626.93	73.680	4130.35
150.00	99.775	7025.06	76.370	4430.44
160.00	100.990	8028.88	82.848	5226.80
170.00	102.205	9044.86	89.007	6086.33
180.00	103.420	10072.99	94.884	7006.13

Table 5 Cont.

Temp., K	$C_p$ , J/(K mol)	${}^aH_T - {}^cH_0$ , J/mol	${}^aS_0$ , J/(K mol)	${}^cH_0 - G$ , J/mol
190.00	104.635	11113.31	100.509	7983.40
200.00	105.850	12165.73	105.907	9015.68
210.00	107.065	13230.29	111.101	10100.92
219.00	108.158	14198.80	115.616	11121.11
220.00	108.280	14307.05	116.110	11237.15
230.00	109.495	15395.93	120.950	12422.57
240.00	110.710	16496.92	125.635	13655.49
250.00	111.925	17610.09	130.179	14934.66
260.00	113.140	18735.47	134.594	16258.97
270.00	114.355	19872.94	138.886	17626.28
273.15	114.738	20233.72	140.214	18065.73
280.00	115.570	21022.53	143.066	19035.95
290.00	116.785	22184.35	147.144	20487.41
298.15	117.775	23140.18	150.394	21699.80
300.00	118.000	23358.23	151.123	21978.67
310.00	119.215	24544.32	155.012	23509.40
320.00	120.430	25742.57	158.817	25078.87
330.00	121.645	26952.94	162.541	26685.59
340.00	122.860	28175.44	166.190	28329.16
350.00	124.075	29410.12	169.769	30009.03
360.00	125.290	30656.98	173.282	31724.54
370.00	126.505	31915.95	176.731	33474.52
380.00	127.720	33187.04	180.120	35258.56
390.00	128.935	34470.33	183.454	37076.73
400.00	130.150	35765.78	186.734	38927.82
410.00	131.365	37073.35	189.963	40811.48
420.00	132.580	38393.04	193.142	42726.60
430.00	133.795	39724.93	196.276	44673.75
440.00	135.010	41068.99	199.367	46652.50
450.00	136.225	42425.16	202.414	48661.15
460.00	137.440	43793.45	205.421	50700.21
470.00	138.655	45173.93	208.390	52769.37
480.00	139.870	46566.59	211.323	54868.45
490.00	141.085	47971.36	214.219	56995.95
500.00	142.300	49388.25	217.081	59152.25
510.00	143.515	50817.34	219.911	61337.28
520.00	144.730	52258.59	222.710	63550.61
530.00	145.945	53711.96	225.478	65791.38
540.00	147.160	55177.45	228.217	68059.73
550.00	148.375	56655.14	230.928	70355.26

\* The significant figures in this table are purely for computational reasons and do not reflect the precision of the data (see text).

Table 6 Thermodynamic functions of crystalline poly(diethyl siloxane)\*

Temp., K	$C_p$ , J/(K mol)	$^cH_T - ^cH_0$ , J/mol	$^cS_0$ , J/(K mol)	$^cH_0 - G$ , J/mol
0.10	0.000	0.00	0.000	0.00
0.20	0.000	0.00	0.000	0.00
0.30	0.000	0.00	0.000	0.00
0.40	0.000	0.00	0.000	0.00
0.50	0.000	0.00	0.000	0.00
0.60	0.001	0.00	0.000	0.00
0.70	0.001	0.00	0.000	0.00
0.80	0.001	0.00	0.000	0.00
0.90	0.002	0.00	0.001	0.00
1.00	0.002	0.00	0.001	0.00
1.20	0.004	0.00	0.001	0.00
1.40	0.007	0.00	0.002	0.00
1.60	0.010	0.00	0.003	0.00
1.80	0.014	0.01	0.005	0.00
2.00	0.020	0.01	0.007	0.00
3.00	0.067	0.05	0.022	0.02
4.00	0.159	0.16	0.053	0.05
5.00	0.310	0.39	0.103	0.13
6.00	0.535	0.80	0.178	0.27
7.00	0.849	1.49	0.283	0.50
8.00	1.257	2.53	0.422	0.85
9.00	1.764	4.03	0.599	1.35
10.00	2.370	6.09	0.815	2.06
15.00	6.507	27.65	2.511	10.02
20.00	11.465	72.53	5.057	28.62
25.00	16.455	142.36	8.145	61.27
30.00	21.295	236.82	11.566	110.17
40.00	30.481	496.12	18.963	262.39
50.00	39.239	844.92	26.723	491.21
60.00	47.585	1279.48	34.624	797.98
70.00	55.458	1794.75	42.549	1183.68
80.00	62.791	2386.73	50.442	1648.65
90.00	69.526	3048.78	58.241	2192.90
100.00	75.671	3775.34	65.891	2813.74
110.00	81.215	4559.94	73.359	3509.51
120.00	86.321	5398.09	80.648	4279.64
130.00	91.006	6285.12	87.754	5122.84
135.00	93.246	6745.72	91.230	5570.34
140.00	95.407	7217.21	94.652	6034.14
150.00	99.597	8192.39	101.378	7014.29

Table 6 Cont.

Temp., K	$C_p$ , J/(K mol)	${}^aH_T - {}^cH_0$ , J/mol	${}^aS_0$ , J/(K mol)	${}^cH_0 - G$ , J/mol
160.00	103.620	9208.83	107.944	8062.25
170.00	107.541	10264.60	114.344	9173.83
180.00	111.400	11359.19	120.593	10347.52
190.00	115.232	12492.36	126.718	11583.98
200.00	119.079	13664.13	132.735	12882.90
206.70	121.714	14470.63	136.701	13785.52
206.70	144.101	17190.63	149.867	13785.52
210.00	144.855	17667.41	152.156	14285.36
220.00	147.140	19127.38	158.947	15840.96
230.00	149.425	20610.21	165.538	17463.53
240.00	151.709	22115.88	171.946	19151.16
250.00	153.994	23644.41	178.186	20902.09
260.00	156.279	25195.78	184.270	22714.42
270.00	158.563	26769.98	190.211	24586.99
273.15	159.283	27270.59	192.054	25188.96
280.00	160.848	28367.06	196.019	26518.26
282.70	161.465	28802.17	197.565	27049.46
282.70	161.465	30642.17	204.035	27049.46
290.00	163.133	31826.95	208.173	28543.22
298.15	164.994	33164.07	212.720	30258.40
300.00	165.417	33469.70	213.742	30652.90
308.50	167.359	34884.00	218.391	32489.62

\* The significant figures in this table are purely for computational reasons and do not reflect the precision of the data (see text).

then given by

$${}^aS_0 = \int_0^{T_x} (C_{pc} - C_{pa}) d(\ln T) + \Delta S_x \quad (12)$$

where  $T_x$  is the melting temperature, 219 K for PDMS, and the recommended isotropization temperature of 308.5 K for PDES. The corresponding entropy change is  $\Delta S_x$ . For the amorphous state of PDMS the residual entropy thus obtained was 3.5 J/(K mol) and was found to be much lower than that of PDES [8.4 J/(K mol)]. Since every mobile unit in a repeating unit of a polymer contributes at an average about 2–4 J/(K mol) to the residual entropy [24], one can assign two mobile units for PDMS and four in case of PDES, indicating that the side chain mobility constitutes two additional mobile units that freeze at the glass transition. It

Table 7 Thermodynamic functions of amorphous poly(diethyl siloxane)\*

Temp., K	$C_p$ , J/(K mol)	${}^aH_T - {}^cH_0$ , J/mol	${}^aS_0$ , J/(K mol)	${}^cH_0 - G$ , J/mol
0.10	0.000	2801.38	8.433	-2800.54
0.20	0.000	2801.38	8.433	-2799.69
0.30	0.000	2801.38	8.433	-2798.85
0.40	0.000	2801.38	8.433	-2798.01
0.50	0.000	2801.38	8.433	-2797.16
0.60	0.001	2801.38	8.433	-2796.32
0.70	0.001	2801.38	8.433	-2795.48
0.80	0.001	2801.38	8.433	-2794.63
0.90	0.002	2801.38	8.434	-2793.79
1.00	0.002	2801.38	8.434	-2792.95
1.20	0.004	2801.38	8.434	-2791.26
1.40	0.007	2801.38	8.435	-2789.57
1.60	0.010	2801.38	8.436	-2787.89
1.80	0.014	2801.39	8.438	-2786.20
2.00	0.020	2801.39	8.440	-2784.51
3.00	0.067	2801.43	8.455	-2776.07
4.00	0.159	2801.54	8.486	-2767.60
5.00	0.310	2801.77	8.536	-2759.09
6.00	0.535	2802.18	8.611	-2750.52
7.00	0.849	2802.87	8.716	-2741.86
8.00	1.257	2803.91	8.855	-2733.07
9.00	1.764	2805.41	9.032	-2724.13
10.00	2.370	2807.47	9.248	-2714.99
15.00	6.507	2829.03	10.944	-2664.87
20.00	11.465	2873.91	13.490	-2604.11
25.00	16.455	2943.74	16.578	-2529.29
30.00	21.295	3038.20	19.999	-2438.23
40.00	30.481	3297.50	27.396	-2201.66
50.00	39.239	3646.30	35.156	-1888.50
60.00	47.585	4080.86	43.057	-1497.44
70.00	55.458	4596.13	50.982	-1027.39
80.00	62.791	5188.11	58.875	-478.11
90.00	69.526	5850.16	66.674	150.50
100.00	75.671	6576.72	74.324	855.69
110.00	81.215	7361.32	81.792	1635.80
120.00	86.321	8199.47	89.081	2490.26
130.00	91.006	9086.50	96.187	3417.81
135.00	93.246	9547.10	99.663	3907.40
135.00	127.721	9547.10	99.663	3907.40
140.00	128.863	10232.55	104.662	4420.14
150.00	131.147	11458.61	113.063	5500.84
160.00	133.432	12840.80	122.056	6688.16
170.00	135.717	14157.26	129.992	7941.38
180.00	138.001	15569.90	138.150	9297.10
190.00	140.286	16887.34	145.104	10682.42

Table 7 Cont.

Temp., K	$C_p$ , J/(K mol)	${}^aH_T - {}^cH_0$ , J/mol	${}^aS_0$ , J/(K mol)	${}^cH_0 - G$ , J/mol
200.00	142.571	18360.91	152.813	12201.69
206.70	144.101	19291.97	157.314	13224.84
210.00	144.855	19812.79	159.938	13774.19
220.00	147.140	21198.76	166.161	15356.66
230.00	149.425	22740.84	173.207	17096.77
240.00	151.709	24217.22	179.393	18837.10
250.00	153.994	25789.80	185.968	20702.20
260.00	156.279	27267.15	191.484	22518.69
270.00	158.563	28900.61	198.880	24526.99
273.15	159.283	29371.93	199.501	25121.77
280.00	160.848	30512.44	203.801	26551.84
282.70	161.465	30873.54	204.779	27017.48
290.00	163.133	32117.57	209.372	28600.31
298.15	164.994	33425.40	213.697	30288.37
300.00	165.417	33775.09	215.054	30741.11
308.50	167.359	35115.37	219.134	32487.47
310.00	167.702	35425.92	220.402	32898.70
320.00	169.986	37085.06	225.540	35087.74
330.00	172.271	38840.41	231.142	37436.45
340.00	174.556	40500.53	235.750	39654.47
350.00	176.840	42316.77	241.298	42137.53
360.00	179.125	44067.30	246.090	44525.10
370.00	181.410	45914.03	251.364	47090.65
380.00	183.694	47665.54	255.664	49486.78
390.00	185.979	49573.16	260.920	52185.64
400.00	188.264	51415.07	265.435	54758.93
410.00	190.548	53353.20	270.448	57530.48
420.00	192.833	55196.09	274.498	60093.07
430.00	195.118	57195.09	279.518	62997.65
440.00	197.402	59128.39	283.807	65746.69
450.00	199.687	61157.90	288.605	68714.35
460.00	201.971	63092.17	292.450	71434.83
470.00	204.256	65182.57	297.273	74535.74
480.00	206.541	67207.25	301.375	77452.75
490.00	208.825	69328.15	305.993	80608.42
500.00	211.110	71353.81	309.667	83479.69
510.00	213.395	73535.58	314.325	86770.17
520.00	215.679	75651.66	318.268	89847.70
530.00	217.964	77863.94	322.734	93185.08
540.00	220.249	79980.98	326.261	96199.96
550.00	222.533	82254.14	330.778	99673.76

\* The significant figures in this table are purely for computational reasons and do not reflect the precision of the data (see text).



is of interest to note that this doubling of mobile units is not reflected in the change in heat capacity at the glass transition. For PDMS  $\Delta C_p$  is 29.24 J/(K mol) and for PDES 34.48 J/(K mol).

\* \* \*

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**Zusammenfassung** – Neue Messungen und Literaturangaben von Polysiloxanen über Wärmekapazität, Umwandlungsparameter, Enthalpien, Entropien und Gibbsche Energien werden vorgestellt und kritisch betrachtet. Das Rechenverfahren ATHAS wurde benutzt, um die Wärmekapazitäten mit einem annähernden Frequenzspektrum in Einklang zu bringen. Es wurden die verschiedenen Kristall- und Mesophasen diskutiert. Die von ATHAS (1990) empfohlenen Werte sind wie folgt: Für Poly(dimethylsiloxan) beträgt der Glasumwandelungspunkt 146 K bei Zunahme der Wärmekapazität um 29.24 J/(K.mol). Die vollständig kristalline Probe schmilzt bei etwa 219 K mit einer Schmelzwärme von 2.75 kJ/mol. Für Poly(diethylsiloxan) beträgt der Glasumwandelungspunkt 135 K bei Zunahme der Wärmekapazität um 34.48 J/(K.mol). Die vollständig kristalline Probe wandelt sich bei 206.7 K um, die Fehlordnungswärme beträgt 2.72 kJ/mol. Die Umwandlung in einen wenig verstandenen "viskosen Kristall", dessen thermodynamische Eigenschaften denen der Schmelze gleichen, erfolgt bei 282.7 K mit einer Umwandlungsenthalpie von 1.84 kJ/mol. Letztendlich verläuft das Schmelzen bei 308.5 K mit einem kleinen endothermen Effekt von etwa 231 J/mol. Wärmekapazitäten, Enthalpien, Entropien und Gibbsche Energien sind für den Bereich 0 K – 550 K tabellarisch angegeben.

**Резюме** — Представлены и критически обсуждены литературные данные и новые измерения полисилоксанов, включающие значения теплоемкостей, параметров перехода, энтальпий, энтропий и энергий Гиббса. Вычислительный метод ATHAS был использован, чтобы привести

теплоемкости в согласие с каким-либо приближенным частотным спектром. Обсуждены различные кристаллы и мезофазы. Найденные методом *ATHAS* (1990) данные для полидиметилсилоксана были следующие: температура стеклования составляла 146 К с увеличением теплоемкости до 29,24 дж/К·моль. Полностью кристаллические образцы плавятся при 219 К с теплотой плавления равной 2,75 кдж/моль. Для полидиэтилсилоксана температура стеклования наблюдалась при 135 К с увеличением теплоемкости до 34,48 дж/К·моль. Полностью кристаллические образцы изменялись до переходного кристалла при 206,7 К с теплотой разупорядочения 2,72 кдж/моль. Переход до «вязкого кристалла» с термодинамическими свойствами близкими к расплаву происходит при 282,7 К с энтальпией перехода равной 1,84 кдж/моль. Окончательное плавление происходит при 308,5 К с небольшой эндотермой около 231 дж/моль. Приведены данные для теплоемкостей, энтальпий, энтропий и энергий Гиббса в температурном интервале 0–550 К.