Short note

Broad band heat capacity spectroscopy in the glass-transition region of polystyrene

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Abstract

The combination of results from temperature modulated DSC (TMDSC) and 3ω-method (HCS) in the glass-transition region allows broad band heat capacity spectroscopy in a frequency range of seven orders of magnitude. In an Arrhenius diagram, the curve for calorimetric data is close to that of dielectric data, except from some remaining problems of temperature calibration. The dynamic glass-transition temperature and the width of the transition interval are determined in the frequency range $10^{-4} < \nu < 10^3$ Hz and compared with DSC measurements on linear cooling (vitrification).

The dynamic calorimetric data are obtained in the liquid equilibrium state, where the dispersion of the glass-transition interval is related to the mean temperature fluctuation of cooperatively rearranging regions (CRR). As expected from the fluctuation approach to glass transition, this temperature fluctuation increases with increasing temperature. This indicates decreasing size of CRRs with increasing temperature. The $a = q/\delta T^* \omega$ parameter is obtained as $a = 6\pm2$ from a comparison of thermal and dynamic glass transition. © 1997 Elsevier Science B.V.

1. Introduction

Combination of different temperature-modulated calorimeters allows the determination of complex heat capacity in a wide frequency range. Results obtained in the glass-transition region of polystyrene by 3ω-method (HCS) [1] and temperature modulated DSC (TMDSC) [2,3] are presented. The dynamic glass-transition temperature and the width of the transition interval are determined in a frequency range of seven orders of magnitude ($10^{\pm4} < \nu < 10^3$ Hz) and compared with DSC measurements on linear cooling (vitrification), dielectric, and dynamic shear spectroscopy. The glass transition from temperature-modulated calorimetry, observed in the equilibrium state of the liquid, is little influenced by non-equilibrium caused by vitrification. Therefore the mean temperature fluctuation of cooperatively rearranging regions (CRR) can be obtained directly from the width of the transition interval [4]. The aim of this paper was to check if both temperature-modulated calorimetric methods give the same results and, thus, allow to determine this mean temperature fluctuation over a wide temperature range.

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2. Experimental

The 168 N polystyrene (PS) sample was from BASF ($\rho = 1.047$ g/cm^3; $M_n = 95,000$ g mol^{-1}; $M_W = 270,000$ g mol^{-1}). DSC measurements were performed to determine the conventional or total C_p and TMDSC to determine the complex heat capacity $C_p^* = C_p' - iC_p''$. Perkin–Elmer DSC-7 and Setaram DSC 121 were used in both the cases. The sample mass was 12 and 230 mg, respectively. The temperature scale of the calorimeters was calibrated in DSC mode according to the recommendation of GEFTA [5] by indium and lead, and was checked in the TMDSC mode by the smectic-to-nematic transition of 8OCB [6]. The determination of complex heat capacity, especially the correction of phase angle, was performed as described in Ref. [7]. The temperature amplitude T_a was about 0.2 K and the underlying cooling rate q_o was nearly proportional to frequency $\nu = 1/t_p$, with $q_o = 0.5$ K min^{-1} for $\nu = 1/60$ Hz. From TMDSC measurements the frequency range $10^{-4} < \nu < 10^{-1}$ Hz is available.

A thermal wave technique, the so-called 3ω-method (HCS) [1], was used in the frequency range $2 \times 10^{-1} < \nu < 2 \times 10^3$ Hz. Several improvements were necessary to measure polymer samples [8]. The temperature wave amplitude was varied between 0.01 and 1 K. This method gives the product of complex heat capacity C_p^*, thermal conductivity κ and density ρ. We assume that the curve shape in the glass-transition region is mainly caused by the complex heat capacity [8].

The temperature scale of the 3ω-apparatus was calibrated using a certified platinum resistor. The DC-component of the heating power causes a stationary temperature gradient of some Kelvin across the sample. This may be the reason for the temperature shift between the data from the 3ω-method and TMDSC measurements around 0.1 Hz, see Figs. 3 and 4 below. The uncertainty of the glass-transition temperature from TMDSC is in the order of 1 K, mainly caused by the uncertainty of maximum determination. For the 3ω-method there is an additional influence of the stationary temperature gradient resulting in a total uncertainty of about 2 K. In the frequency region around 0.1 Hz the uncertainty increases for both methods because the signal-to-noise ratio

decreases. Further investigations are necessary to clarify the discrepancy.

The dynamic glass-transition temperature $T_\alpha = T_\alpha(\omega)$ is determined as the maximum temperature of the imaginary part of heat capacity $C_p''(\omega, T)$ (TMDSC) or of the product $\rho\kappa C_p''(\omega, T)$ (3ω-method) as a function of temperature for given angular frequency $\omega = 2\pi\nu$. To obtain the width of the glass-transition interval a Gaussian function is fitted to the data, see Figs. 1 and 2. Using a fluctuation approach of
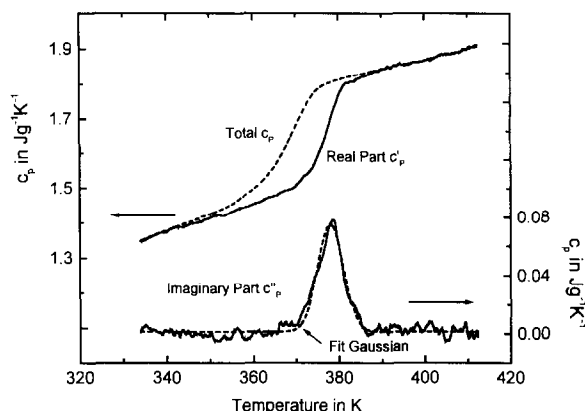

Fig. 1. Examples of real and imaginary part of complex specific heat capacity for polystyrene (PS) obtained by TMDSC (Perkin–Elmer DSC-7) with $t_p = 60$ s; $T_a = 0.2$ K; $q_o = -0.5$ K min^{-1}. The conventional or total c_p was independently measured (Setaram DSC 121) with $q = -0.5$ K min^{-1}.
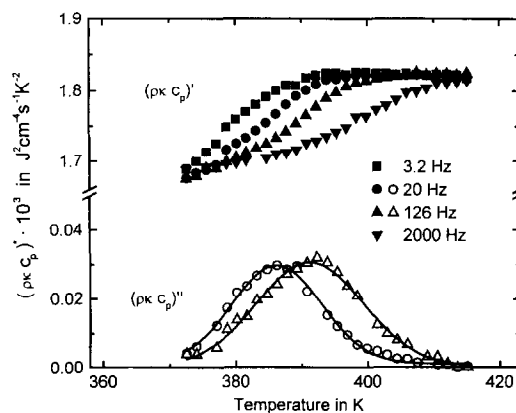

Fig. 2. Examples for heat capacity spectroscopy from the 3ω-method for PS. This method gives the product of thermal conductivity κ, density ρ, and heat capacity C_p. It is assumed that the dispersion is only from $C_p^*(\omega, T) = C_p' - iC_p''$.

glass transition [4], the mean temperature fluctuation δT of cooperatively rearranging regions can be determined as dispersion of the Gaussian function,

$$C_p'' = \frac{A}{2\delta T\sqrt{\pi/2}}\exp\left[-\frac{1}{2}\left(\frac{T-T_\alpha}{\delta T}\right)^2\right] \quad (1)$$

3. Results and discussion

The dynamic glass-transition temperatures T_α from both methods are compared in the Arrhenius diagram Fig. 3. Reasonable data are available in the angular frequency range 10^{-3} to 10^4 rad s^{-1}. Additional WLF-fits (lines) from dielectric (ε'') and dynamic shear (compliance J''; modulus G'') spectroscopy are shown. For PS, the points from heat capacity are close to the results from dielectric spectroscopy. The temperature uncertainty around $\omega = 1$ rad s^{-1} is reflected by the T_α differences: It seems that the curves are mutually shifted by about 4 K. On shifting the 3ω-curves horizontally, all calorimetric data fit well with a WLF-function using nearly the same parameters as for dielectric spectroscopy. At the moment we do, however, not know the exact reason for that shifting. To solve possible temperature calibration problems it may be useful to measure with both methods in an
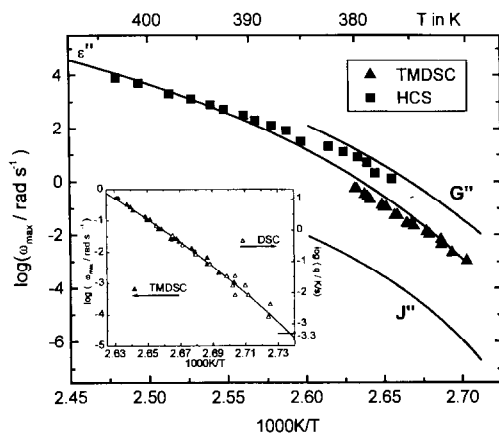

Fig. 4. Mean temperature fluctuation of a CRR from the dispersion of the Gaussian fit to the data from TMDSC and 3ω-method (HCS). The line is a guide for the eyes only.

overlapping frequency range. It seems necessary to expand the frequency range of the 3ω-method to lower frequencies [9] instead of increasing the frequency range of TMDSC because of the limiting time constants of the TMDSC apparatuses available.

Fig. 4 shows the mean temperature fluctuation δT determined from a Gaussian-fit, Eq. (1), of the imaginary part as shown in Figs. 1 and 2. The mean temperature fluctuation at the conventional glass temperature (373 K) is 2.5 K [8,10]. The δT values increase with increasing temperature. This indicates a decreasing number of cooperatively coupled particles with increasing temperature.

The relaxation time τ ($\tau = 1/\omega$) related to glass transitions observed by conventional DSC in cooling mode (vitrification) at a rate q = $-$ 10 K/min is often supposed to be of the order of 100 s. Temperature-modulated calorimetry allows a direct comparison of vitrification and dynamic glass transition (relaxation in thermodynamic equilibrium) and, therefore, a more precise determination of τ. Comparison of dynamic glass-transition temperatures, where the frequency ω is known from the experiment, with vitrification temperatures, where the cooling rates q is known, allows a direct comparison of the influence of q and ω. Low frequency TMDSC data and linear cooling at moderate rates results in two sets of glass-transition temperatures within the overlap interval. To bring both sets in accordance, see inset in Fig. 3, the log(q/ (K s^{-1})) scale for the vitrification temperatures has

Fig. 3. Activation diagram from TMDSC and 3ω-method (HCS) data for PS. The lines correspond to WLF fits from dielectric (ε'') and dynamic shear (G''; J'') spectroscopy, respectively. The inset shows the data from TMDSC and conventional DSC before the shift of 1.2 along the log(q/K s^{-1}) axis (see text).
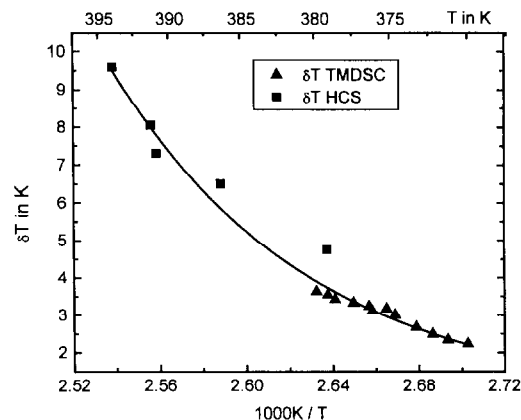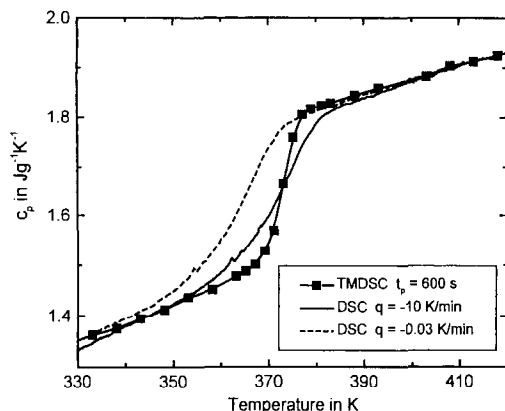
Fig. 5. Quasi-isothermal measured modulus of complex specific heat capacity from TMDSC (Setaram DSC 121; $t_p = 600$ s; $T_a = 0.25$ K; $m_p = 230$ mg) and conventional DSC in cooling mode (Perkin–Elmer DSC-7; $q = -10$ K min^{-1}, $m_p = 27$ mg) with the same glass-transition temperature. The dashed line added indicates the vitrification which is due to an underlying cooling rate of about 0.03 K min^{-1} connected with the quasi-isothermal TMDSC measurement (see text).

to be shifted by an amount of 1.2 ± 0.1. From the formula [4]

$$\omega = \frac{q}{a \cdot \delta T} \qquad (2)$$

using $\delta T = 2.5$ K, we get $a = 6 \pm 2$. This is in agreement with Ref. [11] and measurements on other polymers [12] and other glass-forming compounds [13].

The curve shapes within the glass-transition region can be compared too. In Fig. 5, the specific heat capacity resulting from a linear cooling run (conventional DSC, vitrification) and the modulus $|c_p^*|$ of complex specific heat capacity from a quasi-isothermal TMDSC experiment with the same glass-transition temperatures are shown. The conventional DSC curve is wider than the TMDSC curve, as expected from model calculations taking the influence of non-equilibrium into account [14–16]. The reason for this difference is that the TMDSC curve is measured more or less in the equilibrium state of the melt. To support this, the corresponding vitrification curve caused by the underlying cooling rate of about 0.03 K min^{-1} in the quasi-isothermal TMDSC experiment was estimated, see dashed line in Fig. 5. It is constructed by shifting the measured conventional DSC curve

$(q = -10$ K min$^{-1})$ to the expected glass-transition temperature for $q = -0.03$ K min^{-1} ($\log(q/$ $(K s^{-1})) = -3.3$), see inset of Fig. 3. Only small vitrification effects (widening) can be observed at the low temperature side of the TMDSC curve. Comparing the DSC and the TMDSC curve of Fig. 5, the DSC curve (vitrification) is broadened by a factor of 1.9, in agreement with prior estimations [10].

4. Summary

The combination of results from TMDSC and 3ω-method in the glass-transition region allows heat capacity spectroscopy in a frequency range of seven orders of magnitude. In an Arrhenius diagram, the curve of the calorimetric data is close to that from dielectric measurements.

As the frequency-dependent calorimetric data are obtained in the equilibrium state of the liquid, no influence of non-equilibrium (vitrification) must be taken into account. The equilibrium temperature dispersion of the transformation interval is directly related to the mean temperature fluctuation of cooperatively rearranging regions (CRR) [4]. As expected from the fluctuation approach to the glass transition, the mean temperature fluctuation of the CRRs increases with increasing temperature. This indicates a decreasing size of the CRRs with increasing temperature.

Acknowledgements

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