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New features of the glass transition revealed by the StepScan® DSC

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Abstract The results of StepScan DSC obtained for various oxides, chalcogenides, and organic glasses are discussed in connection with the commonly accepted theory of the glass transition. The new experimental features supporting the apparent idea of a reversible equilibrium being a part of the glass transition that is commonly interpreted as purely kinetic-relaxation phenomenon are discussed. Two alternative methods of the description of the reversible part of StepScan DSC record are compared:the empirical one using the exponential-power function $[1 - \exp(T/T_g)^n]$, and the second one based on the van't Hoff's equation describing the temperature dependence of equilibrium constant in terms of reaction enthalpy, ΔH. The adequacy of the empirical description is rationalized in the framework of the Tool–Narayanaswamy–Moynihan's relaxation theory.

Keywords Glass · Glass transition · Enthalpy relaxation · SpepScan · DSC

Introduction

The kinetic-relaxation nature of the glass transition is commonly accepted and well understood today [1, 2]. The glass transition, that is, the genuine attribute of the glassy state, means here the transition from the metastable thermodynamic equilibrium of the melt to the frozen non-equilibrium structure of the glass reached by cooling of the melt, and vice versa by the heating of the glass. Obviously, the crystallization must be avoided during this process. The kinetics of the glass transition and of the attendant relaxation phenomena describe well the Tool–Narayanaswamy–Moynihan's (TNM) theory [3–6] originating in the Tool's concept of the fictive temperature, T_f [7, 8]. The older hypothesis of the second-order phase transition underlying the glass transition is merely one of textbook historical illustration value today, at least in the case of inorganic glasses [9]. The ambiguity of using the so-called glass transition temperature T_g as a characteristic material constant follows straightforwardly from the kinetic-relaxation character of the glass transition. Therefore, this value is used in technical praxis only in connection with a strict definition of both the experimental procedure of T_g determination and the sample thermal history. The relaxation character of the glass transition implies straightforwardly the characteristic hysteresis of the cooling–heating temperature dependence of state functions such as volume and

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enthalpy as well as the well-known shape of the temperature dependence of the temperature coefficients of these state functions, i.e., of the thermal expansion coefficient and heat capacity. During heating, the last ones typically posses the temperature course with one local maximum (the so-called overshoot) that can be in some cases preceded with one local minimum (undershoot). The classic DSC method is broadly used for measuring the heat capacity temperature dependence in the temperature range of the glass transition. The glass transition temperature is commonly identified with the inflexion point preceding the local maximum. The measurement-heating rate, as well as the cooling rate used for the glass sample preparation, changes, in principle, the shape and all the characteristic temperatures (i.e., those of minimum, maximum, and inflexion point) of the DSC heating curve.

The new experimental techniques, a dynamic differential scanning calorimetry (DDSC) and StepScan® DSC [10–13], bring a new insight into study of the glass transition. Both methods enable to split the glass transition into two types of processes—the fast one (denoted as in-phase, thermodynamic, or storage process) and the slow one (out-of-phase, kinetic or loss process). It was found experimentally that the so-called thermodynamic part of the glass transition is completely independent on the thermal history of glass, and on the direction of temperature change, and, thus, this process depends only on the sample chemical composition [14, 15]. Besides, the thermal history of a glass, including also the exothermic change during the melt → glass transition and the endothermic change in the opposite direction, is, thus, reflected exclusively in the so-called kinetic part of glass transition [14–17].

It is worth mentioning that the experimental finding of this study is, strictly speaking, in contradiction with the commonly accepted theory of the glass transition phenomenon.

The thermodynamic part of StepScan® glass transition record has been the subject of interest in recent studies [18, 19]. It was found that the thermodynamic part could be formally regarded as glass ↔ undercooled melt transition with a conversion degree α dependent (at isobaric conditions) on thermodynamic temperature only. This quasi-equilibrium can be well described by the empirical equation proposed by Holubová et al. [18, 19]

$$\alpha(T) = 1 - \exp[-(T/T_\mathrm{g})^n] \qquad (1)$$

where T is thermodynamic temperature, T_g is the glass transition temperature, which is unambiguously determined from the position of point of inflexion on the reversible part of StepScan DSC record. Thus, in the framework of StepScan® DSC method, the T_g value is considered as the experimental value of the glass transition temperature. The parameter, n, representing the slope of the α versus T curve at T_g temperature, varies in a wide range of values depending on the chemical composition of the non-crystalline material. The conversion degree α is calculated from the temperature dependence of the apparent reversible heat capacity c_p(rev, T) obtained from the StepScan® DSC record:

$$\alpha(T) = \frac{c_p(\mathrm{rev},T) - c_p(\mathrm{rev,glass})}{c_p(\mathrm{rev,melt}) - c_p(\mathrm{rev,glass})} = \frac{c_p(\mathrm{rev},T) - c_{pg}}{\Delta c_p} \qquad (2)$$

where $c_p(\mathrm{rev,melt}) = c_{p\mathrm{m}}/c_p(\mathrm{rev,glass}) = c_{pg}$ is identified with the maximum/minimum value of the measured sigmoid c_p(rev, T) curve and corresponds to the isobaric heat capacity of metastable melt/glass, respectively, at a particular temperature.

Recently, another type of semi-empirical description of the thermodynamic part of StepScan DSC record was proposed [20]. The reversible part of StepScan DSC record of a glass in the region of the glass transition was formally interpreted as a measure of the conversion degree α of the A ↔ B type equilibrium reaction identified with a reversible part of glass ↔ undercooled melt transition. In the case of the standard state of pure substance at the pressure and temperature of the system, the ratio of equilibrium mole fractions x(A), x(B) of A, B can be expressed by the corresponding equilibrium constant K:

$$K(T) = \frac{x(\mathrm{B})}{x(\mathrm{A})} = \frac{x(\mathrm{B})}{1 - x(\mathrm{B})} = \frac{\alpha}{1-\alpha} \qquad (3)$$

or

$$\alpha = \frac{K(T)}{1 + K(T)} \qquad (4)$$

where α is the conversion degree (transformation ratio). The temperature course of the conversion degree, α(T), was expressed in terms of the temperature dependence of the equilibrium constant based on the van't Hoff's equation [21]:

$$K(T) = K_0 \exp(-\Delta H/RT) \qquad (5)$$

where R is the molar gas constant (8.314 J K^{-1} mol^{-1}), T, the thermodynamic temperature, ΔH is the temperature independent formal reaction enthalpy, and

$$K_0 = K_\mathrm{r} \exp(\Delta H/RT_\mathrm{ref}) \qquad (6)$$

where T_ref is an arbitrary reference temperature ($T_\mathrm{ref} =$ 298 K was chosen) and $K_\mathrm{r} = K(T_\mathrm{ref})$ holds. The glass transition temperature, T_i, that is identified with the inflexion point $\alpha_i = \alpha(T_\mathrm{i})$ of the α(T) curve can be calculated by solving the equation:

$$\alpha_i = 1/2 - RT_i/\Delta H \qquad (7)$$

The aim of the present contribution is to compare both these approximations and relate them to the commonly accepted TNM theory of the glass transition.

Theory

Following the Tool's concept of fictive temperature [7, 8], the specific enthalpy, H, can be expressed as a function of the thermodynamic temperature, T, and fictive temperature, T_f:

$$H(T,T_\mathrm{f}) = \int_{T_\mathrm{r}}^{T_\mathrm{f}} c_{p\mathrm{m}}(T')\mathrm{d}T' + \int_{T_\mathrm{f}}^{T} c_{p\mathrm{g}}(T')\mathrm{d}T' \tag{8}$$

where $c_{p\mathrm{m}}$, and $c_{p\mathrm{g}}$ are specific isobaric heat capacities of metastable melt and glass, respectively, and T_r is an arbitrary sufficiently high (to ensure instantaneous formation of metastable equilibrium) reference temperature. Supposing the temperature independence of both specific heat capacities and realizing that fictive as well as thermodynamic temperature is in principle time dependent, the following time dependence of specific enthalpy is obtained:

$$\begin{aligned} H(t) = H[T(t),T_\mathrm{f}(t)] &= H_0 + (c_{p\mathrm{m}} - c_{p\mathrm{g}})T_\mathrm{f} + c_{p\mathrm{g}}T \\ &= H_0 + \Delta c_p T_\mathrm{f} + c_{p\mathrm{g}}T \end{aligned} \tag{9}$$

where

$$H_0 = H(T_\mathrm{r},T_\mathrm{r}) - c_{p\mathrm{m}}T_\mathrm{r} \tag{10}$$

The heat flow can be obtained from the time derivative of enthalpy:

$$\frac{\mathrm{d}q}{\mathrm{d}t} = \dot{q} = \left(\frac{\partial H}{\partial T}\right)_{T\mathrm{f}}\frac{\mathrm{d}T}{\mathrm{d}t} + \left(\frac{\partial H}{\partial T_\mathrm{f}}\right)_{T}\frac{\mathrm{d}T_\mathrm{f}}{\mathrm{d}t} \tag{11}$$

The time course of the fictive temperature, T_f, is obtained within the framework of TNM model [3–6]:

$$T_\mathrm{f}(t) = T(t) - \int_0^t \mathrm{d}t'(\mathrm{d}T/\mathrm{d}t)M[\xi(t) - \xi(t')] \tag{12}$$

where M is the Kohlrausch–Williams–Watts (KWW) relaxation function:

$$M(\xi) = \exp(-\xi^b) \quad 0 < b \le 1 \tag{13}$$

where b is constant, and ξ is the dimensionless relaxation time:

$$\xi(t) = \int_0^t \mathrm{d}t'/\tau(t') \tag{14}$$

where τ is the relaxation time given by the Moynihan's approximation:

$$\tau(T,T_\mathrm{f}) = \tau_0 \exp[xB/T + (1-x)B/T_\mathrm{f}] \tag{15}$$

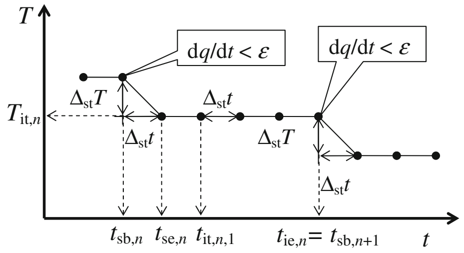

Fig. 1 Schematic drawing of time–temperature schedule during the StepScan® DSC

The StepScan® experiment proceeds via a temperature steps $\Delta_\mathrm{st}T$ realized within the time $\Delta_\mathrm{st}t$ by the constant prescribed heating/cooling rate β ($\beta = \Delta_\mathrm{st}T/\Delta_\mathrm{st}t$). After each temperature step (n-th step dwells from $t_{\mathrm{sb},n}$ to $t_{\mathrm{se},n}$), an isothermal regime follows during which a stationary state is reached. The isothermal regime following the n-th temperature step starts in time $t_{\mathrm{it},n,0} \equiv t_{\mathrm{se},n}$ and dwells until the beginning of the next temperature step, i.e., until the time $t_{\mathrm{sb},n+1}$. The end of the isothermal delay is given by fulfilling the following condition:

$$\dot{q}(t_{\mathrm{it},n,k}) = |H(t_{\mathrm{it},n,k+1}) - H(t_{\mathrm{it},n,k})|/\Delta_\mathrm{st}t < \varepsilon \tag{16}$$

The above heat flux check is repeatedly performed for each $\Delta_\mathrm{st}t$ time interval during the isothermal regime. The reversible isobaric heat capacity is calculated from the enthalpy change taking place during the temperature step:

$$c_{p,\mathrm{rev}}(T_{\mathrm{it},n} + \Delta_\mathrm{st}T/2) = [H(t_{\mathrm{se},n}) - H(t_{\mathrm{sb},n})]/\Delta_\mathrm{st}T \tag{17}$$

while the kinetic part of enthalpy change is formally expressed as "kinetic heat capacity" calculated from the enthalpy change during the isothermal temperature delay

$$c_{p,\mathrm{kin}}(T_{\mathrm{it},n}) = [H(t_{\mathrm{sb},n+1}) - H(t_{\mathrm{se},n})]/\Delta_\mathrm{st}T \tag{18}$$

The abbreviation of particular times and temperatures for the n-th temperature step and succeeding isothermal delay is presented in Fig. 1.

In order to obtain an analytical form of reversible StepScan® curve, it is enough to analyze the cooling curve. At the beginning of the temperature step, the stationary state is established which can be characterized by $T_\mathrm{f} = T$ in the prevailing part of the curve. Only for the low temperature part, where α approaches zero, the stationary state is characterized by constant value of fictive temperature, i.e., $T > T_\mathrm{f} = \mathrm{const.}$ Therefore, it seems to be reasonable to simplify the Eq. 9:

$$\tau(T) \approx \tau_0 \exp(B/T) \tag{19}$$

For the change of dimensionless time $\Delta\xi$ taking part during the temperature step, we then obtain

$$\Delta\xi \approx (\Delta_\mathrm{st}t/\tau_0)\exp(-B/T) \tag{20}$$

It was shown [14, 22] that if relaxation takes place near the metastable equilibrium, then KWW relaxation function can be approximated with the single exponential with sufficient accuracy. In this case, combining Eqs. 17, 9, 12, and 20, we obtain an analytical expression describing the reversible part of StepScan® DSC record:

$$\alpha = \frac{\Delta_{st}T_f}{\Delta_{st}T} = \left\{1 - \exp\left[-\left(\frac{\Delta_{st}t}{\tau_0}\right)\exp\left(-\frac{B}{T}\right)\right]\right\} = \left\{1 - \exp\left[-A\exp\left(-\frac{B}{T}\right)\right]\right\} \qquad (21)$$

where $A = \Delta_{st}t/\tau_0$.

Experimental

Stepwise DSC technique, the StepScan® method (Perkin-Elmer) [10], was used. The temperature step $\Delta_{st}T = 1$ K was used, and heating or cooling rate during the temperature steps of ±1 °C/min and/or ±100 °C/min was applied. The isotherm duration was software controlled. The maximal allowed heat flow difference during isotherm was $\Delta(dQ/dt) = \pm 0.0001$ mW per approximately 10 s before the next step. Both the glass transition temperature and change of isobaric heat capacity, Δc_p, were obtained independent of experimental conditions and thermal history of glass [14].

As_2Se_3 and As_2S_3 bulk glasses were prepared by conventional method of direct synthesis from high-purity elements (5N) in evacuated silica ampoules in a rocking furnace and quenched in air. The oxide glass LiPbPBO ($40Li_2O{:}10PbO{:}10B_2O_3{:}40P_2O_5$) was prepared by melting of oxides and melt was consequently cooled on cold copper plate. The lead–silica glass NBS 711 is a commercial product [23]. The barium crystal glass RONA was taken from the industrial production of the glasswork RONA, Lednické Rovne. The poly(styrene-*co*-acrylonitrile), 75/25, PSA, from BASF was used as a representative of polymer sample. Samples (weighing around 10 mg) were measured into sealed aluminum pans using Pyris 1 DSC (Perkin-Elmer).

Results and discussion

The results of regression analysis of experimental StepScan® data are summarized in Table 1. From the values of standard deviation of approximation, it follows that all the three models describe the experimental data with sufficient accuracy. Moreover, the model of Holubová et al. coincides almost fully with the model based on the TNM theory. The values of glass transition temperature obtained from the model of Holubová are very close to those calculated from the Van't Hoff's model, the T_i values are about 3–5 °C lower in comparison with T_g values of Holubová within the set of studied materials. This simply follows from the fact that the conversion degree in inflexion point of Van't Hoff's model α_i is lower than ½ (see the Eq. 7) whereas for the Holubová's model α_i is close to 0.632. Graphical comparison of experimental data with the results of all the three used models is given in Figs. 2, 3,4, 5, 6, 7. It can be seen that, for all the studied

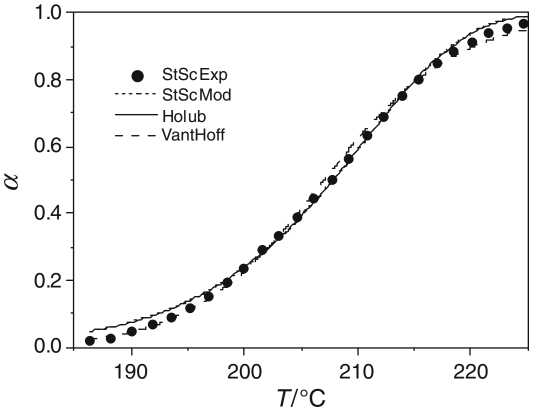

Fig. 2 Comparison of experimental StepScan® record (points) of As_2S_3 glass with empirical models (Holubova et al.—*full line*, Van't Hoff—*dashed line*) and with TNM relaxation theory (*short dash line* fully coinciding with the *full line*)

Table 1 Results of nonlinear regression analysis for empirical models (Holubova et al.—Eq. 1, Van't Hoff—Eq. 4), and for the model based on the TNM relaxation theory Eq. 21

Model	Van't Hoff				Holubova		TNM		
System	$-\log K_r$	ΔH kJ/mol	s_{apr}	T_i/ °C	n	T_g/ °C	$\log A$	B/K^{-1}	s_{apr}
As_2S_3	21.84	328.3	0.014	207	56.7	211	24.40	27200	0.018
As_2Se_3	22.94	371.0	0.020	187	67.7	190	29.18	31150	0.014
LiPbPBO Glass	37.95	421.9	0.033	339	59.3	344	25.51	36232	0.012
NBS711 Glass	41.98	402.0	0.028	464	46.9	471	20.15	34546	0.010
RONA Glass	80.02	711.6	0.025	559	74.5	563	32.09	61801	0.021
PSACN25	10.59	285.1	0.039	105	63.6	108	27.40	24029	0.020

The same values of standard deviations of approximation, s_{apr}, were found for Holubova and TNM model

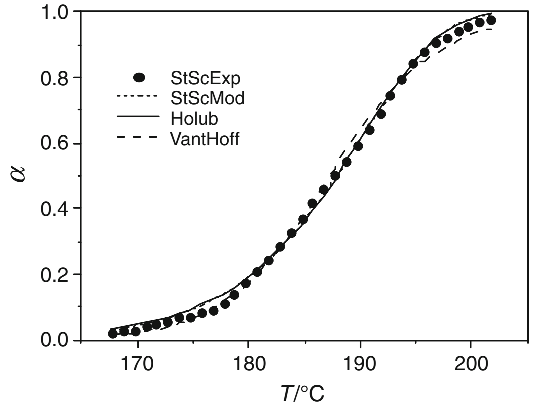

Fig. 3 Comparison of experimental StepScan® record (points) of As_2Se_3 glass with empirical models (Holubova et al.—*full line*, Van't Hoff—*dashed line*) and with TNM relaxation theory (*short dash line* fully coinciding with the *full line*)

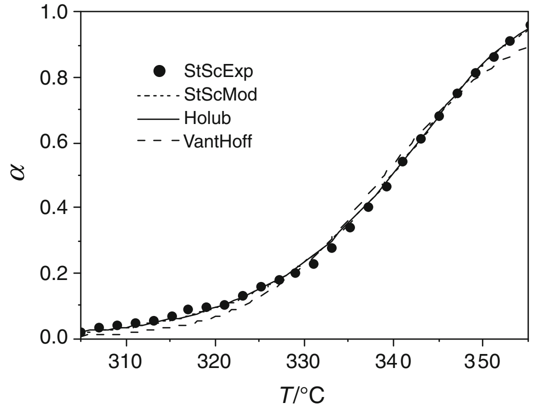

Fig. 4 Comparison of experimental StepScan® record (points) of LiPbPBO glass with empirical models (Holubova et al.—*full line*, Van't Hoff—*dashed line*) and with TNM relaxation theory (*short dash line* fully coinciding with the *full line*)

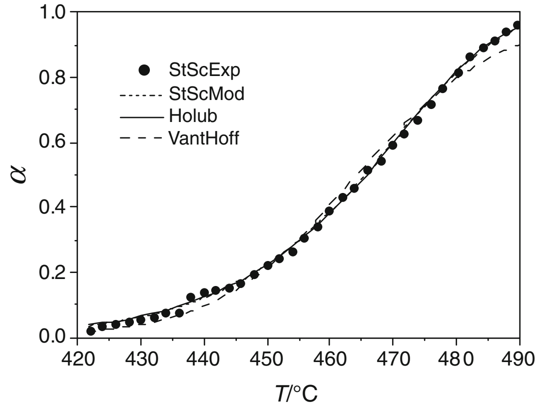

Fig. 5 Comparison of experimental StepScan® record (points) of NBS711 glass with empirical models (Holubova et al.—*full line*, Van't Hoff—*dashed line*) and with TNM relaxation theory (*short dash line* fully coinciding with the *full line*)

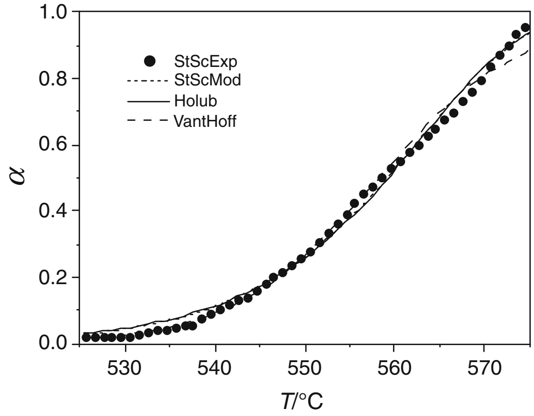

Fig. 6 Comparison of experimental StepScan® record (points) of RONA glass with empirical models (Holubova et al.—*full line*, Van't Hoff—*dashed line*) and with T relaxation theory (*short dash line* fully coinciding with the *full line*)

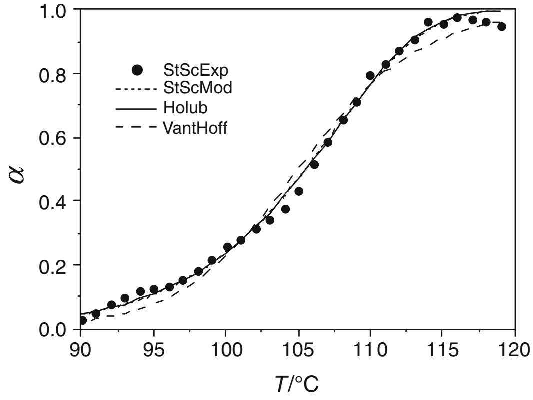

Fig. 7 Comparison of experimental StepScan® record (points) of PSACN25 glass with empirical models (Holubova et al.—*full line*, Van't Hoff—*dashed line*) and with TNM relaxation theory (*short dash line* fully coinciding with the *full line*)

materials, the curves calculated according TNM and Holubová's models fully overlapped. From this point of view, the results of StepScan® DSC can be fully rationalized within the framework of TNM relaxation theory, i.e., on the basis of kinetics of the glass transition. The coincidence with the thermodynamic equilibrium is, thus, probably only an artificial fact following from the similar shape of Van't Hoff's and experimental curves. However, the StepScan® experimental results pointed out the invariance of the results with respect to the heating/cooling rate, β, applied during the temperature step [18, 19]. This fact is in contradiction with our TNM result. Simple rewriting of the Eq. 21 shows the expected dependence on β for constant value of $\Delta_{st}T$:

$$\begin{aligned}\alpha &= \{1-\exp[-(\Delta_{st}T/\tau_0\beta)\exp(-B/T)]\}\\ &= \{1-\exp[-(A'/\beta)\exp(-B/T)]\}\end{aligned} \qquad (22)$$

where $A' = \Delta_{st}T/\tau_0$.

However, the detailed inspection of time–temperature dependence during the StepScan® experiment showed that, especially for higher heating/cooling rates, the prescribed linear dependence within the temperature step is not fulfilled. So far as the details about the Perkin Elmer software used for acquisition and evaluation of StepScan® experimental data are not known to the authors, it is difficult to analyze this situation in more detail. It will be the scope of our future work.

Conclusions

The experimental results obtained by the StepScan® DSC method can be empirically described alternatively by the model of Holubová et al. and by the thermodynamic equilibrium model based on Van't Hoff's equation. The former model is numerically fully equivalent to the model based on the Tool–Narayanaswamy–Moynihan's (TNM) relaxation theory of the glass transition (Table 1).

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