ELSEVIER

Thermochimica Acta 285 (1996) 243–252

thermochimica
acta

Excess energy of polymorphic states or glass over the crystal state by heat of solution measurement

G. Salvetti[a,*], E. Tognoni[a], E. Tombari[a], G.P. Johari[b]

[a] *IFAM del CNR, Via del Giardino 7, 56127 Pisa, Italy*
[b] *Department of Materials Science and Engineering, McMaster University, Hamilton, Ont. L8S 4L7, Canada*

Received 28 August 1995; accepted 12 February 1996

Abstract

The excess internal energy of one polymorph of a material over another may be determined from their heat of solution in a given solvent. (This energy is not to be seen as reversible heat of transformation of the polymorphs.) Thus the difference between the internal energy of amorphous and crystalline forms of sucrose, glucose and glucose monohydrate have been determined from measurement of their heat of solution in water. These differences are 21.2, 15.5 and 28.1 kJ mol^{-1}, respectively. This difference in energy is caused by differences in van der Waals interaction energy, the extent of and the total energy associated with H-bonding in the two solids, and their vibrational frequencies. The implication of these studies and further use of the procedure are discussed in general terms, and it is proposed that this method is more accurate than the usual method of integrating heat capacity–temperature data. The method can be used for determining the excess energy at 0 K of materials which decompose or melt incongruently, and when neither the heat capacity of the high temperature phase nor the heat of phase transformation can be measured.

Keywords: Excess internal energy; Glass; Glucose; Glucose monohydrate; Heat of solution; Polymorphs; Sucrose

---

1. Introduction

To determine the difference between the internal energy, E_{exc}, (or enthalpy, H_{exc} at 1 bar pressure) of two structurally different forms of a material at a certain temperature

---

[*] Corresponding author.

PII S0040-6031(96)02915-2

T, one requires that the heat capacity, C_p, of the two forms be measured from near 0 K to T K and the integral $\int_0^T C_p \mathrm{d}T$ be evaluated for both forms. E_{exc} is then equal to the difference between the values for this integral for the two forms provided no phase transformation occurs between zero and T K. Further, when one needs to determine E^0_{exc}, the difference between the internal energies of two forms of a material at 0 K, C_p data are required to a higher temperature T_1, at which both forms have been transformed into a single third phase, usually a liquid. E^0_{exc} is then equal to the difference (see, e.g., undergraduate text books on thermodynamics).

$$E^0_{\mathrm{exc}} = E^0_1 - E^0_2 = \left(\int_0^{T_{t,1}} C_{p,1} \mathrm{d}T + \Delta H_{\mathrm{t},1} + \int_{T_{t,1}}^{T_1} C_{p,3} \mathrm{d}T \right) + \left(\int_0^{T_{t,2}} C_{p,2} \mathrm{d}T + \Delta H_{\mathrm{t},2} + \int_{T_{t,2}}^{T_1} C_{p,3} \mathrm{d}T \right) \quad (1)$$

where subscripts, 1, 2 and 3 refer to the three forms, 1, 2 and 3, respectively, ΔH_{t} to their heats of reversible phase transformation to the third phase at temperatures $T_{\mathrm{t},1}$ and $T_{\mathrm{t},2}$, and T_1 is a temperature, greater than $T_{\mathrm{t},1}$ and $T_{\mathrm{t},2}$, where phase 3 of heat capacity $C_{p,3}$ exists. This third phase is usually a liquid. When a material rapidly sublimes or decomposes before its melting point is reached, or melts incongruently, this method cannot be used for measurement of its zero-point excess energy, E^0_{exc}. A simpler method for the measurement of E_{exc} of all materials and E^0_{exc} of materials which sublime, decompose or do not melt congruently would, therefore, be useful.

Two forms of a material that do not phase transform at a certain temperature below their equilibrium transformation temperature can be brought from their initially different energy states to the same final energy state also under isothermal conditions at that temperature. This can be done by measuring the heat of solution of the two forms of a material in a particular solvent at a fixed temperature. When this is done the difference between the change in the energy observed for the two forms will be equal to E_{exc} at that temperature. This procedure has the advantage that the usually tedious procedure of C_p measurements at different temperatures is avoided, and the integration of C_p against temperature from near 0 K is not needed.

The heat of solution of inorganic and organic materials has been studied for many years and tables of this heat are available in handbooks of physicochemical data. The heat of solution of organic polymers has also been studied in detail [1–7], with the principal purpose of determining the heat of mixing [1, 2] polymer compatibility for forming blends [3], changes in the configurational and internal energy with temperature [3–5], and for understanding the thermodynamics of polymer solutions in general [6, 7]. Here we use heat of solution measurements to determine the excess energy of three amorphous materials, sucrose, glucose and glucose monohydrate, over their crystalline forms. The excess energy for the first is for its glassy state at 298.16 K, and for the other two is for their highly viscous supercooled liquid states slightly above their calorimetric T_{g}s. Furthermore, we discuss the use of such studies, for other phenomena and other materials.

2. Experimental methods

The microcalorimeter used in an earlier study of C_p and ΔH, the heat release on chemical reaction [8], was modified to accept a 3-mm diameter stainless steel and Teflon constructed sample holder, which contained a weighed amount (7 to 34 mg) of a sample. It was kept at the same temperature as the 1.3 g of distilled water in which the sample dissolved when the sample holder was pushed and submerged in the water. In a typical experiment, weighed amounts of the sample (in its holder) and of water were contained in the same stainless steel tube, which constituted the calorimetric cell, of 4.6 mm internal diameter and 0.2 mm wall thickness, but vertically separated from each other by an air gap of ~ 3 mm and Teflon cap, which prevented water vapour from coming into contact with the sample. The calorimetric cell was in turn contained in a cylindrical cavity (the thermal bath) towards which the heat exchange coefficient was 20 mW K^{-1}. After thermal equilibrium at 298.16 K was reached, the holder containing the sample was pushed into and thus submerged in the water and the temperature change recorded to within 10 μK over a period of 3000 s, until the temperature reached the initial equilibrium value.

A typical plot of the temperature against time for glassy and crystalline sucrose is shown in Fig. 1. This plot was integrated to determine the area it enclosed. A comparison of this integrated area against the area of the standard plots, which were obtained by using known amounts of heat provided to the cell by means of a resistor immersed in the same amount of water, gave the magnitude of the total heat absorbed or evolved during the dissolution of the solid in water.

The so obtained absolute calibration of the microcalorimeter, whose operation for data collecting has been described [8], was tested for both endothermic and exothermic processes by measuring the heat of solution of KCl and KF. Values obtained from averaging 5–6 runs were within 5% of each other. They were found to be consistently 18% higher than literature values for KCl (20.14 kJ mol^{-1}, 17.22 kJ mol^{-1} in the literature), but agreed with the literature values for KF [9].

All chemicals were 99.5+% pure analytical reagent grade, purchased from either Baker Analyzed or Analyticals Carlo Erba. The water used for the purpose was a distilled and ion-exchanged sample commercially available from Angelini, Italy.

Glassy specimens were prepared by melting the crystalline solids in sealed ampoules. Glucose was melted and kept at 148°C and sucrose at 190°C and cooled to ambient temperature. The glassy samples in both cases were light yellow in colour, possibly due to the formation of traces of glucosan, as noted by Parks et al. [10] for glucose, but their C_p was the same as of the colourless samples. Glucose monohydrate glass was melted and kept at 110°C. It was colourless, and completely transparent. The literature values of their glass transition temperatures are 295 K for glucose [11, 12], 340 K for sucrose [12], and 270 K for glucose monohydrate [13], all measured by differential scanning calorimetry with a heating rate of 10 K min^{-1}.

Typical plots of the rate of heat or energy transfer against time observed during the measurements are shown in Fig. 1. Here the exothermic and endothermic processes of dissolution are evident also from the manner at which the rate of energy release approaches zero.

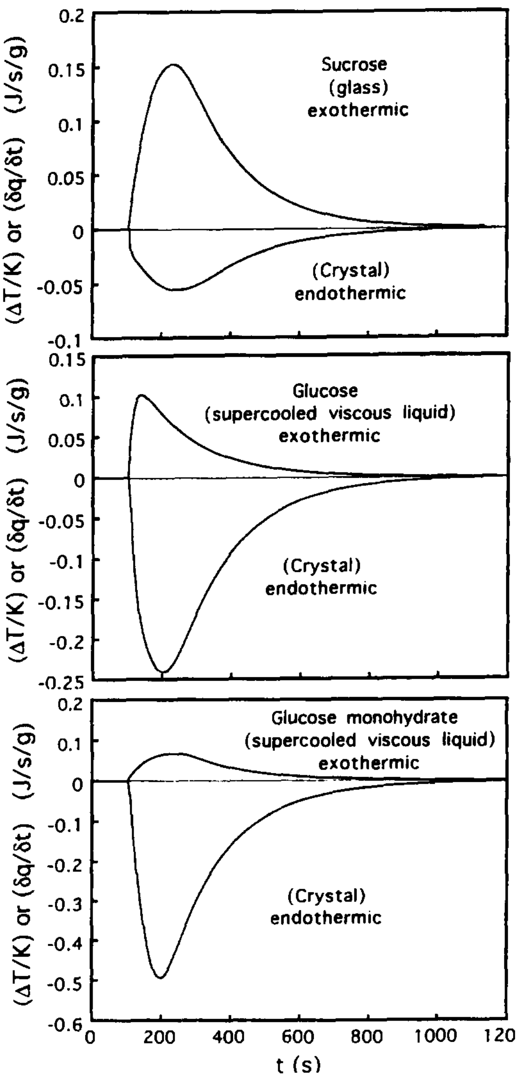

Fig. 1. The absorption and release of heat observed in typical experiments with sucrose, glucose and glucose monohydrate. The mass of the samples are scaled to 1.0 g. The plot is for the change in temperature from the initial value, ΔT, as a function of time. This change ΔT is proportional to the rate of heat exchange, i.e. $\Delta T = K(\partial q/\partial t)$, where K is the instrument constant and $(\partial q/\partial t)$ is the rate of heat transfer. Thus the plot is also equivalent to a plot of $(\partial q/\partial t)$. The integrated area under the curves thus gives q, the total heat absorbed or released. This heat is equal to the heat of solution, i.e. $H^S = -\int_0^\infty (\Delta T/K)\mathrm{d}t$ or $\int_0^\infty (\partial q/\partial t)\mathrm{d}t$. For clarity the starting time for the measurements is arbitrarily shown as 100 s after which the change in ΔT is shown to occur.

3. Results

The heat of solution measured for both the crystalline and glassy state of various materials are given in Table 1, in which the heat of solution of KCl and KF have also been included. This would enable comparison of our data with the values given in the

Table 1
The heat of solution of the glassy and crystalline forms of several substances at 298.16 K in water

Material	Sample mass/mg	H^S/(kJ mol^{-1})
Sucrose (crystalline)	30.95	6.467
	34.10	6.342
	33.00	6.481
Sucrose (glassy)	12.09	−13.788
	15.79	−15.767
	16.65	−14.847
Glucose (crystalline)	27.54	12.163
	24.73	12.264
	40.86	12.196
Glucose (glassy)	18.72	−3.469
	17.17	−3.162
	29.99	−3.365
Glucose monohydrate (crystalline)	19.13	24.490
	34.81	24.165
	25.17	24.024
Glucose monohydrate (glassy)	19.70	−3.700
	24.25	−3.839
	43.20	−3.775
KCl (crystalline)	9.62	20.262
	10.30	20.140
	4.85	20.625
•KF (crystalline)	9.41	−16.559
	10.77	−16.413

literature, which would also enable correction or rescaling of all values if systematic errors were found in a set of data for one material. (A considerable effort on our part failed to show any systematic errors in our data.) Values in Table 1 are given for three samples of each material only, with the mass of the sample being different in each case but the amount of water remaining the same at 1.3 ± 0.02 g. These values are internally consistent, or reproducible, within ± 5%, although the value for KCl differs from that in the literature. The experiments, which were carried out intermittantly over a period of 11 months by the different authors of this paper, yielded the same results.

Thus the average values for the heat of solution in water at 298.16 K are: $+6.43\,\mathrm{kJ\,mol^{-1}}$ for crystalline sucrose (i.e. its dissolution is an endothermic process) and $-14.80\,\mathrm{kJ\,mol^{-1}}$ for glassy sucrose (i.e. its dissolution is an exothermic process). The corresponding values are: $+12.21\,\mathrm{kJ\,mol^{-1}}$ for crystalline glucose and $-3.33\,\mathrm{kJ\,mol^{-1}}$ for glassy glucose; $+24.23\,\mathrm{kJ\,mol^{-1}}$ for crystalline glucose monohydrate and $-3.77\,\mathrm{kJ\,mol^{-1}}$ for glassy glucose monohydrate. (Any systematic error in the measurements, if found, will alter the absolute values of the heat of solution, but not the difference between the heats of solution of the amorphous and crystalline phases.)

4. Discussion

The manner by which the energy of the amorphous form differs from that of the crystalline form, which we use as examples here, and the relationship of their energies to those of their solutions is conveniently seen in the data points given in Fig. 2, where the glass transition temperature, T_g, of each substance taken from the literature [11–13], is indicated. The dissolution of glassy sucrose and supercooled viscous glucose and glucose monohydrate is exothermic, and of their crystalline forms endothermic. So, the absolute energy of their solutions at 298.16 K has a value intermediate between the energies of their amorphous and crystalline forms, i.e. the energy of their solution differs from the absolute energies of the two forms by their respective heats of solution. A short line is drawn through the data points to indicate only the well known observation that C_p and C_V of a glassy material, which are equal to the slope of this short line, are more than those of its crystalline state. It is important to point out that if another solvent such as ionic aqueous solutions or aqueous solution containing organic materials are used, the absolute energy of the solution will change. Thus, we suggest that the data point for the energy of the solution (shown by a cross in Fig. 2) may be, by suitable choice of a solvent, brought to any value along the vertical line at 298.16 K, i.e. the heat

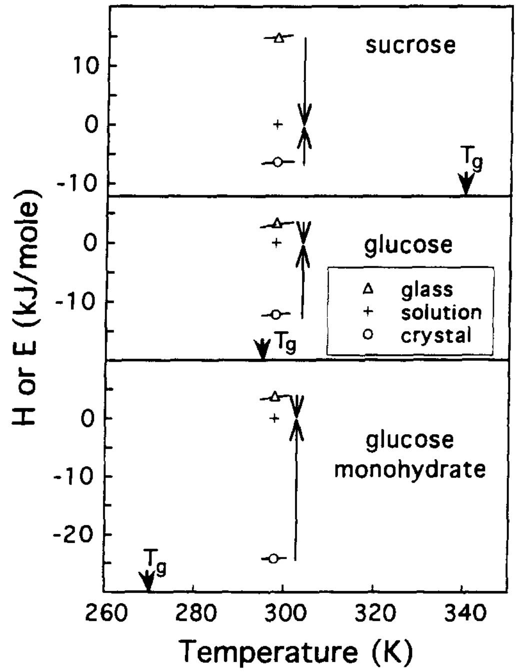

Fig. 2. The heat of solution of the glassy or viscous supercooled and crystalline states of sucrose, glucose and glucose monohydrate. The glass transition temperature, T_g, is indicated. Long arrows indicate exothermic and endothermic changes. The distance between the data points for the two states is equal to E_{exc} or H_{exc}.

of solution can be maximized or minimized, but the difference between the heats of solution of two forms will remain the same.

The excess enthalpy or energy of the glassy or supercooled viscous state is 21.2 kJ mol^{-1} for sucrose, 15.5 kJ mol^{-1} for glucose and 28.1 kJ mol^{-1} for glucose monohydrate at 298.16 K. We now consider the source of the difference between the energy or enthalpy of two forms of a material and give the formalism for measuring E^0_{exc}. A detailed description of the formalism and qualitative representations have been given before [14], so only a brief account may be useful here.

The heat of solution may be seen as a change in either the enthalpy or energy. For our purpose we represent the heat change of the process in terms of the internal energy, instead of enthalpy, as we use a constant pressure, one atmosphere, where the pressure–volume, $p\mathrm{d}V$, term is negligible.

In absolute terms, the difference between the enthalpies or energies of two polymorphs is written as,

$$E_{\text{exc}} = H_{\text{exc}} = (E^0 + \sum E^{\text{i}})_{\text{phase 1}} - (E^0 + \sum E^{\text{i}})_{\text{phase 2}} \tag{2}$$

$$\sum E^{\text{i}} = E^{\text{vibr}} + E^{\text{bond}} + E^{\text{conf}} \tag{3}$$

where E^0 is the energy at 0 K (sum of the lattice and zero point vibrational energies), and E^{i} is the internal energy associated with the ith feature at T above 0 K; i.e., E^{vibr} for the vibrational, E^{bond} for the cohesive van der Waals, covalent and hydrogen bond energy terms as the volume changes, and E^{conf} for the configurational contributions arising from rotational transitions of molecular segments in the structure.

The heat of solution formalism we use is not given in the literature, and so needs to be given here. In strict terms, the heat of solution is written as,

$$H^{\text{S}} = (E^0 + \sum E^{\text{i}})_{\text{soln}} - [(E^0 + \sum E^{\text{i}})_{\text{solu}} + (E^0 + \sum E^{\text{i}})_{\text{solv}}] \tag{4}$$

where the subscripts soln, solu and solv outside the brackets refer to the energy terms for solution, solute and solvent, respectively, and E^0 and $\sum E^{\text{i}}$ are as defined for Eq. (2). The meaning of Eq. (4) is that the magnitude of H^{S} depends also upon the magnitude of E^0_{soln}. If E^0_{soln} is large, H^{S} may be positive; if the former is small the latter may be negative. When the solvent is the same for the dissolution of different phases at a given temperature, $(E^0 + \sum E^{\text{i}})_{\text{solv}}$ is the same for each case, as is $(E^0 + \sum E^{\text{i}})_{\text{soln}}$. Thus, these two terms cancel each other when Eq. (4) is used to obtain H_{exc},

$$E_{\text{exc}} = H_{\text{exc}} = -(H^{\text{S}}_1 - H^{\text{S}}_2), \tag{5}$$

where H^{S}_1 and H^{S}_2 are the heats of solution of the two phases in the same solvent at the same fixed temperature. Thus the measurement of H^{S} yields the energy or enthalpy difference between the different structures of a material at 0 K, plus the different magnitude of van der Waals energy and H-bond energy, and any energy associated with configurations in the different states.

Kauzmann [12] has calculated the enthalpy of the crystalline, glassy, and supercooled liquid phases of glucose from the heat capacity data measured by Parks et al. [10]. As the measured C_p used in these calculations did not extend to temperatures far below 77 K, the error in the integrated area from which Kauzmann determined the value of H may be significant. From Fig. 1 of Kauzmann's paper (p. 225 of Ref. [12]), we determined H_{exc} of glass (or supercooled liquid glucose) over its crystalline phase as 13.7 kJ mol^{-1} at 298 K. The difference between the heats of solution of crystalline glucose and its highly viscous supercooled state at 298.16 K (~ 3 K above its T_g measured for a heating rate of 10 K min^{-1}) determined from this study is 15.5 kJ mol^{-1}. In view of the accuracy of the C_p data, the determination of H from integration of C_p–T plots, and the manner by which Kauzmann estimated H^0_{exc} of glucose from Eq. (1) here (which required C_p data from 0 K and the heat of crystallization of glucose), we consider that the agreement between 13.7 kJ mol^{-1} and 15.5 kJ mol^{-1} is reasonable.

We propose that the heat of solution measurements are preferable to C_p measurements for two reasons:

(1) they are rapid and direct, and

(2) they eliminate the cumulative errors arising from errors in C_p and the heat of phase transformation measurements and thus provide a more accurate value of H_{exc}. It has a further advantage of enabling measurement of the absolute H of a second form of a material when H of at least one of its two forms is already known. This eliminates the need for a set of C_p–T measurements for the second form of the same material.

We now consider how E^0_{exc} can be determined from H^{S} and limited C_p data. Measurement of C_p against the temperature T of two phases yields the difference,

$$\sum E^{\text{i}}_1 - \sum E^{\text{i}}_2 = \int_0^T C_{p,1}\,\mathrm{d}T - \int_0^T C_{p,2}\,\mathrm{d}T \tag{6}$$

where $\sum E^{\text{i}}$ is defined by Eq. (3) and subscripts 1 and 2 refer to the two phases of a material. By combining Eqs. (2), (5) and (6) and rearranging,

$$H_{\text{exc}} = E^0_1 - E^0_2 + \int_0^T (C_{p,1} - C_{p,2})\,\mathrm{d}T \tag{7}$$

On substituting Eq. (5) in Eq. (7)

$$E^0_{\text{exc}} = E^0_1 - E^0_2 = -(H^{\text{S}}_1 - H^{\text{S}}_2) - \int_0^T (C_{p,1} - C_{p,2})\,\mathrm{d}T \tag{8}$$

Thus the difference between the internal energies of two phases at 0 K can be determined from their heat of solution at a particular temperature and the calorimetric enthalpy (known from the C_p measurement) at that temperature. It should be noted that the use of Eq. (8) for determining E^0_{exc} requires no knowledge of the enthalpy of melting or of any other phase transition. Hence E^0_{exc} of materials which melt incongruently, particularly many inorganic and most biological materials, may be determined by our procedure. This seems particularly valuable, because E^0_{exc} of such materials cannot be determined by the usual calorimetric methods. This underscores the significance of the heat of mixing measurements.

We now consider the use of this method for studying the internal energy of amorphous solids, particularly glasses, in their various structural states obtained by annealing, physical ageing or structural relaxation. It is appropriate to recall that one of the characteristics of a glass is that its enthalpy decreases on spontaneous structural relaxation during its physical ageing, or as its fictive temperature, T_f, decreases spontaneously. (T_f is the temperature at which a metastable liquid in internal equilibrium has the same energy as its glass). As this occurs, E^0_{exc} also decreases with T_f, so that the curve for H of a glass plotted against temperature bodily moves closer to that of the crystal, as discussed earlier [14], but not by the same amount at all temperatures because both the vibrational contributions to the enthalpy of a glass, and contribution from the availability of configurational states associated with its sub-T_g relaxations, also decrease, particularly when the glass densifies on ageing. This means that the exothermic H^S will decrease, or the endothermic H^S will increase on structural relaxation during the physical ageing of a glass. So, the heat of solution of a glass will be found to vary with its thermal history. This variation was observed in experiments on vitrified sucrose, whose T_g is 340 K, and thus its structural relaxation occurred during cooling to room temperature and during storage at ambient temperature. The observation seems to confirm that the method used here is adequate for determining also the thermal history and structural relaxation of vitrified solids. This method may probably turn out to be an economic and more accurate alternative to the methods, DSC and adiabatic calorimetry, used currently for determining the change in the energy of a glass on its structural relaxation.

The accuracy with which the excess energy can be determined depends upon whether the heat of solution is endothermic for both polymorphs, or exothermic for both, or whether it is endothermic for one and exothermic for the second. In the first two cases, the difference between the heats of solution of the two polymorphs will be relatively small and may not be accurately determined unless the instrument is sensitive enough for the purpose. Evidently, the accuracy of the method depends upon the position of the curve for the energy of the solution relative to that of the solvent and of the solute. The energy of a solution at a given temperature may lie above the energy of the solvent and of the solute, or between the energies of the solvent and of the solute, or lie below the energies of both the solvent and the solute. The choice of the solvent enables one to have some control on the heat of solution of each form, and even to make the dissolution of one form exothermic and of the other form endothermic in order to determine E^0_{exc} more accurately.

5. Conclusions

Both the procedure given here and the choice of the solvent are advantageous for obtaining accurate values of the excess energy by heat of solution measurement, particularly when the polymorphs do not phase transform at the temperature of interest and their C_p–temperature data are not available. The procedure would be most useful for obtaining the energy difference at 0 K of those polymorphs which decompose on heating before reaching the temperature at which they could transform to a single phase, such as polymorphs that melt incongruently.

Acknowledgements

This research was supported partly by Bilateral Research Agreement. GPJ is grateful for the hospitality and funds in support provided by IFAM del CNR, Pisa, during the period of his stay for this research. *E.* Tognoni is grateful to Edison SpA for a grant in support of this research.

References

[1] U. Bianchi, C. Cumbetti, E. Pedemonte and C. Rossi, J. Polym. Sci., 7 (1969) 845.
[2] F.E. Filisko, Polym. Prep., 15 (1974) 257.
[3] N.E. Weeks, F.E. Karasz and W.J. MacKnight, J. Appl. Phys., 48 (1977) 4668.
[4] F.E. Filisko and R.S. Raghava, J. Appl. Phys., 45 (1974) 4151.
[5] R.S. Raghava and F.E. Filisko, J. Appl. Phys., 45 (1974) 4155.
[6] P.J. Flory, Disc. Faraday Soc., 49 (1970) 7.
[7] C.J.P. Landry and D.M. Teegarden, Macromolecules, 24 (1991) 4310.
[8] M. Cassettari, F. Papucci, G. Salvetti, E. Tombari, S. Veronesi and G.P. Johari, Rev. Sci. Instrum., 64 (1993) 1076.
[9] CRC Handbook of Chemistry and Physics, 1985 edition, p. D-123
[10] G.S. Parks, H.M. Huffman and F.R. Cattoir, J. Phys. Chem., 32 (1928) 1366.
[11] G.P. Johari, J. Chem. Educ., 51 (1974) 23.
[12] W. Kauzmann, Chem. Rev., 43 (1948) 219.
[13] R.K. Chan, K. Pathmanathan and G.P. Johari, J. Phys. Chem., 90 (1986) 6358.
[14] G.P. Johari, Thermochim. Acta, 266 (1995) 31.