

ψ_T . The value of ψ_g during the scanning portion of the underlying linear temperature program is then calculated by linear interpolation between the values derived in the adjoining isothermal portions of the underlying linear temperature program. The method of interpolation is illustrated by FIG. 12.

5. Calculate the instantaneous calibration constant: At each point, the actual heat flow phase ϕ_g , as calculated in the previous step, is used as an argument in a universal calibration function to obtain the specific heat calibration constant K appropriate to the actual experimental conditions extant for that particular point.

6. Calculate the real and imaginary components of the specific heat: C' and C'' are calculated at each point by solving the following set of simultaneous equations:

$$C' \cos(\psi_g + \psi_T) - C'' \sin(\psi_g + \psi_T) = K \phi_{cos}(T_a \omega)$$

$$C' \sin(\psi_g + \psi_T) + C'' \cos(\psi_g + \psi_T) = K \phi_{sin}(T_a \omega)$$

where $T_a = (T_{cos}^2 + T_{sin}^2)^{1/2}$ and ω is the circular frequency corresponding to the applied oscillation's period. The value K in the above equations for calculation of the real component of the specific heat (C') and the imaginary component of the specific heat (C'') is the instantaneous calibration constant calibrated in step 5, above.

7. Smooth the calculated signals: ϕ_{DC} , C' and C'' are smoothed at each point by normalized numerical integration over an interval consisting of exactly an integer number of oscillation periods and centered on that point. Each calculated value is associated with the centroid of the integration interval.

EXAMPLES

The following experimental data were obtained using a Perkin-Elmer DSC-7 "power compensation" Differential Scanning Calorimeter connected to a Perkin-Elmer TAC-7/DX Thermal Analysis Controller that communicates with a Perkin-Elmer Unix 7-Series data station. All samples used in the experiments are readily available commercial products. Sample sizes are as indicated below.

FIG. 4

FIG. 4 shows the glass transition of polystyrene (PS), measured in a cooling run ($\beta_0 = -1$ K/min, Oscillation amplitude $T_a = 1$ K, Period = 100 sec, Sample weight = 17.452 mg).

The heat capacity C_a is calculated from the average heat flow ϕ_D . C_a is equal to the value obtained with a conventional DSC and is identical to C_p . The inflection point in C_a occurs at a lower temperature than that of C' . In contrast to C' , the T_g measured using C_a depends on β_0 . The inflection point of the real (energy storage) part C' , is correlated with the peak in the imaginary (energy loss) part, C'' . Both the shape and the temperature dependence of C' and C'' are in accord with the theories of relaxation in glass transition.

FIG. 5

The heat capacities C_{abs} (absolute heat capacity) and C_a (average heat capacity), and their difference $C_a - C_{abs}$, are shown for the same measurement as in FIG. 4.

FIG. 5 depicts the prior art calculation (from the '775 patent). $C_a - C_{abs}$ indeed exhibits a peak; however, it is located at lower temperature than the glass transition (as calculated from C') and is dependent on the cooling rate β_0 .

As explained with regard to eq. (28), this calculated value is non-quantitative regarding the relaxation process.

FIG. 6

The difference between the prior art ('775 patent) and the present invention is shown for the measurement of FIG. 4. As is apparent, C'' and $C_a - C_{abs}$ exhibit a markedly different dependence on the temperature, with only the former having its peak correctly at the inflection point (glass transition temperature T_g) of the real part and absolute value of the complex specific heat.

FIG. 7

Glass Transition of Polystyrene (PS), measured in a heating run ($\beta_0 = 2$ K/min, Oscillation amplitude $T_a = 1$ K, Period = 50 sec, Sample Weight = 17.452 mg). The sample is identical to that used for the run of FIG. 4.

C_a exhibits the same behavior as seen with a conventional DSC. An enthalphy relaxation peak is superimposed on the glass transition. C' has an inflection point similar to that of FIG. 4.

FIG. 8

Calculation following the prior art ('775 patent). The interpretation of $C_a - C_{abs}$ suffers from the same difficulties as in FIG. 5: only C'' has its peak correctly at the inflection point (glass transition temperature T_g) of the real part and absolute value of the complex specific heat.

FIG. 9

Heating curve for quench cooled PET ($\beta_0 = 2$ K/min, Oscillation amplitude $T_a = 1$ K, Period = 60 sec, Sample Weight = 5.842 mg).

Three transitions can be seen: the glass transition around 70° C., the recrystallization around 120° C. and the melting around 200° C. The glass transition exhibits the same behavior as discussed for polystyrene. The recrystallization is a transition of the strongly undercooled melt in the polymer crystal. The melt is far removed from equilibrium. The transition is possible in only one direction and is therefore only barely seen in the modulated signal. Only C'' has a small peak. C' can be used as a baseline in the evaluation of C_a . As far as the melting is concerned, C' exhibits a change at lower temperatures, while C'' remains unchanged in that range. The peak maximum of C'' occurs at a somewhat larger temperature than that of C' . Using irreversible thermodynamics, these curves give information on enthalpy changes and entropy.

FIG. 10

Calculation following the prior art ('775 patent). $C_a - C_{abs}$ is really the difference between two curves obtained under dissimilar experimental conditions. It can be interpreted only intuitively, and not quantitatively.

FIG. 11

The difference between the prior art ('775 patent) and the present invention is shown for the measurement of FIG. 9: since, as explained with regard to FIG. 9, the recrystallization cannot affect the modulated signal, it is essentially not seen in either C' or C'' while strongly present in C . In contrast, $C_a - C_{abs}$, the prior art "non-rapidly reversible" component, erroneously exhibits a strong peak at the recryst-