Journal of Thermal Analysis and Calorimetry, Vol. 84 (2006) 3, 663–668

THE GLASS TRANSITION
Finite size effect[*]

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The subjects of the paper are the mechanism of vitrification and the glass transition, and a definition of the temperature of the glass transition. A comprehensive description of the structural changes occurring in the amorphous phase ('real' and 'semi-ordered') in a vicinity of the glass transition is presented. One of the major motivation of our studies is to investigate the finite size effect of the glass transition that could be related to the cooperative motion in supercooled liquids. Also, new formula, describing the relaxation time temperature change, is applied in order to better reveal the mechanism of the supermolecular formation under different internal and external factors. The results of the basic methods of thermal analysis, obtained for different polymeric systems, were used in this study. The proposed approach let us correlate the thermodynamic and the structural parameters, which are estimated from the experiments, and describe all well known shapes of the DSC traces, which can be recorded in the glass transition region. Based on positron annihilation lifetime spectroscopy and dilatometric results, the significance of the free and the specific volumes for the activation of the relaxing units is discussed.

Keywords: *glass transition, polymer, structural relaxation, thermodynamics*

Introduction

The glass transition of polymer similar to low molecular substances is accompanied by sharp jump in the heat capacity (specific heat, ΔC_p). The following three contributions should be taken into account [1, 2]:

$$\Delta C_p=\Delta C^{c}+\Delta C^{fv}+\Delta C^{v} \tag{1}$$

where ΔC^{c} is the conformational contribution, resulting from the change of the conformational equilibrium in the glass transition region; ΔC^{fv} is the contribution resulting from the increase of a free volume of the system; ΔC^{v} is the contribution arising from the change of the vibrational frequencies and the anharmonicity of the modes resulting, in turn, from the jump-like change of the compressibility and thermal expansivity. The rigorous determination of the relation between these contributions is a very complex experimental and theoretical problem. Different theories deal with thermal behaviour resulting from the particular molecular and supermoleclar structure of polymers. The main feature of polymeric systems is their local anisotropy, being a consequence of big difference in the inter- and intramolecular interactions. This anisotropy is revealed in the local anisotropy of physical property of final polymeric products or samples, that can be detected by different techniques. One can easy find that the elastic and inelastic effects change the total C_p value that is reflected in the shape of DSC curves, $C_p\rightarrow f(T)$ [3, 4]. It may lead to some specific temperature dependencies of heat capacity of solid polymers. However, remaining in the frame of the phenomenological thermodynamics, one can hardly display the molecular origin of the C_p function changes. The same is true of the entropy and energy functions. However it should be emphasised that every techniques require special sample treatment. Under this action, very often, the local anisotropy and individuality of macromolecules transform to the macroscopic anisotropy, that is especially characteristic of oriented materials. The physical interpretation of different kind of contributions to the total C_p value are discussed widely in literature, e.g. [4]. Summarising, it should be emphasised that all theoretical approaches have shown that all of the contributions are comparable in their values and none of them can be neglected in calculations of ΔC_p.

From the thermodynamic measurements, it is possible to obtained thermodynamic quantities such as the Gibbs free energy (G), enthalpy (H) and entropy (S) of the system over a wide temperature interval. These thermodynamic functions may be evaluated by measuring the heat capacity in the transition temperature region, i.e. below and above the temperature of the glass transition (T_g). Calorimetrically, T_g is usually defined at the midpoint of the $\Delta C_p(T_g)$ value. It should be emphasised, there are kinetic and thermodynamic contributions to the C_p value in the glass transition region. This means that the supercooled liquid may explore all the configurations above T_g whereas the glass is

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1388–6150/$20.00

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trapped kinetically in one of these configurations below T_g. Then, the system can only relax towards that one corresponding to a local minimum of the potential energy. It implicates the existence of a potential energy barrier, which is intrinsic to the occurrence of the glassy state. It was considered that two kinds of structural instabilities/relaxations may occurred: relaxation within the amorphous state with some relaxation time τ_g; relaxation out of the amorphous state into the crystalline state with other relaxation time τ_c [5].

The value of T_g and the shape of C_p are very dependent on the heating and cooling rates of the measurement and on the thermal history of the system. There are three possible scenario for the glass transition observed calorimetrically. Different shapes of the measured C_p curves are presented in Fig. 1. Our earlier study showed that two amorphous fractions can be formed in one system and they exhibit various features, which can be summarised as follow: a) 'real' amorphous phase – typical stepwise transition with relative small $\Delta C_p(T_g)$, T_g at lower range of temperatures (far from T_m), a non-Arrhenius type of the α relaxation (signed as α_g), drastic change of the free volume in the transition range; b) 'semi-ordered' amorphous phase – endothermal peak following the abrupt change of a base line, T_g at higher range of temperatures (closer to T_m), an Arrhenius type of the α relaxation (signed as α_c), no drastic change of a free volume in the transition was observed [5–7].

New interpretation of the DSC curves, obtained for different vitreous systems, is presented. The explanation is based on the earlier proposed concepts of the glass transition and the structural relaxation. The main problem here is the relationship between the energy dissipated during the structural relaxation and the relaxation time, as well as, the connection of G variation with the morphological/structural changes.

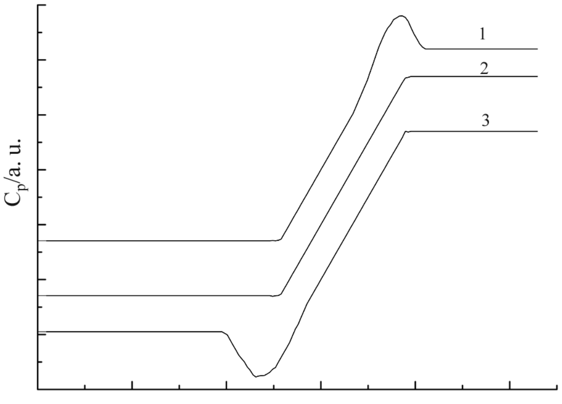

Fig. 1 Sketch of DSC curves which are recorded for the polymeric samples of different thermal histories, e.g. 1 – cold drown, 2 – undeformed, 3 – plastically deformed. Different examples of DSC traces are discussed in details in [4]

Expressions for τ, *H*, *S* and *G* – experimental restrictions

Using the experimental data of the C_p temperature dependence, the thermodynamic quantities can be calculated according with the basic thermodynamic relations:

$$H = H_m - \int C_p \mathrm{d}T \tag{2}$$

$$S = S_m - \int \frac{C_p}{T} \mathrm{d}T \tag{3}$$

$$G = H - TS \tag{4}$$

New formula for the calculation of the temperature dependence of the relaxation time was proposed earlier [5, 7]. This formula recognises both fractions of the amorphous phase therefore the α_g and the α_c relaxations can be described by their own $\tau \rightarrow f(T)$ [5].

$$\tau = \tau_1 \exp\left[\frac{\Delta H_\alpha}{\Delta C_p(T_g)} \frac{1}{T}\right] \tag{5}$$

The enthalpy of activation of the α relaxation was signed as $\Delta H_\alpha = H_i n_\alpha$ (the enthalpy of activation, ΔH_α, is a product of the number of mers taking part in the process (n_α) and the enthalpy of intermolecular interaction (H_i), for explanation [5, 7]). The ΔC_p value was determined at T_g. It was found that this value could be treated as a scaling factor. The application of the scaling factor in the fitting procedure of the τ function give one H_i value for all studied systems if their supermolecular structures are the same. It must be emphasised that the formula describes the dynamics of one system, it means that the thermodynamic parameters, taken from the calorimetric study (DSC), must be exactly pointed out for the system which is the subject of the mechanical or dielectric spectroscopy. The same must be true of the free volume (positron annihilation lifetime spectroscopy – PALS), specific volume (dilatometry – DIL) and the X-ray measurements (wide or small angel X-ray scattering – WAXS or SAXS). However, we can hardly find in literature an adequate set of required data, describing one system, which has been obtained under the same condition. Usually, various experimental techniques have been applied under different conditions or material thermal histories have not been described precisely. The influence of the measurement techniques, with particular attention to PALS, on morphology changes, studied by DSC, was widely discussed in our recent paper [3]. Different sample treatment may introduce incorrect parameter values into the calculations. It was presented for relaxations (signed as γ or α_g) observed in PE samples [7]. If the proper set of the thermodynamic and structural parameters i.e., the set obtained for the same supermolecular structure of the polymeric material, was used for calculations, the common molecular mechanism of the relaxations and the relationships between different structures and the material properties could be found.

Estimation of the characteristic parameters from DMTA data (Eq. (5))

To adopt Eq. (5) for all cases described in literature some assumptions have been taken. It is worth noticing that all assumptions arise from the experimental evidences, and moreover, the parameters, included in the formula, possess physical interpretation. They are evaluated either directly from the measurements or from the results of the formula fitting to experimental data. An example of the fitting DMTA data is presented in Fig. 2a. The results of the fitting, performed for systems of different supermolecular structures, were presented in a previous paper [5]. It was found for the 'semi-ordered' fraction of an amorphous phase that when the kind of crystal units was not changed the same activation enthalpy was obtained for the systems of different thermal histories. Moreover, the amount of the crystalline phase did not influence the activation enthalpy of the α_c relaxation. Owing to the fact that $\Delta H_\alpha = n_\alpha H_i$ and n_α for 'semi-ordered' fraction is constant, it might be concluded that the H_i value also should be constant. The situation for the 'real' amorphous fraction was a little different. The obtained ΔH_α values were different and they were sensitive to the sample thermal history. It means that the α_g relaxation, and hence the glass transition for this fraction, is a process during which the number of 'particles', taking part in the correlated motion, increases with rising temperature. The chosen example describing the variation of the n_α function for the polymer system, during the glass transition, is presented in Fig. 2b. The curve is simulated for the α_g relaxation of side-chain liquid crystal polymer (SCLCP). The relaxation concerns the liberation of the norbornene main-chain in a layer structure (smectic A) [8–10]. The values presented in Fig. 2b exhibits an equivalence of the used experimental method for T_g determination and the physical sense of the measured parameters, i.e. T_0 and T_g. It must be emphasised that almost all fitting gave the n/n_0 values between 0.10–0.15 for T_0(DSC). It might mean that DSC is able to reveal the change of the ΔH function when at least 10% of relaxing units (mers) take part in the transition.

The presented method gives new opportunity for T_g estimation from DMTA as a temperature at which 50% of the relaxing units take part in the process. However, the method defines this temperature in a different way as is presented in literature (one can see for reviewing this subject [11–13]).

Simulation of the C_p and H curves – glass transition region

It is proposed to adopt the simplest model for the C_p curve simulation. One can assumed that below and above the transition, in very narrow temperature ranges, two values could approximate the slight change of C_p, respectively. A sloped straight line might well repro-

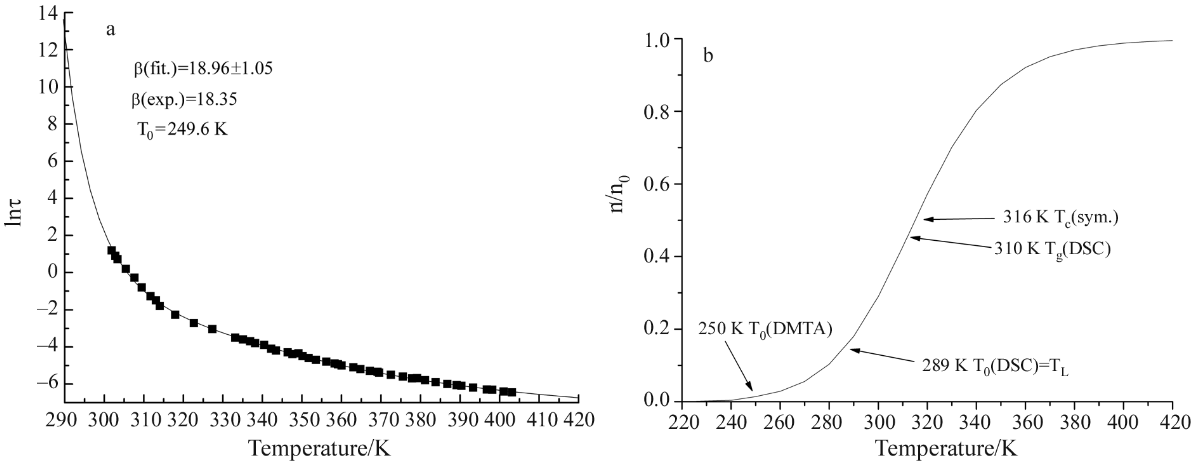

Fig. 2 a – A fitting curve plotted for the α_g relaxation occurred in a side-chain liquid crystal polymer system according to Eq. (5). Points represent the relaxation times evaluated from DMTA experiments. The β values represents the values either obtained in the equation fitting (fit.) or calculated from the definition of this parameter using experimental values (exp.) [5, 7].
b – Temperature dependence of the number of mers taking part in the α_g relaxation: T_C – parameter of the fitting procedure, T_g and T_0 were taken from the DSC measurement and the fitting of the DMTA data: T_0(DSC) in the text is signed as T_L

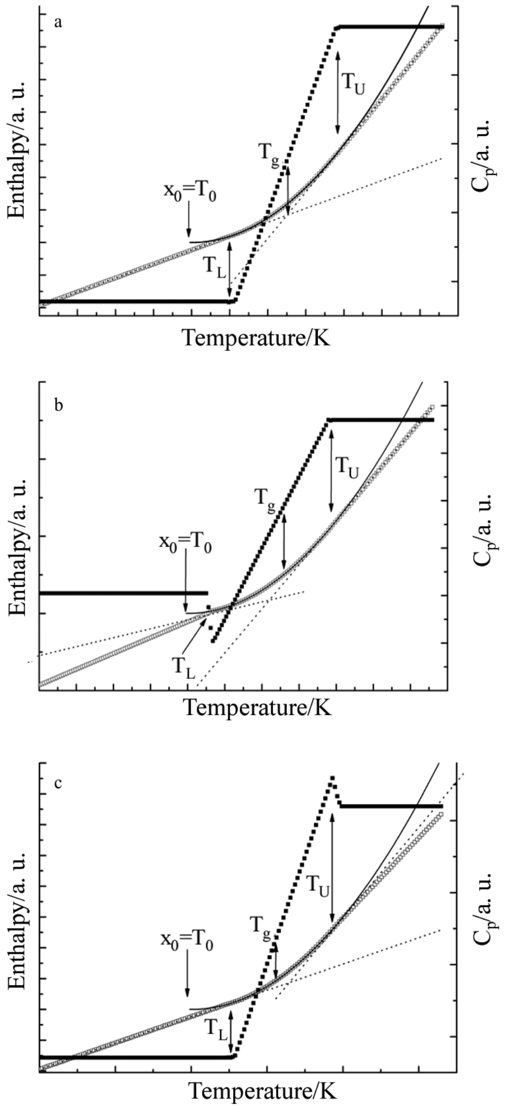

Fig. 3 C_p and H functions, solid and open symbols, respectively, simulated in the temperature range of the glass transition according to the proposed model: a – no peak before and after the transition, b – exothermal peak before the transition, c – endothermal peak after the transition

duce the experimental data inside the transition temperature region. Such assumptions implicate the sloped straight lines below and above transition for the enthalpy function. The polynomial of the second step is adequate for this function representation inside the transition range. If the adequate straight lines of the H functions are tangential to the polynomial at T_L and T_U, below and above the transition, respectively, the smooth C_p curves is obtained (Fig. 3a). If the straight lines are not tangential to the H polynomial function at T_L and T_U, the peaks below (Fig. 3b) and above (Fig. 3c) the transition appear, respectively. The polynomial would reflect, in physical sense, the variation of the n_α function, i.e. the increase of the number of units taking part in the collective motion, which are activated with rising temperature. The x_0 value equals the T_0 value obtained from the fitting of Eq. (5). It is the temperature at which the collective motion begins. The enthalpy as a state function could be represented by four components:

$$\Delta H=\Delta H^{\mathrm{c}}+\Delta H^{\mathrm{fv}}+\Delta H^{\mathrm{co}}+\Delta H^{\mathrm{v}} \qquad (6)$$

where ΔH^{c}, ΔH^{f} and ΔH^{v} reveal the same process as was described for $\Delta C^{\mathrm{c,}}$ ΔC^{f} and ΔC^{v}, respectively. The ΔH^{co} component reflects the H change resulting from the increase of the number of units involving the cooperative motion (structural relaxation).

A comprehensive study of the changes occurring in the amorphous phase by means of mechanical spectroscopy, differential scanning calorimetry, dilatometry, positron annihilation lifetime spectroscopy has shown that the correlation between the free and the specific volumes exists [14]. It has been found that the relative change of the specific volume is much higher than the relative increase of the average radius of the cavity (free volume). Owing to the fact that the average radius value, R, does not give information about the total free volume, its change should not be compared with the specific volume change. The total free volume, $V_F=Rn_c$, is a product of the average radius and the number of cavities, n_c. Unfortunately, one can only estimate the number of the cavities from the experimental data [15]. We have found that this number should decreases with rising temperature [14]. This statement, that the number of cavities decreases, agree with the experimental data found previously for the PMP system [6, 16, 17]. We have found that the relative change of the specific volume is about 3%. In the same temperature range, the relative change of the average radius of the cavity is about 10 times higher. Only decreasing of the number of the cavities would be able to reduce the drastic increase of the product (Rn_c) in such a manner, that the relative change of the total free volume (V_F) would not exceed the relative change of the specific volume. It would mean that the small cavities (at low temperatures) should join into the bigger one as the cooperative motions start to play a significance role for the structural relaxation above T_0. This mechanism could be responsible for the succeeding activation of the units/mers, taking a part in the α relaxation. The mechanism would freeze motion of the centre of gravity of the macromolecules as the temperature lowered. However, segments of the chains and chain ends will still be able to undergo conformational changes even though the centres of gravity of polymer molecules are essentially fixed. As the temperature is lowered still further, even these motions will be suppressed and the system will have passed into glassy state. One can conclude from the experimental results that both the number of available conformations and the rate of

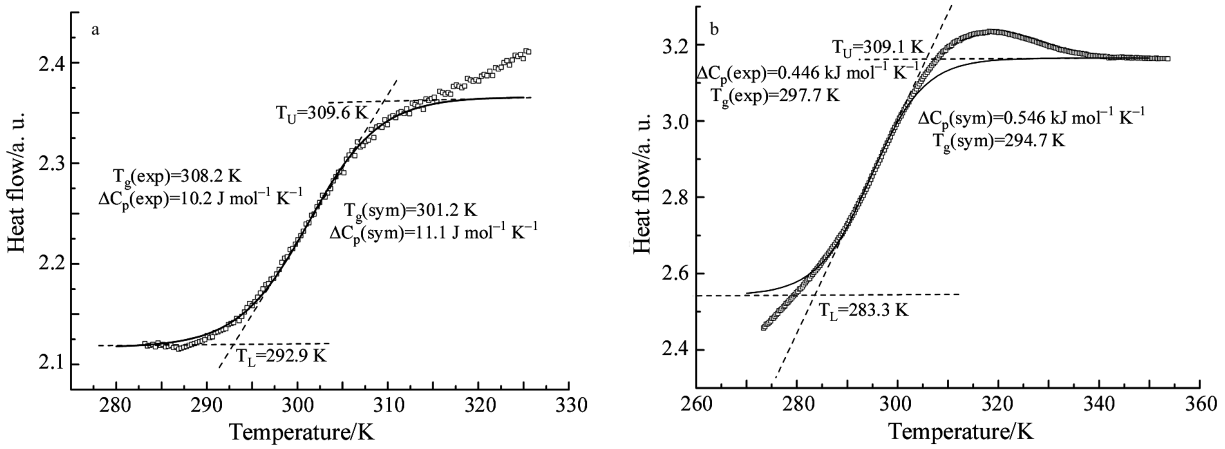

Fig. 4 a – □ – experimental and —– simulated values of the DSC experiments performed for semicrystalline polymer: a temperature range of the glass transition region of the 'real' amorphous phase; b – □ – experimental and —– simulated values of the DSC experiments performed for side-chain liquid crystalline polymer: a temperature range of the glass transition region of the side-chain ('real' amorphous phase)

changing from one to another are decreased because of the following factors: a) a decrease in the average radius of cavities; b) an increase of an energy barrier to rotation. The factors give contributions to the C_p values that is reflected in the polynomial parts of the H function as a succeeding deactivation of mers.

Application to experimental data

Figures 4a and b show the scheme of the estimation of the T_L, T_U and T_g parameters from the DSC trace. The sigmoidal function, $y=A_2+(A_1-A_2)/\{1+\exp[(x-x_0)/\mathrm{d}x]\}$, is proposed for the fitting procedure. This function, additionally, will give the value of ΔC_p, which is equal A_2-A_1. The ΔC_p values, experimental and simulated, are presented in figures. The obtained value of ΔC_p is further used in Eq. (5) for the fitting of the relaxation time spectrum.

The proposed procedure correlates thermodynamic and structural parameters. Its application help us to distinguish two fractions of the amorphous phase that give better description of polymer properties and the phenomenon of the glass transition is better understand. The proposed definition of the relaxation time combines the experimental data of different techniques. Moreover, the equation, applied in this approach, includes only the fitting parameters, which can be compared with the parameters measured in experiments. The mathematical formula gives the answer on a question concerning the origin of the α relaxations, described by the new relations, that is in agreement with the experimental observation. We also receive the information about a degree of order existed in the amorphous phase [5, 7], that could be useful for the description of material properties.

Owing to the fact that this procedure requires application of different experimental techniques and that each technique requires special sample treatment, particularly problematic is the preservation of the same supermolecular structure during each measurement (the same sample thermal history). For example, the piece of the sample for DSC investigation must be cut down directly from the same specimen which is prepared for mechanical, dielectric or X-ray measurements [18]. In other case, there is no sense to compare the results, as is very often done for DSC and DETA.

Conclusions

The linear approximation of the C_p data gives satisfied analytical description of the experimental results in the glass transition region. It gives opportunity for the calculation of the components of the state function and their physical interpretation. The interpretation recognises four components of the state function for the processes occurred in the temperature range of the glass transition. The proposed approach let us correlate the thermodynamic and the structural parameters, which are estimated from the experiments. The C_p linear approximation describes all found in experiments shape of the DSC traces in the glass transition region.

The finite size of the glass transition in a temperature scale is postulate. Although this transition is revealed by calorimetry between T_L and T_U, it starts at much lower temperature T_0 when the correlated motion of the relaxing units (mers in the case of macromolecules) has begun.

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Received: August 1, 2005
Accepted: November 15, 2005

DOI: 10.1007/s10973-005-7163-0