

HEAT CAPACITY FUNCTIONS OF POLYSTYRENE IN GLASSY AND IN LIQUID AMORPHOUS STATE AND GLASS TRANSITION DSC and TMDSC study

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The heat capacity or the specific heat is for any crystalline, partially amorphous or completely amorphous substance or material a significant thermodynamic property. The glass transition may be regarded as the melting point of amorphous substances and materials, a transition property of an outstanding technical importance. A crucial point is the fact that the presence of a glass transition is an unequivocal proof of an amorphous content of a material. Furthermore, the change of the specific heat at the glass transition temperature enables the quantitative determination of the amorphicity on a relative or absolute level of any substance or material. The absolute determination of the amorphicity affords a calibration with a reference corresponding to the material under investigation. The crystallinity for this reference substance must be known from the preparation and or by any independent analytical method.

The literature data for the specific heat and the glass transition of polystyrene were collected and evaluated. Data were found for the specific heat in literature from 10 to 470 K. The data were unified for each of the reported temperature in a mean value and the corresponding standard deviation was determined. An excellent conformity was found in the glassy state of polystyrene with standard deviations lower than 0.7%. The standard deviations above the glass transition were considerably higher.

All these literature data were transferred for each of the literature sets separately into linear specific heat functions in the vicinity of the glass transition. One set of our measurements performed with the DSC 204 and with polystyrene SRM 705a as sample material was additionally integrated in the mean of these functions for the glassy state and the liquid amorphous state respectively. The addition of our results gave practically no change of the mean coefficients and only a decrease of the standard deviations. In such a way, the data with the best statistical base for the specific heat of polystyrene are listed in this paper ('Conclusions').

The glass transition as a transition in and out of a non-equilibrium state, the glassy state, is sensitive to all kind of influences such as thermal and mechanical treatments as well as to the selected experimental conditions. Therefore, certain standardized conditions procedures must be fulfilled to get reproducible data. The literature data for the glass transition temperature were also used to get a mean value. However, two values were omitted for the formation of the mean, because the authors reported values, which were too low on the base of impurities present. The mean value of the glass transition for polystyrene is according to the literature 369 ± 2 K. A mean value of 370 ± 2 K was extrapolated for an infinite molecular mass.

The DSC and TMDSC measurements for the three thermodynamic properties reported in this paper, namely the specific heat, the glass transition temperature and the corresponding change of the specific heat gave results without significant differences compared with the literature values.

Atactic polystyrene is a rather ideal polymer together with sapphire as calibration substance to elucidate and validate the DSC and TMDSC procedures for the determination of the specific heat and the glass transition.

Keywords: DSC, glass transition temperature, glassy and liquid amorphous state, polystyrene, specific heat, specific heat change, standard reference material, TMDSC

Introduction

Heat capacity functions are an important thermodynamic characterization for practically all chemical substances as well as for technical materials and especially also for polymers. Thermodynamic functions are always quantitative descriptions of a chemical substance or a material and are practically meaningless in a qualitative form with the only exemption for didactic reasons.

Polystyrene (PS) is introduced as an amorphous polymer for a possible reference material for the determination of the heat capacity functions and the

glass transition for testing of DSC and TMDSC instruments. The transformation of the measured heat flow curves into thermodynamic functions, namely into specific heat functions affords an instrumental calibration with sapphire as a preferred substance. The heat capacity functions for PS and the comparison of the experimental data with the literature values, presented in this paper as mean values, are a rather ideal proof for the functionality and the precision of DSC as well as temperature modulated DSC instruments including the involved evaluation procedures. In analogy to the polystyrene, the oligomer

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n-hexatriacontane is proposed in a publication as rather ideal reference substance for the determination of the resolution of DSC instruments using the ratio of the melting peak to the height of the minimum between the lambda and the melting peak as the characteristic parameter [1].

There is a rather evident difference between materials or substances which are ideally crystalline and materials or substances, which are partially or completely amorphous. Namely, the glass transition is a typical phenomenon only observed for amorphous or partially amorphous substances. The more or less sharp step-wise change in the heat capacity functions is an absolute prove of an existing amorphicity of a substance or a material. Furthermore, the quantification of this change of the heat capacity for each of the substance under investigation allows the determination of the content of the amorphous phase [2]. Two conditions have to be fulfilled for quantification; first the substance or material must always be of the same chemical and physical composition. And second, a calibration is afforded not for the qualitative statement of the amorphicity, however, for its quantification. Ideal and experimentally easy is the correlation between a completely amorphous sample of a given substance as reference phase and the measured difference of the heat capacity functions at the glass transition. It should be mentioned here that DSC and the TMDSC measurements for the determination of the change of the heat capacity and the related glass transition temperature are the state of the art methods, hitherto not achieved with any other physicochemical instrumentation. This statement is true in consideration of the straightforward determination, the sensitivity achieved, the easiness of the sample handling and the ratio of the benefit to costs for such a measurement and their evaluation. Complementary methods applied for the proof of the amorphicity and its quantitative determination are among others the X-ray diffraction and the solution calorimetry.

The new experimental data on the glass transition temperature and the heat capacity functions reported here were measured for polystyrene with the DSC 204 F1 Phoenix from Netzsch-Gerätebau GmbH. The instruments are calibrated for specific heat measurements using sapphire as reference material. The calculation of the heat capacity functions for the two states and the evaluation of the analytically essential change at the glass transition temperature from measured heat flow curves by DSC are for any sample material extremely straightforward. Additionally, the easiness to obtain the heat capacity functions from measured curves for polystyrene using the DSC 204 in applying the software Proteus[®] from Netzsch is demonstrated. Parallel measurements were

performed using the same DSC, however, with temperature modulation.

An absolute and relative comparison of the measured heat capacity functions for polystyrene with literature values is presented in this paper. These comparisons are performed with different mean values for polystyrene obtained from literature and also with a unique data set, namely the heat capacity data given for the Standard Reference Material 705a from NIST [3]. The latter data set has been obtained by adiabatic calorimetry. The data for the heat capacity should be only applied for measurements of the SRM 705a, provided the polymer has not been heated above 350 K [4].

The adiabatic measurements performed with appropriate calorimeters yielding certainly data of the highest accuracy. However, the DSC and the temperature modulated DSC allow a rapid determination of such data with a much smaller sample mass. One subject of this paper is the verification of the repeatability and the accuracy of the data obtained with DSC measurements for the reference material used, namely polystyrene. The DSC enables a direct measurement of the heat flow curve. The thermodynamic and therefore absolute level for the specific heat is achieved with a calibration of the instrument using preferably sapphire as reference substance and treating the heat flow curve by an algorithm. The heat capacity functions, normally obtained for the glassy and the liquid amorphous state are representing thermodynamic functions for the substance or material under investigation, of course on a certain accuracy level.

The elaboration of data and especially also the determination of the glass transition temperature and the heat capacity functions are discussed in literature and in several normative regulations. The extended discussions are caused by the fact that the glass transition is a solid-state transition, which does not allow a clear thermodynamic classification. Normally, it is assigned as of second order; however, several aspects are influenced by the history of the material and by kinetic effects. The glass transition temperature as well as the change of the specific heat function from a glassy state into the liquid amorphous state is rather sensitive to the conditions of pretreatment and the measurement such as heating and cooling rates, tempering with time interval and selected temperature, sample size, mechanical stress. An extreme change of the viscosity is observed at the glass transition. This change is not so obvious, yet very crucial for a number of technical applications mainly of technical materials. It should be mentioned here, that quite different phenomena in nature are also depending on the behavior of amorphous or partially amorphous materials.

It seems obvious, that such facts, which are not observed for a first order transition, make a regulation or normative procedure for an analytical determination of the glass transition temperature and the related change of the specific heat rather difficult. In contrary, the procedure for a determination of a melting point and an enthalpy of fusion is a straightforward analytical task. The results obtained for a purity determination are rather insensitive to the chosen experimental condition and to the thermal history as long as one is dealing with substances, which are chemical and physical stable at the melting region. Certain precautions must be also fulfilled, but mainly in respect to the sample material under investigation. Details about the purity measurements and purity determinations according to the premelting were reported by Marti [5].

Our attempt has been directed towards several goals:

- to collect literature data for the specific heat functions and the glass transition temperature for polystyrene and to generate data sets of mean values together with error limits;
- to get an estimation of the reproducibility and the accuracy of our measurements for the specific heat functions performed with the DSC 204 F1 Phoenix[®] and the also with the TMDSC procedure;
- to compare the mean value of the heat capacity per mole obtained by our measurements for the polystyrene SRM 705a with the values reported by NIST;
- to compare the specific heat capacities measured with our DSC instrument and the TMDSC procedure for SRM 705a with the mean values from literature;
- to discuss the existing evaluation procedures for the determination of the glass transition temperature T_g ;
- to discuss the importance of the different temperatures assigned within the glass transition such as the 'thermodynamic glass transition temperature', the onset glass transition temperature, the Δc_p half-step temperature, the initial and the final temperatures of the glass transition;
- to discuss the relation of the different glass transition temperatures in respect to technical applications;
- to discuss the data presented in literature for polystyrene obtained with TMDSC method.

Experimental

Material and methods

All our measurements were performed with the DSC 204 F1 Phoenix[®], equipped with the τ -sensor and the μ -sensor, respectively. The evaluation of the DSC and TMDSC were executed by the Netzsch soft-

ware Proteus[®]. The Standard Reference Material SRM 705a for atactic polystyrene has been characterized by physicochemical methods by the NIST [3]. The certified material was used for our measurements of the heat capacity by DSC and TMDSC. The sample masses were measured with a microbalance CP2P from Sartorius. The calibration of the DSC 204 F1 Phoenix in respect to the temperature and the enthalpies has been executed with Sapphire. The caloric calibration was performed using six reference materials according to the Netzsch procedure for enthalpy calibration. We selected aluminum pans with pierced lids and nitrogen as purge gas.

Literature values

Data for the heat capacity and the specific heat of atactic polystyrene in the glassy state as well as in the liquid amorphous state have been searched for in the literature. The literature data found for polystyrene are collected in Tables 1a and b. All collected data were obtained by adiabatic calorimetry with one exception. The data range from 10 to 470 K. Marsh [7] covers the temperature range from 10 to 460 K. Each of the literature data set in Tables 1a and b shall be described shortly in the following.

The data given by NIST [3] is restricted to one material of polystyrene with narrow molecular mass distribution, namely the SRM 705a. The SRM 705a is delivered in 5 g units. The material is physico-chemically and analytically characterized and is recommended for the calibration of instruments used for the determination of the molecular mass and for use in the checking of DSC and DTA instruments. The molecular mass is slightly dependent on the method of determination; the average molecular mass according to light scattering for SRM 705a is $179300 \pm 740 \text{ g mol}^{-1}$. The value is according to the sedimentation equilibrium $189800 \pm 2100 \text{ g mol}^{-1}$. The heat capacity measurements were obtained by adiabatic calorimetry. The certificate gives the heat capacity in $\text{J mol}^{-1} \text{ K}^{-1}$ for the repeating unit $[-\text{C}_8\text{H}_8-]$ with a molecular mass of 104152 g. The temperature range 10 to 350 K is the recommended temperature range for calibration. The data are valid when the heating rate approaches zero. These heat capacity values listed for SRM 705a are estimated to be within 0.2% of the real values, provided the material has not been heated above 350 K. The values by NIST are listed in Tables 1a and b as specific heat values in $\text{J g}^{-1} \text{ K}^{-1}$.

Karasz *et al.* [6] reported data for atactic polystyrene as received and also for annealed material. The average molecular mass according to light scattering for the material used by Karasz, namely N.B.S. No. 706 was indicated with $258000 \text{ g mol}^{-1}$. The calo-

Table 1a Selected literature data for the specific heat of atactic polystyrene, collected for the temperature range 10 to 200 K

<i>T</i> / K	NIST [3] SRM 705a/ J g ⁻¹ K ⁻¹	Karasz <i>et al.</i> [6] as received/ J g ⁻¹ K ⁻¹	Karasz <i>et al.</i> [6] annealed/ J g ⁻¹ K ⁻¹	Marsh [7]/ J g ⁻¹ K ⁻¹	Abu-Isa, Dole [9]/ J g ⁻¹ K ⁻¹	ATHAS [10] exp./ J g ⁻¹ K ⁻¹	Mean lit. values ¹ / J g ⁻¹ K ⁻¹	Stand. dev. of mean lit. values/ %
10	0.0321			0.0321		0.0320	0.0320	0.004
15	0.0673							
20	0.1033			0.1033		0.1034	0.1033	0.002
25	0.1379							
30	0.1699					0.1678	0.1689	0.11
35	0.1993							
40	0.2262			0.2266		0.2221	0.2250	0.15
45	0.2510							
50	0.2739					0.2689	0.2714	0.25
60	0.3159			0.3159		0.3108	0.3142	0.17
70	0.3543					0.3493	0.3518	0.25
80	0.3905			0.3908		0.3857	0.3890	0.17
90	0.4250	0.4255				0.4207	0.4237	0.15
100	0.4581	0.4573		0.4580		0.4548	0.4570	0.08
110	0.4903	0.4897				0.4885	0.4895	0.05
120	0.5241	0.5229		0.5242		0.5221	0.5233	0.05
130	0.5563	0.5567				0.5558	0.5563	0.02
140	0.5899	0.5911		0.5895		0.5898	0.5901	0.04
150	0.6242	0.6263				0.6242	0.6249	0.00
160	0.6592	0.6621		0.6596		0.6591	0.6600	0.07
170	0.6950	0.6987				0.6947	0.6961	0.01
180	0.7359	0.7359		0.7316		0.7311	0.7326	0.11
190	0.7695	0.7737				0.7682	0.7705	0.17
200	0.8081	0.8123		0.8084		0.8062	0.8088	0.13

¹mean of the selected literature values for the corresponding temperature

Table 1b Literature data for the specific heat of atactic polystyrene, collected for the temperature range 210 to 470 K. Values are given for each of the literature only for the temperature intervals reported. See the text for the explanations to each of the literature set cited here. Literature data for the specific heat capacity are mainly measured by adiabatic calorimetry with one exception [10]

<i>T</i> /K	NIST [3] SRM 705a/ J g ⁻¹ K ⁻¹	Karasz <i>et al.</i> [6] as received/ J g ⁻¹ K ⁻¹	Karasz <i>et al.</i> [6] annealed/ J g ⁻¹ K ⁻¹	Marsh [7]/ J g ⁻¹ K ⁻¹	Abu-Isa, Dole [9]/ J g ⁻¹ K ⁻¹	ATHAS [10] exp./ J g ⁻¹ K ⁻¹	Mean lit. values ¹ / J g ⁻¹ K ⁻¹	Stand. dev. of mean lit. values/ %
210	0.8476	0.8515				0.8452	0.8481	0.18
220	0.8881	0.8835		0.8881	0.8579	0.8851	0.8806	0.57
230	0.9293	0.9265			0.9008	0.9217	0.9196	0.65
240	0.9717	0.9695		0.9717	0.9436	0.9615	0.9636	0.53
250	1.0139	1.0125			0.9865	1.0026	1.0039	0.63
260	1.0571	1.0555		1.0571	1.0293	1.0450	1.0488	0.54
270	1.1003	1.0985			1.0721	1.0883	1.0898	0.65
280	1.1435	1.1415		1.1445	1.1150	1.1324	1.1354	0.55
290	1.1877	1.1845			1.1578	1.1773	1.1773	0.52
300	1.2319	1.2275		1.2319	1.2007	1.2228	1.2232	0.48
310	1.2760	1.2705			1.2435	1.2689	1.2658	0.57
320	1.3211	1.3135	1.1793		1.2863	1.3154	1.3121	0.53
330	1.3653	1.3565	1.3607		1.3292	1.3624	1.3548	0.66
340	1.4104	1.3995	1.4060		1.3720	1.4097	1.4014	0.61
350	1.4556	1.4425	1.4514			1.4574	1.4517	0.33
360		1.4855	1.4967	1.5007		1.5054	1.4971	0.42
370		1.5285				1.5536	1.5411	1.26
380		1.8510		1.8675	1.8217		1.8467	1.34
390		1.8860			1.8471		1.8665	1.95
400		1.9210		1.9299	1.8725		1.9078	1.78
410		1.9560			1.8979		1.9269	2.91
420		1.9910		1.9923	1.9233		1.9688	2.28
430		2.0260			1.9487		1.9873	3.87
440		2.0610		2.0547	1.9741		2.0299	2.80
450		2.0960			1.9995		2.0478	4.83
460		2.1310		2.1171	2.0249		2.0910	3.33
470		2.1660			2.0503		2.1082	5.78

¹mean of the selected literature values for the corresponding temperature

Table 2 The linear functions of the specific heat of atactic polystyrene are collected. These functions were calculated from the data given in Tables 1a and b for the corresponding literature. The glass transition temperatures given by the authors are listed and also the corresponding specific heat capacity values for the liquid amorphous and the vitreous state. In addition the differences of the specific heat capacities are shown for the relevant glass transition temperature

Source	Sample identification, history	Linearization limits/K	$c_{p,vit}=aT+b/J \text{ g}^{-1} \text{ K}^{-1}$	$c_{p,liq-am}=aT+b/J \text{ g}^{-1} \text{ K}^{-1}$	T_g/K	$c_{p,liq-am} \text{ at } T_g^g / \text{J g}^{-1} \text{ K}^{-1}$	$c_{p,vit} \text{ at } T_g^g / \text{J g}^{-1} \text{ K}^{-1}$	$\Delta c_p \text{ at } T_g^g / \text{J g}^{-1} \text{ K}^{-1}$
NIST SRM 705a Certificate 1990 [3]	SRM 705a, as received	220–350	$c_{p,vit}=0.004373 T-0.078236$					
Karasz <i>et al.</i> 1965 [6]	NBS No. 706 as received, vacuum dried at 80°C for 24 h	220–470	$c_{p,vit}=0.00430 T-0.06250$	$c_{p,liq-am}=0.0035 T+0.5210$	357 ²	1.7705	1.4726	0.298
Karasz <i>et al.</i> 1965 [6]	NBS No. 706 annealed from 480 to 290 K at 10 K h ⁻¹	293–379	$c_{p,vit}=0.00453 T-0.135554$	$c_{p,liq-am}=0.00302 T+0.71706$	365 ²	1.819	1.518	0.301
Marsh 1987 [7]	NIST SRM 705, 706, 1478 amorphous heat capacity data from experiments	200–460	$c_{p,vit}=0.00431 T-0.06056$	$c_{p,liq-am}=0.00312 T+0.68170$	370	1.836	1.534	0.302
ATHAS 1996 [10]		240–500	$c_{p,vit}=0.00457 T-0.14409$	$c_{p,liq-am}=0.00255 T+0.91328$	370	1.8568	1.5468	0.310
Abu-Isa, Dole 1965 [9]	PS from Dow Chemical Co., as received	223–430	$c_{p,vit}=0.00428 T-0.08454$	$c_{p,liq-am}=0.00254 T+0.85646$	366	1.786	1.4819	0.304
Mean values stand. dev. of mean					369±2	1.814±0.01	1.511±0.01	0.303±0.002

¹Literature data evaluated in this paper by linear regression for the glassy and the liquid amorphous state

²Values not used for mean, 0.8% volatile material not removed by drying and annealing [8]

rimetric instrument applied for the measurement of the heat capacity was a wide temperature range modification of an adiabatic design. The data were presented by Karasz as specific heat capacities for the temperature range of 90 to 474 K and for the annealed sample from 293 to 378 K. The precision of the instrument was previously to the measurements with polystyrene assessed by Karasz *et al.* with the determination of the heat capacity of a standard sample of alumina. The errors in the heat capacity were estimated to an average of $\pm 0.2\%$ up to about 400 K, and for higher temperatures to about $\pm 0.4\%$.

Marsh [7] reported the heat capacities of atactic polystyrene as mean values for three different standard reference materials, namely SRM 705 and SRM 1478 both references with a narrow molecular mass distribution and the latter with a mass-average mean of $374000 \text{ g mol}^{-1}$. The SRM 706 was characterized with a broad molecular mass distribution. The heat capacity was measured with adiabatic calorimetry for the temperature ranges 10–360 K, 6–380 K and 20–470 K, respectively. Marsh states that the heat capacities in the glassy state below 340 K are relatively insensitive to the molecular mass distribution and the thermal history. However, above the glass transition temperature the heat capacity is highly reproducible for the individual sample. A kinetically influenced glass transition occurs around 370 K.

Wunderlich reported in the Athas Databank two sets of data, namely in 1993 from internal energy modes calculated heat capacities [8] over a temperature interval from 0.1 to 1000 K. The second data set ‘polystyrene experimental data’ were given in the glassy state from 10 to 370 K [10]. Only the latter set has been integrated in this paper.

Abu-Isa and Dole [9] reported specific heat functions for an atactic polystyrene of a high purity received from The Dow Chemical Co. with a high molecular mass ($240000 \text{ g mol}^{-1}$). The values in Table 1b were calculated from these functions, which were given in the glassy state from 220 to 338 K and in the amorphous liquid state from 378 to 548 K.

The specific heat functions from the literature data and also for the calculated mean are graphically presented in the following for the glassy and the liquid amorphous state.

The data for the specific heat of polystyrene presented in Tables 1a and b have been transferred for each of the data sets into specific heat functions for the glassy and also for the liquid amorphous state. The functions were calculated from the data sets by a linear regression according to the following equation

$$c_{p,i} = a_i T + b_i \quad (1)$$

where i – vit, lq-am, vit – corresponds to vitreous or glassy phase, lq-am – corresponds to liquid amorphous phase.

The data from the NIST Certificate for the SRM 705a are shown in Figs 1a and b together with the corresponding equations. In Fig. 1a is the specific heat function of polystyrene shown from 10 to 350 K and also the corresponding polynomial equation. Figure 1b represents the linear equation of the specific heat function for the glassy state of polystyrene in the temperature interval from 220 to 350 K.

In addition, the data are also presented with a linear function.

The specific heat functions obtained from the mean literature values, namely the mean of the data calculated for all selected temperatures of Table 1b, are presented in Fig. 2 for the range from 300 to 420 K.

The glass transition temperatures were collected from the literature and represented in K. The only exception is the glass transition temperature for the sample NBS No. 706, because Karasz [6] did not give a value and the specific heat curve reveals a relaxation peak. The glass transition temperature of 357 K was evaluated by us according to the procedure described by Mathot [11] for glass transitions revealing such a relaxation peak. Finally, the glass transition tempera-

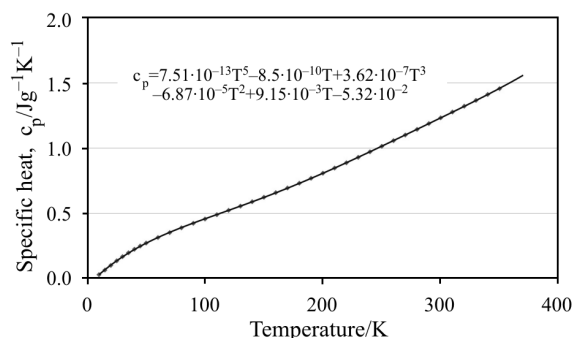


Fig. 1a Non-linear specific heat function for polystyrene SRM 705a in the glassy state calculated from NIST Certificate for the range of 10 to 350 K

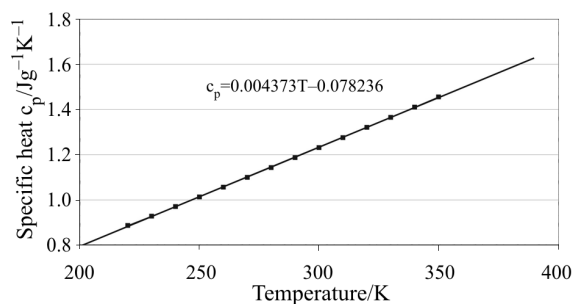
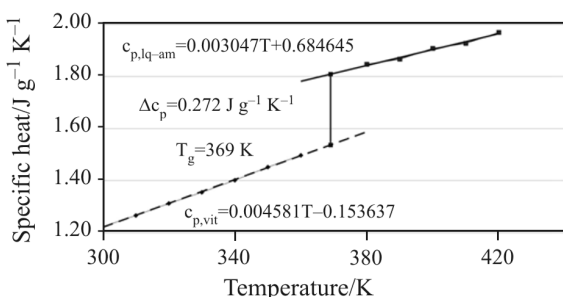


Fig. 1b Linear specific heat function for polystyrene SRM 705a in the glassy state calculated from NIST Certificate for the range 220 to 350 K

Table 3a Evaluation of mean literature data (see mean literature values in Table 1b, column 8) to get the coefficients for the linear specific heat functions of atactic polystyrene. The change of the specific heat at the $T_g=369$ K is calculated from the corresponding data of these functions

$c_{p,vit}=aT+b$ linearization range 300–360 K/J g ⁻¹ K ⁻¹	$c_{p,lq-am}=aT+b$ linearization range 380–420 K/J g ⁻¹ K ⁻¹	T_g /K	Δc_p at T_g /J g ⁻¹ K ⁻¹
$c_{p,vit}=4.581 \cdot 10^{-3}T-0.153637$	$c_{p,lq-am}=3.047 \cdot 10^{-3}T+0.684645$	369	0.272

**Fig. 2** Specific heat functions for atactic polystyrene in the glassy and in the liquid amorphous state determined from the mean literature values presented in Table 1b. Linear approximations in the vicinity of the glass transition temperature are shown

ture was taken as the mean from the selected values in the cited literatures. The two values from Karasz *et al.* were omitted because the authors reported about a considerable content of impurities. The mean value and its standard deviation is $T_g=369\pm 2$ K (Table 2).

The change of the specific heat at this glass transition temperature is given in Fig. 2 with $c_p=0.272$ J g⁻¹ K⁻¹ calculated with the specific heat functions of the mean literature values (Table 3a).

All in Tables 1a and b presented literature data sets for the specific heat are collected in Table 2 for each of the literature incorporated in this paper as linear functions representing the two states of polystyrene.

The specific heat values at these glass transition temperatures have been taken from the extrapolated linear functions. The differences of the specific heats for the liquid amorphous state and the glassy state have been calculated and are also presented in Table 2. The linear functions were calculated for the given temperature limits, namely for the glassy state within the lower limit and the glass transition temperature and in the liquid amorphous state within the glass transition and the upper limit.

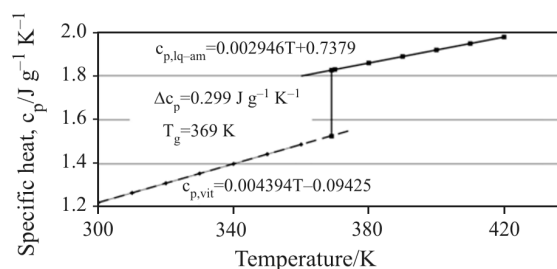
In another step, the change of the specific heat at the glass transition temperature was calculated as the

difference between the values in the liquid amorphous and the glassy state. The change of the specific heat for the mean value of the glass transition temperature is evaluated as $c_p=0.303\pm 0.002$ J g⁻¹ K⁻¹.

Tables 3a and b comprises two mean values for all the data shown in Table 2.

The specific heat functions in Table 3a for the glassy and the liquid amorphous state are presented as the specific heat functions obtained by the data of the selected literatures and evaluated for each of the reported temperatures as the mean data point (Fig. 2).

The second mean is the so-called mean function of the single specific heat functions calculated from the literature data in Table 2. These functions were unified into a single function for the vitreous state and for the liquid amorphous state, respectively. This was achieved by the formation of the mean of the coefficients for the linear functions and therefore the standard deviations could be calculated. The mean functions for the glassy and the liquid amorphous state of atactic polystyrene are shown in Table 3b as well as in Fig. 3 for the temperature range 300 to 420 K. The change of the specific heat was calculated for the mean value of the glass transition temperatures of 369 K. The error of the Δc_p was determined by the specific heat functions transferred by the standard deviations of the coefficients for the linear equations.

**Fig. 3** Mean functions of the specific heat for atactic polystyrene. The mean of the coefficients for the linear functions were taken from the cited equations for the given publications shown in Table 2**Table 3b** The second set of specific heat functions as representing mean equations for the glassy and the liquid amorphous state, represented by the linear coefficients were calculated by the mean values of the captioned coefficients for the selected and evaluated literatures for the atactic polystyrene

$c_{p,vit}=aT+b$ linearization range 300–360 K/J g ⁻¹ K ⁻¹	$c_{p,lq-am}=aT+b$ linearization range 380–420 K/J g ⁻¹ K ⁻¹	T_g /K	Δc_p at T_g /J g ⁻¹ K ⁻¹
$c_{p,vit}=(4.394\pm 0.051) \cdot 10^{-3}T-(9.425\pm 1.493) \cdot 10^{-2}$	$c_{p,lq-am}=(2.946\pm 0.166) \cdot 10^{-3}T+(0.7379\pm 0.0631)$	369±2	0.303±0.002

These coefficients were determined by the greatest influence of the corresponding standard deviations.

DSC experiments and results

DSC experiments have been undertaken with different sample sizes of polystyrene SRM 705a and also with different heating rates. The idea was to investigate the experimental conditions for measurements of the specific heat and to check the accuracy and the reproducibility of the DSC method. The calibration with sapphire, the baseline stability and the evaluation and transfer of the measured heat flow curves into functions of the molar heat capacities or the specific heat are parts of the investigations.

The reproducibility and the accuracy were proofed with a measurement of 19.404 mg polystyrene SRM 705a in the DSC 204 equipped with the μ -sensor. The sample was cooled to -50°C with 20 K min^{-1} and heated to 140°C with 2.5 K min^{-1} , in total four consecutive cycles. The baseline corrected heat flow curves for the first scan of 19.404 mg polystyrene SRM 705a and for 27.788 mg of sapphire are shown in Fig. 4a. These heat flow curves are evaluated with the Netzsch software Proteus[®] for a determination of the specific heat curve. Equal evaluations were performed for the additional 3 cycles and all four curves are presented in the temperature interval from 280 to 410 K in Fig. 4b. Additionally, the specific heat values are listed for selected temperatures in the vitreous and in the liquid amorphous state for a comparison in Fig. 4b.

The SRM 705a, supplied in small rodlets obtained by the granulation process following the polymerization, reveals in the first DSC scan a relaxation peak in the glass transition region.

The data evaluated from the four consecutive measurements of the specific heat shown in Fig. 4b are collected in Table 4 as mean values from 240

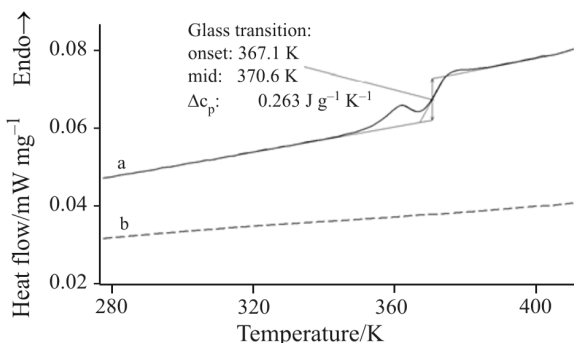


Fig. 4a DSC curves of polystyrene SRM 705a with a sample mass of a – 19.404 mg and for sapphire with b – 27.788 mg, first heating for PS with a heating rate of 2.5 K min^{-1} . The μ -sensor was installed in the DSC 204

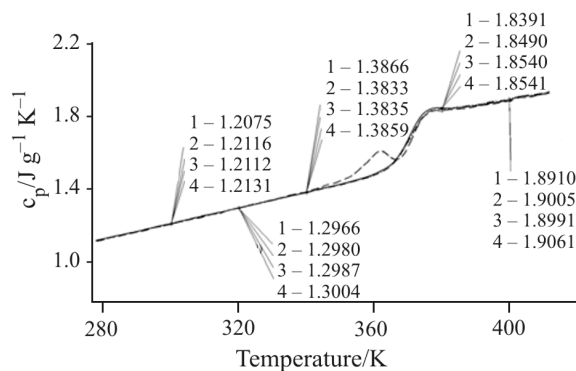


Fig. 4b Temperature dependence of the specific heat of atactic PS, sample size 19.404 mg, heating rate 2.5 K min^{-1} ; four consecutive runs from 280 to 410 K. The consecutive curves are indicated with 1 – 4

410 K in intervals of 10 K. The reproducibility, given as relative values of the standard deviation of the experimental mean, is shown in Table 4. In addition, the deviations of our experimental mean values from the NIST [3] as well as from the mean literature values were calculated according to Eq. (2) and the values obtained are also listed.

$$r_e = \frac{c_p^{\text{Lit.}} - c_p^{\text{exp}}}{c_p^{\text{Lit.}}} 100 \quad (2)$$

In Fig. 5 the functions of the specific heat for atactic polystyrene SRM 705a are presented for the vitreous as well as for the liquid amorphous state. The functions were calculated from the mean values of the four consecutive measurements using a sample mass of 19.404 mg. The difference of the specific heat between the liquid amorphous and the vitreous phase is calculated as $\Delta c_p = 0.296\text{ J g}^{-1}\text{ K}^{-1}$ for the glass transition temperature of 371 K. This value was experimentally determined from the heat flow curve.

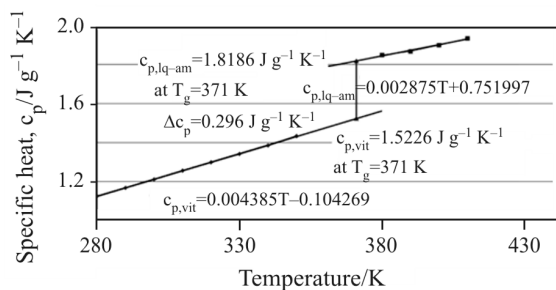
In another experiment with the same material using the sample mass of 10.896 mg we determined the specific heat values from the heat flow curve. The sample was heated from 220 to 410 K with a heating rate of 2.5 K min^{-1} . The calibration was performed using sapphire with a mass of 28.163 mg. The results for the measured specific heats are shown in Table 5 as well as in Fig. 6. Comparisons are made with PS from NIST, namely SRM 705a and the mean literature values and the standard deviations are presented.

TMDSC experiments and results

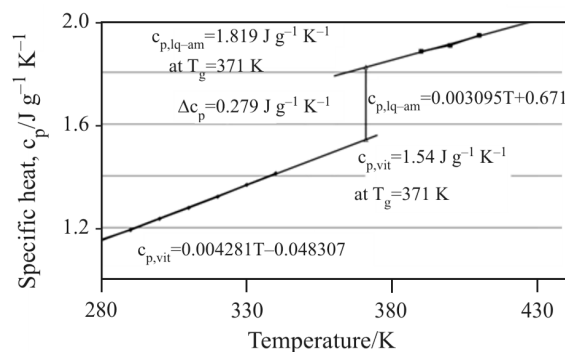
The DSC 204 F1 equipped with the τ -sensor has been extended to perform temperature modulated experiments. The method has been thermodynamically evaluated with the determination of the specific heat and the glass transition temperature applying the reference material for atactic polystyrene, namely

Table 4 Reproducibility and accuracy of c_p determinations from our DSC measurements with 19.404 mg atactic polystyrene, comparison with NIST data for SRM 705a and the mean literature values (Table 1b)

T/K	Exp. mean of 4 curves ¹ / $J g^{-1} K^{-1}$	Reproducibility/ %	NIST [3] SRM 705a/ $J g^{-1} K^{-1}$	Deviation exp. from NIST/ %	Mean lit. values/ $J g^{-1} K^{-1}$	Deviation exp. from mean lit./ %
240	0.9465	0.11	0.9717	2.6	0.9636	1.8
250	0.9877	0.11	1.0139	2.6	1.0039	1.6
260	1.0277	0.08	0.0571	2.8	1.0488	2.0
270	1.0859	0.09	1.1003	1.3	1.0898	0.4
280	1.1242	0.13	1.1435	1.7	1.1354	1.0
290	1.1673	0.09	1.1877	1.7	1.1773	0.9
300	1.2109	0.12	1.2319	1.7	1.2232	1.0
310	1.2553	0.12	1.2760	1.6	1.2658	0.8
320	1.2984	0.08	1.3211	1.7	1.3121	1.0
330	1.3416	0.07	1.3653	1.7	1.3548	1.0
340	1.3848	0.08	1.4104	1.8	1.4014	1.2
350	1.4328	0.52	1.4556	1.6	1.4517	1.3
360	1.5094	2.72			1.4971	-0.8
370	1.6561	0.90			1.5411	-7.5
380	1.8491	0.35			1.8467	-0.1
390	1.8673	0.21			1.8665	0.0
400	1.8992	0.31			1.9078	0.5
410	1.9342	0.20			1.9269	-0.4

¹19.404 mg PS NIST SRM 705a, 4 consecutive runs, 2.5 K min⁻¹**Fig. 5** Specific heat functions for atactic polystyrene in the glassy and the liquid amorphous state as mean functions for four consecutive runs with a sample mass of 19.404 mg. Calculations were made from the experimental mean values from Table 4, second column

SRM 705a. Experimental conditions such as crucible types, sample size and shape, underlying heating rate, modulation parameters were tested. The sample of polystyrene with 12.570 mg was cooled to 220 K and then heated to 430 K using a heating rate of 2 K min⁻¹ under sinusoidal modulation, applying cycles of a period of 90 s and an amplitude of 0.3 K. Linear cooling to 220 K was executed with 20 K min⁻¹. The second heating was made under equal conditions as the first one. The temperature segment around the glass transition of polystyrene is shown for the second heating in Fig. 7 over the temperature interval from 340 to

**Fig. 6** Linear functions of the specific heat and change of the specific heat at the glass transition for atactic polystyrene SRM 705a with a mass of 10.896 mg, determined for the vitreous phase with data in the limits 290–340 K and for the liquid amorphous phase within the limits 385–405 K

400 K. The measured heat flow forced by the sinusoidal temperature modulation is registered. The total heat flow curve as well as the relevant glass transition temperatures and the corresponding change of the heat capacity, evaluated by the Proteus[®] software, are documented.

The TMDSC heat flow curves for first and second heating have been transferred to the specific heat functions by using sapphire with a mass of 12.720 mg as calibration substance. The mean of the experimen-

Table 5 Accuracy of specific heat determination for polystyrene SRM 705a using a sample mass of 10.896 mg and applying a heating rate 2.5 K min⁻¹ shown in comparison with the NIST SRM 705a data and with the mean literature values

T/ K	Exp. values/ J g ⁻¹ K ⁻¹	NIST [3] SRM 705a/ J g ⁻¹ K ⁻¹	Dev. exp. from NIST/ %	Mean lit. values/ J g ⁻¹ K ⁻¹	Dev. exp. from mean lit./ %
240	0.9835	0.9717	-1.2	0.9636	-2.1
250	1.0251	1.0139	-1.1	1.0039	-2.1
260	1.0648	1.0571	-0.7	1.0488	-1.5
270	1.1172	1.1003	-1.5	1.0898	-2.5
280	1.1548	1.1435	-1.0	1.1354	-1.7
290	1.1909	1.1877	-0.3	1.1773	-1.2
300	1.2344	1.2319	-0.2	1.2232	-0.9
310	1.2763	1.2760	0.0	1.2658	-0.8
320	1.3196	1.3211	0.1	1.3121	-0.6
330	1.3654	1.3653	0.0	1.3548	-0.8
340	1.4096	1.4104	0.1	1.4014	-0.6
350	1.4680	1.4556	-0.9	1.4517	-1.1
360	1.6062			1.4971	-7.3
370	1.6299			1.5411	-5.8
380	1.8675			1.8467	-1.1
390	1.8807			1.8665	-0.8
400	1.9037			1.9078	+0.2
410	1.9426			1.9269	-0.8

¹10.896 mg PS NIST SRM 705a, heating rate 2.5 K min⁻¹

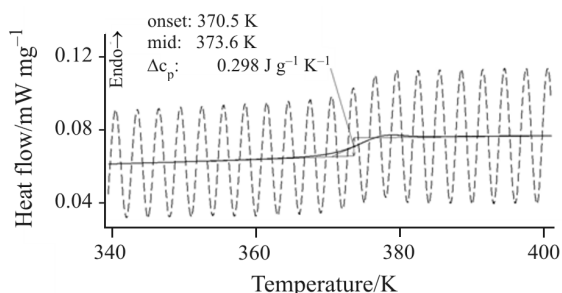


Fig. 7 TMDSC for atactic polystyrene SRM 705a with sample of 12.570 mg. Experimental conditions: underlying heating rate 2 K min⁻¹, sinusoidal modulation, period 90 s, amplitude 0.3 K. Represented are for the second scan the modulated heat flow and the mean value of the heat flow rate (total heat flow)

tal values for the heat capacities are compared in Table 6 with the values from NIST for SRM 705a and also with the mean literature values from Table 1b.

The evaluation of the specific heat for the TMDSC experiment on atactic polystyrene SRM 705a with a mass of 16.120 mg is presented for the first heating in Fig. 8. The measurements with the polystyrene and the calibration with sapphire were performed under identical experimental condition as applied for the determinations of the specific heat described above for the sample of 12.570 mg. The evaluation with the software Proteus[®] supplies the total

specific heat and the reversing and non-reversing c_p or the real and complex heat capacity curves. The accuracy of the specific heat capacity values are evaluated from the temperature modulated measurement using the second heating and specifically the part of the reversing c_p . The evaluated curves, namely the total heat capacity function and the reversing and non-reversing c_p are shown in Fig. 8. The specific heat values measured for PS SRM 705a and taken from the reversing c_p are comprised in Table 7, also

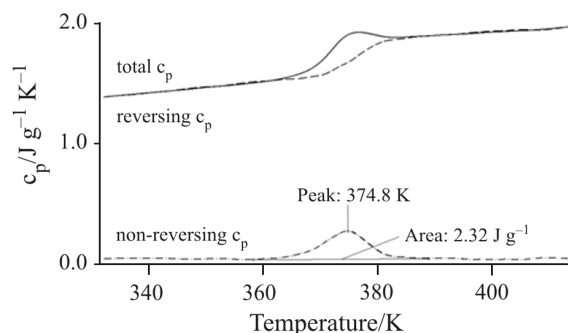


Fig. 8 TMDSC for atactic polystyrene SRM 705a with sample mass of 16.120 mg. Experimental conditions: underlying heating rate 2 K min⁻¹, sinusoidal modulation, period 90 s, amplitude 0.3 K. Represented are the total, the reversing and the non-reversing specific heat curves for the temperature region from 330 to 410 K. Calibration was performed with sapphire of 12.720 mg

Table 6 Experimental values and their mean of the specific heat for atactic polystyrene of 12.570 mg for the first and the second heating. Comparison of the data measured by TMDSC with literature values

T/K	Exp. values ¹ 1 st heating/ J g ⁻¹ K ⁻¹	Exp. values ¹ 2 nd heating/ J g ⁻¹ K ⁻¹	Experimental mean/ J g ⁻¹ K ⁻¹	NIST [3] SRM 705a/ J g ⁻¹ K ⁻¹	Dev. exp. mean from NIST SRM 705a// %	Mean lit. values/ J g ⁻¹ K ⁻¹	Dev. exp. mean from mean lit. values/%
240	0.9391	0.9409	0.9400	0.9717	3.3	0.9636	2.4
250	0.9876	0.9947	0.9912	1.0139	2.2	1.0039	1.3
260	1.0322	1.0378	1.0350	1.0571	2.1	1.0488	1.3
270	1.0737	1.0746	1.0742	1.1003	2.4	1.0898	1.4
280	1.1165	1.1121	1.1143	1.1435	2.6	1.1354	1.9
290	1.1548	1.1518	1.1533	1.1877	2.9	1.1773	2.0
300	1.2005	1.1926	1.1966	1.2319	2.9	1.2232	2.2
310	1.2446	1.2391	1.2419	1.2760	2.7	1.2658	1.9
320	1.2870	1.2803	1.2837	1.3211	2.8	1.3121	2.2
330	1.3324	1.3229	1.3277	1.3653	2.8	1.3548	2.0
340	1.3730	1.3686	1.3708	1.4104	2.8	1.4014	2.2
350	1.4215	1.4120	1.4168	1.4556	2.7	1.4517	2.4
360	1.4643	1.4546	1.4595			1.4971	2.5
370	1.5456	1.5052	1.5254			1.5411	1.0
380	1.7949	1.7484	1.7717			1.8467	4.1
390	1.8469	1.8289	1.8379			1.8665	1.5
400	1.9076	1.8902	1.8989			1.9078	0.5
410	1.9736	1.9492	1.9614			1.9269	-1.8

¹12.570 mg PS NIST SRM 705a, reversing c_p evaluated from TMDSC for the 1st and 2nd heating**Table 7** Specific heat values for a sample of 16.120 mg atactic polystyrene SRM 705a measured by TMDSC, second heating, comparison of experimental data with literature data

T/K	Exp. values 2 nd scan ¹ / J g ⁻¹ K ⁻¹	NIST [3] SRM 705a/ J g ⁻¹ K ⁻¹	Dev. exp. from NIST/ %	Mean lit. values/ J g ⁻¹ K ⁻¹	Dev. exp. from mean lit./%
240	0.9732	0.9717	-0.2	0.9636	-1.0
250	1.0098	1.0139	0.4	1.0039	-0.6
260	1.0545	1.0571	0.2	1.0488	-0.5
270	1.0983	1.1003	0.2	1.0898	-0.8
280	1.1424	1.1435	0.1	1.1354	-0.6
290	1.1828	1.1877	0.4	1.1773	-0.5
300	1.2282	1.2319	0.3	1.2232	-0.4
310	1.2692	1.2760	0.5	1.2658	-0.3
320	1.3134	1.3211	0.6	1.3121	-0.1
330	1.3473	1.3653	1.3	1.3548	0.6
340	1.3906	1.4104	1.4	1.4014	0.8
350	1.4376	1.4556	1.2	1.4517	1.0
360	1.4766			1.4971	1.4
370	1.5564			1.5411	-1.0
380	1.8160			1.8467	1.7
390	1.8791			1.8665	-0.7
400	1.9144			1.9078	-0.3
410	1.9355			1.9269	-0.4

¹16.120 mg PS NIST SRM 705a, reversing c_p evaluated from a second heating in TMDSC

for the second heating, together with the literature values from NIST and the elucidated mean literature values. Relative deviations from both of the literature data sets are also shown.

The experimental values presented as linear specific heat functions in Table 8 are data from several experiments, namely DSC measurements with 19.404, respectively 10.896 mg polystyrene. The functions with TMDSC were determined for the sample with 12.570 mg by using the data points obtained as mean values and for the experiment with 10.896 mg with a single data set. A comparison with the corresponding specific heat functions as mean values from literature shown in Table 3b is made available.

Glass transition

The glass transition as a change of an amorphous or partially amorphous substance or material from a solid into a liquid state or vice versa has a certain similarity with the melting process. Quite a number of physical characteristics are influenced by these transitions. The molecular arrangement changing from a highly ordered crystalline structure is transferred during the melting process into a liquid. The amorphous structure, however, randomly arranged in the glassy state, but with a certain structure for the nearest molecular distances is changing during the glass transition more or less gradually into a liquid state which is rather highly viscous. The glass transition affects – of course also the melting process – quite a number of properties of the substances and materials under investigation, namely among others the specific heat, the specific volume, the enthalpy, the entropy, the refracting index, the dielectric constant, the viscoelastic behavior. Formally and widely accepted in thermal analysis is the statement that a glass transition is a second-order phase transition. There are functional behaviors at the glass transition which are in favor of

such a thermodynamic description, namely that the function for the enthalpy and the volume only reveal an increased slope for the liquid amorphous state compared with the value in the glassy state. Furthermore, that the specific heat and the thermal expansion coefficient show at the glass transition temperature two discrete values which are higher for the liquid amorphous state than for the glassy state.

The experimental facts proof that the glass transition is depending on mechanical, chemical (solidification after the chemical production processes) and also the thermal history. Specifically, the change of the experimental conditions in cooling and heating for a given sample will also influence the glass transition of an amorphous polymer or of an amorphous substance. The changes are related to the existence of a non-equilibrium state, a fact that can be observed in two ways. The first is a shift of the glass transition temperature even up to a few Kelvin. This shift is depending on the polymer under investigation, its treatments starting with the solidification and ending with the selected conditions during the actual measurement. The second change is related to endothermic processes overlapping with the glass transition. These enthalpy changes can be observed on heating or on cooling under certain cooling and heating rates. This second observation is also not only based on thermal history, but also on all kind of physical, chemical and mechanical treatments. The endothermic peak overlapping the glass transition on heating depends in its quantitative size and temperature position within or near the glass transition on the history of the polymer and also on the experimental conditions selected. Of course, such changes must be based on physico-chemical phenomena, which must have an influence on the quality or the physical structure of the glassy phase formed. There are equilibrium theories existing, one developed by Gibbs and DiMarzio [12], however, these theories could never be experimentally supported. A thermodynamic phase transition in-

Table 8 Specific heat functions for polystyrene SRM 705a obtained from experimental data. Comparison the specific heat functions evaluated from our measurements using DSC and TMDSC with literature mean values

Method/ source	Sample mass/ mg	No. of measurements	$c_{p,vit}=aT+b/J \text{ g}^{-1} \text{ K}^{-1}$	$c_{p,lq-am}=aT+b/J \text{ g}^{-1} \text{ K}^{-1}$
DSC	19.404	4	$c_{p,vit}=4.385 \cdot 10^{-3}T-0.104269$	$c_{p,lq-am}=2.875 \cdot 10^{-3}T+0.751997$
DSC	10.896	1	$c_{p,vit}=4.281 \cdot 10^{-3}T-0.048307$	$c_{p,lq-am}=3.095 \cdot 10^{-3}T+0.67100$
TMDSC	12.570	2	$c_{p,vit}=4.333 \cdot 10^{-3}T-0.101800$	not sufficient data
TMDSC	16.120	1	$c_{p,vit}=4.175 \cdot 10^{-3}T-0.026150$	$c_{p,lq-am}=3.938 \cdot 10^{-3}T+0.330740$
Exp. mean c_p functions+ standard dev.			$c_{p,vit}=(4.294 \pm 0.045) \cdot 10^{-3}T - (7.013 \pm 1.953) \cdot 10^{-2}$	$c_{p,lq-am}=(3.303 \pm 0.324) \cdot 10^{-3}T + (0.5846 \pm 0.1291)$
Literature mean c_p functions+ standard dev.			$c_{p,vit}=(4.394 \pm 0.051) \cdot 10^{-3}T - (9.425 \pm 1.493) \cdot 10^{-2}$	$c_{p,lq-am}=(2.946 \pm 0.166) \cdot 10^{-3}T + (0.7379 \pm 0.0631)$

dependent of the existing order, however, would require that the phases be in equilibrium in the temperature region of the transition.

The solid-state of a glassy polymer must be described thermodynamically as a non-equilibrium state depending on the kinetics of treatment. Therefore, quite different glassy states exist for a given polymer in respect to energetic situation caused by the density of the domain arrangement of the polymer structure. In addition to the thermodynamic variables of state, an internal order parameter is necessary for the description of the glassy state. This parameter was introduced by Fox and Flory [13] as the so-called free volume. This volume and also the enthalpy of vitrification, which is exothermic, depend among other parameter in the glassy state on the time scale of passing through the glass transition region. The time interval for the existence of the semi-liquid phase before the final glassy state is formed, allows the polymer molecules different relaxation movements of the whole molecule or of molecular segments. Such molecular movements are based on translatory and rotational diffusion. The viscosity of a polymer increases within the glass transition region by cooling down, the free volume is getting smaller and cooperative movements or jump processes are restricted more and more to smaller chain segments of the polymer molecules. The theoretical considerations of a polymer structure and its rotational diffusion were first published by Kuhn *et al.* [14]. The two extremes of the vitrification of a polymer are the quenching with liquid nitrogen and the other one, when the cooling rate for the polymer is close to zero. The first case allows practically no relaxation and the second case leads to a glassy state with an utmost stability and the lowest value of the free volume possible for a given polymer.

The different properties of a polymer affected by the glass transition make it obvious that several analytical methods may be applied for its investigation and for its analytical quantification. Each of the instrumental methods applied reveal a different sensitivity, which is a normal analytical fact. However, the glass transition temperatures which are measured for the same polymer applying several instrumental techniques are often not in agreement with differences up to 10 K. The kinetic dependence of the structure of the glassy state and the nature of the dependent, measured variable are the explanation for this fact.

The above statements of the complexity of the glass transition from a non-equilibrium state into a liquid amorphous state is for an analytically correct determination of the glass transition temperature and the change of the heat capacity at this temperature a real challenge. Of course, this is true for all of the analytical methods applied for the specific task. Let us re-

strict to the DSC and the TMDSC instrumentation. First of all, the analysis may be performed on two different levels, namely first on a thermoanalytical level with the evaluation of heat flow curves. The second procedure is an evaluation of the specific heat function, which is obtained from the heat flow curve by calibration preferably with the reference substance sapphire. The sapphire enables an outstanding calibration for the specific heat. The evaluation of the specific heat function for the glass transition temperature and the Δc_p for this temperature is on a thermodynamic level, which is always within the existing error limits a quantitative data set. The normative guidelines are neither consistent nor often based on heat flow curves. As an example for the glass transition, typical for guidelines, the following temperatures are given for possible evaluation of a glass transition: the glass transition temperature as inflexion point of the specific heat curve, as intersection with the half line of the change of the heat flow or the specific heat with the corresponding curve, the bisector of angle between the extrapolated specific heat curves below and after the glass transition. All these evaluated temperatures assigned as the glass transition are spread over several Kelvin. Additionally, the onset temperature is defined as a threshold value for the deflection from the practically linear specific heat function before the glass transition. Another onset is the so-called extrapolated onset as the intersection of the inflection line with the linear extrapolated specific heat curve below the glass transition. Corresponding end points as a threshold value and as an extrapolated endset are also defined.

The crucial point is the physico-chemical evaluation of the glass transition, a transition that is extremely important for a great many of technical applications.

Literature values for the glass transition temperature of PS were reported first by Tammann as a transformation observed at 368 K [15]. Fox and Flory [13] measured the glass transition temperature for PS with different molecular masses and reported for the extrapolation to a value with an infinite molecular mass the function shown in Eq. (3).

$$T_{g, \text{inf}} = T_{g, \text{exp}} + 1.1 \cdot 10^5 / M \quad (3)$$

where $T_{g, \text{inf}}$ – glass transition temperature for a polymer with an infinite molecular mass, $T_{g, \text{exp}}$ – measured glass transition temperature for a polystyrene with molecular mass M .

The literature values for the glass transition temperature are comprised for different proveniences of PS in Table 9. The molecular mass is given for the different samples as mean value in respect to the mass distribution. The measured and reported values for

Table 9 Literature data for the glass transition temperature of polystyrene. The molecular masses are given as mean values. Additionally the glass transition temperatures are corrected for the value obtained for an infinite molecular mass. The function for this extrapolation is taken from Fox and Flory [13]

Source	Sample identity, history	Molecular mass ¹ /g mol ⁻¹	$T_{g,exp}/K$	$T_{g,\infty}/K$
Karasz [6]	NBS No. 706 as received, vacuum dried at 80°C for 24 h	$2.6 \cdot 10^5$	$(357)^2$	–
Karasz [6]	NBS No. 706 annealed from 480 to 290 K at 10 K h ⁻¹	$2.6 \cdot 10^5$	$(362)^2$	–
Marsh [7]	NIST SRM 705, 706, 1478	$3.7 \cdot 10^4$	370	373
ATHAS [10]	amorphous heat capacity data from experiments	–	370	370
Abu-Isa, Dole [9]	PS from Dow Chemical Co., as received	$2.6 \cdot 10^5$	366	366
Fox and Flory [13]	–	$8.5 \cdot 10^4$	373	374
Beevers [16]	–	$7 \cdot 10^4$	368	369
Mean values			369.4 ± 1.2	370.4 ± 1.4

¹Mass-average molecular mass, ²values not used for mean

the glass transitions are collected in this table as well as the glass transition temperature extrapolated for an infinite high molecular mass.

Experiments and results on the glass transition

Experiments with polystyrene as Standard Reference Material SRM 705a from NIST were performed for the determination of the glass transition temperature in using the DSC 204 F1 Phoenix[®]. The μ -sensor was installed for the DSC measurements and the τ -sensor for the TMDSC.

DSC method was applied for a sample of PS with 23.235 mg and the curves are presenting this sample with different thermal history. The sample was heated to 410 K with a heating rate of 10 K min⁻¹. The cooling to 300 K was achieved with a free cooling procedure (estimated mean cooling rate about 1 K min⁻¹). The additional cooling from 300 to 220 K was performed with 5 K min⁻¹. A heating rate of 10 K min⁻¹ was applied for the measurement through the glass transition region to 410 K. This sample of polystyrene was then quenched within the sample crucible with liquid nitrogen. The consecutive heating with 10 K min⁻¹ was stopped at 410 K. The two DSC curves are presented in Fig. 9. The software Proteus[®] was used for the evaluation of the glass transition in respect to the characteristic temperatures and for the determination of the change of the specific heat at the glass transition temperature at the midpoint (intersection of the bisector of angle line with the curve).

The results are included in Table 10.

The glass transition of 16.120 mg polystyrene is shown in Fig. 10 measured and evaluated with the TMDSC. The reversing heat flow has been separated from the total heat flow curve and therefore the influ-

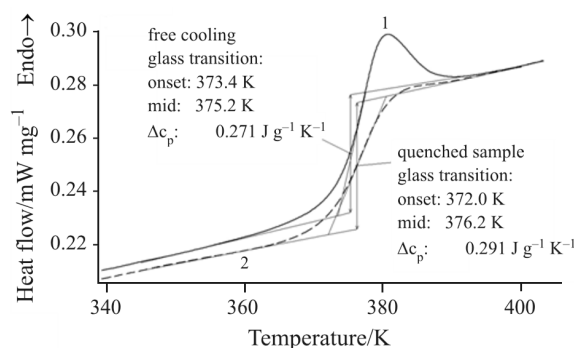


Fig. 9 DSC heat flow curves with a sample of polystyrene of 23.235 mg. 1 – with the sample free cooled to 300 K and restarted at 220 K. The heating rate was 10 K min⁻¹ to 410 K. 2 – obtained after quenching with liquid nitrogen applying the same heating rate with the start also at 220 K

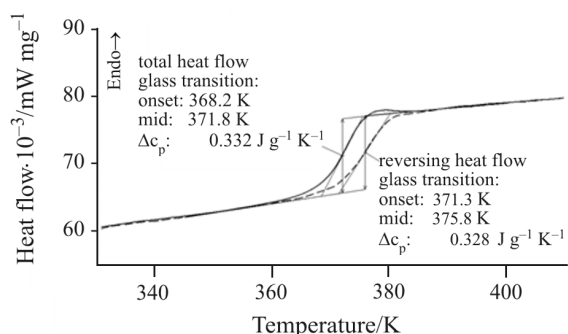
ence of the relaxation enthalpy to the evaluation of the glass transition temperature is eliminated.

A sample of polystyrene with 19.404 mg was used for consecutive runs. The first curve was obtained with sample material SRM 705a as received and heating with 2.5 K min⁻¹ from 280 to 410 K. The sample was then cooled to 220 K with a rate of 20 K min⁻¹ and heated up with 2.5 K min⁻¹. The same procedure was repeated another two times. The standard evaluations as for the sample with 23.235 mg were performed.

Another group of measurements was performed using four samples with sample masses between 3 and 8 mg. The cooling of the samples was identically, namely 0.1 K min⁻¹ from 410 to 310 K. The heating rate was selected with 2, 10, 50 and 100 K min⁻¹. DSC curves were evaluated for the glass transition temperature, the change of the specific heat during the transi-

Table 10 Glass transition temperatures, midpoint, the change of the specific heat at the T_g for polystyrene SRM 705a are collected. Also the relaxation peak, if existing is given quantitatively. Results for DSC and TMDSC measurements and for samples with different thermal histories are shown

Experimental method	Mass/mg	Thermal history	Heating rate/ K min ⁻¹	Relaxation peak/ J g ⁻¹ K ⁻¹	T_g (mid) corrected ¹ / K	Δc_p at T_g / J g ⁻¹ K ⁻¹
DSC	19.404	as received, 1 st heating	2.5	1.5	371	0.263
		410 to 220 K 20 K min ⁻¹ 2 nd heating		0.1	370	0.283
		3 rd heating		0.2	370	0.269
		4 th heating		0.1	370	0.285
DSC	23.235	free cooling from 410 K	10	0.8	373	0.271
		quenched N ₂ , liq.		0	374	0.291
DSC	7.82	cooling 0.1 K min ⁻¹ from 410 to 310 K	2	1.3	371	0.293
DSC	7.9	identical	10	2.3	376	0.337
DSC	4.67	identical	50	1.4	386	0.370
DSC	3.16	identical	100	0.3	388	0.395
TMDSC total heat flow	16.120	cooling 20 K min ⁻¹ from 410 to 330 K 2 nd heating	2 90s, 0.3 K	1.4	372	0.332
Reversing heat flow		identical	identical	0	376	0.328
Total heat flow		identical history 1 st heating	identical	2.5	371	0.312
Reversing heat flow		identical	identical	0	377	0.299

¹heating rate influence corrected from corresponding indium measurements**Fig. 10** Temperature modulated heat flow curves, presented for 16.120 mg polystyrene as total heat flow and in form of the reversing heat flow for the glass transition region. Influence of the relaxation peak to the glass transition temperature

tion and for the relaxation enthalpy. The results are shown in the Table 10.

Another measurement was undertaken, however with the temperature modulated DSC instrument. Polystyrene with a sample mass of 16.120 mg was cooled with 20 K min⁻¹ to 220 K. The sample was ex-

posed to a temperature modulated experiment with the following conditions: underlying heating rate 2 K min⁻¹ to the temperature at maximum of 410 K, sinusoidal modulation with 90 s cycles and an amplitude of 0.3 K. The total and the reversing c_p curves are presented in Fig. 8. The temperature modulated DSC curves – total and reversing heat flow curves – were evaluated for the glass transition data. The results are also included in Table 10.

Discussion

The heat capacity or the specific heat of polymers, organic and inorganic substances are essential thermodynamic functions. There are three groups of substances existing, first crystalline substances which reveal a continuous specific heat function for the temperature region of the existence for a given solid state. The second group is amorphous and the third are partially amorphous substances or materials. The most important indicator of an amorphous content for any substance or material is the glass transition. The

change of the specific heat at the glass transition temperature allows a quantification of the amorphicity of a substance. The existence of an amorphous content in a crystalline substance can be decisive for its stability and its applicability in quite different industrial areas. On the other hand, the glass transition temperature for polymers and materials restricts its application to certain temperature limits within the glassy or within the liquid amorphous state. In special cases also the pressure limits may play a role for specific applications.

Phase changes are normally related to an enthalpy change. Only rather exceptional solid state transformations such as specific polymorphic transitions may reveal an infinitely small enthalpy change.

Let us estimate the enthalpy ratio for a first order transformation, for a glass transition and compare it also with the energy uptake by an amorphous material with increasing temperature caused by the heat capacity. The ratios obtained for these transitions expose the demands on quality for the sensitivity and the resolution of instrumentation such as the DSC and TMDSC [1] in respect to the determination of the specific heat and the glass transition on a high quality level. First, the enthalpy ratio of the melting of a crystalline substance, phenacetin is selected as reference to compare with the enthalpy change for a glass transition, namely for polystyrene as an example. The melting point of phenacetin is 407 K and the enthalpy of fusion is 181 J g^{-1} [5]. The glass transition of polystyrene at 369 K reveals a specific heat change of $0.3 \text{ J g}^{-1} \text{ K}^{-1}$ (Table 2). The glass transition covers a temperature region of about 7 K, if we approximate this transition with the tangent at the inflexion point and the extrapolated on- and end-set. The enthalpy uptake of polystyrene over this temperature interval is estimated with 1 J g^{-1} . The physical expression of the comparison for the enthalpy changes shows in our case the 181 times higher enthalpy level for the transition of the crystalline state of phenacetin at the melting point to the value for the transition of the glassy state of polystyrene. The next comparison of the energy uptake is also made with polystyrene. The slope of the specific heat function for the glassy state is given in Table 3b as mean literature value $4.4 \cdot 10^{-3} \text{ J g}^{-1} \text{ K}^{-2}$. The enthalpy of about $2 \cdot 10^{-3} \text{ J g}^{-1}$ is necessary for the temperature increase of 1 K for atactic polystyrene having a molecular mass of about $1.8 \cdot 10^5$ within a temperature region of about 300 to 360 K. The enthalpy ratio of the enthalpy uptake of glassy polystyrene for the increase of 1 K to the melting process of phenacetin is 1 to $9 \cdot 10^4$ and the ratio to the enthalpy change of the glass transition of polystyrene is 1 to 500. The requirements on a DSC instrument or on a TMDSC for a heat capacity determina-

tion with a rather high precision are exceptional. The control of the precision of a DSC or TMDSC instrument in performing a reference measurement with a suitable reference material is a perfect test for the functionality of an instrument and its caloric calibration as well as a validation of the evaluation procedures for the applied software.

One of the central aims of this paper was a literature search for data existing for the specific heat of polystyrene. The literature data could be found in the temperature interval from 10 to 470 K. Six sets of data could be considered as valuable and are shown in Tables 1a and b. Each of the data sets was reported in different temperature intervals. The data sets allowed to obtain a mean value with a standard deviation on different statistical levels, one mean data had to be calculated with only two values, namely for 470 K. The standard deviations of the specific heat data from literature can be split into three precision regions as demonstrated in Fig. 11.

The first is overlapping the temperature interval from 10 to 210 K with a relative standard deviation for the specific heat of polystyrene of better than 0.2% and with a mean value of 0.09%. The next interval is 220 to the glass transition region of 360 K with a relative deviation of about 0.5%. The relative deviations above the glass transition from 370 to 470 K reveal a completely different picture, namely a practically linear function increasing in the given interval from 0.6 to 6%. The reproducibility or the precision of the specific heat values for the glassy state of atactic polystyrene, especially in consideration of the different provenances is excellent. The higher standard deviations in the temperature region above the glass transition to 470 K should find an explanation. The whole temperature region, namely from 10 to 470 K imposes no technical problems in any of the three intervals for the instrumentation as the literature data were obtained with one exemption by adiabatic

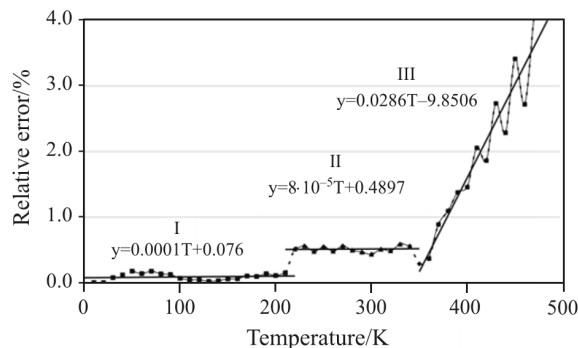


Fig. 11 The relative standard deviations of the mean literature values for the specific heat data from 10 to 470 K comprised in Tables 1a and b. Linear functions were calculated for the three existing accuracy intervals in respect to temperature

calorimetry, a method which is of an outstanding precision. Reasons for the behavior must be found in relation with the properties of polystyrene. The molecular movements of polystyrene are strongly increased in the liquid amorphous state compared with the glassy state. Chemical impurities such as monomers, oligomers, impurities from the polymerization among other substances will be present in any quality of polystyrene. Physical impurities, in a strict definition of the molecule also chemical impurities, are present in any polymer as molecules, namely polystyrene molecules with a smaller or greater molecular size compared to the average mean. The physical impurities are created during the polymerization. The molecular mass distribution and the mean value is mainly depending on the production pathway and production conditions selected. The molecular mass distribution has a minor influence on the specific heat as long as the standard deviation from the mean value is restricted to a few percent, which is the case for all the samples polystyrene for the literature data integrated in this paper as well as for the atactic polystyrene SRM 705a used in the experiments of this paper.

The question is now about the influence of all these possible impurities on the specific heat functions near the glass transition. The impurities are in the glassy state arranged in the loops and between the molecular chains of the polystyrene, or in the so-called free volume. The frozen-in structure of the polystyrene molecules restricts the movements of monomers, oligomers and other chemical impurities to certain small domains. Therefore, the contribution to the specific heat by these impurities is rather limited. Above the glass transition as well as during this transition also the main chain structure of polystyrene starts to get in motion, preferably in hindered rotational diffusion of segments [13, 14].

The movements of chain segments are extremely reduced by decreasing temperature in the glassy state already a few degrees below the glass transition temperature. The whole freezing-in is stepwise from chain movements to rotations of the phenyl rings and finally to mere bond oscillations. Finally, the glassy state approaches nearly the energy level of a crystalline state. Of course, the highly ordered crystalline structure cannot be reached. Furthermore, the final non-equilibrium state achieved on cooling depends also on the kinetic of the cooling process. Wunderlich and Bodily [17] reported about the glassy state of polystyrene revealing a frozen-in state, restriction to atomic oscillations, below 230 K. The specific heat function for polystyrene SRM 705a according to NIST [3] shows in Fig. 1a a rather broad change of the slope to a higher value around 190 K. Additionally, a stepwise increase of the standard deviation at 210 K is

indicated in Fig. 11 for the mean specific heat values of the literature data (NIST, Karasz, Marsh, and Athas). The increase of the standard deviation can be explained by the change of the molecular motions in the polystyrene, which enables an additional contribution of an enthalpy, sensitive to all or to specific impurities of the different qualities of polystyrene used for the reported measurements.

Another phenomena indicating a similar change is the weak transition, the so-called '50°C transition' observed for polystyrene [17]. The transition, also called β -transition is broad, overlaps an interval from 300 to 360 K and is observable by different methods such as the brittle point, the increasing viscosity important for tensile properties, the change of the dynamic mechanical loss, and also a NMR line width broadening. Dielectric constant and ultrasonic adsorption measurements show a decrease at 300 K. The explanation of this solid state transition beginning below the glass transition is a freezing-in of partial rotations of the phenyl groups, which is completed at about 300 K. This is a similar behavior as observed for the lambda transition of *n*-hexatriacontane, which is described as a hindered chain rotation, however occurring in a sharp temperature interval as a cooperative phenomenon [1].

The influence of physical and chemical impurities on the glass transition temperature is even more pronounced as in the case of the specific heat. Many impurities which can be dissolved in the corresponding polymer such as monomers, solvents, softeners react similar to an eutectic impurity in crystalline substances [5]. Therefore the results on the glass transition temperature given by Karasz in Tables 2 and 9 are omitted in this paper for the calculation of the mean. Karasz explained depressions in the order of several degrees by the presence of 0.8% of volatile materials, which could apparently not be removed by a drying procedure. Specifically, the polystyrene NBS 706 as received, however vacuum dried at 80°C gives a glass transition temperature, which is 12°C lower than the reported mean value. The glass transition temperature was 7°C below the mean even after annealing from 207 to 20°C with a cooling rate of 10 K h⁻¹. Similar findings of impurities which are strongly resisting any vacuum or thermal treatments may exist in organic molecules with a distorted crystalline structure. The physicochemical explanation of such low activities or partial pressures for low molecular impurities at considerable high temperatures and in this way a hindered diffusion process for these molecules out of the main substances could be a rather high interaction enthalpy between the main component and the guest molecules.

Table 2 contains linear functions of the specific heat in the glassy and in the liquid amorphous state in the vicinity of the glass transition for all the literature data integrated in our paper. The glass transition temperatures according to the literature and also the corresponding change of the specific heat are also presented. The glass transition temperature is as a mean calculated for selected values with 369 ± 2 K. The mean of the change of the specific heat at the mean value for the glass transition temperature is 0.303 ± 0.002 J g⁻¹ K⁻¹. The difference of the specific heat values at the glass transition calculated with the mean of the specific heats from the single literature data is 0.303 ± 0.01 J g⁻¹ K⁻¹. The standard deviations for the latter difference are 5 times greater. It can be explained by the fact that systematic errors of the single literature data are identical for the glassy as well as for the liquid amorphous state. Therefore, some of the systematic errors are eliminated by the calculation of the mean values for each of the reported literature. The mean values of the glass transition and the corresponding change of the specific heat are according to the literature on a high precision level.

The mean values for the specific heat functions in the vicinity of the glass transition for atactic polystyrene were calculated from the mean literature values. The calculated data are shown in Table 3a. Here, the mean of the data points for each of the temperatures were calculated and with the obtained data the linear functions in both of the states determined. The functions are also presented in Fig. 2.

In another approach, the mean functions of the specific heat for atactic polystyrene are collected for the two states in Table 3b. Here, the specific heat functions for each literature data set were determined and then the mean coefficients and their standard deviations were calculated. The latter approach seems obviously the correct one.

The first measurement with 19.404 mg polystyrene SRM 705a is presented in Fig. 4a as heat flow curve together with the curve for sapphire. The curve for polystyrene shows a relaxation peak at the beginning of the glass transition. The relaxation is not observed in the following consecutive curves obtained by heating with 20 K min⁻¹ to 410 K after identical cooling procedures to 220 K with 20 K min⁻¹. The relaxation is certainly caused by the solidification process during the polymerization of PS.

The calibration runs with sapphire are necessary to transfer the heat flow curves into the specific heat functions. The four consecutive runs for 19.404 mg polystyrene are shown in Fig. 4b. The specific heat curves reveal an outstanding reproducibility of the DSC 204 with relative standard deviations better or equal than 0.5%. Two values in the glass transition re-

gion, namely for 360 and 370 K have to be omitted because of the relaxation peak in the first scan. The mean values and the reproducibility for the specific heat are compared in Table 4 with literature values. The deviations from the NIST SRM 705a and from the mean of all the literature values are below 3% with a mean value of about 1.5%.

The specific heat functions calculated for the data of the four consecutive runs (Fig. 5) are in excellent agreement with the data for the mean functions of the literature values by comparing the coefficients of the linear functions and the standard deviations. The same statement holds for the evaluated glass transition temperature as well as for the corresponding change of the specific heat.

The single measurement with a sample mass of 10.896 mg PS reveals practically the same excellent agreement with the literature data for the specific heat functions in the glassy and in the liquid amorphous state.

The temperature modulated measurements for the determination of the specific heat functions afford also a caloric calibration preferably performed with sapphire. In such a way, a transformation can be executed for any heat flow curve on a thermodynamic level. Quite a number of results on specific heat functions in literature, even for polystyrene are only published on arbitrary scales. The Netzsch software Proteus[®] enables a straightforward treatment of the heat flow measurements of a sample together with a calibration into specific heat functions. Figure 7 demonstrates the sinusoidal temperature modulation as well as the total heat flow curve for the second scan with 12.720 mg polystyrene. The mean of the first and second heating for the specific heat values of polystyrene show the same accuracy level in comparison with the results obtained by the classical DSC method. The representation of the total specific heat functions separated into a reversing and a non-reversing part allows presenting the glass transition without a relaxation enthalpy. This example represents one of the benefits from the temperature modulated technique, namely the separation of overlapping effects under certain restrictions.

The glass transition temperatures for polystyrene taken from the literature presented in Table 9 are within temperature limits from 366 to 373 K omitting the data from Karasz. The mean value is 369 ± 2 K. The extrapolation to an infinite molecular mass is not changing to much yielding a mean value of 370 ± 2 K. This fact is based on the high molecular masses of the polystyrene material used.

Conclusions

DSC and TMDSC allow the determination of the heat capacity or specific heat as well as the glass transition temperature for substances and materials in a straightforward procedure with a considerable accuracy. To achieve results of a high quality affords certain requirements in quite different areas. The instrumentation used for such a measurement must be of a high quality. The same holds for the software. The whole procedure starting with the sample handling to the elucidation of the data needs a careful treatment. The sample handling is too often regarded as unimportant, which is certainly not a safe starting point for the generation of data with a high accuracy. Dynamic calorimeters are dealing with thermal resistances to the pans and to the sample material. Indium used to calibrate for the thermal resistance to the sample is the procedure of choice, however not ideal. Additionally, the pans used, the sample size and the sample form as well as the sample contact to the pan are crucial points. All necessary calibrations such as the temperature and enthalpy calibration should be carefully performed.

To transfer the directly measured heat flow curves into specific heat functions needs a calibration, made preferably with sapphire. Such a procedure is necessary for the DSC as well as for the TMDSC. Only arbitrary specific heat curves are often reported for the latter method because the calibration step is omitted. The thermal resistance has consequences, normally not to the measured enthalpy, however to the corresponding temperature of the sample. Specific heat curves of a high accuracy afford a correct assignment of temperature and enthalpy. The measurement of specific heat curves together with the elucidation of data using proper calibration procedures is the only way for a validation of this analytical procedure. Many of the above mentioned instrument and sample related areas are discussed in literature [1, 2, 5, 18].

Atactic polystyrene is a rather well known material as a representative of amorphous polymers. It is applied as reference substance for many different physico-chemical determinations. The SRM 705a from NIST is a valuable standard, however only reported for the glassy state of polystyrene. The glass transition and the liquid amorphous state are of course of a higher complexity, but scientifically and technically of great interest. Of a cardinal importance in our study was the evaluation of the literature for the existing data on the specific heat and the glass transition of polystyrene.

The literature data collected as mean values for the specific heat over the temperature interval from 10 to 470 K reveal an excellent agreement with standard deviations for the glassy state of better than

0.7%. Different reasons may be alleged for the much higher standard deviations of 0.6 to 6% above the glass transition up to 470 K. First, there are only three data sets reported in literature for the amorphous state. Second, the energetic contributions of the physical and chemical impurities to the specific heat are considerably higher in the liquid amorphous state compared to the glassy state. Additionally, the literature data for each of the cited authors were transferred into linear specific heat functions in the vicinity of the glass transition for both of the physical states. The two sets of coefficients could be used to get a mean specific heat function representing all the reported polystyrene data, one for the glassy and the second for the liquid amorphous state. No literature values had to be excluded as outlier or had to be integrated with a lower mass in case of the specific heat. As a conclusion more data for the liquid amorphous state could improve the situation especially also in using the polystyrene SRM 705a.

The DSC and TMDSC equipment, namely the DSC 204 F1 Phoenix[®] with the software Proteus[®] were used to determine the specific heat of polystyrene SRM 705a as well as the characteristic values for the glass transition. The own experimental approach has been planned and was executed to proof and to validate the instrumental methods and the software procedures for the DSC and the TMDSC. Such a goal can only be achieved, if a literature base exists. Such a base only separated as information into single publications are of a minor value, because a general proof of the accuracy is impossible. It seems of an absolute necessity to evaluate such published data, if existing, and to examine the information critically. Of course, there is no absolute correct way for this task, because such a comparison could yield in conformity or in discrepancy of the data. The difficult question is then, for the latter case the judgment of the possible facts.

In this context, we observed both of these possible cases. The literature data for the specific heat were extremely consistent for the glassy state of polystyrene. The data for the liquid amorphous state spread increasing with the temperature difference to the glass transition up to 6%. Explanations for this spread are the small number of data and the influence of impurities, which may differ for each polystyrene reported in literature. The glass transition temperature showed data which differ in the order of up to 12°C. Impurities, which could only partially removed were the explanation of the authors [6].

Several series of measurements with the SRM 705a were executed and evaluated during our investigations. One set of measurements was made with 19.404 mg polystyrene SRM 705a using the DSC 204. The data obtained as mean values of this set

of 4 measurements, represented by the two linear functions were nearly identical with the mean values for the linear functions reported in the literature. Therefore, these measurements of our study were integrated in the mean values of all the specific heat functions taken from the literature.

The overall mean of the specific heat functions (means of the corresponding coefficients) are means of 7 data sets in the glassy state and 6 in the liquid amorphous state. The equations for the best mean at present, which can be given for the specific heat functions in $\text{J g}^{-1} \text{K}^{-1}$ for polystyrene are as follows:

$$c_{p, \text{vit}} = (4.393 \pm 0.043) \cdot 10^{-3} T - (9.5668 \pm 1.2696) \cdot 10^{-2}$$

$$c_{p, \text{li-am}} = (2.934 \pm 0.165) \cdot 10^{-3} T + (0.74025 \pm 0.05646)$$

The new data introduced from our experiments into the selected literature values cause practically no shift in the mean values for the linear coefficients and in addition the standard deviations are reduced. This fact proofs the high quality and excellent accuracy of the data obtained with the DSC 204 F1 Phoenix[®] and also of the software Proteus[®]. Furthermore, the fact that the specific heat functions measured with a DSC are lying within the functions calculated for the literature data, measured with adiabatic calorimeters is indicating a new area.

The specific heat data measured with the TMDSC is also of a high accuracy.

The glass transition temperature and the corresponding change of the specific heat characterize the glass transition of polystyrene. The glass transition often described as a second order transition is in reality a transition from a non-equilibrium state into a liquid amorphous state. The physical quality of the glassy state, generated by the mechanical and thermal history of the polymer as well as by the selected condition of the heating from the glassy state may influence the measured glass transition. Therefore, certain conditions must be fulfilled to receive reproducible data. The literature data gave a mean value for the glass transition of polystyrene of 369 ± 2 and 370 ± 2 K for the extrapolation to an infinite high molecular mass and a corresponding change of the specific heat of $0.303 \text{ J g}^{-1} \text{K}^{-1}$. The data measured by us with the DSC and the TMDSC using the polystyrene SRM 705a correspond rather well with these literature data.

As a final conclusion, the determination of the specific heat with any DSC or TMDSC equipment demands an appropriate sample preparation, an excellent instrumentation and an adequate software. Atactic polystyrene of an outstanding quality in respect to physical and chemical impurities is an excel-

lent polymer for the test of any selected procedure in the area of the specific heat and the glass transition.

The glass transition temperature as a non-equilibrium transition needs for a reproducible data generation a standard procedure for a given substance or material under investigation. Another approach for the measurement of the glass transition has to be taken in case the thermal history of the sample should be investigated, namely in omitting in advance of the sample measurement any thermal and mechanical stress.

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