OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 1, No. 6, June 2007, p. 277 - 280

Capability of conventional Differential Scanning Calorimetry (DSC), temperature modulated DSC (MDSC) and StepScan DSC for the glass transition phenomenon study

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The results and limits in the glass transition study by conventional differential scanning calorimetry (DSC), temperature modulated DSC (MDSC) and StepScan DSC are compared. Bulk glassy As_2S_3 was used as appropriate model glass. It was found that nonreversing (kinetic) processes affected in fundamental way the results obtained especially by conventional DSC, but indispensable influence on MDSC results was also found. On the other hand no influence of kinetics was observed when StepScan DSC was used. Reversing (thermodynamic) part of StepScan DSC was found to be completely independent on the experimental conditions in the glass transition region. This result has shown that explanation of glass transition phenomenon is still far from being complete.

(Received April 3, 2007; accepted April 25, 2007)

Keywords: Glass transition, DSC, Temperature modulated DSC, MDSC, StepScan DSC, Arsenic trisulfide

1. Introduction

The development of differential scanning calorimetry (DSC) technique in last two decades was done by introduction of commercially available calorimeters with temperature modulation, MDSC^{TM}, by TA Instruments. Using conventional heat-flux DSC whose heating block temperature is sinusoidally modulated and so the sample temperature is modulated in the same manner about a constant ramp. The resulting instantaneous heating rate varies sinusoidally about the underlying heating rate (average heating rate). The average heat flow is called total heat flow. This one is the only quantity that is available and hence it is the only quantity that is always measured in conventional DSC experiments. The sample temperature and the amplitude of instantaneous heating flow are measured and finally, using Fourier transformation of the experimentally obtained data, the quantity termed reversing heat flow is obtained. The nonreversing heat flow is the difference between the total heat flow and the reversing heat flow and represents heat flow due to kinetically hindered process. Process is called reversing if the system responds in a reversible way on the timescale of the experiment (or faster) and nonreversing if the system is either too slow to respond reversibly on the timescale of the experiment or if it is irreversible altogether (on any timescale). In case of MDSC it means that the reversing process is in-phase with temperature modulation and nonreversing process with some phase lag is out-of-phase.

Reversing isobaric heat capacity can be determined by MDSC using the magnitude of heat flow and heating rate obtained by averaging over one modulation period. As a complex heat capacity has been defined, see [1], the nonreversing heat flow recalculation to the nonreversing heat capacity has also been used.

More detailed information about MDSC one can found in [2-4] and references therein.

More recent and from MDSC^{TM} essentially different technique, StepScan DSC by Perkin-Elmer, is based on adapted enthalpic method of isobaric heat capacity, C_p, determination to the high sensitive power-compensated apparatus. This method allows equilibration of the system after each step in a series of small step increases (decreases) in temperature. The area under the resulting curve (the total enthalpy change in the step) is evaluated and divided by the temperature step to give the heat capacity at the midpoint of the temperature step. Enthalpic changes connected with possible kinetic effects are recorded in the timescale during equilibration after each one temperature step. StepScan DSC method allows obtaining not only C_p at the midpoint of the temperature step but also enthalpic changes connected with slow processes (compare to the time of temperature change) after temperature step. As a result two curves are obtained. The first of them is the temperature dependence of C_p (reversible part) and the second one is the temperature dependence of slow processes' enthalpy changes (irreversible part); these parts have been termed by Perkin-Elmer as thermodynamic and kinetic ones, respectively.

The result obtained by StepScan DSC seems to be close to this one obtained by MDSC, but two crucial differences should be stressed. Firstly, when TMDS is used, the sample temperature is continually periodically changed, aside from the extent of possible kinetic effects, whereas in the case of StepScan DSC the software-controlled variable isotherm duration allows the sample to achieve the state close to the thermal equilibrium at each temperature step. Secondly, no special mathematical operation, like Fourier transformation, is needed to obtain results by StepScan DSC.

In spite of a lot of theoretical works have been addressed to the physical meaning of both reversing and nonreversing components, see e.g. [3-5] and references cited in, one can only hardly say that this problem has been resolved. Having this in mind it seems to be more useful to compare all three available DSC techniques each other.

The main aim of our work is to compare the results obtained by conventional DSC, MDSC and StepScan DSC in the glass transition region of model glass.

2. Experimental

Bulk glass of As_2S_3 (5N purity) was used as model glass. Its advantage is facile preparation in high purity, stoichiometric composition and great reluctance of undercooled melt against crystallization. The power-compensated differential scanning calorimeter Pyris 1 operated with Pyris software (both Perkin-Elmer) capable of working in all three modes under study was used.

A typical sample weight of small pieces of bulk glass was 8-10 mg. Sample was sealed into aluminium pans. An empty pan was used as a reference sample and matched to within the sample pans by ± 0.05 mg.

Calorimeter was carefully calibrated and nitrogen gas of precisely regulated constant flow 20 ml/min. (FMA 550 mass flow controller, Omega) was used as a purging gas.

DSC mode was used with heating rates successively 1, 10, 20, 50 and 100 K/min. For experimental curves, see Fig. 1.

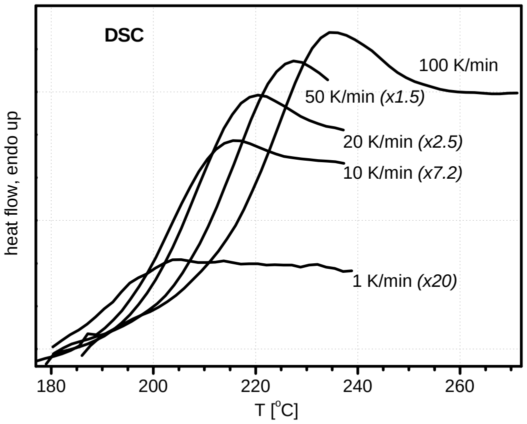

Fig. 1. Conventional DSC results. Number in brackets is magnification factor.

Dynamic DSC (DDSC) is the Perkin-Elmer version of MDSC. To avoid possible confusion the MDSC will be used as a common mark for temperature modulated DSC, despite of calorimeter manufacturer. Dynamic mode operated with saw-tooth modulation was used with period 40 s, temperature amplitude 0.75 K and heating/cooling rates 2/-1, 4/-2 and 10/-5 K/min. These experimental conditions correspond to underlying heating rate 0.5, 1.0 and 2.5 K/min, respectively. For temperature dependence of reversing C_P, see Fig. 2.

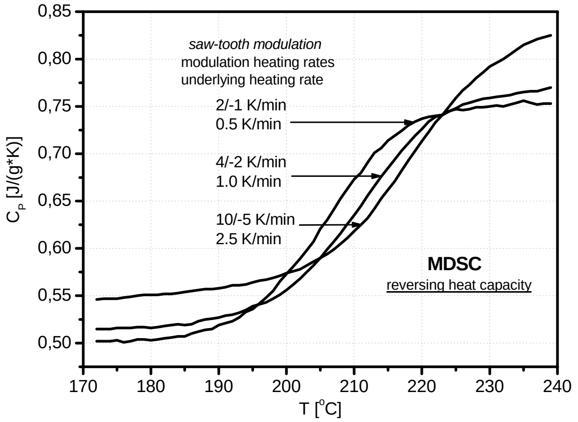

Fig. 2. Reversing C_P dependence on T obtained from MDSC measurements. For details, see text.

StepScan DSC experiments were carried out with temperature step 1 K, heating rates in the temperature step successively 1, 10 a 100 K/min and isotherm duration either 60 sec. or with maximal allowed heat flow difference ± 0.1 μW per approx. 2 sec. before next step. The experimental set up corresponds to average underlying heating rate 0.50, 0.91 and 0.99 K/min, respectively. For results, see Fig. 3.

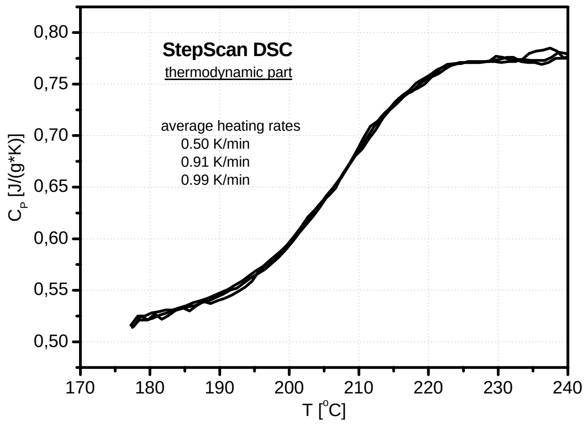

Fig. 3. StepScan DSC thermodynamic (reversing) part at different average heating rates, see text.

3. Results and discussion

In the glass transition temperature range the influence of three available DSC methods on the determination of glass transition temperature, T_g, was studied. T_g was determined as a temperature of half change of heat flow (DSC) or isobaric heat capaciy, ΔC_p (MDSC, StepScan DSC). Results are collected in Fig. 4.

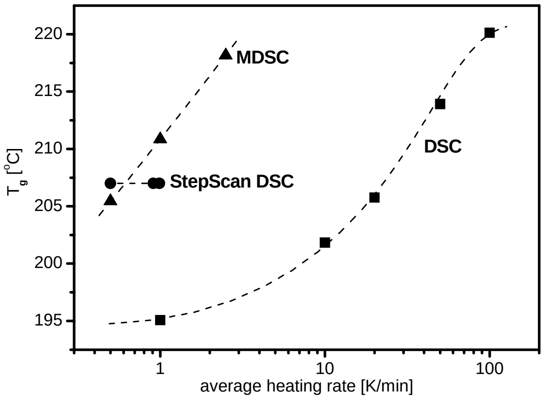

Fig. 4. Heating rate dependencies of T_g, obtained by indicated DSC methods.

The T_g dependence on the heating rate obtained by conventional DSC was significant as it is well-known and is discussed elsewhere [6-14].

Results obtained by MDSC show still distinguishable dependence of T_g on heating rates (more correctly on underlying heating rates) even though these rates are slow at all. The T_g values are from 10 °C up to 22 °C higher comparing with conventional DSC results at the comparable heating rates. Furthermore, it must be stressed that with increasing underlying heating rate besides the glass transition temperature also temperature dependence of isobaric heat capacity, C_p, has been shifted up but without changing of isobaric heat capacity change at glass transition, ΔC_p, see Fig. 2.

From above mentioned follows that experimental MDSC dependencies have been moved up in both axis when underlying heating rate increases. It means that MDSC requires both careful calibration and choice of experimental set up. It is well known that both T_g and C_p depend not only on frequency but also on amplitude of temperature modulation (it means on mean rate of temperature change). It seems to be clear that MDSC reversing heat flow is in fact not fully in phase with the temperature change. The permanent periodical change of sample temperature probably causes that sample is not close to thermal equilibrium, especially in the case when reversing process is attended by some slow nonreversing one. The glass transition is one of typical examples.

The values of C_p given by StepScan DSC are independent on the average heating rate and in consequence of that T_g value remains unchanged, see Figs. 3 and 4.

Average heating rate is governed both by the temperature step heating rate and duration of following isotherm. The isotherm duration is variable, depending on the amount and average relaxation time of kinetic processes at the given temperature. It means that the average heating rate of the one step can differ more or less from the other one at every heating-isotherm step. It can be simply said that in every step the StepScan DSC method will wait for termination of all processes being slower then experimental time of the temperature step, of course within the instrument sensitivity. As follows, the heat flow of nonreversing (kinetic) process is effectively separated from reversing (thermodynamic) one and so the temperature dependence of isobaric heat capacity, and from it T_g, can be determined without influence of both thermal history of glass and experimental conditions. As we have shown previously, Step Scan DSC enables to determine the glass transition temperature from heating scan as well as from cooling scan dependent on chemical composition only [14,15].

From obtained results follows one crucial question whether or not the glass transition is the kinetic effect at all. To test possibility of solving of this problem by StepScan DSC, the heating scan was stopped in the glass transition region and was continued after 30 minutes isotherm (sufficient long time to reach thermal equilibrium, because at this temperature the mean relaxation time is of order of hundred seconds). At this moment it occurs to everybody that separation of experimentally obtained heat flow into reversing and nonreversing ones could presents only software separation of entirely kinetic processes. In such case as well as in the case that the glass transition is entirely kinetic effect, both reversing and nonreversing (kinetic) parts should change during the sufficiently long isotherm. Comparison of results obtained without and with inserted isotherm, however, shows clearly that only kinetic overshoot disappeared after isothermal dwell whereas the sigmoidally shaped reversing part remains unchanged, see Fig. 5.

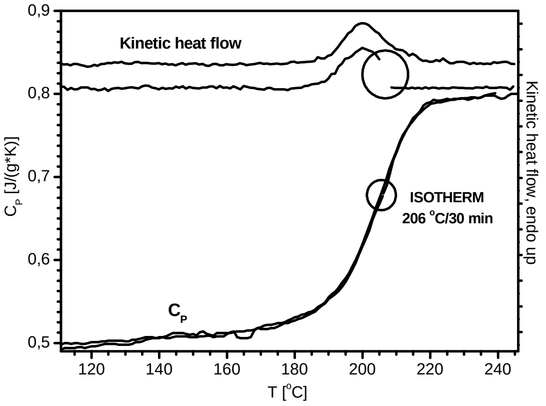

Fig. 5. StepScan DSC measurements in the glass transition range of As_2S_3 bulk glass. Reversing parts are labeled C_p, the nonreversing ones are labeled Kinetic heat flow. For details, see text.

This result, along with previous finding that reversible part (and consequently T_g) depends only on the chemical composition of glass [14,15], shows that the commonly used concept that glass transition is entirely kinetic process is probably not fully realistic. It should be stressed at this moment that well known T_g dependence on the thermal history of glass and on the experimental conditions, when conventional DSC is used, can be caused by superimposition of the slow kinetic effects on the sigmoidally shaped glass transition C_p change, for more details see [14].

4. Conclusion

The glass transition of glassy arsenic trisulfide was measured to test capabilities of three DSC techniques: conventional DSC, temperature modulated DSC (MDSC) and StepScan DSC. As one can expect the significant dependence of the glass transition temperature on experimental conditions was found by conventional DSC, but surprisingly indispensable dependencies were also found when MDSC was used. The isobaric specific heat capacity $C_p(T)$, determined by MDSC, was also dependent on the experimental parameters. On the other hand, both the glass transition temperature and $C_p(T)$ were found by the StepScan DSC to be independent on the experimental conditions. It is important to emphasize that step heating rate in StepScan DSC experiments should not be too high, typically is used between 10 – 20 K/min. When higher step heating rate is chosen the total enthalpy change in the step can be evaluated with indispensable error.

It has been demonstrated, by means of the StepScan DSC, that the reversing (thermodynamic) part is really independent on the experimental time in the glass transition range, contrary to nonreversing (kinetic) part. From it follows that glass transition is very probable not only kinetic effect, as it has been commonly assumed based on both viscosity and conventional DSC measurements. One can conclude that explanation of glass transition is still far from being complete and obtained results raise further questions.

Acknowledgements

This work was supported by the project of the Ministry of Education of the Czech Republic MSM 0021627501.

Authors cordially thank to prof. S. A. Kasap from University of Saskatchewan, Canada, for helpful discussions on MDSC technique.

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