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ORIGINAL CONTRIBUTION

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A description of the glass transition measured by temperature modulated differential scanning calorimetry

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Abstract The temperature modulated differential scanning calorimetry (TMDSC) technique can be used for heat capacity spectroscopy in the low frequency range. Measured property is the complex heat capacity $C^* = C' - iC''$. The frequency dependent relaxation transition measured by TMDSC occurs in the temperature range of the thermal glass transition. Thus, the non-equilibrium of the glassy state influences the TMDSC curves. An experimental evidence is the dependence of the shape of the C'-curve on the thermal history. A theoretical description of the influence of the non-equilibrium state on the spectroscopic curves is presented. This description is based on the Tool–Narayanaswamy–Moynihan model.

Key words Temperature modulated differential scanning calorimetry – heat capacity – glass transition – relaxation – polystyrene

Introduction

The non-equilibrium process can be measured in the conventional differential scanning calorimeter (DSC). In the following this process will be named as thermal glass transition (TGT).

Another appearance of the glass transition is the so-called α-relaxation that can be measured in a relative large frequency range using spectroscopic methods. Such investigations are carried out frequently at relative high frequencies in the super-cooled melt (meta stable equilibrium). In the thermal case we call this relaxation as thermal dynamical glass transition (DGT). The experiments in this frequency range can be described using the linear response theory [1, 2].

At relative low frequencies (typically below 200 mHz) the thermal relaxations (DGT) can be investigated by temperature-modulated differential scanning calorimetry (TMDSC) [3]. In the TMDSC, a temperature program is applicable that can be described as a superposition of the linear scanning rate with a periodic temperature perturbation [4]. Thus, using this technique the phenomenon of the thermal glass transition and the thermal dynamical glass transition can be measured simultaneously.

If the underlying scanning rate β_0 and the amplitude of the temperature perturbation T_a is sufficiently small, the measured heat flow is a superposition of an underlying component (related to the conventional DSC signal) and a periodic component. From the periodic component the frequency-dependent complex heat capacity can be calculated [5]:

$$C^* = C' - iC'' , \tag{1}$$

The underlying component as well as the conventional DSC curve yields the heat capacity C_β. Measurements of the glass transition of polymers indicate the C^* depends on the frequency as well as on underlying heating rate. Under certain conditions a hysteresis in the C^*-curves between cooling and heating occur [6, 7]. This result pointed out that the transition from the equilibrium to a non-equilibrium states (i.e. the TGT) influences the frequency dependent C^*-measurements. Such behaviour is well known for other spectroscopic methods as dielectric spectroscopy [8, 9].

For a description of TMDSC measurements in the glass transition region it is necessary to consider the influence of the non-equilibrium state on the measured C^*-curves. As an example we investigate the influence of the non-equilibrium state on the DGT of polystyrene (PS) at slow frequencies and represent a method for its description based on the so-called Tool–Narayanaswamy–Moynihan model.

Description of thermal relaxations

The thermal relaxation transition in the PS melt can be described as a linear process [1, 2]. The thermal relaxation is determined by a relaxation function ϕ. A common example for ϕ is the Kohlrausch–Williams–Watts (KWW) function [10, 11].

$$\phi(t) = \exp(-(t/\tau)^{\beta_{\mathrm{KWW}}}) \tag{2}$$

another one is the Havriliak–Negami (HN) function [12]

$$\phi(\omega) = \frac{1}{(1 + (\mathrm{i}\omega\tau)^{\beta_{\mathrm{HN}}})^{\gamma_{\mathrm{HN}}}} , \tag{3}$$

where β_{KWW}, β_{HN} and γ_{HN} are parameters which describe the asymmetry and width of the relaxation function. In contrast to the KWW-function, the HN-function has two parameters, thus it is a very flexible function without initial restriction of the shape of ϕ.

In the equilibrium state the temperature dependence of the relaxation time τ is given by the Vogel–Fulcher–Tammann (VFT) equation [13]

$$\lg\left(\frac{1}{\tau}\right) = \lg(\omega) = A - \frac{B}{T - T_{\mathrm{V}}} , \tag{4}$$

where A, B and T_{V} are parameters.

In contrast, thermal glass transition measured by conventional DSC is a non-linear effect. However, it is possible to describe this transition with the same relaxation function ϕ as in the equilibrium state. One method for this is based on the fictive temperature T_{f}. The fictive temperature characterized the actual structure of the sample. The actual structure influences the molecular relaxation behavior. One relation that describes the temperature and structure dependence of the relaxation time is the so-called Tool–Narayanaswamy–Moynihan (TNM) equation [14–16]:

$$\tau = \tau_0 \exp\left[\frac{x\Delta h^*}{RT} + \frac{(1-x)\Delta h^*}{RT_{\mathrm{f}}}\right] , \tag{5}$$

where x is the non-linearity parameter and Δh^* the activation energy. The influence of the structure is represented by the fictive temperature T_{f}. For $x = 1$, Eq. (5) is a Arrehenius equation. This is in contrast to the VFT-behaviour. Therefore, the TNM equation is valid only in a relative small temperature range around the glass transition temperature. For TMDSC experiments this condition should be approximately correct.

The fictive temperature characterizes an apparent temperature of the cooperative motions. It describes the entropy change of the cooperative modes as a function of temperature. In the melt T_{f} is identical to the temperature T of the thermal bath. If the sample is cooled at a constant rate, T_{f} becomes constant in the glassy state. The fictive temperature can be determined from the heat capacity curve C_β measured in the conventional DSC run [17]

$$T_{\mathrm{f}}(T) = T_{\mathrm{r}} + \int_{T_{\mathrm{r}}}^{T_1} \left(\frac{C_\beta(T) - C_{\mathrm{g}}(T)}{C_{\mathrm{e}}(T) - C_{\mathrm{g}}(T)}\right) \mathrm{d}T , \tag{6}$$

where $C_{\mathrm{e}}(T)$ and $C_{\mathrm{g}}(T)$ are the extrapolated heat capacity curves of the melt and the glassy state, respectively. The reference temperature T_{r} is chosen in the equilibrium melt and T_1 represents another temperature in the glassy state.

Experimental

The sample was commercial Polystyrene (PS-168N; BASF) with a molecular weight $M_{\mathrm{w}} = 1.7 \times 10^5$ g/mol ($M_{\mathrm{w}}/M_{\mathrm{n}} = 2.8$). The sample mass was 6.818 mg. The TMDSC measurements were performed using a Perkin–Elmer DSC 7 in the DDSC mode. The input parameters were selected in such a manner that the temperature program is equal to an underlying rate $\beta_0 = \pm 2$ K/min and a temperature amplitude $T_{\mathrm{a}} = 0.5$ K. The used frequencies f_0 are 36 and 18 mHz.

At first, the sample was measured in the cooling run from 160 to 70 °C. After that, the heating run followed without additional annealing. The measured heat flow was calibrated [18, 19] and the real and imaginary part of the complex heat capacity were calculated.

Results and discussion

In Fig. 1 a typical TMDSC curve of PS is shown. The TGT can be seen in C_β. At the used frequency the DGT occurs at higher temperatures. This transition is represented in

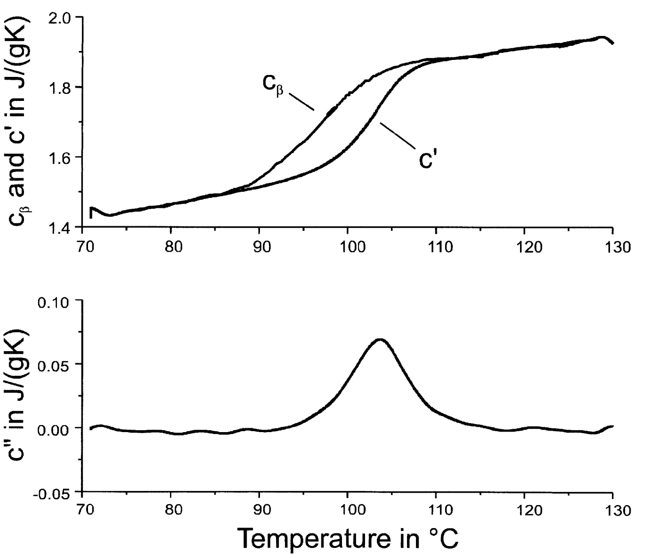

Fig. 1 Specific heat capacities of polystyrene in the glass transition region ($m = 6.818$ mg, $\beta_0 = -0.5$ K/min, $T_a = 1$ K, $f_0 = 40$ mHz)

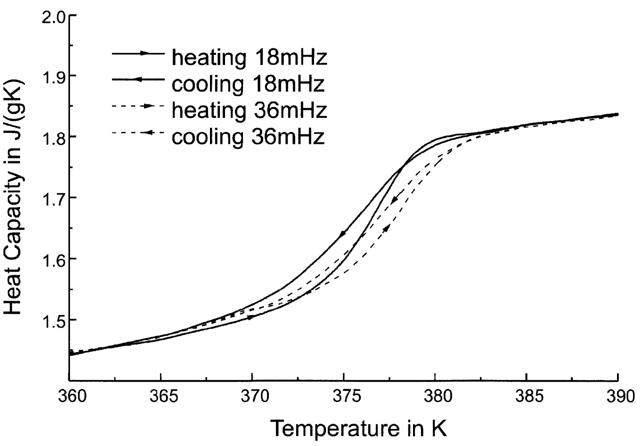

Fig. 2 Real part of the specific heat capacity of polystyrene (6.818 mg) in the glass transition region at different frequencies ($T_a = 0.5$ K, $\beta_0 = \pm 2$ K/min)

a C'-step and a C''-peak. Figure 2 shows the cooling and heating C'-curves. At both frequencies a hysteresis between the heating and cooling curves is detected. At a lower frequency, the difference between heating and cooling increases. Such hysteresis effects cannot be explained by means of the linear response theory. The reason of the hysteresis is the influence of the freezing process during the thermal glass transition on the relaxation process measured in the frequency-dependent experiment.

In the liquid the temperature of the thermal bath T is identical to the fictive temperature T_f. If the heat capacity curve C_β differs from the heat capacity of the liquid C_e than is $T_f > T$ and the sample is in the non-equilibrium state. As shown in Fig. 1, the low-temperature part of the DGT (detected in the C'-step) takes place in the region where the system changes to the non-equilibrium state. In other words, we expect non-linear effects (hysteresis) in the C'-curve if T_f differs from T. In such a non-equilibrium state the actual entropy is not only a function of the temperature but also dependent on the thermal history. Therefore, the entropy during a cooling run is different from that of a heating run at the same temperature. This difference in the actual state is the reason of different relaxation times at the same temperature. Because the temperature range of the DGT shifts to higher temperatures if the frequency is increased, the influence of the non-equilibrium state on the C'-curves should decrease with increasing frequency. This corresponds to the experimental results in Fig. 2.

The fictive temperatures can be used for the interpretation of the hysteresis. The basis of a phenomenological description of such TMDSC results in the Fourier-transformed (frequency-dependent) complex relaxation function

$$\phi(T,\omega_0) = \frac{C^*(T,\omega_0) - C_{st}(T)}{\Delta C(T)} = \phi'(T,\omega_0) - i\phi''(T,\omega_0)\,, \tag{7}$$

where $C_{st}(T)$ is the extrapolated heat capacity function of the glassy state and $\Delta C(T)$ is the difference of both the extrapolated curves of the glassy and the liquid state. ω_0 is connected to the frequency f_0 ($\omega_0 = 2\pi f_0$). Equation (7) can be used for the description of the measured TMDSC curves.

A very flexible model function to describe $\phi(T,\omega_0)$ is the HN-function (Eq. (3)). The original HN-function is frequency dependent. ϕ is a function of temperature because the relaxation time τ depends on T. To consider the influence of the non-equilibrium state in the relaxation function, the fictive temperature must be regarded in $\tau(T)$. Equation (5) complies with this condition. Thus $\phi(T,\omega_0)$ reads

$$\phi(T,\omega_0) = \frac{1}{\left(1+\left(i\omega_0\tau(T_r)\exp\left[\frac{x\Delta h^*}{R}\left(\frac{1}{T}-\frac{1}{T_r}\right)+\frac{(1-x)\Delta h^*}{R}\left(\frac{1}{T_f(T)}-\frac{1}{T_f(T_r)}\right)\right]\right)^{\beta_{HN}}\right)^{\gamma_{HN}}} \tag{8}$$

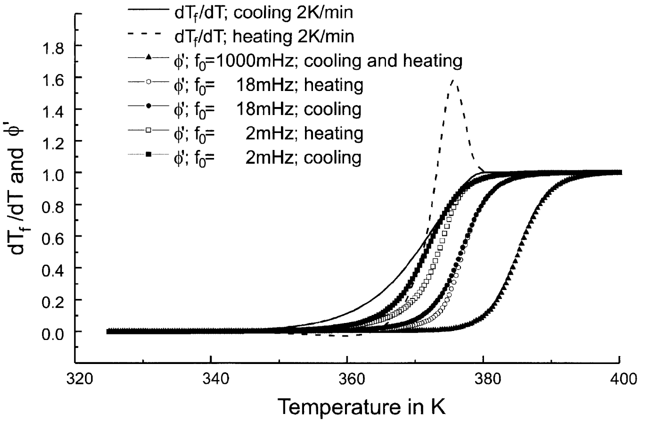

Fig. 3 Model calculations of the relaxation functions $\mathrm{d}T_\mathrm{f}/\mathrm{d}T\,(T, \beta_0)$ and $\phi'(T, \omega_0)$ for a cooling as well as a heating run. For parameters see the text

where T_r is a reference temperature. The calculation of the real and imaginary parts of the HN-function is reported in ref. [20]. For calculation of the relaxation function the fictive temperature and the parameters in Eq. (8) must be known.

Results of model calculations (using Eq. (8)) are presented in Fig. 3. $\phi'(T)$-curves are plotted for cooling and subsequent heating runs. The underlying heating rate β_0 is 2 K/min. The frequencies are 1 Hz, 30 mHz and 2 mHz. The function $T_\mathrm{f}(T)$ is determined from conventional DSC measurements at the scanning rate β_0. For T_r the glass transition temperature of 369 K is chosen. The correlated relaxation time is estimated from the approximation of Heinrich and Stoll ($\tau(T_\mathrm{g}) = \beta_0/15$ K) [21] to τ (369 K) = 450 s. The respective parameters are taken from the literature ($\beta_\mathrm{HN} = 0.7$, $\gamma_\mathrm{HN} = 0.99$ [22], $\Delta h^*/R = 69\,500$ K and $x = 0.46$ [23]). For comparison the functions $\mathrm{d}T_\mathrm{f}/\mathrm{d}T$ are plotted in this diagram as well. $\mathrm{d}T_\mathrm{f}/\mathrm{d}T$ is determined from conventional DSC measurements using Eq. (6).

At a frequency $f_0 = 1$ Hz the distance between the DGT and the TGT is more than 15 K. Almost in the total temperature range of the DGT is $T_\mathrm{f} \cong T$. As a result, the ϕ' curves of the cooling and heating run are identical. With decreasing frequency the measured DGT shifts to lower temperatures. The difference between T_f and T decreases and consequently the influence of the non-equilibrium state on the DGT curves increases. The model calculation shows a difference between heating and cooling scans at $f_0 = 33$ mHz. The hysteresis increases with decreasing frequency.

A comparison between Fig. 2 and Fig. 3 shows that the above-mentioned model describes the measured curve shape of TMDSC measurements in the glass transition region qualitatively. Differences between the experimental and the calculated curves might be caused by the parameters selected.

Conclusions

In a TMDSC experiment slow thermal relaxation is measured close to the glass transition. If an underlying scanning rate appears, the measured curve looks like a superposition of a conventional DSC curve (determined by the underlying scanning rate) and a dynamic (frequency dependent) experiment. However, the underlying temperature change influences the dynamic results as shown experimentally. The reason for this is that the equilibrium states successively stays in the range of the thermal glass transition. This can be described using the fictive temperature. T_f is in the range of interest different to the external temperature. By considering this effect the TMDSC curves in the glass transition region can be described.

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