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Dedicated to Professor Bernhard Wunderlich on the occasion of his 65th birthday

THE GLASS TRANSITION TEMPERATURE OF POLYSTYRENE
Results of a round robin test

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Abstract

A round robin test was performed to determine the reliability of values for the glass transition temperature T_g as determined by DTA on polymers. Ten different instruments were involved. The test material was high molecular weight polystyrene. Values for T_g (midpoint) were reported in the range 107°C±2 K. The respective heat flow curves differed considerably in shape. In the literature a T_g of 100°C is often given for polystyrene. The discrepancy between this value and the value of 107°C found in the round robin test is due to three differences: the thermal history of the sample, the evaluation of the heat flow curves, and the effect of finite sample size.

Keywords: glass transition temperature, polystyrene

Introduction

In 1964 B. Wunderlich, D. M. Bodily and M. H. Kaplan published a seminal paper on the glass transition of polystyrene [1]. Since those days there has been an ever increasing interest in the phenomenon of the glass transition, both in experimental and theoretical physics [2, 3]. The development of modern DTA- and DSC-instruments made possible the rapid determination of the glass transition temperature T_g of polymeric materials [4, 5]. When skilfully performed it is meanwhile possible to analyse the glass transition quantitatively. But, when dealing with results from DTA-experiments on the level of applied research and quality control in industry one is confronted with very elemental questions such as: Do different DTA-instruments yield the same glass transition temperature T_g for the same material – as they should within certain limits? How large are the typical deviations between the results obtained with different instruments? How does the T_g-value which is determined according to different norms compared with the corresponding value from, e.g., Wunderlich's compilation – the ATHAS-Table [4]? What are the reasons for possible differences between given T_g-values? These are the questions which are addressed in the following.

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In the next chapter I present the results of a round robin test on high molecular weight polystyrene (PS). The test involved ten different DTA/DSC-instruments in seven different laboratories. We were interested in the scatter of the actual values for T_g as well as in the shapes of the heat flow curves in the glass transition region. As will be seen, the average T_g-value of 107°C obtained in the round robin test differed substantially from the value of 100°C which is often cited in the literature and which is also listed in the ATHAS-Table [4]. In Chapter 3 some precision data from the literature for T_g of PS are chosen as basis for Chapter 4, where I show that the apparent discrepancy can be explained by taking into account the thermal history of the sample, the evaluation of the heat flow curves, and the effect of finite sample size.

Results of the round robin test

Six manufacturers of DTA/DSC-instruments participated in the test. Together with two instruments from our lab ten different DTA/DSC-instruments were used for the test, cf. Table 1. As test material we chose high molecular weight polystyrene without any additives ($Mw=374000$, $Mw/Mn=2.5$). This material is known to be uncritical in DTA-experiments, i.e. it shows a well-defined and narrow glass transition and no degradation effects in the temperature range of interest. The molecular weight is high enough to be close to the limit of infinite chain length within some tenth of a degree of T_g [6]. The material was supplied to the participants of the test in the form of moulded platelets of 1 mm thickness.

The procedure for testing was prescribed according to a German norm (DIN 53765) as follows: cooling of the sample (10–20 mg) to a temperature below T_g–50 K, waiting for equilibrium (1–2 min), heating with 20 K min^{-1} to T_g+50 K (first run), holding for 1–2 min, cooling with 20 K min^{-1} to T_g–50 K,

Table 1 Types of instruments involved in the round robin test

Manufacturer	Type of instrument
C3 Analysentechnik	Seiko
Mettler	TA 4000, DSC 30
	DSC 12E
	TA 8000
Netzsch	DSC 200
Perkin-Elmer	DSC 7
SETARAM	DSC 141
TA Instruments	DSC 2910
	DSC 912
Shimadzu	DSC 50

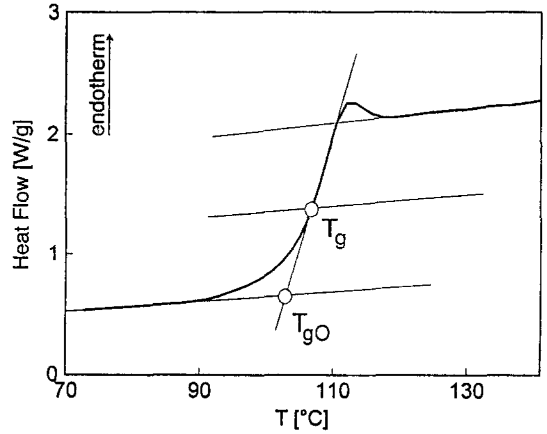

Fig. 1 Heat flow curve taken on polystyrene at the glass transition with definition of the glass transition temperature T_g as the midpoint temperature

holding for 1–2 min, heating with 20 K min^{-1} to T_g+50 K (second run). The glass transition temperature of the material is taken as the midpoint temperature determined in the second run. The midpoint temperature is defined in the usual way as the temperature of half step-height at the glass transition, see Fig. 1. Note that the German norm differs with respect to ASTM 3418 in two points. First, the cooling rate is taken to be 20 K min^{-1} (ASTM 3418: quench cooling). Second, ASTM 3418 suggests the extrapolated onset temperature T_{go} for the definition of T_g whereas DIN 53765 prescribes the midpoint-temperature for the glass transition temperature T_g.

For each instrument T_g and T_{go} of the second run was determined from the respective heat flow curves. Figure 2 shows the result of the round robin test. It is found that the T_g-values scatter around 107°C within ±2 K. The scatter in the values for the extrapolated onset temperature is somewhat larger. This finding is in agreement with the results of a round robin test discussed in Ref. [7]. Figure 3 exhibits the heat flow curves which were recorded with the ten instruments in the respective second run. The curves have been shifted, stretched/compressed and – in some cases – reflected along the horizontal to make them comparable. I must emphasize that the succession of the curves in Fig. 3 does not coincide with the succession of instruments listed in Table 1. As is evident from this compilation, one is still far from safe grounds in DTA/DSC-experiments. As long as heat flow curves from different instruments differ in such a drastic way, any quantitative evaluation of a heat flow curve in the glass transition region with respect to theories on relaxational phenomena must be regarded with scepticism.

Though the measurements were not performed in the c_p-mode, values for the step height at the glass transition were nevertheless determined from the curves in Fig. 3 and related to the change of the heat capacity Δc_p at the transition via

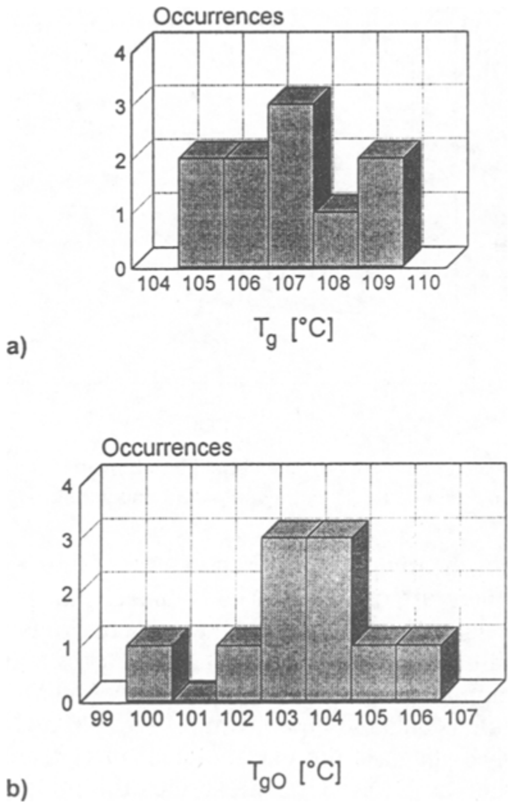

Fig. 2 Results of the round robin test with ten different types of DTA/DSC-instruments. The histograms show how often a value was reported in a given range [T– 0.5 K, T+0.5 K]. a) Midpoint temperature T_g, b) Extrapolated onset temperature T_{go}

$\Delta c_p = \Delta p/\beta$ where Δp is the change in heat flow at the transition and β is the heating rate. One obtains Δc_p-values in the range 0.26 to 0.31 J (g K)$^{-1}$ neglecting two outliers. These values compare sufficiently well with the value for PS given in the ATHAS-Table, $\Delta c_p = 0.30$ J (g K)$^{-1}$ [4].

T_g-values of polystyrene from the literature

The round robin test yielded an average T_g-value for PS of 107°C. In the literature a value of 100°C is often assumed or explicitly given [4]. Before explaining the reasons for this apparent discrepancy it is interesting to check how trustworthy the T_g-value of 100°C is. Table 2 presents T_g-values of polystyrene taken from reliable sources (which, of course does not imply that these are the only reliable sources). In order to make the original data comparable they must be extrapolated to common conditions. First, it must be observed that the

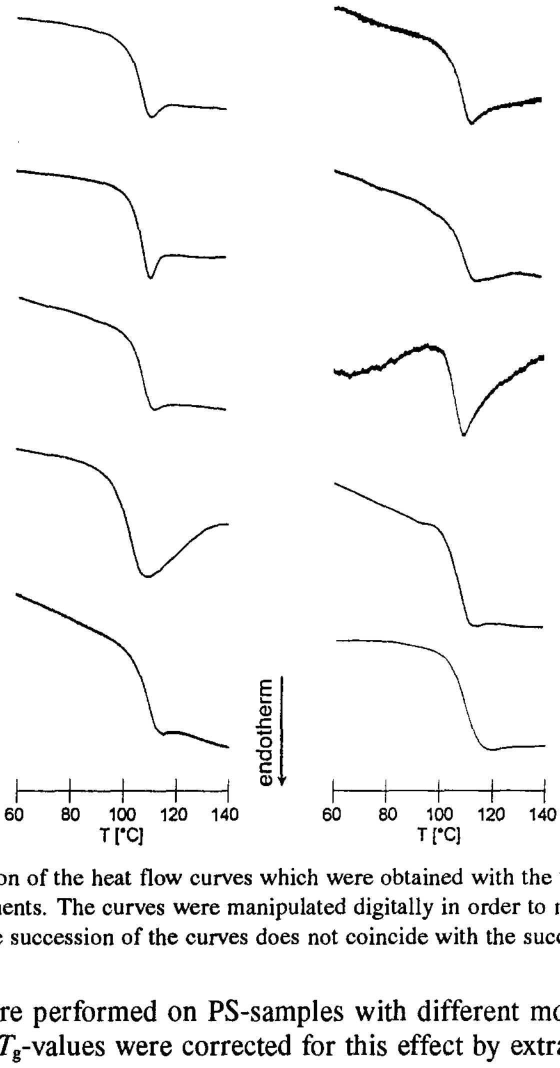

Fig. 3 Comparison of the heat flow curves which were obtained with the ten different types of instruments. The curves were manipulated digitally in order to make them comparable. The succession of the curves does not coincide with the succession in Table 1

experiments were performed on PS-samples with different molecular weights. The respective T_g-values were corrected for this effect by extrapolation to infinite molecular weight according to the following equation [6].

$$T_{g\infty} = T_g + K/M_n \tag{1}$$

where K is taken to be 128000 according to Aras and Richardson [6]. In a second step, the data must be corrected for the rate with which the samples were cooled to the glassy state before performing the actual determination of T_g in a heating run. Wunderlich *et al.* found that T_g is affected by the cooling rate q_- according to the following relation [1].

$$T_g = T_{go} + \alpha \log(q_- /\mathrm{K\ min^{-1}}) \tag{2}$$

where α =4 K. Here, we take $T_g = T_{g\infty}$. The respective values for $T_{g\infty}$ and T_{go} are listed in Table 2. In Ref. [6] two values for $T_{g\infty}$ were given according to two different choices of the parameter K in Eq. (1).

Table 2 displays T_g-values in the range 96.9 to 99.8°C for polystyrene which was cooled at a rate of 1 K min^{-1} into the glassy state prior to the measurement. In the following we use a value of 98°C as the average taken from Table 2. The value of 100°C from the ATHAS-Table [4] is slightly above this range. But, it must be remembered that most samples which are examined in routine experiments were cooled at rates much larger than 1 K min^{-1}, typically in the range of 10 K min^{-1} to 100 K min^{-1}. In those cases the glass transition is expected to occur at 102 or 106°C, respectively. A further complication occurs since there is no general agreement as to the parameter α in Eq. (2). Wunderlich *et al.* derived α =4.03 K [1]. Richardson found α =2.5 K [8]. Recently, Toratani *et al.* determined this parameter to be α =2.1 K [10]. For simplification, a value of α =4 K is used in the following chapter.

Table 2 Glass transition temperatures taken from the literature and corrections for infinite molecular weight ($T_{g\infty}$) and cooling rate of 1 K min^{-1} prior to the measurement (T_{go})

Ref.	Cooling rate/ K min^{-1}	M_n	T_g/ K	$T_{g\infty}$/ K	T_{go}/ K	T_{go}/ °C
6	5	various		374.7	371.9	98.9
				372.9	370.1	97.0
8	1	37000	468.2	371.6	371.6	98.5
1	1	357000	372.5	372.9	372.9	99.8
9	20	36000	371.6	375.2	370.0	96.9

Solving the discrepancy between T_g =100°C and T_g =107°C

As discussed in the foregoing chapter, precision data of polystyrene yield T_g=98°C (±1 K) using a cooling rate of 1 K min^{-1} prior to the heating run. In the round robin test a value of 107°C was determined. The apparent discrepancy between these two values can be traced back to three effects:

1. In the round robin test a cooling rate of 20 K min^{-1} was prescribed. According to equation 2 this leads to a shift ΔT_{g1} of the glass transition temperature of approximately $\Delta T_{g,\text{rate}}$=5 K compared to a sample which was cooled at 1 K min^{-1}.

2. As can be seen in Fig. 2 the step in the heat flow curves at the glass transition is followed by a hump. This hump is caused by enthalpy relaxation. In the present case, this effect occurs since the heating rate equals the cooling rate. A comprehensive discussion of this effect has been given by Richardson [5]. As regards the physics of the glass transition it is no longer sensible to take the mid-

point temperature for the definition of the glass transition temperature when enthalpy relaxation occurs [5, 6, 8]. Instead, one should use the temperature where the enthalpy curves from the glassy and the liquid state intersect. Richardson gives a simple method how to derive this temperature from heat flow curves [5, 6, 8]. Comparing the set of parameters for cooling and heating rates which were used in our round robin test with experiments performed by Richardson and Savill [9] one finds that the use of the midpoint temperature yields a T_g-value about $\Delta T_{g,\mathrm{relax}}=3$ K above the glass transition temperature which is derived using the method of intersecting enthalpy curves.

3. The third effect which contributes to the shift of T_g is the finite thermal conductivity of the polymer sample and the imperfect contact between sample and crucible. Figure 4 illustrates this effect. There is a linear correlation between sample weight and the glass transition temperature. The sample weight for the determination of T_g in a typical experiment is 10–20 mg. The corresponding T_g-value is shifted by about $\Delta T_{g,\mathrm{mass}}=2$ K to higher temperatures as compared to the extrapolated value at zero mass. In addition, Fig. 4 shows the influence of varying thermal contact between sample and crucible. A smoothed (by grinding) platelet filling the diameter of the pan has a better thermal contact than shavings. Due to the high molecular weight of the polystyrene which was used in our experiments this difference in thermal contact still exists after heating to T_g+50 K in the first run. Similar effects have been reported by Richardson [8].

Adding the three contributions one finds:

$$\Delta T_g = \Delta T_{g,\mathrm{rate}} + \Delta T_{g,\mathrm{relax}} + \Delta T_{g,\mathrm{mass}} = 10\ \mathrm{K} \tag{3}$$

Taking the average value from Table 2 $T_{g,\mathrm{lit.}}$ and adding ΔT_g, one arrives at a value of 108°C for the glass transition temperature of high molecular weight polystyrene as measured by DSC with a cooling rate of 20 K min^{-1} prior to the

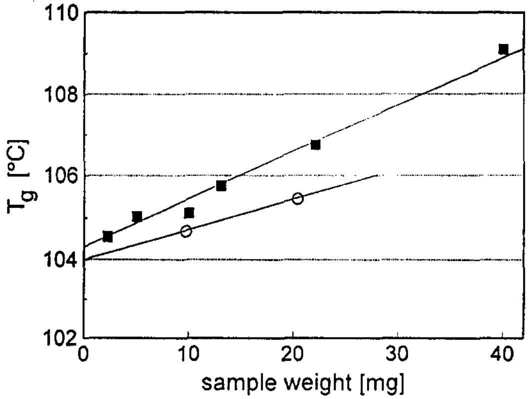

Fig. 4 Dependence of T_g on sample weight. ■ : shavings, O: smoothed (by grinding) platelet

second run. This value compares favourably with the mean value of 107°C found in the round robin test.

In Wunderlich's book 'Thermal Analysis' a set of specific heat curves measured on polystyrene are depicted in Fig. 4.34 [4]. If one evaluates the data from this set taken on the sample which was cooled at 5 K min^{-1} prior to the heating run one finds from this figure $T_g=105.2$°C. Transforming this value into the value corresponding to a cooling rate of 20 K min^{-1} according to Eq. 2 one arrives at $T_g=105.2\text{°C}-4\text{ K}(\log 5-\log 20)=107.6\text{°C}$. This value lies well within the range of data obtained in the round robin test.

Summary

The value for the glass transition which is determined in DTA/DSC-experiments depends on (1) the thermal history of the sample, on (2) the interpretation of the heat flow curve and on (3) instrumental effects. The latter include the shift of T_g because of the finite thermal conductivity of the sample. Precision data on polystyrene taken from the literature were corrected for point (2) and (3) and yielded $T_g=98\text{°C}\pm1$ K in the limit of infinite molecular weight and for the case that the sample was cooled at a rate of 1 K min^{-1} into the glassy state prior to the measurement. The value of 100°C which is given in literature as the glass transition temperature of polystyrene can be viewed as an easy to memorize figure. A round robin test on high molecular weight polystyrene with the participation of ten different types of DTA/DSC-instruments yielded $T_g=107\text{°C}\pm2$ K (midpoint temperature). In this test the samples were cooled from T_g+50 K at a rate of 20 K min^{-1} to the glassy state prior to the heating run. The discrepancy between the values 98 and 107°C is caused by the different cooling rates of 1 and 20 K min^{-1}, respectively, by the fact that no correc- tion for enthalpy relaxation was performed and by the shift due to the finite mass of the sample.

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